



MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES



INVESTIGATION OF BEHAVIOURS OF PHASE CHANGED CRYSTALS IN THE PRESENCE OF ADDITIVES

SEVGİ POLAT

Ph.D. THESIS

Department of Chemical Engineering

Thesis Supervisor

Prof. Dr. Perviz SAYAN

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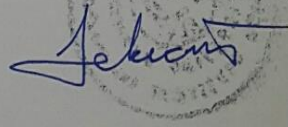
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ÖZET

KATKILAR VARLIĞINDA FAZ DEĞİŞTİREN KRİSTALLERİN DAVRANIŞLARININ İNCELENMESİ

Bu çalışmada, polimorfik özellik gösteren glisin ve pseudo-polimorf kalsiyum sülfat hemihidratın faz dönüşümü saf ortamda ve çeşitli katkıları varlığında incelenmiştir. İlk olarak, polimorfik açıdan β -glisinin α -glisine dönüşümü su/etanol ortamında saf, laurik, bütirik, oleik, miristik, asetik, tartarik ve sitrik asit varlığında; farklı ultrasonik şiddetlerde ve değişen UV ışıma varlığında incelenmiştir. Polimorfik faz dönüşümü ultrasonik hızın sürekli olarak ölçülmesiyle takip edilmiştir. Bu dönüşümü doğrulamak amacıyla elde edilen kristallerin XRD analizi yapılmıştır. SEM ve morfoloji analiz sonuçlarına göre, hem şekil parametrelerinin hem de kristallerin boyutlarının kullanılan katılardan önemli ölçüde etkilendiği belirlenmiştir. Ayrıca, kristaller TGA, elementel analiz ve FTIR ile karakterize edilmiştir. Termal analiz sonucunda elde edilen veriler ve izokonversiyonel yöntemeye dayanan çeşitli kinetik modeller kullanılarak aktivasyon enerjileri hesaplanmıştır. Kinetik sonuçlar, kullanılan katkı maddelerinin, bozunma sürecinde glisin kristallerinin ortalama aktivasyon enerjisinde artışa yol açtığını göstermiştir. Tezin ikinci bölümünde, kalsiyum sülfat hemihidratın kalsiyum sülfat dihidrata pseudo-polimorfik faz dönüşümü saf ortamda ve katkı maddesi olarak kullanılan trikarballik, glutamik ve propiyonik asit varlığında incelenmiştir. Faz dönüşümü sürekli iletkenlik ölçümleri ile takip edilmiştir. Dönüşüm süreci boyunca elde edilen kristallerin karakterizasyonu detaylı bir şekilde yapılmıştır. Ayrıca, kesikli bir kristalizörde dönüşüm süresince katkıların adsorpsiyonu; temas süresi, katkı konsantrasyonu ve sıcaklık parametreleri açısından incelenmiştir. Adsorpsiyon karakteristikleri izoterm, kinetik ve termodinamik özellikler açısından değerlendirilmiştir. Kalsiyum sülfat hemihidratın dihidrata dönüşüm sürecinde propiyonik asidin hızlandırıcı, trikarballik ve glutamik asidin ise geciktirici olarak kullanılabileceği ortaya koyulmuştur.

Anahtar kelimeler: Polimorfizm, faz transformasyonu, glisin, kalsiyum sülfat hemihidrat, katkı, ultrasonik etki, UV ışıma, izokonversiyonel yöntem, adsorpsiyon.

ABSTRACT

INVESTIGATION OF BEHAVIOURS OF PHASE CHANGED CRYSTALS IN THE PRESENCE OF ADDITIVES

In this study, phase transformation of glycine (polymorph) and calcium sulfate hemihydrate (pseudo-polymorph) was investigated in the absence and then the presence of various additives. Firstly, the phase transformation of β -glycine to α -glycine in a water/ethanol media was investigated in terms of its polymorphism in pure media and in the presence of lauric, butyric, oleic myristic, acetic, tartaric and citric acid, different intensities of ultrasonic irradiation and varying intensities of UV radiation. The polymorphic phase transformation was continuously monitored by in-line measuring of the ultrasonic velocity. The XRD technique was applied for the phase analysis of the crystals to confirm the polymorphic transformation. Based on the combination of SEM and morphology analyses, it was found that not only the shape parameters but also the size of the crystals obtained were significantly affected by the additives used. The crystals obtained were further characterized by means of TGA, elemental analyzer and FTIR. The attained thermal data were utilized to calculate the activation energy using various kinetic models based on the isoconversional method. The kinetic results revealed that the addition of the additives used led to increase in the average activation energy of the glycine crystals during decomposition process. In the second part, pseudo-polymorphic phase transformation of calcium sulfate hemihydrate to calcium sulfate dihydrate was performed in the absence and then the presence of tricarballic, glutamic and propionic acid used as the additives. The phase transformation was continuously followed by conductivity measurements. The structure of the samples obtained during this process was characterized detailed. Furthermore, the adsorption of the additives during the transformation process was studied in a batch-type crystallizer with respect to contact time, additive concentration and temperature. The adsorption characteristics were investigated by means of evaluating the isotherm, kinetic and thermodynamic properties. While propionic acid can serve as a good accelerator for the transformation process from calcium sulfate hemihydrate to dihydrate, tricarballic and glutamic acids can be used as the retarder.

Keywords: Polymorphism, phase transformation, glycine, calcium sulfate hemihydrate, additive, ultrasonic irradiation, UV radiation, isoconversional methods, adsorption.

CLAIM FOR ORIGINALITY

The ability of a compound to exist in crystalline form, where each form has the same chemical structure but different molecular compositions in the crystal lattice, is called polymorphism [1]. Polymorphs can significantly vary depending on their physical and chemical properties, in addition to their structures. These properties include solubility, refractive index, melting point, filtration characteristics, compressibility, vapor pressure, crystal structure, density, enthalpy of fusion, hardness, chemical and physical stability, and heat capacity, which are considered to be important factors for controlling the quality and properties of the final product depending on its application in industrial processes [2]. Polymorphism is frequently encountered in crystallization of various organic and inorganic materials, primarily in drug molecules. One of the most widely known and studied organic substances that exhibits polymorphic behavior is glycine. Glycine, commonly used by living organisms on Earth to build proteins, is the simplest amino acid. Glycine is found in three different crystalline forms: α , β and γ with different relative stabilities and structures [3]. The applications of glycine in the food, chemical, cosmetics and pharmaceutical industries have focused attention on its properties from many different standpoints [4]. Studies on glycine's thermodynamic properties in aqueous solutions have considerable importance in life science, biotechnological development, and industrial processes [5]. A thorough grasp of the phase transformation process of glycine is needed, both for control of polymorphism and in the production of high-quality final products with desired physical properties. Previous studies have revealed that operating conditions of crystallization, such as pH, temperature and initial concentration, additives and ultrasound can affect phase transformation and physical properties of the end-products. Therefore, using additives to control phase transformation and physical properties has received considerable attention [6]. This is the first study that investigates the effects of lauric, butyric, oleic and myristic, acetic, tartaric and citric acid on the phase transformation of glycine. These fatty and carboxylic acids were selected as the additive due to its high efficiency, ease of handling, non-toxicity, and availability. The lack of studies on the use of these additives in the β -glycine/ α -glycine transformation and the absence of a detailed shape analysis to determine the shape factor also contributed to this preference. Particle shape factors should be determined to obtain a high-quality product with desired properties. A detailed identification of the crystal shape by interpreting and depicting the

shape parameters will contribute to different industrial uses of glycine. Furthermore, as an important physical property of polymorphic crystals, the stability of the crystals should be examined to improve the quality of the as-obtained crystals and to obtain detailed information of crystal polymorphs formed. To date, no previously reported study has focused on the storage stability of glycine polymorphs precipitated using a liquid antisolvent method in the presence of ultrasonic irradiation. A better understanding of the stability of crystals is of great importance to increase the productivity of the glycine transformation process. Therefore, the one of the purposes was to determine the influence of ultrasonic irradiation on the morphology and storage stability. Moreover, the thermal characteristics of the glycine crystals were investigated detailed in this study. Although the studies have reported the thermal decomposition kinetics of pure glycine, no study has been published on the kinetic analysis glycine crystals in the presence of the additives used. The kinetic parameters obtained are critical for defining the transformation process in terms of thermal aspect and increasing the productivity of the transformation process. Therefore, the other purpose of this study is to investigate the effects of fatty and carboxylic acids on thermal decomposition behavior and calculate the activation energies of the crystals obtained in a pure and additive media using various kinetic models.

In the second part, calcium sulfate which is of great importance for a number of industries, especially the medical, construction and ceramic industries was studied detailed. There are three forms of calcium sulfate that are able to be formed, depending on crystallization conditions: calcium sulfate dihydrate, calcium sulfate hemihydrate, and calcium sulfate anhydrite. Calcium sulfate dihydrate, which is obtained through the hydration of calcium sulfate hemihydrate, has become increasingly important due to its wide application in industry [7]. Extensive efforts have gone into producing products with the desired quality and specifications. In this study, tricarballic, glutamic and propionic acid were preferred as the additive. The effects of these additives have not been investigated and the exact role of their use as the additives for transformation process has not yet fully indicated, and no kinetic and adsorption studies have been reported on the transformation process. It is believed that the usage of these additive would lead not to only increase the productivity of the transformation processes but to also obtain a product having the desired properties.

SYMBOLS

A	: Pre-exponential or frequency factor (min^{-1})
b_T	: Temkin isotherm constant related to the heat of adsorption (J/mol)
C	: Constant
C_e	: Equilibrium additive concentration (mg/L)
C_i	: Initial additive concentration (mg/L)
E	: Activation energy (kJ/mol)
f(x)	: Reaction model
g(x)	: Integrated form of the reaction model
k(T)	: Reaction rate constant
K_F	: Freundlich adsorption constant (mg/g)(L/mg) ^{1/n}
K_L	: Langmuir binding constant (L/mg)
K_T	: Equilibrium binding constant (L/mg)
k₁	: Pseudo-first order rate constant (1/min)
k₂	: Pseudo-second order rate constant (1/min)
n	: Empirical parameter relating the adsorption intensity
n	: Reaction order
R	: Ideal gas constant (8.314 J/mol.K)
p(u)	: Temperature integral
q_e	: Adsorption capacity at equilibrium (mg/g)
q_m	: Maximum adsorption capacity (mg/g)
q_t	: Adsorption capacity at time t (mg/g)
R_L	: Dimensionless equilibrium parameter or adsorption intensity
T	: Absolute temperature (K)
V	: Volatile content

V	: Volume of the solution (L)
V*	: Effective volatile content
W	: Mass of the adsorbent (g)
W_f	: Final sample mass (mg)
W_o	: Initial sample mass (mg)
W_t	: Sample weight at time t (mg)
x	: Conversion or weight loss rate
β	: Heating rate (K/min)
ΔG°	: Gibbs free energy change (kJ/mol)
ΔH°	: Standard enthalpy change (kJ/mol)
ΔS°	: Standard entropy change (kJ/mol)

ABBREVIATIONS

ATR	: Attenuated total reflection
BET	: Brunauer-Emmett-Teller
CaSO₄	: Calcium sulfate anhydrite
CaSO₄·0.5H₂O	: Calcium sulfate hemihydrate
CaSO₄·2H₂O	: Calcium sulfate dihydrate
DAEM	: Distributed activation energy model
DSC	: Differential scanning calorimetry
DTG	: Differential thermogravimetric
FTIR	: Fourier transform infrared
FWO	: Flynn-Wall-Ozawa
KAS	: Kissinger-Akahira-Sunose
SEM	: Scanning electron microscopy
TEM	: Transmission electron microscopy
TG	: Thermogravimetric
TGA	: Thermogravimetric analysis
MS	: Mass spectrometer
XRD	: X-ray diffraction

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1. INTRODUCTION

1.1. The Purpose of the Study

Polymorphism is frequently encountered in crystallization of various organic and inorganic materials, primarily in drug molecules. One of the most widely known and studied organic substances that exhibits polymorphic behavior is glycine [8]. Glycine is the simplest amino acid and has widespread use in the chemical, cosmetics, pharmaceutical, and food industries. Its three polymorphs under atmospheric temperature and pressure are the γ , α , and β forms, which are the most stable polymorph of glycine, the metastable polymorph of glycine, and the unstable polymorph of glycine, respectively [3,4,9-11]. α -Glycine at room temperature is stable and spontaneously crystallizes from aqueous solution. Both β and γ nucleation are usually obtained only under certain conditions, such as in the presence of alcohol and additives, or with technical processes at extreme temperatures [12,13].

Substances incorporating solvent in their crystal lattice show a special type of polymorphism. These substances are called solvates or hydrates, if water molecules are part of the crystal structure. Solvates and hydrates are summarized with the term “pseudo-polymorphs” [14]. Calcium sulfate is one of the most significant inorganic compounds and is used for a variety of purposes in the ceramic, construction, fertilizer, plastic, paper and medical industries [15,16]. It can be crystallized in three different forms: calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and calcium sulfate anhydrite (CaSO_4) [17]. The pseudo-polymorphic phase transformation process of calcium sulfate hemihydrate to the dihydrate form in particular has come to the attention of several researchers due to a wide range of different industrial applications [18].

Polymorphs and pseudo-polymorphs generally have different chemical and physical properties, including stability, crystal shape, compressibility, melting point, thermal conductivity, heat capacity, density, and dissolution rate [19]. These differences in chemical and physical properties result in the need to handle and process the materials differently [20]. Thus, the control of polymorphism and pseudo-polymorphism are of great importance for efficient crystal production [1]. Several studies reveal that crystallization parameters like pH, temperature, initial concentration, and solvent type used can affect

phase transformation and thus the physical properties of the end products [21-24]. Some studies have indicated that different polymorphs can be formed with different physical properties when systems are irradiated with ultrasound [25-27]. Previous studies also showed that the presence of additives has significant effects on phase transformation. Thus, the use of additives to control phase transformation and physical properties has gained popularity.

In the present study, taking all this into consideration, the transformation of β -glycine to α -glycine was investigated, both in pure media and in the presence of various fatty and carboxylic acids. Particle shape factors were quantitatively determined. In addition, kinetic models were used to determine the effect of the additives on the thermal decomposition behavior of the crystals obtained both in pure media and in the additives media, and to explain the kinetic characteristics and calculate the activation energies for the decomposition of the glycine crystals. The other purposes of this study are to investigate the effects of UV radiation of different intensities on the crystallization behavior of the polymorph of β glycine to α glycine in a water–ethanol system and to determine the influence of ultrasonic irradiation on the morphology and storage stability of glycine, and finally, to detect the impact of sonication on the time taken for the phase transformation from the β to the α form of glycine.

In terms of pseudo-polymorphism, the aim of this paper was to determine the effects of tricarballic, glutamic and propionic acid on the transformation of calcium sulfate hemihydrate to its dihydrate form. The average particle size, crystal morphology and functional groups of the samples were determined and compared between pure and impure media. In addition, the adsorption isotherms, kinetics and thermodynamics of the additives on the transformation process were comprehensively examined and carboxylic acids adsorbed amounts were determined as a function of temperature.

1.2. Polymorphism and Pseudo-Polymorphism

Polymorphism is a material's ability to exist in more than one crystal form in which its chemical structure remains the same, but the molecular arrangement in the crystal lattice is different [1]. Although the chemical composition of the two polymorphs is the same, they are regarded as two distinct compounds because their physical and chemical

properties, such as particle size, solubility, stability, compressibility, melting point, viscosity and crystal form, are different [28]. Accordingly, the full characterization of all possible polymorphs is extremely important, especially in the pharmaceutical industry, thereby any transformation that occurs during production or storage can be prevented and selected polymorphs can be crystallized [29].

The term “pseudo-polymorphism” indicates substances involving a stoichiometric or non-stoichiometric amount of solvent in their crystal lattice. When water molecules are introduced into their crystal structures, they are referred to as solvates or hydrates. Similar to polymorphs, the various pseudo-polymorphs of a substance can have significantly different physical properties. However, pseudo-polymorphs become different chemical substances if solvents are added into their structures and thus, their physical and chemical properties may change [14]. A schematic representation of a polymorph and pseudo-polymorph is presented in Figure 1.1 [30].

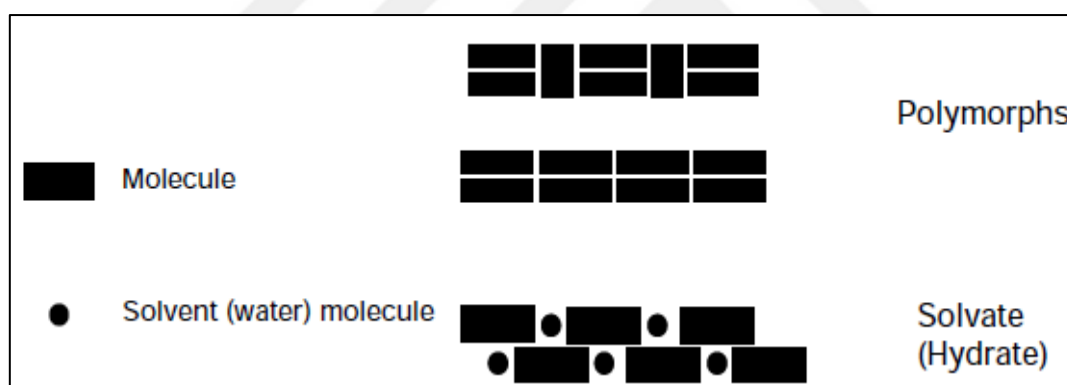


Figure 1.1. Schematic representation of polymorph and solvate [30].

1.3. Phase Transformation

A system’s physical nature can be expressed in terms of its phases and it is possible to change the number of phases by adjusting one or more of three variables, such as temperature, pressure and concentration. On the other hand, the chemical nature of a system can be defined in terms of its components and the number of components is constant for any given system. The phase rule is stated using the equation shown below:

$$P+F=C+2 \quad (1.1)$$

where F is the degrees of freedom of the system, C is the number of components and P is the number of phases [31].

A phase transformation can be categorized into two groups from a thermodynamic point of view: Enantiotropy and monotropy. When polymorphs cannot be changed, their crystals have monotropic forms. A polymorph is a stable solid over the entire temperature range up to its melting point due to its monotropic form. Accordingly, the real transition point of the polymorph is not observed below its melting point. On the other hand, at temperatures above the melting point, it can be said that a virtual or extrapolated transition point may be obtained as a result of the thermodynamic aspects. When polymorphs have enantiotropic crystal forms, a reversible transition point, which is also known as an equilibrium point, is observed at temperatures below the melting point of either polymorph. Thus, both polymorphs have a specific temperature range over which they are thermodynamically stable solids [32].

1.4. Glycine

Glycine is the simplest non-essential amino acid present in living organisms, which has attracted a great deal of attention as a model compound in polymorphism studies [33]. The chemistry of the polymorphic forms of glycine has been of great interest to the food and chemical industry, especially in cosmetics in regard to the production of complicated molecules as well as in the pharmaceutical industry, which is facing the increasing demand for new drugs. Three polymorphs of glycine (α -, β - and γ -form) can be crystallized, mostly simultaneously, from an aqueous solution under ambient conditions [9,10]. These polymorphs are different from each other in terms of the arrangement of the $+NH_3-CH_2-COO^-$ zwitterions through hydrogen bonding. At ambient temperature, the α -form of glycine is present in a pure aqueous solution and can be crystallized. For the crystallization of the β - and γ -forms, the glycine dimers in an aqueous solution of the α -form are decomposed; under near equilibrium conditions, crystallization occurs to form the α -form, whereas under non-equilibrium conditions, the β - and γ -forms are formed. Under ambient conditions, the γ -form is the most stable form, which is followed by the α - and β -forms. At elevated temperature, the stability of the α -form is increased, which is then followed by the γ - and β -forms. The β -form is less stable under both reaction conditions and rarely exists. The α -form can be easily formed, whereas the γ -

form can only be crystallized under special conditions [34-36]. Figure 1.2 shows the molecular structure of the glycine polymorphs.

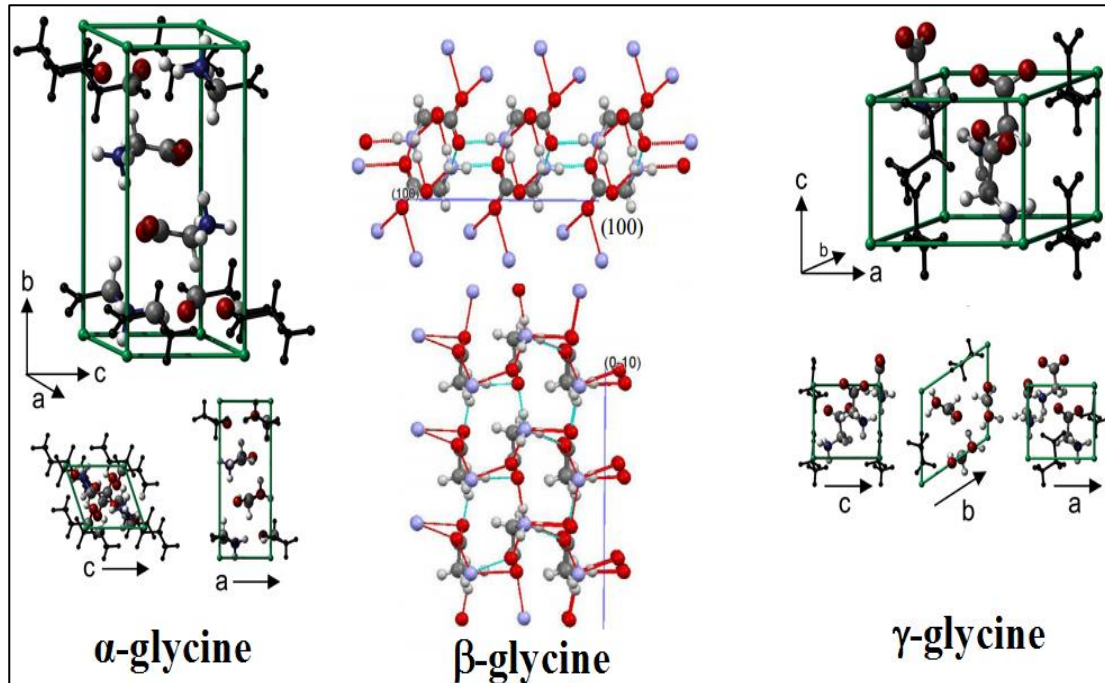


Figure 1.2. Molecular structure of the glycine α , β and γ polymorphs [37,38].

1.5. Calcium Sulfate

Calcium sulfate, a calcium salt, forms naturally as the mineral gypsum; it is one of the most important inorganic materials, with applications in industrial and environmental processes [39]. Contrarily, it can emerge on an undesirable scale inside heat exchangers, pipes, boilers, or seawater desalination equipment, or as a by-product during manufacture of boric and phosphoric acids [7]. Calcium sulfate occurs in three forms: calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and calcium sulfate anhydrite (CaSO_4) depending on crystallization conditions such as supersaturation, temperature, and pH [40]. Calcium sulfate dihydrate has shown to be a stable phase until 97°C and transforming into calcium sulfate hemihydrate in the temperature range $97\text{--}150^\circ\text{C}$; above this temperature anhydrite form becomes a stable phase [41]. The transformation process of calcium sulfate hemihydrate to the dihydrate form in particular has come to the attention of several researchers due to a wide range

of different industrial applications, and commonly, the influences of various additives on this transformation process have been studied [18]. Figure 1.3 shows the different modifications of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ ($x=0.0-2.0$).

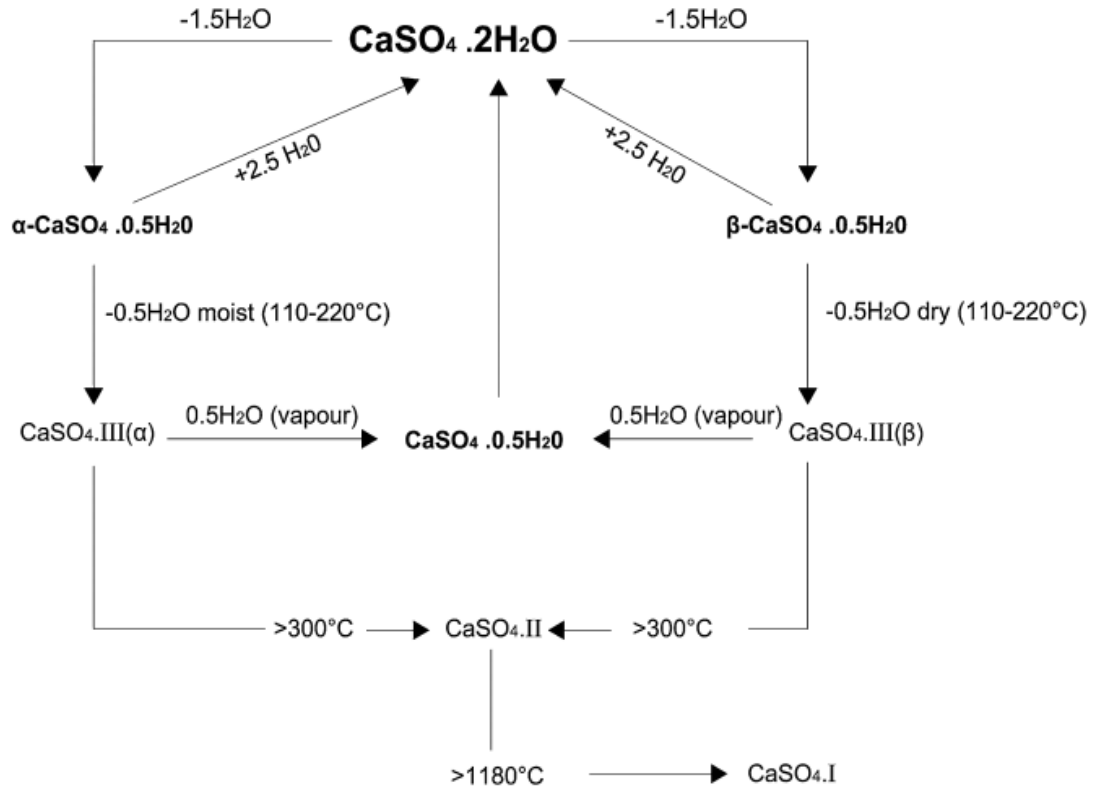


Figure 1.3. Different modifications of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ ($x=0.0-2.0$) [42].

1.6. Effects of Additives or Impurities

Impurities or additives can affect the rates of nucleation and crystal growth, often (or usually) with an effect disproportionate to the amount involved. Part per million levels of impurity have been shown to profoundly influence the size, shape, and rate of growth of some industrially important compounds. Especially impurities or additives are known to profoundly affect crystal morphology [32]. The crystal shape depends on the relative growth rate of the crystal faces. Major impact on the face growth rate is due to the effect of impurities (desired, for example, additives, and undesired) as well as solvents. Depending on the species of the impurity, the molecule may selectively incorporate into the crystal lattice and may block or inhibit the growth of the face. Docherty and

coworkers classify additives as disruptive or blocker type molecules. The disruptive effect of an additive is presented in Figure 1.4.

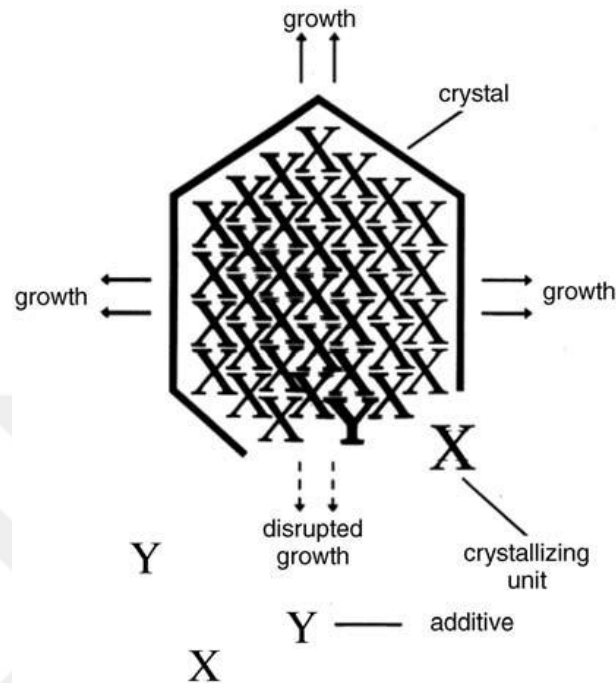


Figure 1.4. Disruptive effects of additives [43].

It is seen that one part of the molecule can incorporate into the crystal lattice (due to the structural similarity), whereas one part of the molecule is significantly different in structure. The adsorption of the new growth layer will be disturbed here, since incorporation of the structural different moiety of the molecules is not possible. The disruptive effect has impact on the growth rate of the face. The inhibited growth of a crystal surface and the thus caused change of the crystal habit [30].

1.7. Fatty Acids

A fatty acid is a carboxylic acid, a group of compounds containing a carboxyl group and expressed as $R-C(O)OH$, where $C(O)OH$ is the structure of carbon, oxygen, and hydrogen atoms that comprises the carboxyl group and R is the remainder of the molecule. Specifically, fatty acids are saturated or unsaturated carboxylic acids with a chain of non-aromatic compounds (also known as aliphatic compounds, one of two classes of compounds made up of carbon and hydrogen). Fatty acids are thus composed

of just three elements in various configurations: carbon, oxygen, and hydrogen [44].

Fatty acids have important roles in signal-transduction pathways; cellular fuel sources; the composition of hormones and lipids; the modification of proteins; and energy storage within adipose tissue (specialized fat cells) in the form of triacylglycerols [45]. Furthermore, fatty acids play roles outside the body; they are used as lubricants, in cooking and food engineering, and in the production of soaps, detergents, and cosmetics [46].

1.7.1. Types of fatty acids

The fatty acids can be generally classified into two groups as follows: saturated and unsaturated fatty acids. Figure 1.5 shows the example of saturated and unsaturated fatty acids structure.

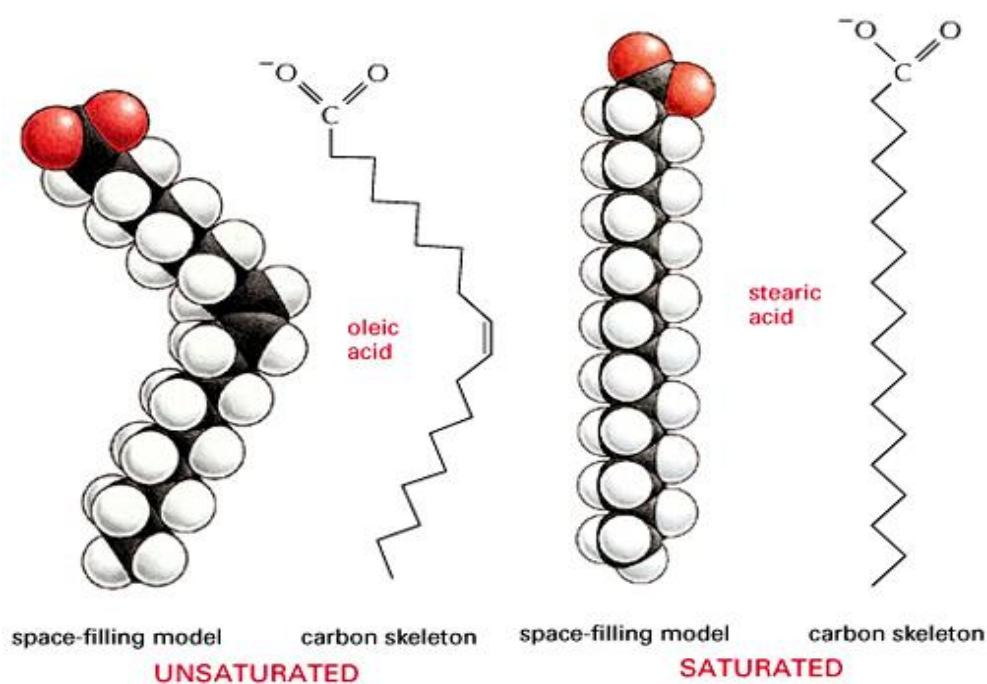


Figure 1.5. Unsaturated and saturated fatty acids [47].

Saturated fatty acids are saturated with hydrogen, and most are straight hydrocarbon chains with an even number of carbon atoms. The most common fatty acids contain 12–

22 carbon atoms. They are typically solid at room temperatures. Table 1.1 shows a list of the most common saturated fatty acids.

Table 1.1. The list of the most common saturated fatty acids [48].

Name	Scientific name	Molecular wt.
Propionic	Propanoic	74.1
Butyric	Butanoic	88.1
Valeric	Pentanoic	102.1
Caproic	Hexanoic	116.1
Oenanthic	Heptanoic	130.1
Caprylic	Octanoic	144.2
Pelargonic	Nonanoic	158.2
Capric	Decanoic	172.3
Undecylic	Undecanoic	186.3
Lauric	Dodecanoic	200.3
Myristic	Tetradecanoic	228.4
Palmitic	Hexadecanoic	256.4
Margaric (Daturic)	Heptadecanoic	270.4
Stearic	Octadecanoic	284.4

Fatty acids with double bonds are unsaturated – either monounsaturated (1 double bond) or polyunsaturated (>1 double bond). Table 1.2 shows the list of the most common unsaturated fatty acids. Monounsaturated fatty acids contain one carbon-carbon double bond, which can be found at different positions throughout the fatty acid chain. The majority of monounsaturated fatty acids are between 16 and 22 carbons in length, and contain a cis double bond. Polyunsaturated fatty acids contain more than one double bond and they are produced only by plants and phytoplankton, and are essential to all higher organisms [45,49].

Table 1.2. The list of the most common unsaturated fatty acids [50].

Formula	Common Name	Melting Point
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	Palmitoleic Acid	0 °C
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	Oleic Acid	13 °C
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	Linoleic Acid	-5 °C
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	Linolenic Acid	-11 °C
$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{CO}_2\text{H}$	Arachidonic Acid	-49 °C

1.8. Carboxylic Acids

Carboxylic acid, any of a class of organic compounds in which a carbon (C) atom is bonded to an oxygen (O) atom by a double bond and to a hydroxyl group (–OH) by a single bond. A fourth bond links the carbon atom to a hydrogen (H) atom or to some other univalent combining group. The carboxyl (COOH) group is so-named because of the carbonyl group (C=O) and hydroxyl group [51].

1.9. Kinetic analysis

The basic kinetic equation for the rate dx/dt of solid-state thermal decomposition is expressed as

$$\frac{dx}{dt} = k(T) f(x) \quad (1.2)$$

where t , $k(T)$ and $f(x)$ indicate the reaction time, the reaction rate constant, and the reaction model, respectively, and x denotes the conversion or weight loss rate. The conversion of decomposed sample is given by:

$$x = \frac{W_0 - W_t}{W_0 - W_f} \quad (1.3)$$

where W_0 and W_f are the initial and final sample mass, respectively, and W_t is the sample weight at time t . The rate constant $k(T)$ can be defined by an Arrhenius-like equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (1.4)$$

where A is the pre-exponential or frequency factor (min^{-1}), E is the activation energy (kJ/mol), T is the absolute temperature (K), and R is the ideal gas constant (8.314 J/mol.K).

The constant heating rate, β , (K/min) is defined as

$$\beta = \frac{dT}{dt} \quad (1.5)$$

For non-isothermal analysis substitution of Eq. (1.5) in Eq. (1.2) gives the relation:

$$\frac{dx}{dt} = \beta \frac{dx}{dT} = k(T)f(x) = A \exp\left(-\frac{E}{RT}\right)f(x) \quad (1.6)$$

Integration of Eq. (1.6) gives

$$\int_0^x \frac{dx}{f(x)} = g(x) = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} p(u) \quad (1.7)$$

where $p(u)$ and $g(x)$ show the temperature integral and the integrated reaction model, respectively. Eq. (1.7) can be solved by making certain approximations, depending on the applied kinetic method. In the present study, the activation energy was determined using the isoconversional method as this method provides a practical solution, enables determination of the effect of activation energy for decomposition and does not require the assumptions necessary with specific reaction models. Using the isoconversional method, even complex processes, including those involving many reactions simultaneously, can also be described. Therefore, for calculation of the activation energy, various kinetic models that are based on the isoconversional method can be used.

In this study, evaluations were performed based on the Flynn-Wall-Ozawa (FWO), Friedman, Starink, and Kissinger-Akahira-Sunose (KAS) models, which are the most frequently used for thermal decomposition kinetics [52-54]. The general model equations and the plotting methods are shown in Table 1.3.

Table 1.3. The general kinetic model equations for FWO, Friedman, Starink and KAS models.

Kinetic model	General model equations	Plotting method
FWO	$\ln(\beta) = \ln\left(\frac{AE}{Rg(x)}\right) - 5.331 - 1.052 \frac{E}{R} \frac{1}{T}$	$\ln(\beta)$ vs $(1/T)$ Slope= $-1.052E/R$
Friedman	$\ln\left(\beta \frac{dx}{dT}\right) = \ln\left(\frac{dx}{dt}\right) = \ln[Af(x)] - \frac{E}{RT}$	$\ln(\beta dx/dT)$ vs $(1/T)$ Slope= $-E/R$
Starink	$\ln\left(\frac{\beta}{T^{1.92}}\right) = C - 1.0008 \frac{E}{RT}$	$\ln(\beta/T^{1.92})$ vs $(1/T)$ Slope= $-1.0008E/R$
KAS	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(x)}\right) - \frac{E}{RT}$	$\ln(\beta/T^2)$ vs $(1/T)$ Slope= $-E/R$

The activation energy for the decomposition reaction of the crystals obtained in pure and in the presence of additive can be calculated by using the slope of the plots obtained by using the above linearized forms of the equations.

In the present study, a simplified distributed activation energy model (DAEM) was also used to determine thermal kinetic parameters including the activation energy of the crystals obtained from a pure solution or solutions containing 500 ppm of the different carboxylic acid additives (acetic, tartaric and citric acid). The DAEM model assumes that the decomposition mechanism requires many reactions, which have different activation energies that show the changes in the bond strengths of the species and are irreversible, independent, parallel and first order. DAEM is especially compatible with the experimental data, which was obtained under low heating temperature conditions in the range of 5–40 °C/min [55]. For this reason, heating rates of 5, 10 and 20 °C/min were used in this study. The main features of this well-known method are given below.

The integral form of the thermal decomposition can be expressed using equation (1.8).

$$1 - V/V^* = \int_0^\infty \exp\left(-\frac{A}{\beta} \int_0^T e^{-E/RT} dT\right) f(E) dE \quad (1.8)$$

where V refers to the volatile content at absolute temperature T , V^* is the effective volatile content, A is a frequency factor, E is the activation energy and R is the universal gas constant.

The distribution curve, $f(E)$, can be expressed using equation (1.9).

$$\int_0^{\infty} f(E) dE = 1 \quad (1.9)$$

The DAEM given in equation (1.10) was obtained using the Miura–Maki modification [56] of equation (1.10).

$$V / V^* = 1 - \int_E^{\infty} f(E) dE = \int_0^E f(E) dE \quad (1.10)$$

where E refers to the activation energy at a specific temperature. With relevant integral calculations, the Arrhenius equation of the simplified DAEM can be expressed using equation (1.11).

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT} \quad (1.11)$$

Equation (1.11) provides the calculations used for the kinetic parameters of the thermal decomposition process under both inert and oxidative conditions. The plot of $\ln(\beta/T^2)$ vs. $1/T$ is a linear line at each fractional transformation and from the slope and intercept of this line it is possible to calculate the activation energy and frequency factor, respectively.

1.10. Theoretical Equations for Adsorption

It is well known that adsorption defines as the accumulation of a substance at a surface or interface. It is one of the most important techniques with extensive application in industrial and environmental processes. In the literature, there are several studies and various industrial applications on adsorption especially in water treatment, construction and medical industries [57-61]. In the current study, the adsorption technique was used to determine the quantity of the adsorbed additive, and to gain information about the detailed adsorption characteristics.

1.10.1. Adsorption isotherms

The adsorption isotherms are important both to describe the interaction between adsorbate and adsorbent in equilibrium and to provide fundamental information on the process. There are various isotherm models proposed in published literature. In this study, the most frequently used three isotherm models, which are Langmuir, Freundlich and Temkin were employed. While Langmuir isotherms assume monolayer adsorption, including homogeneous interactions with the solute, the Freundlich isotherm is associated with multilayer adsorption onto the heterogeneous adsorbate surface [62,63]. Moreover, the Temkin model was also used to investigate the adsorption isotherm in this study. This isotherm predicts that adsorption energy decreases linearly with surface coverage because of the interaction between adsorbent particles and the adsorbate [64]. The isotherm parameters obtained from the Langmuir, Freundlich and Temkin models at different temperatures were calculated with the help of the linear expressions, and their respective expressions are given in Table 1.4.

Table 1.4. Adsorption isotherm models and their linear expressions.

Isotherms	Linear expression	Y-axis	X-axis
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e}$	C_e
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$	$\ln C_e$
Temkin	$q_e = B \ln K_T + B \ln C_e$	q_e	$\ln C_e$

In addition to linear form, the non-linear form of the Langmuir model equation is given below in Eq. (1.12).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1.12)$$

where q_e (mg/g) is the adsorbed amount at equilibrium concentration, q_m indicates the maximum adsorption capacity (mg/g), K_L is the Langmuir binding constant (L/mg), C_e is the equilibrium additive concentration (mg/L).

The dimensionless equilibrium parameter, or the adsorption intensity (R_L), based on the essential characteristics of Langmuir isotherm, can be defined by Eq. (1.13) below.

$$R_L = \frac{1}{1 + K_L C_i} \quad (1.13)$$

where C_i (mg/L) is the initial additive concentration. The parameter R_L shows the favorability and feasibility nature of the adsorption. In general, there are four probabilities: $R_L=0$ (irreversible adsorption); $0 < R_L < 1$ (favorable adsorption); $R_L=1$ (linear adsorption); and $R_L > 1$ (unfavorable adsorption) [65].

The Freundlich isotherm is often applied for heterogeneous adsorption surfaces and for when active sites have different energies [66]. The non-linear form of the Freundlich equation is shown below in Eq. (1.14).

$$q_e = K_F C_e^{1/n} \quad (1.14)$$

In Freundlich isotherm models, K_F (mg/g)(L/mg)^{1/n} and n are the constants indicating the relative adsorption capacity and intensity of adsorption, respectively. The values of n and $1/n$ give information regarding the favorability of adsorption and heterogeneity factor, respectively. In general, $n > 1$ shows that the type of adsorption isotherm is favorable and that greater n values are associated with higher adsorption intensities. The expression $0 < (1/n) < 1$ is an indication of the adsorption intensity of the surface heterogeneity, and as the $1/n$ value approaches zero, the heterogeneity of the surfaces increase [63].

The Temkin model is also used to model adsorption isotherms. The Temkin isotherm is basically used to determine the interactions between the adsorbents and additives to be adsorbed assuming that the free energy of adsorption is a function of the surface coverage [67]. The Temkin model is described using Eq. (1.15) below.

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (1.15)$$

$$B = \frac{RT}{b_T} \quad (1.16)$$

where K_T is the equilibrium binding constant (L/mg). The constant b_T shows the Temkin isotherm constant related to the heat of adsorption [68].

1.10.2. Adsorption kinetics

Kinetics is a major parameter used to evaluate adsorption processes. The adsorption kinetic models provide important details for designing of sorption systems and for selecting optimum operating conditions [69,70]. In this study, uptake kinetics of the additives sorption on the adsorbent was analyzed using four kinetic models: pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models.

The pseudo-first-order model proposed by Lagergren takes into account the adsorption kinetics process of the solid-liquid phase based on adsorption capacity [71]. The pseudo-second-order model is designated for evaluating the chemisorption kinetics [72]. The other popular model, Elovich, considers the chemical interaction between the adsorbate ions and the surface sites [73]. Apart from these three models, the intra-particle diffusion model takes into account the diffusion effects of the adsorption kinetics. This model provides comprehensive information for expressing the transportation process of adsorbate molecules. In the case when the adsorption process is controlled by intra-particle diffusion, the model should show a linear plot, and this plot should pass through the origin [74]. Otherwise, it suggests that the intra-particle diffusion is not a rate-controlling step and it could include other mechanisms. The models used and their linear expressions are shown in Table 1.5.

In addition to linear form, the non-linear form of the pseudo-first order model equation is shown below in Eq. (1.17).

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1.17)$$

where q_e and q_t are the specific amounts of the additive adsorbed (mg/g) at equilibrium and time t (min), respectively. The expression k_1 is the pseudo-first order rate constant (1/min) [75].

Table 1.5. Adsorption kinetic models and their linear expressions.

Kinetic model	Linear expression	Y-axis	X-axis
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$	$\log(q_e - q_t)$	t
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$	t
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	q_t	$\ln t$
Intraparticle diffusion	$q_t = k_p t^{0.5} + C$	q_t	$t^{0.5}$

The adsorption data were also studied in terms of a pseudo-second order mechanism. The non-linear forms of the pseudo-second order reaction are given below by Eq. (1.18).

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (1.18)$$

where k_2 is the second order constant, q_e and q_t are the amounts of additive adsorbed at equilibrium and time t , respectively [76].

1.10.3. Adsorption thermodynamics

The values of certain thermodynamic parameters (i.e., standard enthalpy change (ΔH°), standard Gibbs free energy change (ΔG°), and standard entropy change (ΔS°), must be taken into consideration to understand the mechanism of the spontaneous process [77].

ΔG° is a critical factor for determining the spontaneity of the process, and it can be calculated using Eq. (1.19) below.

$$\Delta G^\circ = -RT \ln K_e \quad (1.19)$$

where T is the absolute temperature (K) and R is the gas constant (8.314 J/mol K). The adsorption equilibrium constant can be defined by Eq. (1.20) below.

$$K_e = \frac{q_e}{C_e} \quad (1.20)$$

where q_e and C_e are equilibrium concentrations of adsorbed carboxylic acid on the adsorbent and in the solution, respectively.

Using the Van't Hoff equation, the equilibrium constant can be expressed in terms of enthalpy change (ΔH°), and entropy change of adsorption (ΔS°) in terms of functions of temperature [78].

$$\ln K_e = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (1.21)$$

1.11. Literature Sources of Glycine and Calcium Sulfate Hemihydrate

Glycine is the smallest protein-forming amino acid and is an all-purpose material, employed in different applications in various fields. The polymorphism phenomenon exhibited by glycine adds to its merits [13]. A thorough grasp of the phase transformation process is needed, both for control of polymorphism and in the production of high-quality final products with desired physical properties. Previous studies have revealed that operating conditions of crystallization, such as pH, temperature, initial concentration, and additives, can affect phase transformation and physical properties of the end-products. Therefore, using additives to control phase transformation and physical properties has received considerable attention [2]. Some studies indicate that different polymorphs can be formed with different physical properties with the presence of additives in crystallization media [79]. Hrkovac et al. explored the effects of sodium chloride and oxalic acid used as additives on glycine crystallization. They found that both additives and their amounts affected the solubility, the width of the metastable zone, crystal size distribution, and crystal morphology of glycine [8]. A similar study performed by Yang et al. used sodium chloride as the additive, which had significant effects on the nucleation and polymorphic transformation of glycine. The presence of that additive caused a change in the nucleation of γ -glycine [80]. Another study performed by Losev et al. examined the impacts of various carboxylic acids such as acetic, oxalic, malonic, succinic, maleic,

glutaric, and L-malic acid on glycine polymorphism. Except for glutaric acid, all other acids studied affected the polymorphism of glycine [81].

Some studies have indicated that different polymorphs can be formed with different physical properties when systems are treated with ultrasound. Nii and Takayanagi [25] performed a study to investigate the impact of high-frequency ultrasound on the crystallization behavior of the polymorphs of glycine in a water–ethanol system. The transformation between β and α forms was carried out in non-sonicated and sonicated media. Ultrasonic transducers operating at 1.6 MHz and 20 kHz were used and the influence of ultrasonic frequency was investigated by comparing the resulting crystals produced by these two ultrasound frequency. They found that the crystal size was reduced at low frequency ultrasound; however, ultrasound enhanced both the growth rate of α -glycine crystals and the incorporation of microcrystals into larger crystals. Renuka et al. [26] studied to determine the higher ultrasonic frequency effects on the nucleation and growth characteristics of glycine. The experiments were performed at different ultrasound frequencies in the range of 1–10 MHz. They found that higher ultrasound yielded a higher nucleation rate but with a smaller crystal size compared to the crystals obtained in the absence of ultrasound. A similar study performed by Louhi-Kultanen et al. [27] showed that ultrasound affected the crystal morphology and crystal size distribution of glycine.

In addition, astrobiologists are interested in the potential role of glycine – being the simplest amino acid –in the origin of life on Earth and in evolution. Furthermore, glycine is seen to be important because scientists have actually spotted the molecule beyond Earth. Glycine has been found in bodies in the solar system and in meteorites, and there are also numerous studies that reveal glycine exists in meteorites that have fallen to earth [33,82]. Therefore, scientists have been constantly interested in the potential role of glycine beyond Earth, and this subject has drawn the attention of numerous research groups. Previously conducted studies have indicated that ultraviolet radiation can be a parameter in the formation of glycine [83-85].

Calcium sulfate is one of the most significant inorganic compounds and is used for a variety of purposes in the ceramic, construction, fertilizer, plastic, paper and medical industries [15,16]. The transformation process of calcium sulfate hemihydrate to the dihydrate form in particular has come to the attention of several researchers due to a wide

range of different industrial applications, and commonly, the influences of various additives on this transformation process have been studied [18]. Additives such as metal ions [86], amino acids [87], carboxylic acids [88] and inorganic salts [89] have been found to greatly impact the quality of the product and the transformation process. The crystal-specific characteristics such as crystal size distribution, purity, shape or size can be changed, along with the transformation rate that can be accelerated or retarded by an additive in the media. Wang and Meldrum [41] investigated the influence of the various additives: poly acrylic acid, poly-sodium-4-styrene sulfonate, sodium triphosphate and magnesium chloride, on the intermediate phases, stabilities and morphology of calcium sulfate. They found that these additives had an inhibitory effect on calcium sulfate precipitation, and they significantly affected the crystal morphology. Boisvert et al. explored the retarding effects of the additive sodium poly(acrylate), which is a polyelectrolyte, on the transformation of calcium hemihydrate to dihydrate [90]. While the adsorption of the additive on hemihydrate did not inhibit its dissolution, the adsorption on dihydrate did retard the crystal growth. Another study, performed by Azimi and Papangelakis, examined the influence of sulfate and chloride salts during the hydration of calcium sulfate hemihydrate and determined that the addition of NaCl accelerated the transformation, but that NiSO_4 caused inhibition [39]. In a study conducted to examine the effect of a citric acid additive on the transformation process, it was found that low citric acid concentrations blocked calcium sulfate dihydrate nucleation and growth [91]. Similar research was also performed by Badens et al. where citric acid, as well as adipic, malic, and meso-tartaric acid, were used to determine their influence on the transformation process [92]. The retarding effect of the citric and malic acid were shown to be stronger than that of the other additives. In the Baden study, the adsorption mechanism of the additives at the surface of the samples was explained. The influence of additives on transformation can involve different mechanisms. Yet the main mechanism is the physical or chemical binding of the additives onto the crystal surface. Studies have also shown that even a small amount of these additives adsorbed by the crystal structure changes the nucleation rate, shape of the crystals, crystal growth and their agglomeration or dispersion behavior, and surface properties [42,91].

2. MATERIALS AND METHODS

2.1. Materials

The analytical-grade pure powdered α -glycine, ethanol, calcium sulfate dihydrate, fatty acids such as lauric acid, butyric acid, oleic acid and myristic acid, carboxylic acids such as acetic acid, tartaric acid, citric acid, propionic acid, glutamic acid and propane-1,2,3-tricarboxylic acid (tricarballic acid) were procured from the Merck Company. Triple-distilled water was used in all experiments.

2.2. Transformation of β - to α -Glycine Experiments

2.2.1. Effect of fatty and carboxylic acids on polymorphic transformation of glycine

The polymorphic phase transformation of β -glycine to α -glycine was investigated using a 2L-capacity double-jacketed cylindrical glass crystallizer with a 130 mm internal diameter and 150 mm length. The crystallization experiments were carried out at a constant 25 ± 0.1 °C temperature and 75 rpm stirring speed. The crystallizer's inner temperature was controlled by means of a thermostat. A paddle type Teflon stirrer with a width of 75 mm and 70mm height was chosen as the stirrer type. All experimentation was performed in triplicate. A schematic representation of experimental set-up is given in Figure 2.1.

The process for the transformation of β -glycine to α -glycine was performed as follows: At the beginning of the experiment, according to solubility data at 25 °C, the appropriate amount of α -glycine was dissolved in 500 ml of triple distilled water and filtered using a membrane filter with a nominal pore size of 0.45 μ m. The saturated and filtered solution of α -glycine was placed in the crystallizer, stirred well at 75 rpm, and kept at 25 °C in media. After reaching thermal equilibrium, polymorph β was produced from anti-solvent crystallization. The volume fraction of ethanol used as anti-solvent in the suspension was 0.67. When the anti-solvent cooled to 5 °C was rapidly mixed with the saturated solution, the β form appeared instantly and then slowly transformed into the α form. An ultrasonic sensor (LiquiSonic 30, SensoTech GmbH, Germany) measuring the ultrasonic velocity of the solution with 0.01 m/s accuracy was placed in the crystallizer to continuously monitor the transformation process. This sensor emits longitudinal ultrasonic waves with very low frequency and these waves do not have a cavitation effect in the suspension. All data

related to the change in ultrasonic velocity with respect to time was recorded online from the computer and used to determine transformation time.

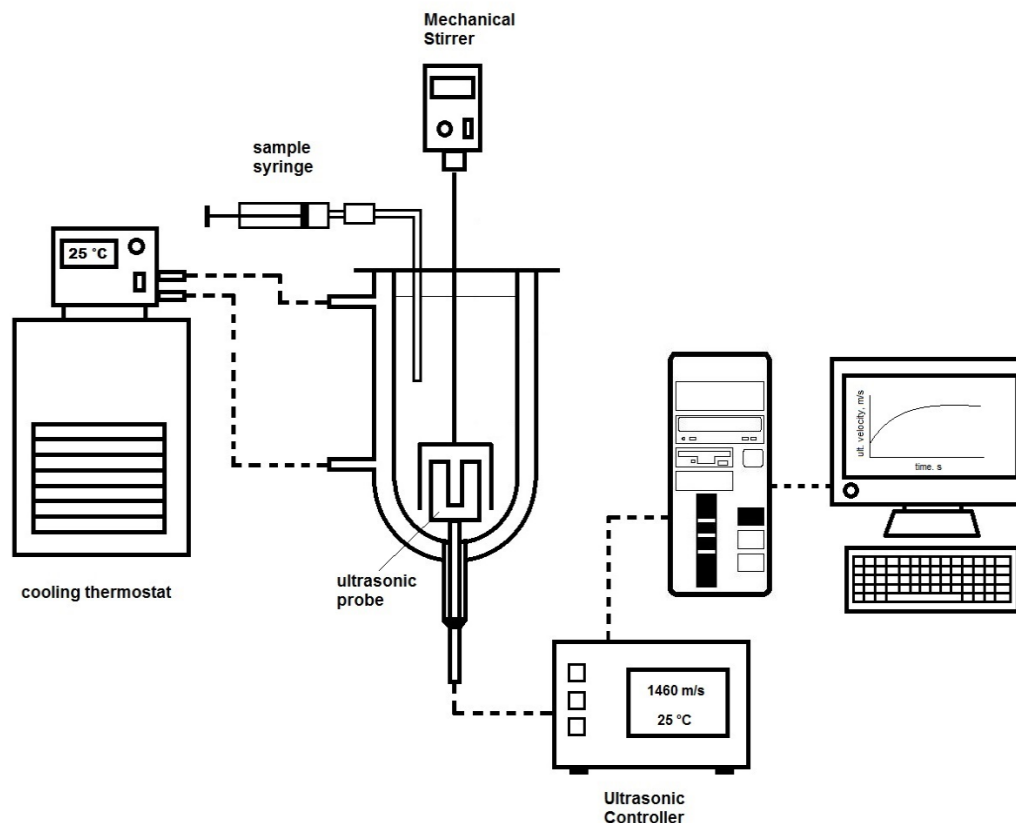
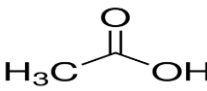
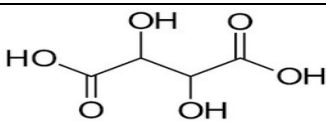
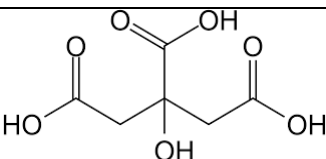


Figure 2.1. Experimental set-up for fatty and carboxylic acids media.

The experiments were performed at three different concentrations of 50, 100, and 250 ppm using lauric acid, butyric acid, oleic acid and myristic acid as the additives and at constant 500 ppm acetic acid, tartaric acid and citric acid concentrations. Fatty acids and carboxylic acids were added to the crystallization media with ethanol. The general properties of these carboxylic acids including acetic acid (monocarboxylic acid), tartaric acid (dicarboxylic acid) and citric acid (tricarboxylic acid) are shown in Table 2.1.

During phase transformation process, both pure and additive media, the samples were taken from the crystallizer at specific time intervals using a syringe. Once the sample was taken, it was immediately filtered and dried. X-ray diffraction (XRD) analysis and microscopic analysis of the samples taken were performed. After the transformation process was completed, various analyses were carried out to characterize the end product obtained in a non-additive media and in the presence of fatty and carboxylic acids.

Table 2.1. Properties of carboxylic acids.

Carboxylic acid	Chemical formula	Molecular weight (g/mol)	Chemical structure
Acetic acid	C ₂ H ₄ O ₂	60.05	
Tartaric acid	C ₄ H ₆ O ₆	150.09	
Citric acid	C ₆ H ₈ O ₇	192.12	

2.2.2. Effect of ultrasonic irradiation on polymorphic transformation of glycine

To determine the influence of ultrasonic irradiation on the polymorph transformation, an ultrasonic probe was directly immersed into the suspension and ultrasound was applied at the top of the crystallizer with a titanium tip. A schematic representation of experimental set-up is given in Figure 2.2.

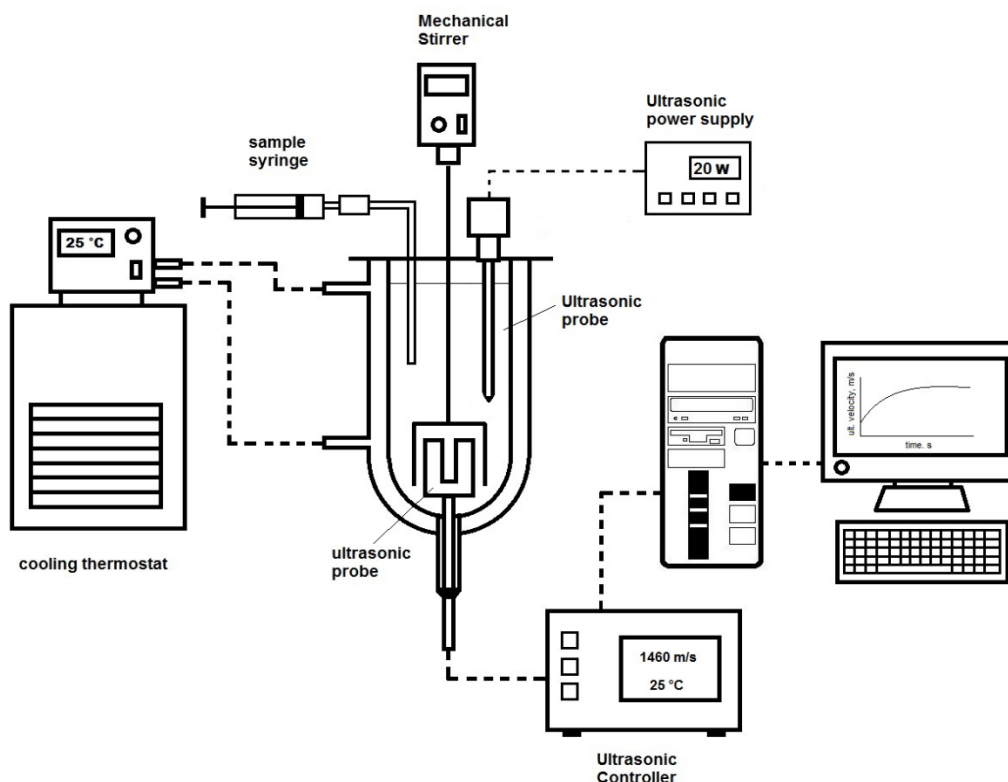


Figure 2.2. Experimental set-up for ultrasonic irradiation media.

Bandelin ultrasound homogenizer Sonopuls HD 2200 equipped with a 3 mm diameter immersion probe was used as the ultrasonic source, working at 20 kHz frequency and 200 W maximum power. The experiments were conducted at three different ultrasonic powers of 20, 30, and 40W. During the transformation process, both without and with ultrasonic irradiation, the samples were withdrawn from the crystallizer at regular time intervals, quickly filtered, and then the solid phase was dried and analyzed.

2.2.3. Effect of UV radiation on polymorphic transformation of glycine

Eight, twelve and twenty Watt, high energy, short wavelength (254 nm) ultraviolet lamps were used as UV radiation sources to investigate the effects of ultraviolet radiation and its intensity on the glycine transformation process. As shown in Figure 2.3, an appropriate intensity UV radiation source was also placed in the crystallizer, within the quartz tube, at the beginning of the experiments.

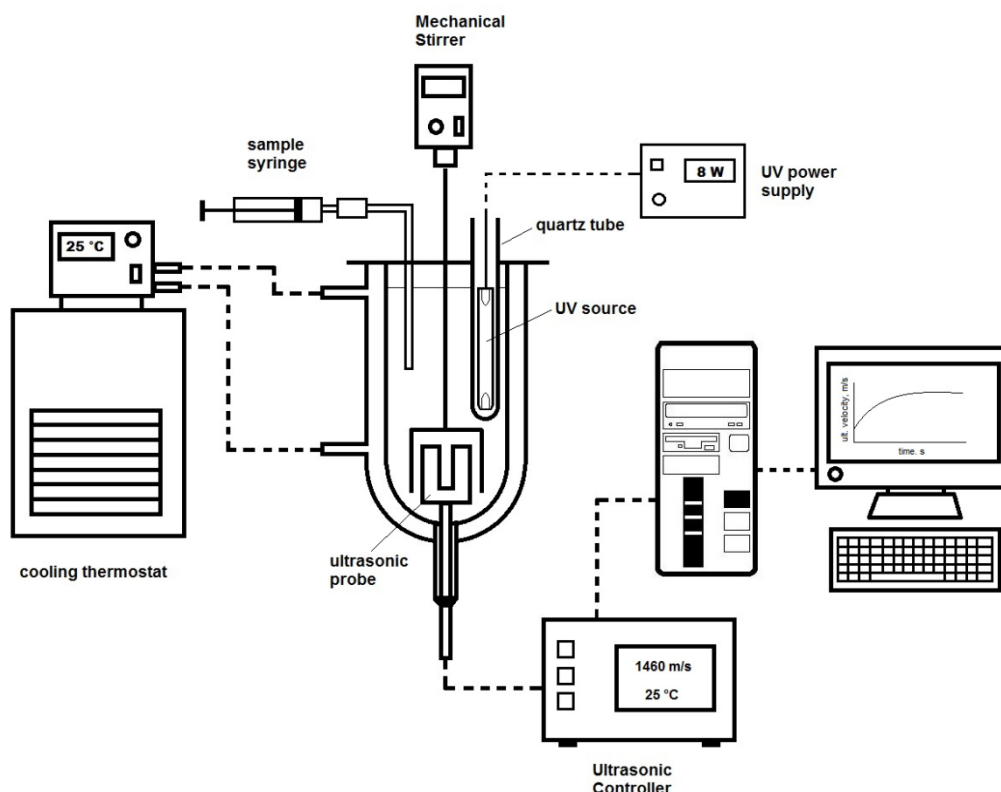


Figure 2.3. Experimental set-up for UV radiation media.

In order to demonstrate the possible effects of UV radiation and its intensity on glycine phase transformation, all experiments were repeated in the presence of a selected model additive. The use of additive was also beneficial for in-depth investigation of UV radiation impact on glycine crystals. Among the various types of carboxylic acids, propane-1, 2, 3-tricarboxylic acid was preferred in the current study due to its cost effectiveness, high efficiency, availability and easy handling. The experiments were carried out at 500 ppm additive concentration.

During the transformation process, the suspension was withdrawn from the crystallizer at chosen time intervals, quickly filtered, and then the solid phase was dried. The solid phase was subjected to various analyses for characterizing the end product obtained in pure media and in the presence of varying UV radiation sources.

2.2.4. Analysis

2.2.4.1. XRD analysis

The phase identification of the crystals was completed by X-ray diffraction (Bruker D2 Phaser Table-top Diffractometer) equipped with an X-Ray tube containing a copper anticathode. The XRD patterns were recorded over a 2θ range between 10° and 50° using a step size of 0.01. The same particle sizes and the same amount of samples were used in the experiments. The particle size of the crystals between 38 and 45 μm was used for the XRD analysis.

Quantitative phase analysis of the samples was accomplished using the Rietveld refinement method employing the Materials Analysis Using Diffraction (MAUD) software developed by Wenk, Matthies & Lutterotti and Ferrari & Lutterotti.

2.2.4.2. SEM and morphology analysis

SEM analysis was performed using a Zeiss EVO LS 10 device to evaluate the surface morphology of the crystals and to investigate the effects of additives on glycine crystals. To get a better insight into the size and shape characteristics of the crystals obtained with and without additives, the crystals were characterized using a Malvern Morphologi G3 instrument. This instrument allows analysis of the shape and size parameters by means of scanning and recording the images of all measured crystals. The $10\times$ lens was utilized for

all the analysis.

2.2.4.3. Particle size and elemental analysis

The particle size of the crystals was determined by means of the laser diffraction particle size analyzer (Malvern Mastersizer 2000). For the analysis, the crystals were dispersed in α -glycine saturated solution. The suspension was put into the particle size analyzer by using the feeding module and then the analysis was carried out. The results were recorded in the range of 0.1 to 1000 μm and approximately 10.000-15.000 particles counted for each analysis.

The elemental analysis of the crystals was carried out using a LECO 628 Series CHN elemental analyzer.

2.2.4.4. FTIR analysis

A Fourier transform infrared (FTIR) spectra of the crystals with and without additives was recorded using a Perkin Elmer Spectrum 100 model Fourier Transform Infrared Spectrometer in the range of 4000 to 650 cm^{-1} to obtain more information about the functional groups of the crystals.

2.2.4.5. TG analysis

Thermogravimetric analysis (TGA) was applied by using Setaram LABSYS Evo Thermal Analyzer to evaluate the thermal behavior of the crystals obtained in pure media and in the different additive media. The thermal decomposition of crystals obtained was examined between 30 and 800 $^{\circ}\text{C}$ under inert atmosphere. The experiments were applied to a 10 ± 0.1 mg sample with a 20 mL/min nitrogen flow and three different heating rates (5, 10 and 20 $^{\circ}\text{C}/\text{min}$).

2.2.4.6. TG/FTIR/MS analysis

The crystals obtained in pure media and in the presence of additives were simultaneously analyzed via thermogravimetric analysis (TGA) coupled with a mass spectrometer (MS) (Pfeiffer Omni Star) and a Fourier transform infrared (FTIR) spectrum to characterize the crystalline product and to detect gas produced by the phase transformation of glycine. The

transfer line for TGA/MS and TGA/FTIR were heated up to 190 and 225 °C, respectively. During the TGA/MS analysis, the scanning was performed in a range from 2 to 150 m/z under an electron impact ionization energy of 70 eV. FTIR spectra were recorded in the range of 4000 and 650 cm⁻¹.

2.2.4.7. DSC analysis

Differential scanning calorimetry (DSC) was also used to determine the polymorphic forms of the crystals. 5 ± 0.5 mg of the sample was taken in an aluminum pan and heated over the temperature range between 30 and 400 °C at a heating rate of 10 °C/min under a constant N₂ flow rate.

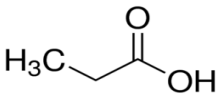
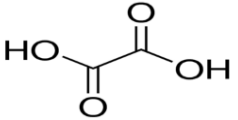
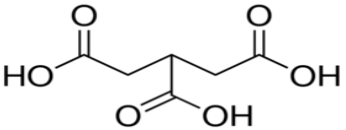
2.2.4.8. Filtration analysis

Filtration speed measurements were performed by using a Millipore standard laboratory vacuum filtration at a constant pressure of 700 mbar. Once the transformation process was complete, 250 ml of suspension extracted from the crystallizer was transferred to the filtration unit, and then collection time for each 10 ml of filtrate under constant pressure was measured and recorded. At the end of the process, total filtrate volume and filter cake height were measured. The obtained results were evaluated according to Darcy's law, whereby glycine filtration characteristics like average specific cake resistance and average cake porosity were calculated.

2.3. Transformation of calcium sulfate hemihydrate to dihydrate experiments

The transformation process of calcium sulfate hemihydrate to calcium sulfate dihydrate was carried out in both the absence and the presence of the additives in a batch type crystallizer. The batch crystallization experiments were performed in a 500 mL cylindrical double-jacketed glass crystallizer. As the additives, propionic acid, glutamic acid and propane-1,2,3-tricarboxylic acid (tricarballic acid) were used at several concentrations, ranging from 250 ppm to 2500 ppm, to determine the effects of these additives at different concentrations on this transformation process. The general characteristics of these carboxylic acids including propionic acid (monocarboxylic acid), glutamic acid (dicarboxylic acid) and propane-1,2,3-tricarboxylic acid (tricarboxylic acid) are represented in Table 2.2.

Table 2.2. Characteristics of carboxylic acids.

Carboxylic acid	Chemical formula	Molecular weight (g/mol)	Chemical structure
Propionic acid	$C_3H_6O_2$	74.08	
Glutamic acid	$C_5H_8O_4$	90.03	
Propane-1,2,3-tricarboxylic acid	$C_6H_8O_6$	176.12	

The crystallizer inner temperature was adjusted by circulating water from the thermostated bath into the crystallizer jacket, with the stirring performed via a magnetic stirrer at 300 rpm constant stirrer rate. The pH was continuously controlled during the transformation process and the suspension pH was kept constant at 2.5. This value was determined by pre-experiments which were performed before in the same crystallization system for three different carboxylic acid concentrations. The initial pH values of saturated solution were measured ranging from 5.5 to 2.5 for different additives concentrations at 20 °C, respectively. The biggest change in pH was observed for 2500 ppm carboxylic acids concentration. By taking into account of these results, all experiments were carried out at 2.5 pH. The pH values were adjusted by addition of diluted sulfuric acid solution from a different line via a peristaltic pump and measured by using a pH meter which was connected to a pH control unit. The transformation process was followed by continuous recording of conductivity values using a conductometer (WTW inoLab Cond Level 2). Figure 2.4 shows the experimental set-up.

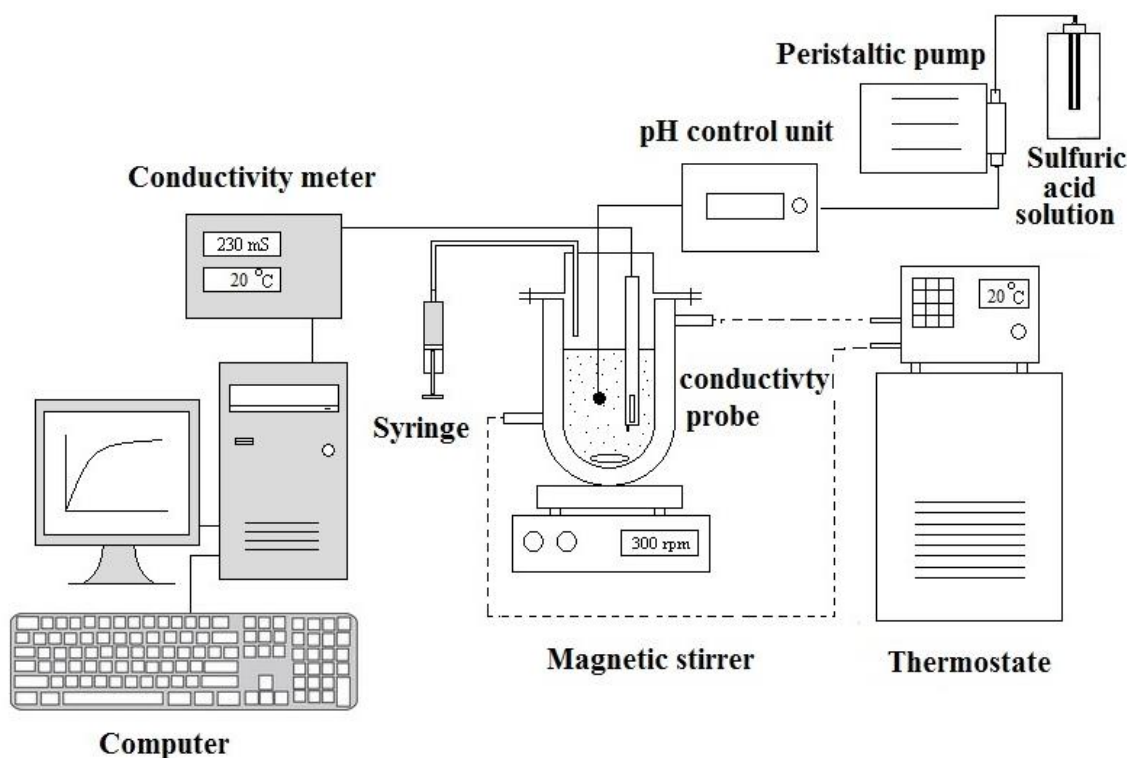


Figure 2.4. Experimental set-up.

The transformation procedure was performed in pure media as follows: 400 mL of saturated calcium sulfate solution was placed into the crystallizer, stirred well at 300 rpm, and kept at 20 °C. In the presence of propionic acid, glutamic acid and propane-1,2,3-tricarboxylic acid, at the beginning of the experiments, a previously determined required amount of analytical grade carboxylic acids studied, corresponding to a given concentration, was also put into the crystallizer. 100, 400 and 1000 mg propionic acid, glutamic acid and propane-1,2,3-tricarboxylic acid was added to the crystallizer for 250, 1000 and 2500 ppm additive concentrations, respectively. Next, 10 g of calcium sulfate hemihydrate was added into the solution to obtain a suspension. During the transformation process, suspension samples of 10 mL were taken from the crystallizer at selected time intervals and quickly filtered through syringe filters that had a nominal pore size of 0.45 μm . The filtrate was then examined using the Thermo Scientific Evolution 300 UV-Vis Spectrophotometer to detect the influence of initial carboxylic acid concentration, temperature and contact time on the transformation process. The initial additive concentration, contact time and temperature varied within a range of 250-2500 mg/L, 0-150 min and 20-40 °C respectively.

The amount of the additive adsorbed per unit mass of the adsorbent (q_e) was determined by the mass balance equation,

$$q_e = \frac{(C_i - C_e) \times V}{W} \quad (2.1)$$

where C_i and C_e is the initial and equilibrium additive concentration (mg/L), W is the mass of adsorbent (g) and V is the solution volume (L).

At the end of each experiment, meaning at the completion of the transformation process, the entire suspension was taken from the crystallizer and filtered to determine the character of the samples obtained in the absence and the presence of carboxylic acids studied. The solid part obtained from the filtration was washed with saturated calcium sulfate solution. The crystals were then dried at room temperature to a constant weight. These crystals were used to perform the various analyses. For the first analysis, the crystal size distributions were determined via a laser diffraction particle size analyzer (MALVERN 2000). Next the samples were subjected to morphology observations using a scanning electron microscopy (SEM) to investigate the crystal habit change. The crystal structure was identified by X-ray diffraction (XRD) using Cu $K\alpha$ radiation. The surface area of the crystals obtained in pure media and in the presence of additive were measured by means of Brunauer–Emmett–Teller (BET) nitrogen adsorption method. Moreover, the obtained crystals were analyzed simultaneously via thermogravimetric analyzer (TGA) coupled with a fourier transform infrared spectrometer (Thermo Nicolet IZ 10) and a mass spectrometer (Pfeiffer Omni Star) to characterize the samples. The transfer lines between TGA and FTIR and TGA and MS were kept at 225 °C and 190 °C, respectively. FTIR spectra were recorded between 4000 and 700 cm^{-1} at 4 cm^{-1} resolutions with 32 scans, whereas the MS analysis was in the 2 to 150 m/z range. Lastly, a Fourier transform infrared spectrometer (ATR-FTIR) analysis was performed to determine the functional groups of the samples.

3. RESULTS AND DISCUSSION

3.1. The Results of Lauric Acid Effects on Polymorphic Phase Transformation of Glycine•

3.1.1. Ultrasonic velocity measurement

The ultrasonic velocity through liquid media is a physical property that depends on the density and adiabatic compressibility of the media, which changes with temperature, concentration and pressure. Changing the ultrasonic velocity of a solution has been successfully used to measure the in-situ changes in concentration of a solute. The polymorphic phase transition can be monitored using the change in the ultrasonic velocity; the change in the concentration and thereby the change in the ultrasonic velocity can be observed during the polymorphic phase transition due to the dependence of the ultrasonic velocity on the concentration [93]. Therefore, the polymorph transformation process of β -glycine to α -glycine in pure media was monitored through online measurement of the ultrasonic velocity in this study. The results of polymorphic phase transformation of β -glycine to α -glycine crystals, as monitored by ultrasonic velocity measurement, are illustrated in Figure 3.1.

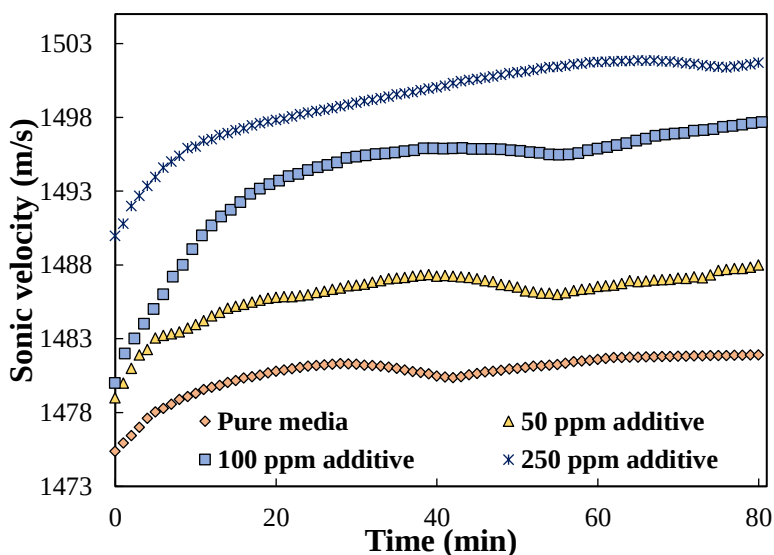


Figure 3.1. Variation of ultrasonic velocity in terms of time for the crystals obtained in pure solution and solutions containing different concentrations of lauric acid.

• Polat, S., Sayan P. (2018) Kinetic analysis and polymorphic phase transformation of glycine in the presence of lauric acid. *Journal of Crystal Growth*, 481, 71-79.

The results of the ultrasonic velocity measurement obtained in the presence of different lauric acid concentrations are presented in Figure 3.1. Examining the ultrasonic velocity curves obtained in the pure media, it was seen that the transformation process of β -glycine to α -glycine occurred in three steps. The initial step was related to the dissolution of the β -glycine crystals. With the dissolution of β -glycine, the ultrasonic sound velocity of the solution increased rapidly. Then, a sharp change were observed at 42 minutes. This point indicated the formation of nuclei from dissolved β -glycine. The last step, where the ultrasonic velocity started to rise again, involved the growth of α -glycine crystals. In pure media, the transformation process was observed to be completed within 45 minutes. As can be seen from Figure 3.1, the same stages observed in the transformation process of β -glycine to α -glycine were also seen in the presence of additive media. Yet, the transformation rate fluctuated with the addition of lauric acid to crystallization media. Compared to the pure media, the phase transformation time for the crystals obtained in additive media changed significantly depending on the additive concentration. For example, in 50 ppm additive media, it took 54 min for the crystals to form, while in 100 and 250 ppm additive media, it took 59 min and 77 min, respectively. From the ultrasonic velocity results, it was found that the transformation rate decreased with the increase of the additive concentration, but that with lauric acid, the transformation time was prolonged. This change observed in transformation rate resulted in changes to the morphological and shape properties of the glycine crystals.

3.1.2. XRD and microscopy analysis

In this study, where the phase transformation process of β -glycine to α -glycine was examined in pure and impure media, XRD analyses were performed to identify which polymorphic form had crystallized. Figure 3.2 shows the XRD spectra of the crystals obtained in pure media at different times. At $t=0$ min, the characteristic peak of β -glycine was observed at 18° , an indication that the crystals obtained at the initial stage of the experiment were polymorph β . At $t=15$ and 35 min, the β characteristic peak, as well as the new peaks characterizing the α -glycine, were detected at 15° , 20° and 29° . It was found that the crystals obtained at this time were a mixture of polymorphs β and α . With the increase of time, the intensity of the characteristic β -glycine peak decreased and the reflection of α -glycine peaks increased. At $t=45$ min, the XRD spectra obtained in pure

media showed that the β -glycine peak disappeared completely and that the crystals obtained were in the α -form. These results agree with those reported by the studies in the literature [81,94]. Furthermore, the XRD peaks obtained were compared to the structures in Cambridge Structural Database and validated [95,96]. The transformation process monitored by XRD analysis is consistent with the ultrasonic velocity measurement.

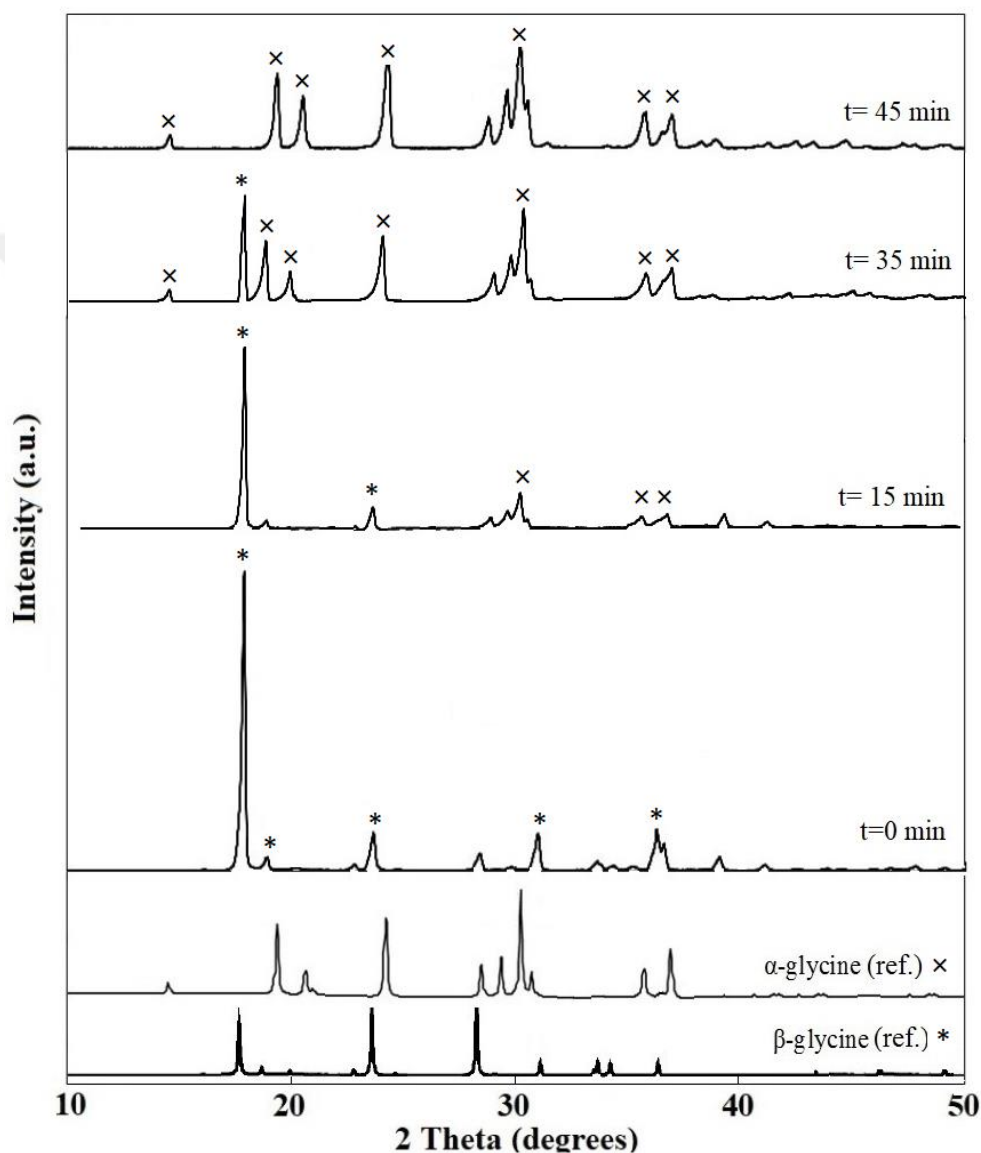


Figure 3.2. XRD spectra of the crystals obtained in pure solution.

The XRD spectra of the end-crystals obtained at different lauric acid concentrations are given in Figure 3.3, where the results indicate that all the crystals obtained were of the α

form. However, the addition of lauric acid to crystallization media led to changes in the peak intensities of the crystals obtained; that is, the peaks obtained increased with higher concentrations of additive. As stated in the literature, these changes may be caused by the incorporation of additive molecules within the crystal lattice. In this circumstance, structural imperfections and internal strains occur in the individual lattice symmetry and thus, unlike in pure media, shifts and changes occur when the additive is present [97].

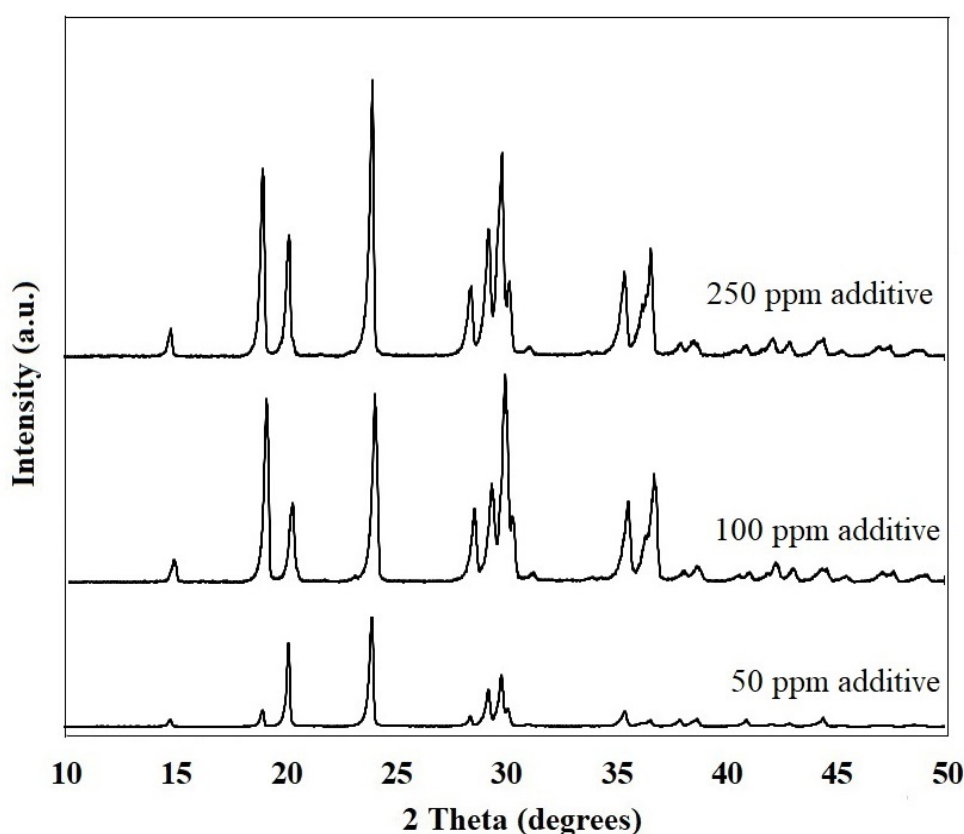


Figure 3.3. XRD spectra of the crystals obtained in solutions containing different concentrations of lauric acid.

In addition to XRD analysis, microscopy analysis were carried out to confirm which polymorphic form crystallized and to investigate the crystal habit change. The optical microscopy images of the crystals in pure medium are given in Figure 3.4.

The crystals formed at the start time, i.e. $t=0$, were completely in β form and were in the form of needles. This result is in accordance with previous studies [98]. The α -glycine

crystals began to form as the process continued, whereas β -glycine crystals began to dissolve. The β and α glycine crystals coexist in the same medium. α -glycine crystals were prismatic smooth crystals and had a very different morphology than β -glycine. The needle-shaped crystals disappeared completely from the medium and transformed into prismatic α -glycine structures after transformation. These results are supported by the XRD patterns.

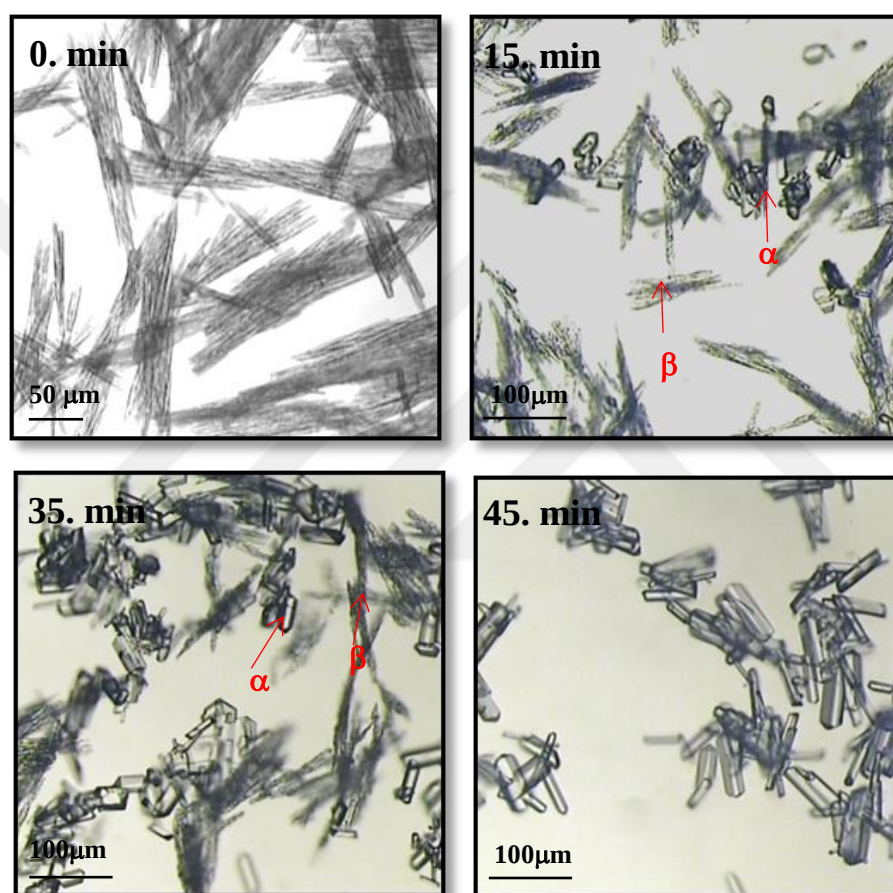


Figure 3.4. Microscopic images taken at different times for pure media during the polymorphic transformation.

3.1.3. SEM analysis

The SEM analyses of α -glycine crystals obtained in pure media and in the presence of different additive concentrations were performed to detect the impact of lauric acid on glycine morphology. The results are given in Figure 3.5. Normal prismatic-shaped crystals with smooth surface were obtained in pure media. This result agreed with the literature [25,99].

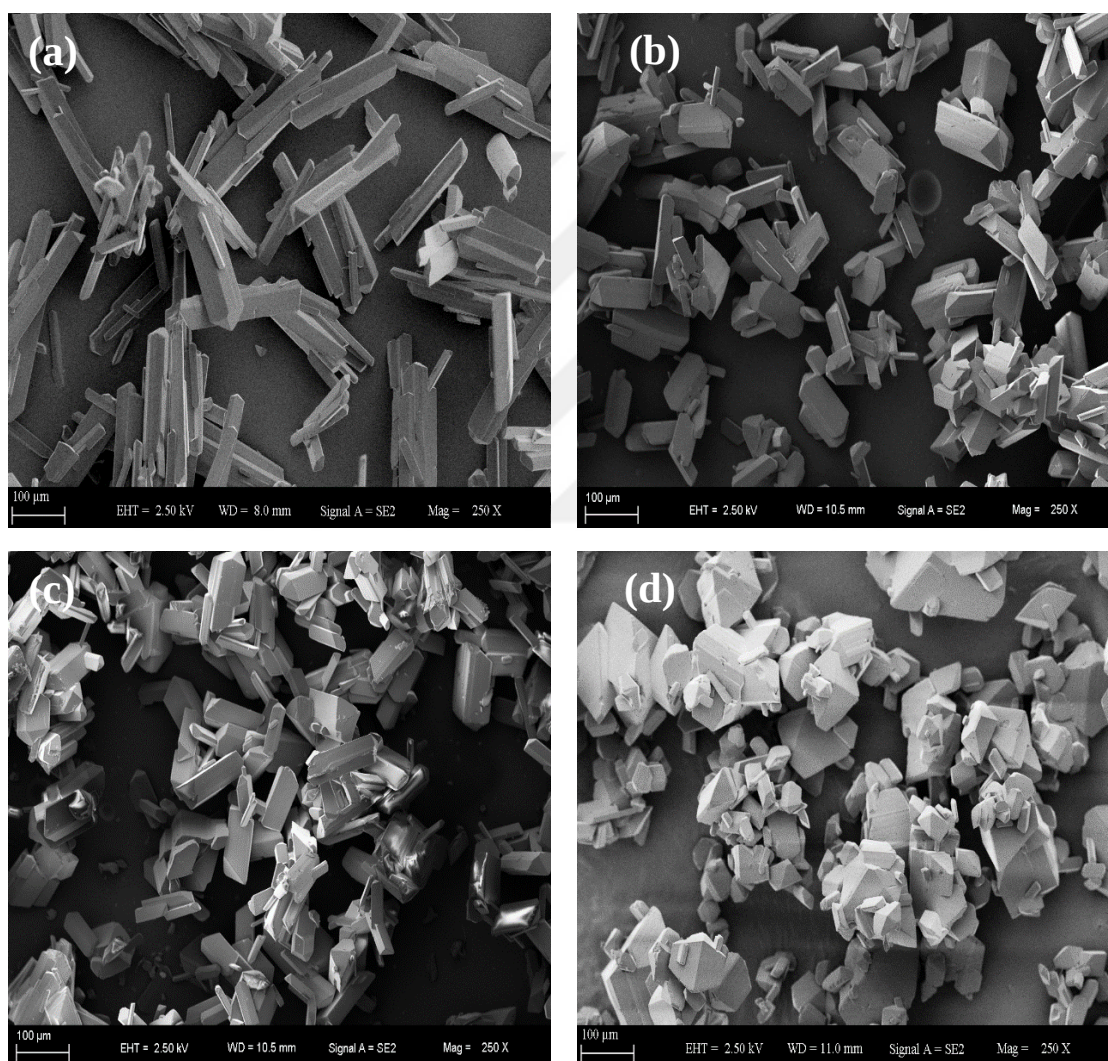


Figure 3.5. The SEM images of the glycine crystals obtained in (a) pure solution and (b-d) solutions containing different concentrations of lauric acid (b) 50 ppm, (c) 100 ppm and (d) 250 ppm.

It can be seen that the crystals obtained in 50 ppm lauric acid retained basically the same morphology. However, the length and width of the crystals changed compared to the pure media. It was also noticed that the thickness of the crystals started to increase. As the concentration of lauric acid increased to 100 ppm, the crystal thickness further increased. In Figure 3.5, it clearly shows that the crystals obtained in the presence of 100 ppm additive were shorter, in terms of length, and that the crystals had more volume due to increases in their width. The crystals obtained in the presence of 250 ppm lauric acid completely lost the rod form. The shape of the crystals varied in size, from big to small. It was also detected that the addition of lauric acid to the media caused the formation of agglomerates. With the higher additive content, the agglomeration tendency increased even more. However, the agglomerates formed at the highest additive concentration had weaker bonding compared with those at 50 and 100 ppm, and they dispersed in an easier manner due to the hydrodynamic conditions of the media.

The morphology of the glycine crystals, which was clearly visible in the SEM images, changed according to the degree of increase of lauric acid concentration. This change occurred when the crystals took on a different form depending on the change in their length to width ratio. The variations of morphology could be due to the adsorption of additive on the surface of the crystals.

3.1.4. Morphology analysis

A detailed morphological analysis was carried out using a Malvern Morphologi G3 device to better understand the influence of lauric acid on glycine morphology, and to describe the particle shape parameters quantitatively. To this purpose, first, the images for the crystals obtained in pure media and in the presence of 250 ppm concentration of additive were taken. Next, the shape values, like circularity, elongation, and convexity were determined, the results of which are given in Figure 3.6. The crystals obtained in pure media had a long, homogenous, and non-circular prismatic shape. The addition of lauric acid resulted in changes in size and shape. Crystals obtained in the presence of lauric acid were smaller in shape and their lengths significantly shorter. As was the case seen in the SEM analysis, the crystals lost their rod shape, becoming slightly circular, and thereby developed a different appearance.

To obtain detailed information on the shape of the crystals and to ascertain the quantity of the different shapes of the crystals, particle shape factors, including circularity, elongation, and convexity, were determined. Circularity is calculated as the proportion of the circumference of a circle that has the same area as the particle to the circumference of the image of the real particle, whereas elongation is calculated using $[1 - \text{width}/\text{length}]$. Circularity and elongation values range between 0 and 1, where the circularity of a perfect circle is 1, while for a narrow rod, the value is close to 0. The elongation of a circle, on the other hand, is 0, while a rod has a high elongation value. Convexity, as another shape factor, is calculated by dividing the perimeter of a convex hull by the perimeter of the real particle. The convexity of a straight shape is 1, while the convexity of a skewed object approaches 0 [100,101].

Figure 3.6 shows the circularity, elongation, and convexity values of the crystals. The high-sensitivity (HS) circularity value of the crystals obtained in pure media was 0.552, while it reached 0.624 in the presence of lauric acid. This indicates that the crystals attained a relatively more circular shape. The decrease in the elongation value from 0.517 to 0.429 with the addition of the additive also served as evidence to this change. The convexity value was almost the same for both media.

To calculate the agglomeration tendency of the crystals, width-length ratios were calculated by dividing the width of the crystals by the length of the crystals. The width-length ratio in the pure media was 0.483, while it reached 0.571 with the addition of lauric acid, which indicates that the agglomeration of the crystals increased in terms of shape analysis. Images obtained from SEM and Morphologi G3 analyses supported this view.

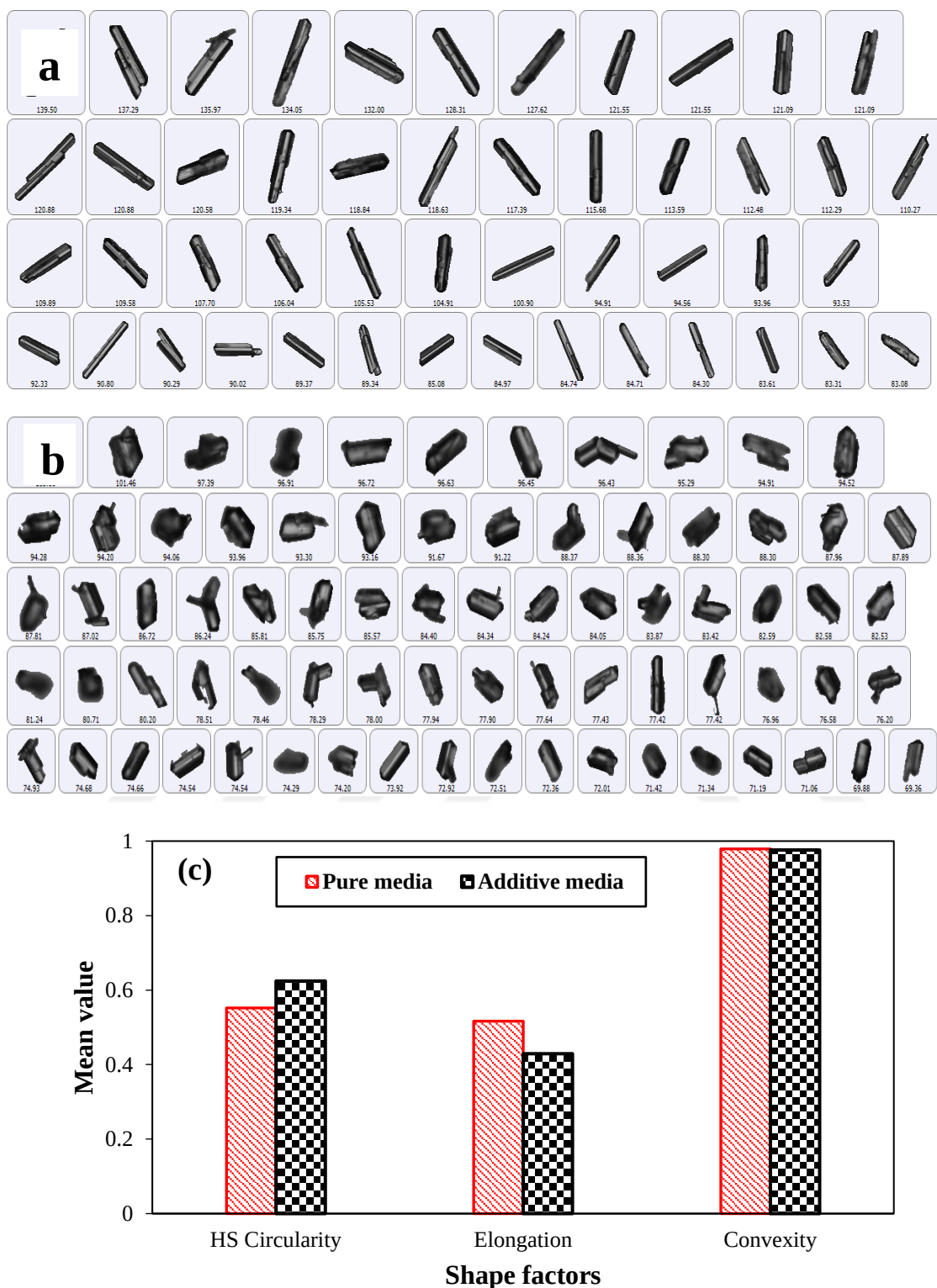


Figure 3.6. The shapes of the crystals obtained in (a) pure solution and (b) solution containing 250 ppm lauric acid. (c) Variation of the shape factor values of the crystals.

3.1.5. Thermal decomposition characteristics of α -glycine crystals

The thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) curves of the α -glycine crystals obtained in the absence and in the presence of 250 ppm lauric acid at different heating rates are presented in Figure 3.7. According to the TGA and DTG curves, the thermal decomposition of the crystals obtained in pure media can be divided into two stages. In the first stage, the thermal decomposition of the glycine crystals at 5 °C/min started at 245 °C and ended at 300 °C, with the maximum decomposition temperature being at 281 °C. The total weight loss was about 50%, and this loss could be attributed to the decomposition of the amino group. At higher temperatures, the lower weight loss of about 30% occurred due to the decomposition of the carboxyl group in the glycine. In this stage, the decomposition rate was slower than that of the first stage and it covered a wider temperature interval of between 316 ° and 480 °C, which was determined by the DTG curve. The results obtained were compatible with those from the literature [102]. The characteristic decomposition temperatures such as initial temperature, T_i , maximum peak temperature, T_{max} , and final temperature, T_f , for the crystals obtained in pure media are given in Table 3.1.

Table 3.1. Characteristic decomposition temperatures (°C) of the crystals obtained in pure and impure media for each heating rate.

Media	Heating Rate (°C/min)	First decomposition step			Second decomposition step		
		T_i	T_{max}	T_f	T_i	T_{max}	T_f
Pure	5	245	281	300	316	380	460
Media	10	253	286	326	326	389	520
	20	280	305	340	359	397	535

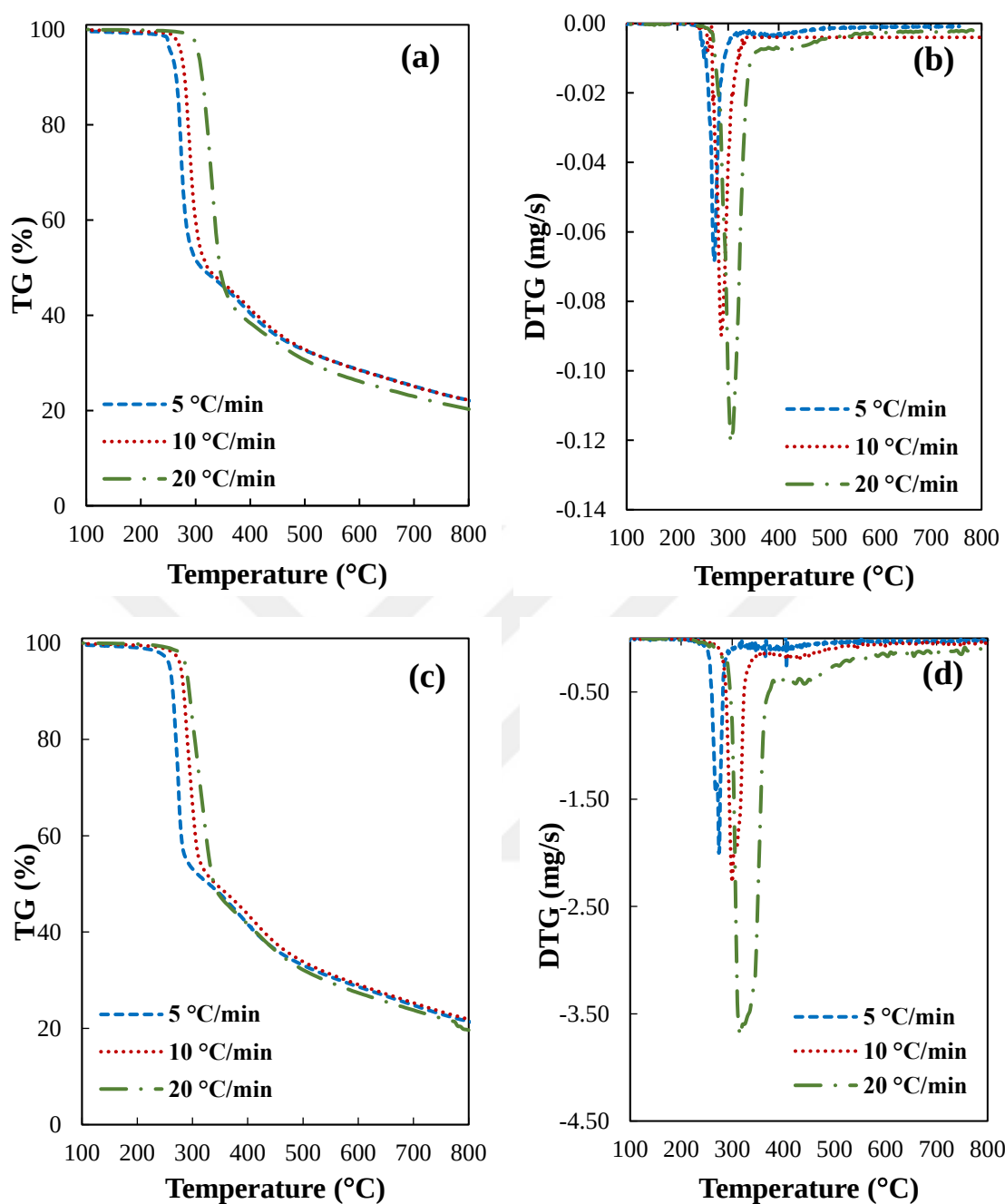


Figure 3.7. (a) TGA and (b) DTG curves of glycine obtained in pure solution, (c) TGA and (d) DTG curves of glycine obtained in solution containing 250 ppm lauric acid.

The same decomposition trend was observed for the 10 and 20 °C/min heating rates, with the maximum peak temperatures being observed at 286 and 305 °C, respectively. It was clear that the changing heating rates caused the decomposition temperature to shift higher

and also affected the completion of the decomposition process. This situation could be explained by the increasing thermal lag resulting from the higher heating rate. Compared to the TGA and DTG curves of the crystals produced in the absence and in the presence of additive, it was found that the addition of lauric acid to the crystallization media resulted in a considerable shift of the initial and final decomposition temperature, as well as the maximum peak temperature. For instance, the main decomposition stage for the crystals obtained in the absence and in the presence of additive at 10 °C/min occurred within the temperature ranges of 253 and 326 °C and 260 and 340 °C, respectively.

As clearly shown in Figure 3.7, the maximum peak temperature increased by about 8 °C for each heating rate in the presence of additive. This shift could have been caused by the additive in the media, and if so, it would indicate that the lauric acid adsorbed on the crystal surface. In addition to changing temperature, differences in total weight loss were seen in the presence of 250 ppm lauric acid. The final solid residues at the completion of the thermal decomposition process were determined as 20.8% and 19.7% for crystals in the absence and in the presence of lauric acid, respectively. The higher total mass loss in the additive media could be attributed to variations in the lauric acid content of the samples.

3.1.6. Kinetic analysis

In terms of both practical and industrial applications, it is important that the influence of additive on the thermal decomposition characteristics and kinetics of α -glycine crystals be thoroughly understood. For this purpose, the activation energy, which is an essential kinetic parameter, was examined using different kinetic models for the crystals obtained in pure and impure media. In this study, where the main decomposition region was within the temperature range of 245 to 340 °C, the greatest weight loss zone observed was taken into consideration to calculate the activation energy. The standard isoconversional plots of FWO, Friedman, Starink, and KAS in the conversion range of 0.1 to 0.9, with an interval of 0.1 for the crystals obtained in pure media, are presented in Figure 3.8.

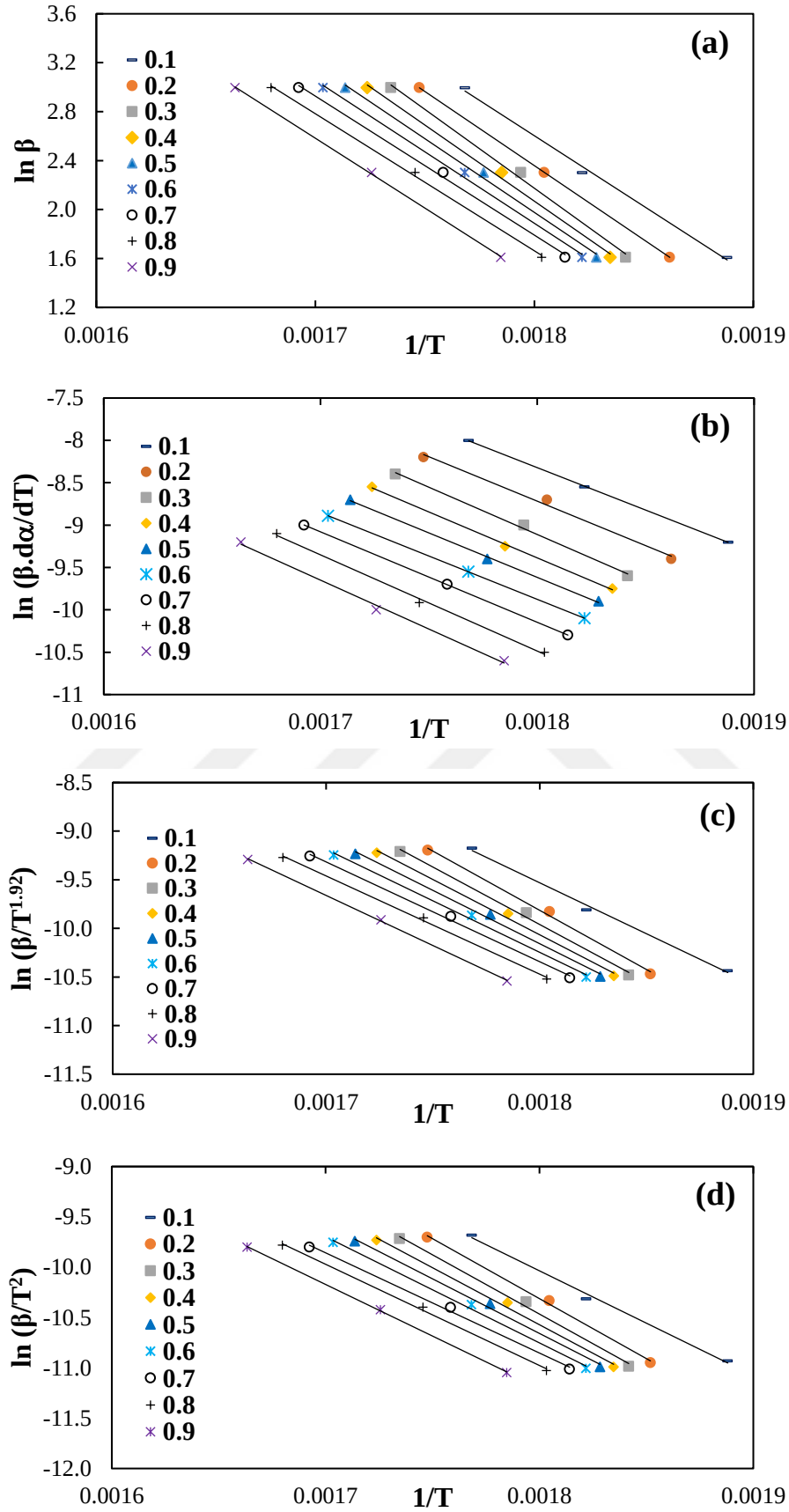


Figure 3.8. The plots of (a) FWO, (b) Friedman, (c) Starink and (d) KAS models.

The activation energy was determined from the slope of plotted lines for each model. When all the lines were examined, it was observed that the lines were in parallel with one another and correlated well with the studied models. The calculated values of activation energy and correlation coefficient (R^2) are given in Table 3.2.

Table 3.2. The activation energy (E, kJ/mol) and R^2 values of the crystals obtained in the absence and in the presence of lauric acid using the FWO, Friedman, Starink, and KAS models.

Media	α	FWO		Friedman		Starink		KAS	
		E	R^2	E	R^2	E	R^2	E	R^2
Pure media	0.1	91.1	0.9963	83.3	0.9998	87.1	0.9956	86.4	0.9953
	0.2	95.8	0.9999	87.3	0.9911	101.2	0.9965	99.1	0.9976
	0.3	94.0	0.9963	92.8	0.9963	98.2	0.9955	97.5	0.9954
	0.4	90.5	0.9962	90.1	0.9988	94.5	0.9953	94.2	0.9953
	0.5	87.4	0.9965	87.2	0.9986	91.1	0.9957	90.2	0.9962
	0.6	90.2	0.9997	90.9	0.9999	88.0	0.9963	87.7	0.9963
	0.7	88.6	0.9986	89.6	0.9999	85.3	0.9969	82.8	0.9969
	0.8	87.8	0.9976	94.4	0.9957	83.9	0.9982	83.6	0.9982
	0.9	90.3	0.9971	96.0	0.9967	85.6	0.9996	85.3	0.9996
	Average	90.6		90.2		90.5		89.6	
Additive media	0.1	116.2	0.9926	106.7	0.9999	113.4	0.9913	110.9	0.9932
	0.2	111.4	0.9923	98.93	0.9987	108.2	0.9909	107.2	0.9924
	0.3	104.5	0.9893	96.92	0.9999	100.9	0.9872	104.8	0.9869
	0.4	99.65	0.9841	95.16	0.9979	95.78	0.9809	103.8	0.9807
	0.5	98.54	0.9816	99.57	0.9984	94.55	0.9778	93.64	0.9801
	0.6	96.73	0.9986	96.41	0.9981	92.58	0.9917	92.27	0.9917
	0.7	94.31	0.9999	100.8	0.9980	98.53	0.9982	97.25	0.9974
	0.8	88.56	0.9986	97.82	0.9967	95.53	0.9982	95.21	0.9982
	0.9	90.17	0.9933	100.5	0.9971	93.77	0.9999	93.47	0.9999
	Average	99.99		99.20		99.25		99.84	

The calculated activation energy values with respect to conversion degree for the crystals obtained in pure media were very close to each other, with high R^2 values. It was determined that the R^2 values varied within a range of 0.9911 and 0.9999 and that the obtained lines were parallel with one another. This situation indicates that the

decomposition of the pure crystals had similar kinetic characteristics for all conversion values and did not include any parallel, consecutive, complex reactions. The decomposition was only related to the removal of the amino group.

The average activation energy of the crystals obtained in pure media under the FWO, Friedman, Starink and KAS models was calculated as 90.6, 90.2, 90.5, and 89.6 kJ/mol, respectively. Although the activation energy calculated for the KAS model was determined to be slightly lower than that of the other studied models, these values were nearly the same for all models studied, and they were in good agreement with each other. In effect, this indicates that the model equation fitted the experimental data well and the values obtained were reliable and accurate.

As shown in Figure 3.9 the addition of lauric acid to the media resulted in a considerable increase in the activation energies, meaning that the minimum energy required to initiate reaction was higher. The average activation energy values obtained from the FWO, Friedman, Starink and KAS models were 99.99, 99.20, 99.25, and 99.84 kJ/mol, respectively.

As seen in Table 3.2, the activation energy increment was around 10% in the presence of 250 ppm lauric acid. Compared to the pure media, with the additive media, fluctuation was observed in the values of the activation energies calculated with different conversion values. These values fell within the wide interval of 88 and 116 kJ/mol.

The changes and fluctuations that occurred in the activation energy of the crystals obtained in the presence of additive shows that the lauric acid adsorbed on the crystal surface and that the sample content changed. Compared to the pure media, the decomposition of the glycine crystals containing lauric acid needed more energy to start to decompose, had a slower reaction rate and involved a more complex interaction. The lauric acid therefore affected the decomposition of the crystals because it adsorbed on the crystal surface and changed the diffusion characteristics. The results obtained by kinetic analysis were consistent with DTG results. The presence of lauric acid in the media led to a shift to higher temperature in both of the maximum peak temperatures and increased the values of activation energy.

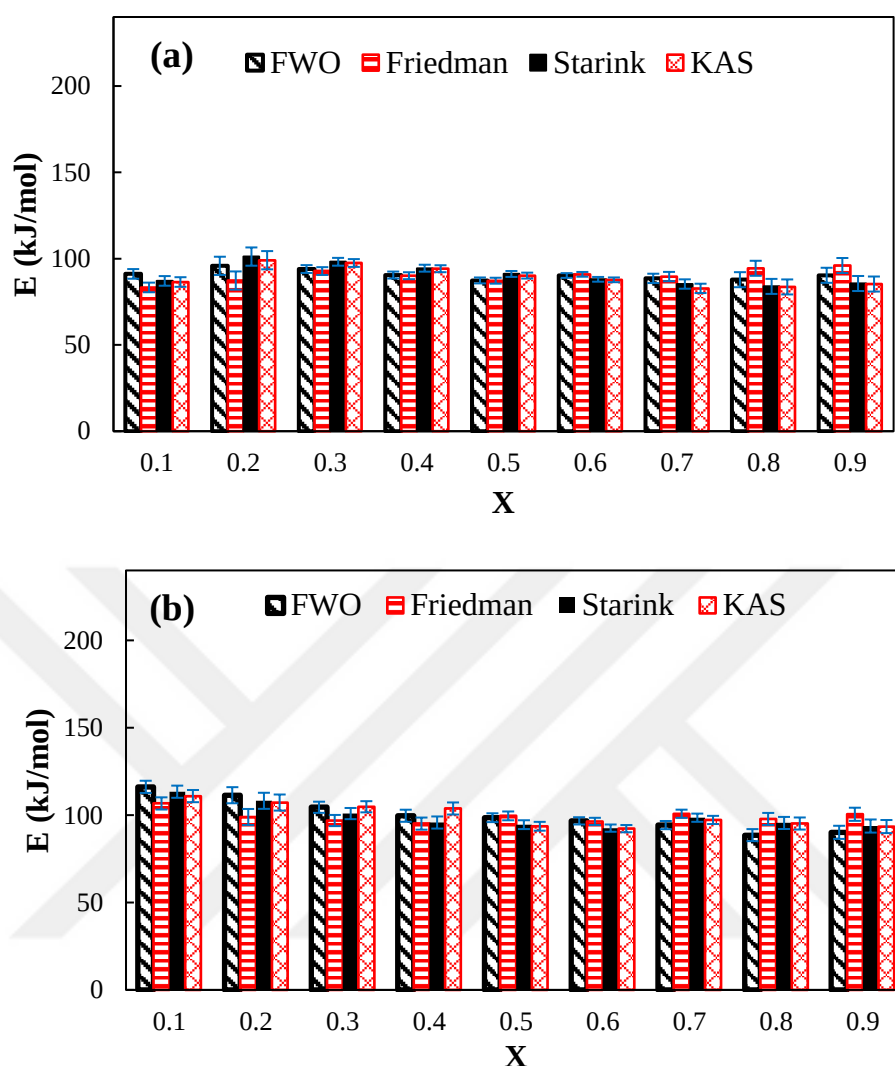


Figure 3.9. Variation of activation energy with respect to conversion degree for the crystals obtained a) in pure media and b) in the presence of 250 ppm lauric acid.

3.1.7. Elemental and FTIR analysis

Elemental analysis, which was used to identify the elemental composition of the samples, was performed on the crystals obtained in pure media and in the presence of 250 ppm lauric acid to determine the effect of additive on the C, H, and N composition of the crystals. The crystals obtained in pure media consisted of 31.99% C, 6.69% H, and 18.55% N. The addition of lauric acid to media resulted in a slight variation in elemental composition. The composition of the crystals obtained in 250 ppm lauric acid was 32.17% C, 6.72% H, and 18.50% N. This result reveals that the C and the H contents slightly increased because of the presence of additive on the crystal surface.

In addition to elemental analysis, FTIR analysis was used to characterize the crystals, to determine the functional groups and to understand the binding of the additive to the crystal surface. Figure 3.10 presents the FTIR spectra of the crystals obtained in the absence and in the presence of 250 ppm lauric acid. The obtained spectra for pure media agreed with the those found in the studies published in the literature [103,104].

The absorbance band between 2200 and 3300 cm^{-1} and the peak seen at 1499 cm^{-1} were related to N–H stretching vibrations of the NH_3^+ group. The absorbance peaks at 1599 and 1406 cm^{-1} were attributed to the asymmetric and symmetric stretching vibration of the COO^- group, respectively. The peak seen at 1444 cm^{-1} can be attributed to the presence of the bending vibration of the C–H bonds of the CH_2 group. In addition, the other peaks at 891 and 693 cm^{-1} were related to C–C symmetric stretching and O–C=O bending vibrations, respectively.

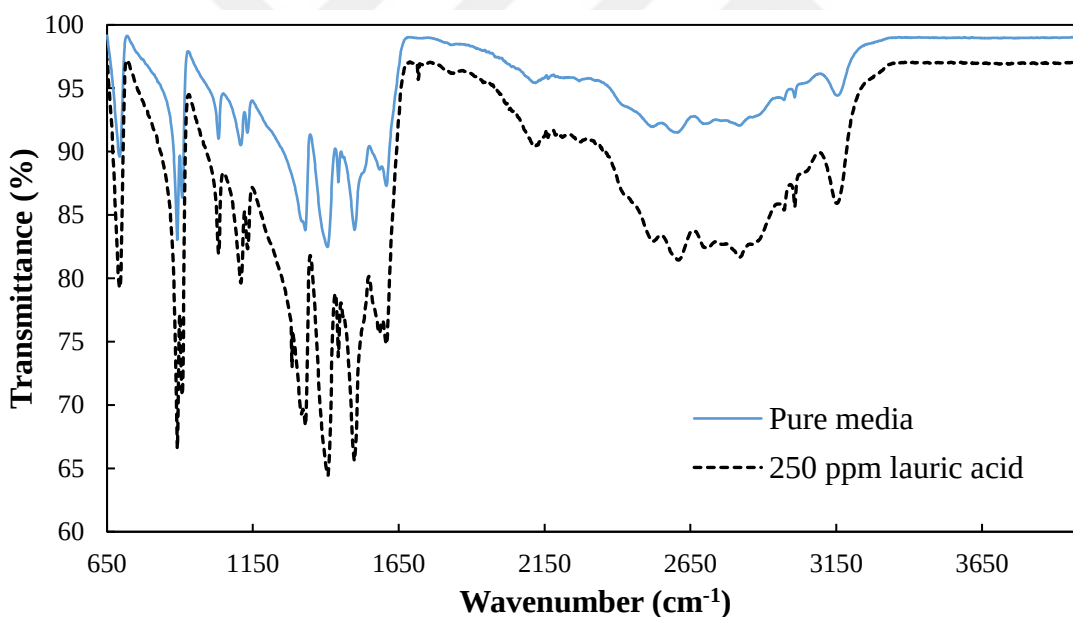


Figure 3.10. FTIR spectra of the crystals obtained in pure solution and solution containing 250 ppm lauric acid.

All peaks that characterize α -glycine crystals were detected in the presence of lauric acid. In contrast to the FTIR spectra obtained in the pure media, the crystals obtained in the impure media had distinct peaks at 1718 cm^{-1} and 1285 cm^{-1} , which were attributed to the C=O stretching and C–O stretching vibration of the carboxylic group in lauric acid [104]. Moreover, a slight shift and increase in intensity of the peaks were observed. These results

obtained were compatible with the elemental analysis results and confirmed that the lauric acid adsorbed on the crystal surface.

3.1.8. Filtration analysis

Both SEM and morphological analysis results show that the morphology and structure of α -glycine crystals change in the presence of lauric acid. To determine the effect of this change on the filtration characteristics of α -glycine, the filtration rates are measured in non-additive media and in the presence of different concentrations of lauric acid. The filtration rate measurements were evaluated according to Darcy's law [105] to determine the specific cake resistance and the average cake porosity. The results are given in the Figure 3.11.

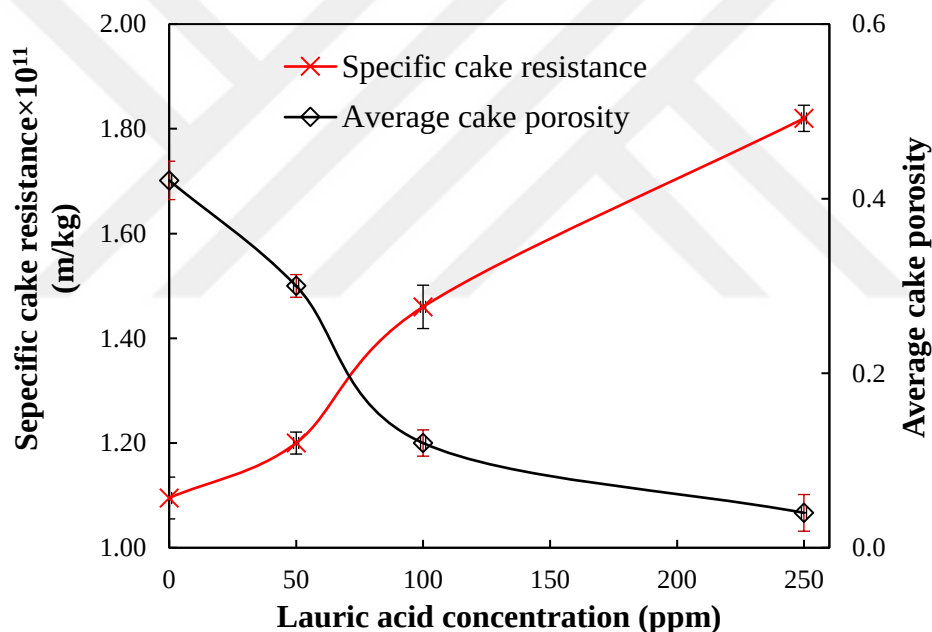


Figure 3.11. Variation of the specific cake resistance and average cake porosity values of the crystals obtained in the absence and presence various lauric acid concentrations.

The specific cake resistance and the average cake porosity values for pure medium were calculated as 1.095×10^{11} m/kg and 0.421, respectively. As the concentration of lauric acid increased to 250 ppm, the specific cake resistance value increased to 1.82×10^{11} m/kg, while the average porosity value decreased to 0.04. This can be attributed to the morphological change and decrease in the average particle size of the crystals.

3.2. The Results of Butyric Acid Effects on Polymorphic Phase Transformation of Glycine•

3.2.1. Ultrasonic velocity measurement

The transformation of the β phase to α phase was determined using an ultrasonic velocity measurement technique. During the phase transformation process the composition of the solution changed, which resulted in a change of sound velocity in the media. The variations in the ultrasonic velocity values are shown in Figure 3.12.

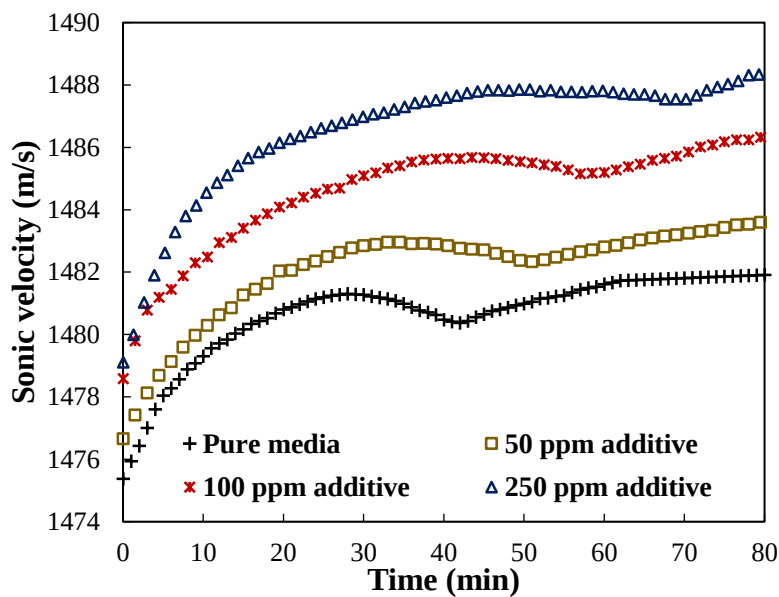


Figure 3.12. Variation of ultrasonic velocity versus time for the crystals obtained in pure media and in the presence of different butyric acid concentrations.

The ultrasonic velocity curves obtained in pure media and in the presence of butyric acid concentrations demonstrate an increase in ultrasonic velocity, a transition, a decrease due to the transition period, and an increase due to the formation of the new phase. The increase in ultrasonic velocity from the beginning to the transition period is due to the dissolution of the β -glycine. This process is prolonged by the increase in concentration of butyric acid added to the medium. This shows that butyric acid prolongs the phase transformation process of glycine.

• Polat, S., Sayan P. (2018) The Characterization and Polymorphism of α -Glycine in the Presence of Butyric Acid. *Advanced Powder Technology*, 29 (9), 1968-1976.

In pure media, the phase transformation time was 45 minutes. The transition time was 54, 63, and 70 minutes for 50, 100, and 250 ppm butyric acid concentrations, respectively.

3.2.2. XRD analysis

The XRD analysis of the final product obtained by the transformation process with different butyric acid concentrations is shown in the Figure 3.13. The crystals obtained in all three butyric acid concentrations were in α -glycine form, as shown in Figure 3.13. The intensities of the α -glycine characteristic peaks increased due to the increase in butyric acid concentration.

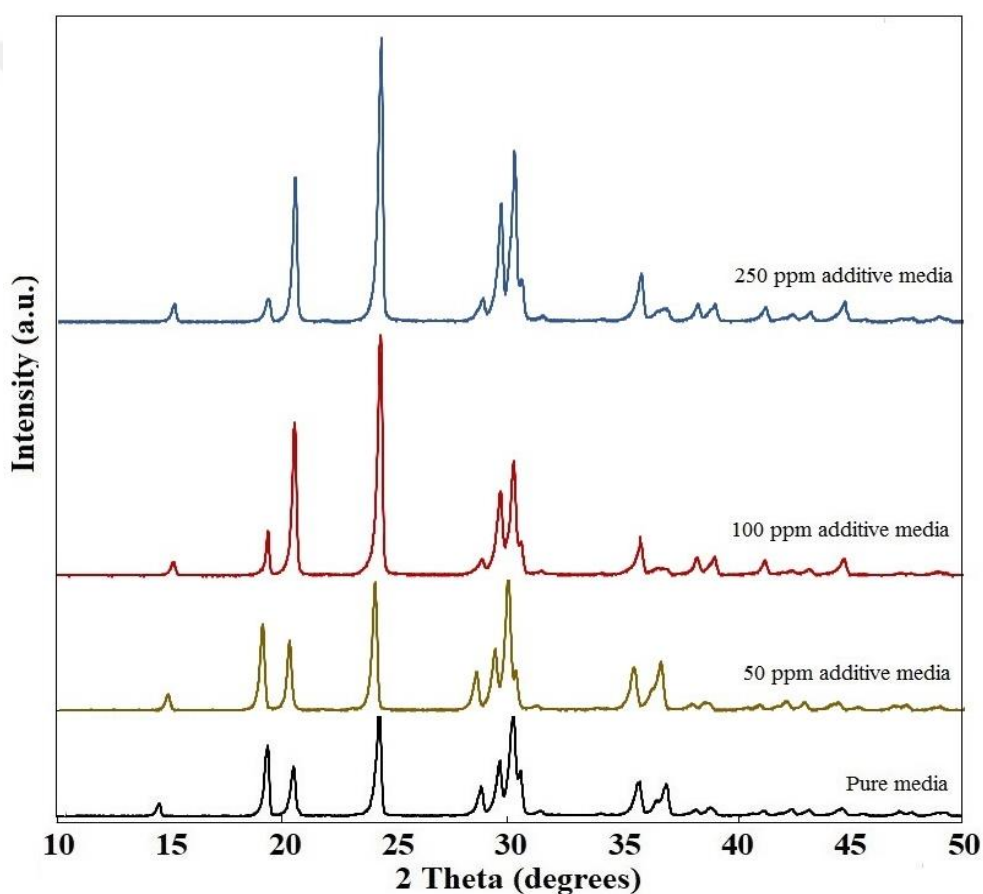


Figure 3.13. XRD results of the crystals obtained in the presence of butyric acid with varying concentrations.

The peak intensities of the crystals obtained in pure medium at $\theta = 23^\circ$ is 2000. This value was measured as 5000 at 250 ppm butyric acid concentration. This increase in

intensities may be due to changes in internal structures caused by the adsorption of butyric acid on the crystal surface.

3.2.3. SEM analysis

SEM analysis was performed to investigate the influence of butyric acid on α -glycine crystal morphology with pure and impure media, and the results are given in Figure 3.14. The crystals obtained by completing the transformation of β -glycine to α -glycine in pure medium had a smooth prismatic structure consistent with the results of previous studies [5]. The average particle size of the crystals is 85 μm . The average aspect ratio, or the ratio of the width to the length of the crystals, is 0.483.

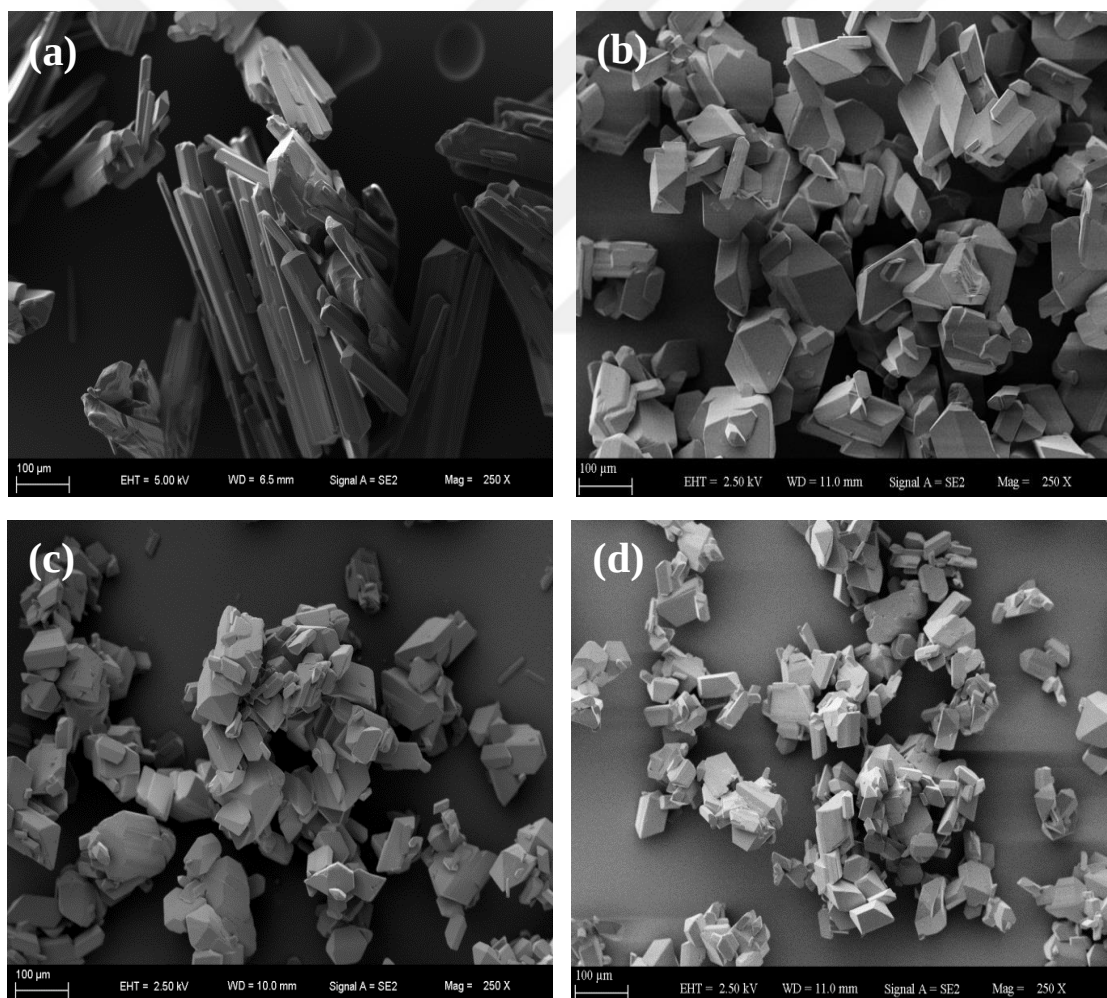


Figure 3.14. SEM images obtained a) in pure media b) in the presence of 50 ppm butyric acid c) in the presence of 100 ppm butyric acid d) in the presence of 250 ppm butyric acid.

Both the average particle size and the aspect ratio of the crystals obtained changed and the crystals tended to grow on each other in the presence of 50 ppm butyric acid. In the presence of 100 ppm butyric acid, the crystals grew onto each other more rapidly and began to partly lose their shape. The variation in aspect ratio of crystals was observed over a wider range. The crystals began to lose their homogeneous appearance in the pure medium and the agglomeration in crystals also began. The addition of 250 ppm butyric acid to the crystallization media led to a significant increase in the agglomeration tendency and caused a distinctive decrease in the average particle size. The crystals with 250 ppm butyric acid agglomerated and the average particle size of the crystals is 51 μm . The aspect ratio of the crystals obtained is 0.713. Crystals formed may be due to the defects on the crystal surfaces that cause morphological change. The resultant crystals are morphologically quite different from each other. In each butyric acid concentration, the rod-like structure of the crystals was replaced by crystals with shorter and more compact structures when compared to a pure media. The variations of morphology could be due to the adsorption of additive on the surface of the crystals.

3.2.4. Morphology analysis

A detailed shape analysis was performed using a Malvern Morphologi G3 instrument to better characterize the quantitative change in the crystal morphology seen in SEM imaging. Figure 3.15 shows the analysis of commonly used shape factors like elongation and HS (High Sensitivity) circularity values of crystals obtained in a pure media with different butyric acid concentrations. Results show the elongation value decreased from 0.517 to 0.287 as the butyric acid concentration increased. The HS circularity value increased from 0.552 to 0.720. The crystals were transformed from a rod structure into a shorter and rounded form. These results aligned with the SEM results. Another shape parameter that can be used to characterize the morphology of the obtained crystals is convexity. Convexity is calculated by dividing the convex hull perimeter by the actual particle perimeter. The convexity value of the crystals was 0.979 for pure medium and 0.990 for 250 ppm butyric acid.

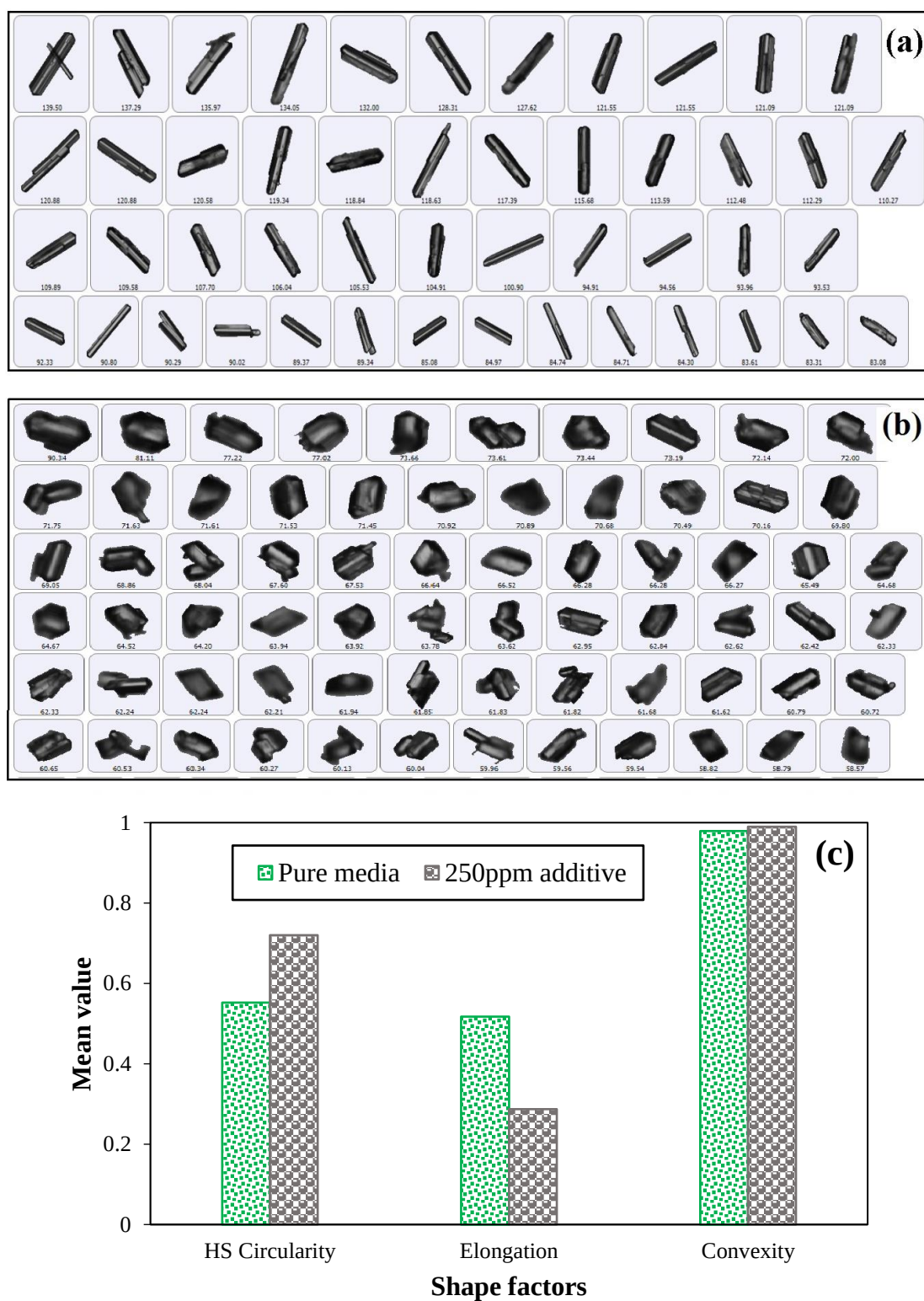


Figure 3.15. The shapes of the crystals obtained in (a) pure solution and (b) solution containing 250 ppm butyric acid. (c) Variation of the shape factor values of the crystals.

3.2.5. Thermal characteristic of the α -glycine crystals

The TG and DTG curves of the crystals obtained in the presence of 250 ppm butyric acid for the heating rate of 5, 10 and 20 °C/min are shown in Figure 3.16. As mentioned 3.1.5 part, thermal decomposition of α -glycine crystals obtained in pure media involved a two-stage thermal degradation process.

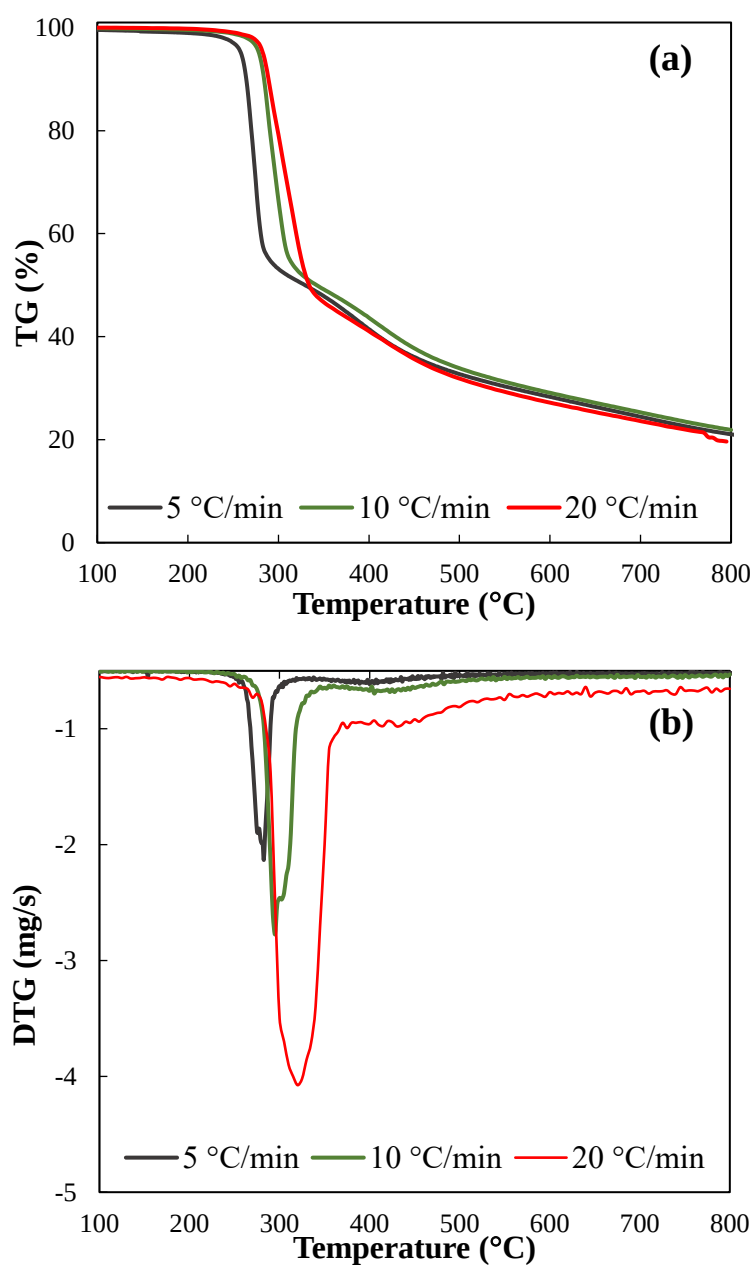


Figure 3.16. a) TG b) DTG curves of the crystals obtained in the presence of 250 ppm butyric acid at 5, 10 and 20 °C/min heating rate.

The first stage includes the decomposition of the amino group (approximately 50%), and the second stage includes the thermal decomposition of the carboxyl group constituent of glycine (approximately 30%) [102]. The peak intensities of the first and second stages of the thermal decomposition vary. The intensity of the first stage is higher than that of the second stage. The peak temperatures for these stages are 281 °C and 380 °C, respectively. Analysis of the TG and DTG curves obtained in the presence of additive media show peak temperatures shifted towards higher temperatures.

3.2.6. Kinetic analysis

Figure 3.17 and Table 3.3 show the activation energy values as a function of conversion between 0.1 and 0.9 with an interval 0.1 for the crystals with and without additive between 245 °C and 340 °C.

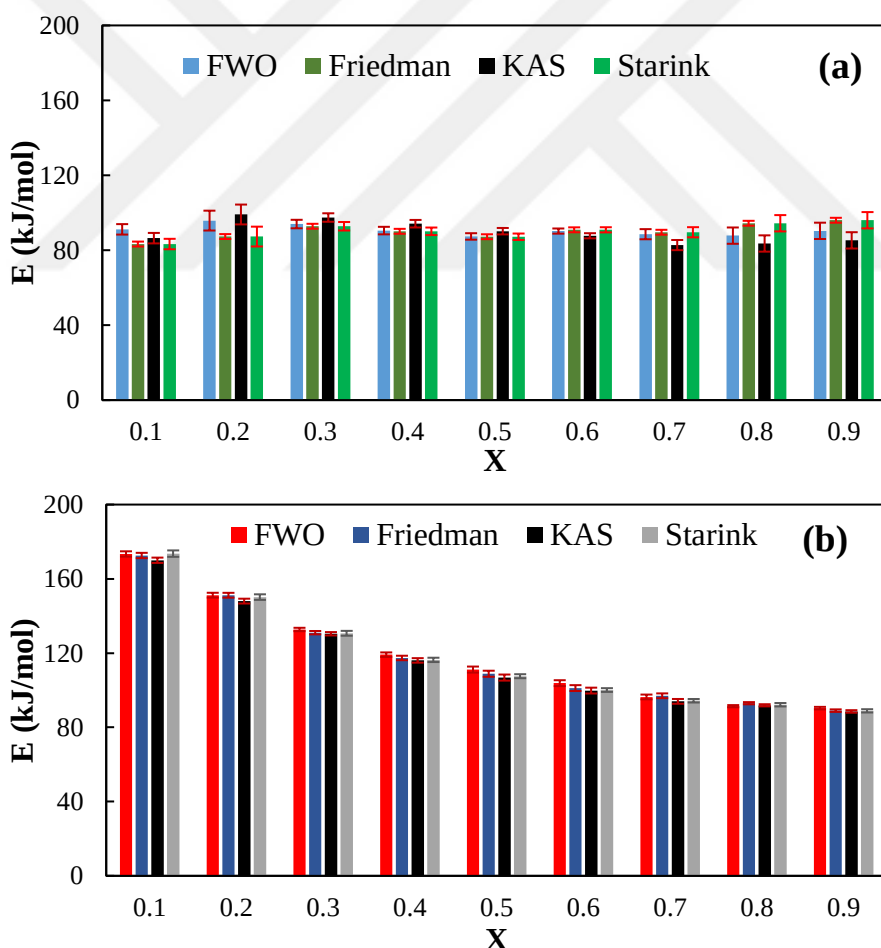


Figure 3.17. Variation of activation energy with respect to conversion degree for the crystals obtained a) in pure media and b) in the presence of 250 ppm butyric acid.

Table 3.3. The activation energy (E, kJ/mol) and R^2 values of the crystals obtained in the absence and in the presence of butyric acid using the FWO, Friedman, Starink, and KAS models.

Media	α	FWO		Friedman		Starink		KAS	
		E	R^2	E	R^2	E	R^2	E	R^2
Pure media	0.1	91.1	0.9963	83.3	0.9998	87.1	0.9956	86.4	0.9953
	0.2	95.8	0.9999	87.3	0.9911	101.2	0.9965	99.1	0.9976
	0.3	94.0	0.9963	92.8	0.9963	98.2	0.9955	97.5	0.9954
	0.4	90.5	0.9962	90.1	0.9988	94.5	0.9953	94.2	0.9953
	0.5	87.4	0.9965	87.2	0.9986	91.1	0.9957	90.2	0.9962
	0.6	90.2	0.9997	90.9	0.9999	88.0	0.9963	87.7	0.9963
	0.7	88.6	0.9986	89.6	0.9999	85.3	0.9969	82.8	0.9969
	0.8	87.8	0.9976	94.4	0.9957	83.9	0.9982	83.6	0.9982
	0.9	90.3	0.9971	96.0	0.9967	85.6	0.9996	85.3	0.9996
	Average	90.6		90.2		90.5		89.6	
Additive media	0.1	173.4	0.9912	170.0	0.9909	173.6	0.9982	172.6	0.9972
	0.2	151.2	0.9937	148.0	0.9993	150.2	0.9963	151.2	0.9965
	0.3	132.7	0.9901	130.4	0.9990	130.7	0.9891	131.0	0.9899
	0.4	119.1	0.9922	116.1	0.9986	116.3	0.9894	117.4	0.9906
	0.5	111.1	0.9883	106.8	0.9980	107.5	0.9757	108.9	0.9954
	0.6	103.8	0.9990	99.8	0.9976	100.1	0.9965	101.1	0.9908
	0.7	96.4	0.9981	94.0	0.9990	94.3	0.9999	97.0	0.9944
	0.8	91.4	0.9991	91.9	0.9936	92.2	0.9996	93.0	0.9928
	0.9	90.3	0.9989	88.6	0.9919	88.9	0.9989	89.0	0.9993
	Average	118.8		116.2		117.1		117.9	

The presence of butyric acid significantly increases the activation energy of glycine crystal decomposition, showing a high linear correlation coefficient (R^2 values of >0.9953). The activation energy change as a function conversion is between 90 and 173 kJ/mol and the average value for the crystals obtained in the presence of 250 ppm butyric acid is 118.8, 116.2, 117.1 and 117.9 kJ/mol for FWO, Friedman, Starink and KAS models, respectively. The percent deviation values, which were obtained using different models and found fairly good, validate the accuracy and reliability of the calculated activation energy values obtained by means of different kinetic models and multi heating rates. The small differences obtained in activation energies were due to the estimations

and calculations used to solve the temperature integral for the derivation of iso-conversional model equations. The reaction mechanism causes the calculated activation energy for pure media depending on conversion degree to be close to one another. The thermal degradation process was not included in the complex and competitive reactions in pure media. The addition of butyric acid to the crystallization media causes a fluctuation in activation energy. The α -glycine crystals with additive media required a higher activation energy value during thermal decomposition process due to the butyric acid content. This could be consistent with the adsorption of the butyric acid to the crystal surface.

3.2.7. FTIR and elemental analysis

FTIR spectrometry was utilized to determine whether butyric acid adsorbed on the crystal surface or not. It also helped to characterize the structure of the α -glycine crystals obtained in the absence and the presence of 250 ppm butyric acid media. This spectrum is given in Figure 3.18. As mentioned 3.1.6 part, the FTIR spectrum obtained in pure media is consistent with the results of previous studies [103].

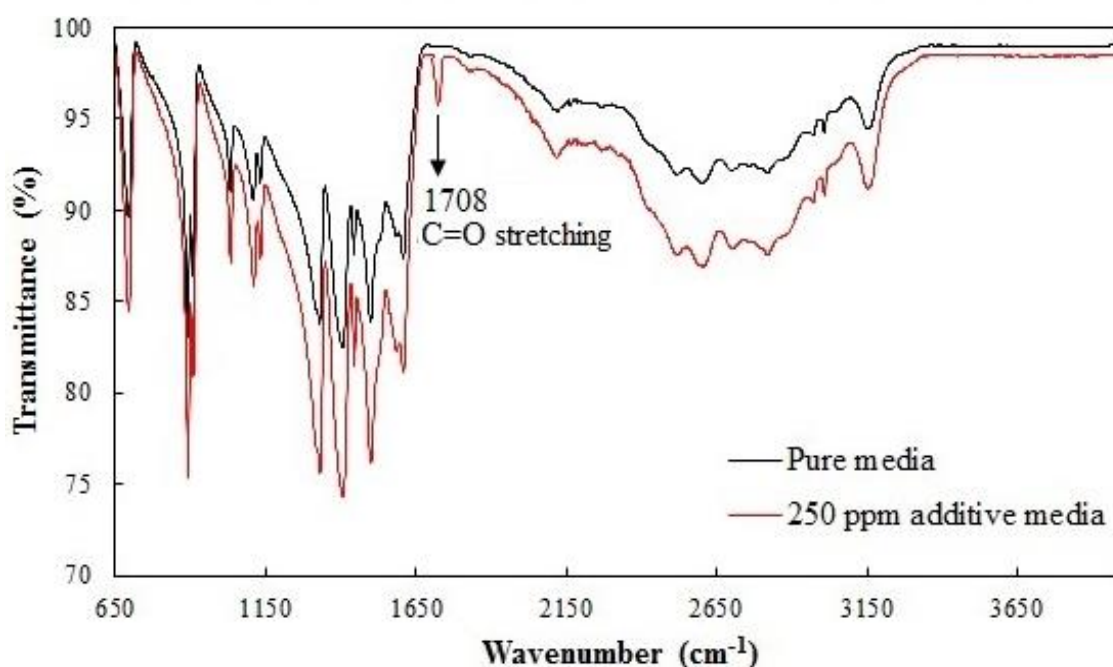


Figure 3.18. FTIR spectra of the crystals obtained in pure media and in the presence of 250 ppm butyric acid.

Crystals obtained in the presence of the additive had a peak that differed from glycine at about 1700 cm^{-1} . The peak intensities increased significantly. FTIR analysis shows adsorption of butyric acid on the crystal surface.

An elemental analysis was conducted to further characterize the crystals and to determine the elemental composition of the α -glycine with and without butyric acid. The elemental content of α -glycine crystals obtained in pure media is 31.99% C, 6.69% H, and 18.55% N. The elemental analysis result showed good concordance with the theoretical formulation. The elemental analysis gave 32.20 % C, 6.73 % H, and 18.46 % N for the crystals obtained in 250 ppm butyric acid media. Crystals with additive had higher C and H contents but lower N content when compared to pure media. This result confirms the interaction between glycine and butyric acid during phase transformation.

3.2.8. Filtration analysis

To determine the effect of butyric acid on the filtration characteristics of α -glycine, the filtration rates are measured in non-additive media and in the presence of different concentrations of butyric acid. The specific cake resistance and the average cake porosity results are given in the Figure 3.19.

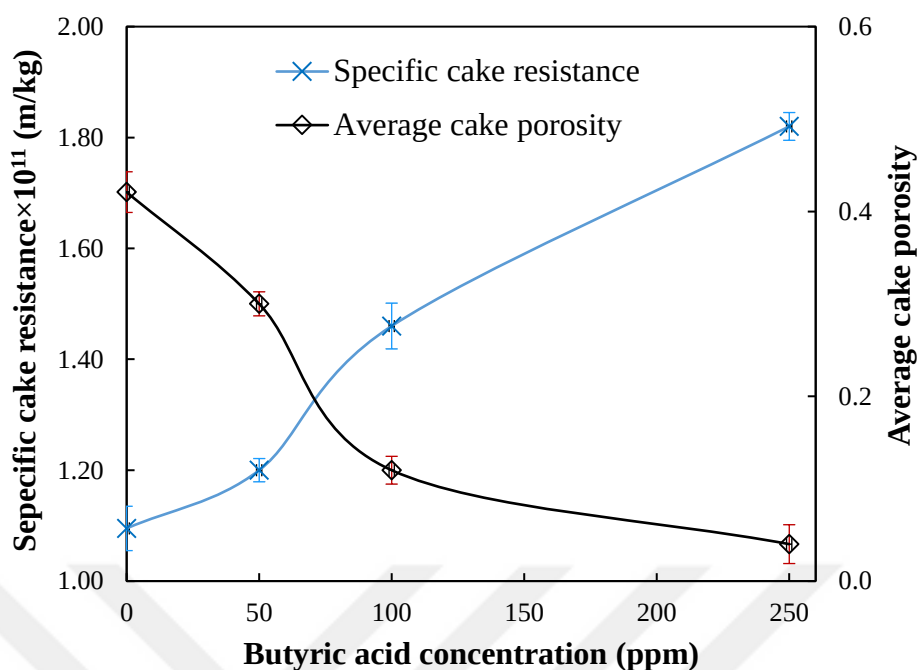


Figure 3.19. Variation of the specific cake resistance and average cake porosity values of the crystals obtained in the absence and presence various butyric acid concentrations.

The specific cake resistance and the average cake porosity values for pure medium were calculated as 1.095×10^{11} m/kg and 0.421, respectively. As the concentration of butyric acid increased to 250 ppm, the specific cake resistance value increased to 1.66×10^{11} m/kg, while the average porosity value decreased to 0.031. This can be attributed to the morphological change and decrease in the average particle size of the crystals.

3.3. The Results of Oleic Acid Effects of on Polymorphic Phase Transformation of Glycine*

3.3.1. Ultrasonic velocity measurement

Ultrasonic velocity values measured in the experiments where the transformation process of β -glycine to α -glycine was studied in pure media and in the presence of different oleic acid concentrations are given in the Figure 3.20.

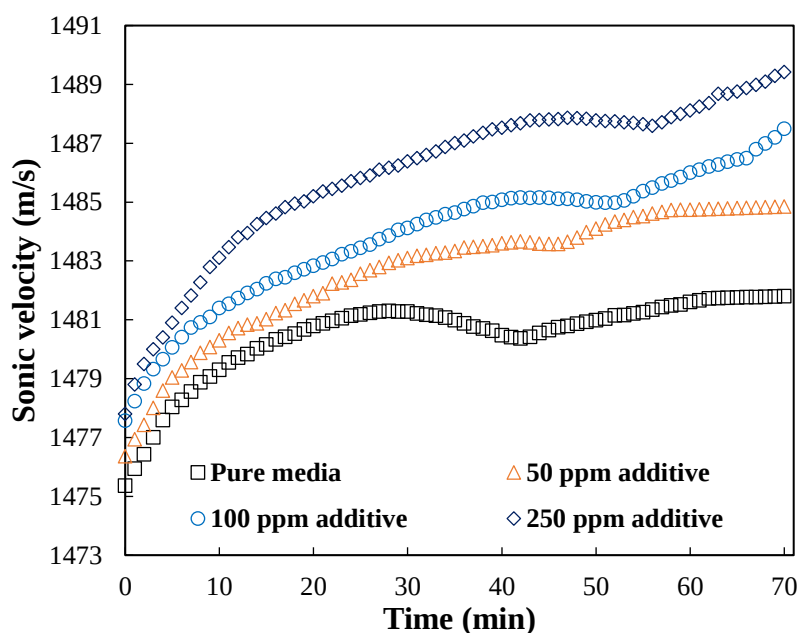


Figure 3.20. Variation of ultrasonic velocity versus time for the crystals obtained in a) pure media, and in the presence of b) 50 ppm oleic acid c) 100 ppm oleic acid d) 250 ppm oleic acid.

When time-dependent ultrasonic velocity changes of crystals produced in pure media were examined, as mentioned before the transformation process of β -glycine to α -glycine occurred in three stages. This behavior observed in the transformation process of β -glycine to α -glycine was also observed in all experiments carried out in the presence of oleic acid. Whereas the transformation process was completed in 45 minutes in pure medium, the duration was determined to be 50, 55, and 59 minutes at 50, 100, and 250 ppm oleic acid concentrations, respectively. The transformation rate was slowed by the

* Polat, S., Sayan P. (2018) Evaluation of solvent-mediated phase transformation of glycine using oleic acid: Morphology and characterization study. Chinese Journal of Chemical Engineering, In press.

addition of oleic acid. These results showed that there was a relationship between transformation time and oleic acid concentration. At 50 ppm oleic acid concentration, the additive had almost no effect on transformation time, whereas at higher concentrations, the additive tended to prolong the transformation time. The increase in the transformation time caused the morphology of the crystals and the particle shape parameters to change.

3.3.2. XRD analysis

The XRD measurements were performed both to follow the transformation process of β -glycine to α -glycine and to identify the crystal structures. The follow-up of the transformation process performed by XRD analysis was in one-to-one concurrence with the follow-up with ultrasonic velocity measurements. Taking that into consideration, the completion of the transformation time for the crystals obtained at different oleic acid concentrations was determined from velocity measurement curves; the XRD results of the samples taken during these times are shown in the Figure 3.21.

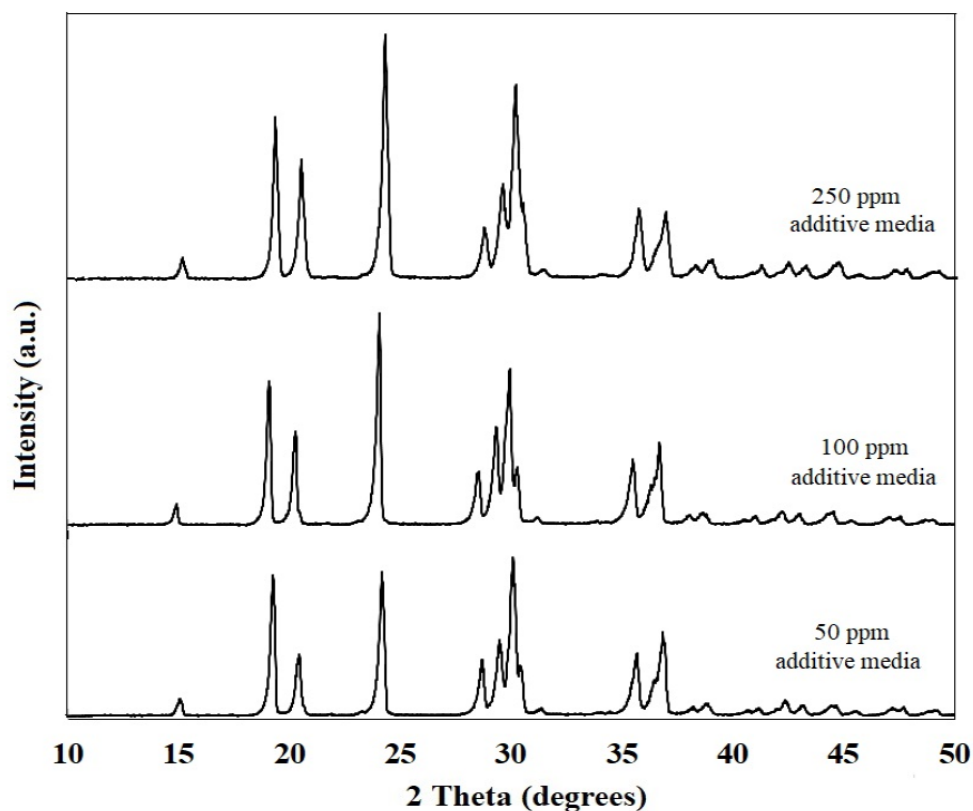


Figure 3.21. XRD results of the crystals obtained in the presence of different oleic acid concentrations.

The XRD profiles of all crystals obtained in the presence of oleic acid present the typical peaks of α -glycine; however, their peak intensities changed. The characteristic peak intensities of α -glycine increased as the concentration of oleic acid increased. This increase in intensity could result from the incorporation of additive molecules within the crystal lattice. In this circumstance, internal strains and structural imperfections occur in the individual lattice symmetry. Hereby, shifts and changes take place when the additive is present compared to those in the pure media [97].

3.3.3. SEM analysis

To determine the effects of oleic acid on glycine morphology, the SEM images of the glycine crystals with and without oleic acid contained are shown in the Figure 3.22. In agreement with the existing literature reports, the crystals obtained in pure media were prismatic with a regular rod shape and a smooth surface [25,97]. The SEM images show that both the length and the width of the crystals containing additive changed compared to those in pure media. The crystals obtained in the presence of 50 ppm oleic acid shortened lengthwise, and the crystals gained volume due to increases in their width. The crystals grew on each other, leading to formation of crystal aggregates. The same situation was also observed for crystals in the presence of 100 ppm oleic acid, and shorter crystals were obtained. As the crystals grew on each other, more dense crystal aggregates were formed compared with those in 50 ppm additive media.

As the crystal aggregates were broken by the hydrodynamic conditions of the media, partial deformations were observed on the crystal surface. Crystals retained their rod form despite shortening and increase in volume. The crystals obtained in the presence of 250 ppm oleic acid completely lost the rod form. The crystals obtained were similar in appearance and were uniformly stable. The aggregates formed during the phase transformation had weaker bonding compared with those at 50 and 100 ppm and were easily dispersed by the hydrodynamic conditions of the media. The morphology of the glycine crystals, which was clearly visible in the SEM images, varied depending upon the increase in oleic acid concentration. This change occurred as crystals acquired a different form depending on the change in the length to width ratio of the crystals.

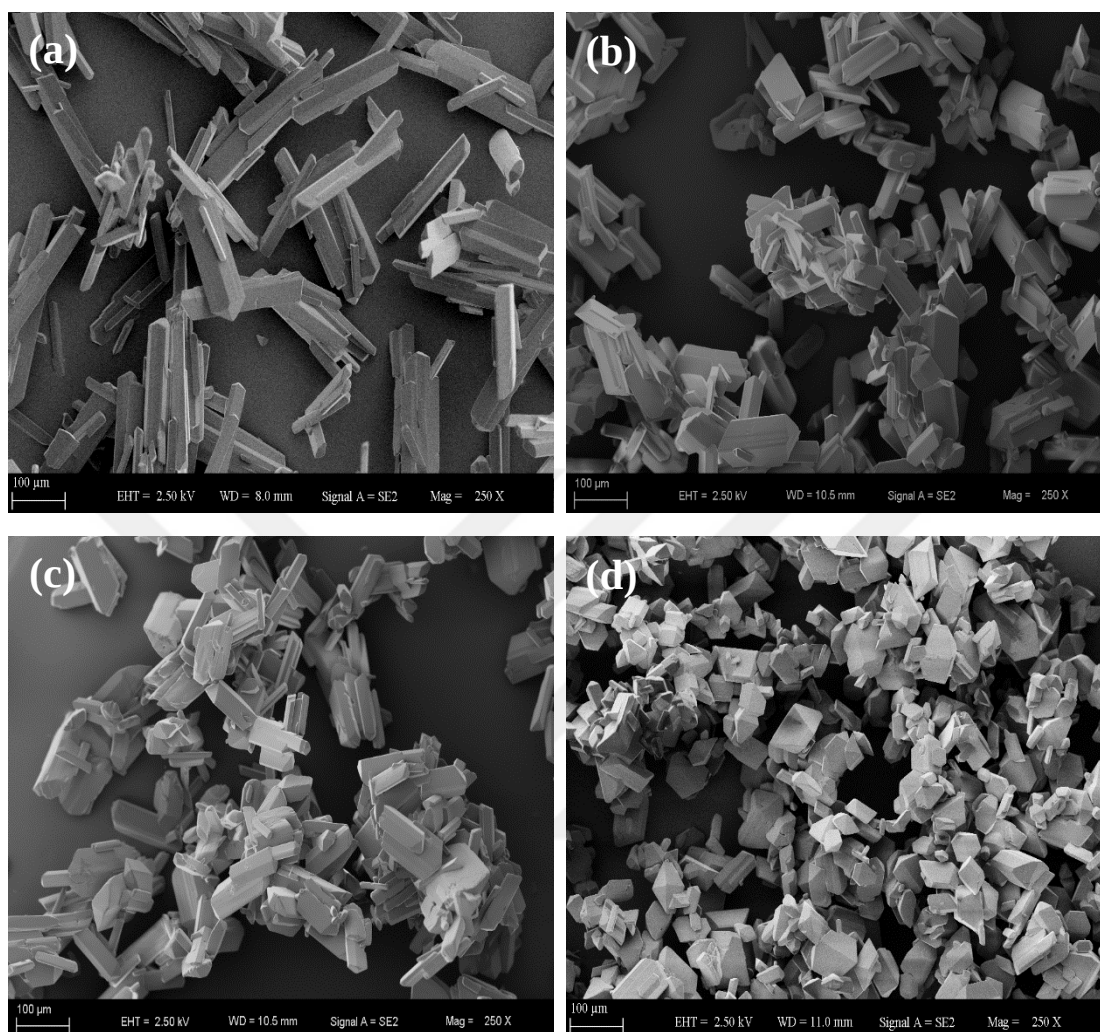


Figure 3.22. The SEM images of the glycine crystals obtained in a) in pure media, and in the presence of b) 50 ppm c) 100 ppm d) 250 ppm oleic acid concentrations.

3.3.4. Morphology analysis

The morphological analysis was performed detailed using a Morphologi G3 instrument to better demonstrate the effect of oleic acid on glycine morphology, and to describe the particle shape parameters quantitatively. In the evaluation of crystals in the Morphology G3 device, some of the images for the crystals produced in pure media and in the presence of 250 ppm additive are presented in Figure 3.23. The crystals obtained in pure media were long, uniform, and rod-shaped without roundness. The addition of oleic acid caused the differences in size and shape of the crystals. The crystals obtained in the presence of

oleic acid were smaller in size, and the crystals lengths decreased significantly. Like results obtained from SEM analysis, the crystals lost their rod form, and their shapes gained a different appearance by slight rounding.

To obtain more information about the shape of the crystals and to quantify the shape of the crystals, the particle shape factors such as circularity, elongation, and convexity were determined. Circularity is the ratio of the perimeter of a circle with the same area as the particle divided by the perimeter to the actual particle image, and elongation is determined as $[1 - \text{width}/\text{length}]$. Both circularity and elongation values range from 0 to 1: the circularity of a perfect circle is 1, whereas this value for a narrow rod is closer to 0. The elongation value of a circle is 0 whereas a rod has a high elongation. The other shape factor, convexity, is calculated by dividing the convex hull perimeter by the actual particle perimeter. The convexity of a smooth shape is 1, whereas the convexity of a very irregular object is closer to 0. [100,106,107]. Circularity, elongation, and convexity values of the crystals are given in Figure 3.23.

The high sensitivity (HS) circularity value of the crystals produced in pure media was 0.552, but this value was 0.678 in the presence of oleic acid. This was an indication that the shape of the crystals transformed to a more rounded form. The decrease of the elongation value with the additive supported this change. The convexity value was determined to be about 0.960 for both media. Aspect ratios obtained by dividing the width of the crystal by its length were also calculated to determine the agglomeration tendency of the crystals. The aspect ratio mean value was 0.483 in pure media increased to 0.649 with the addition of oleic acid to the media, indicating that agglomeration of the crystals increased in terms of shape analysis. The images obtained from SEM and Morphology G3 analyses support this view.

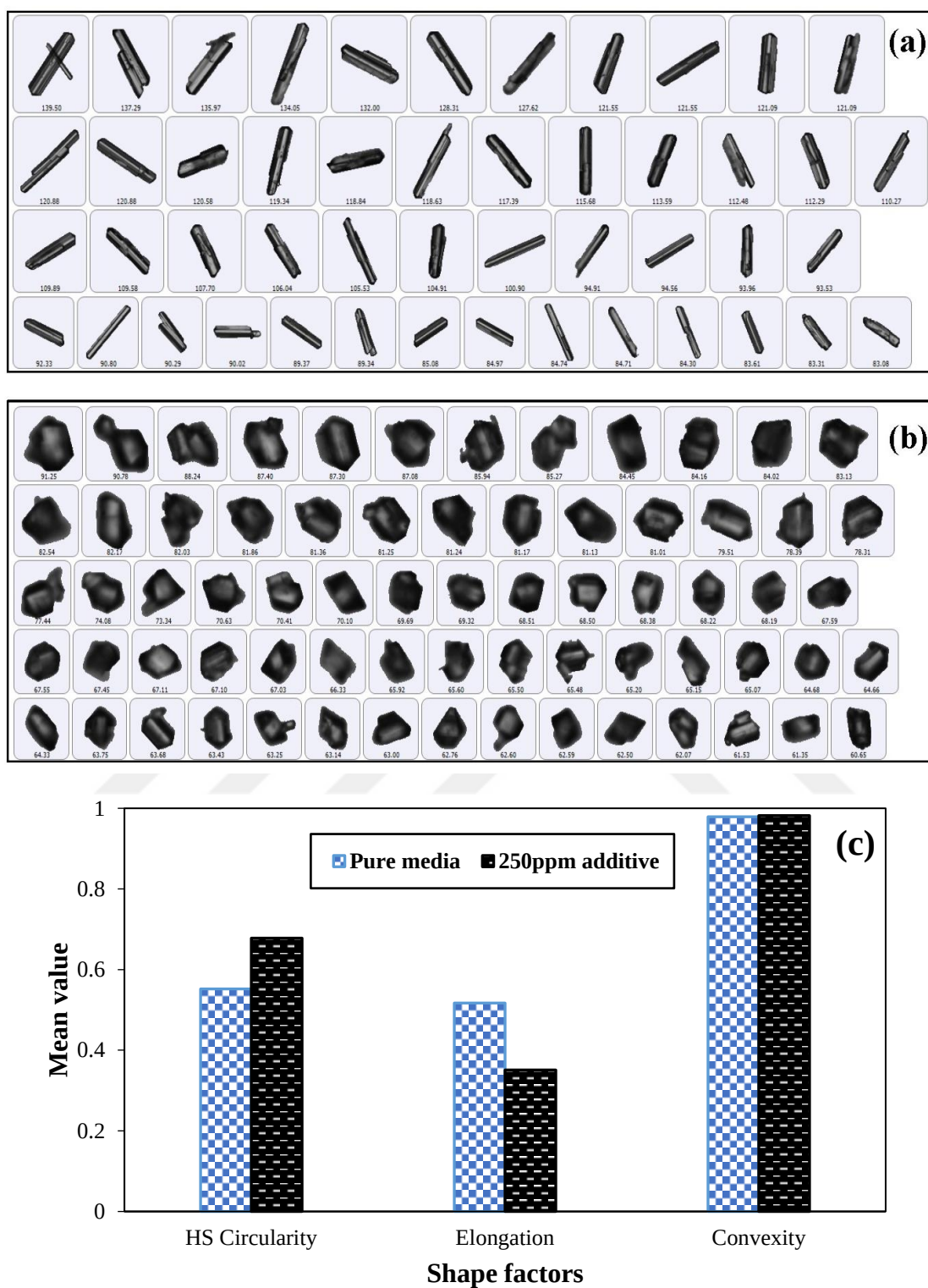


Figure 3.23. The shapes of the crystals obtained in (a) pure solution and (b) solution containing 250 ppm oleic acid. (c) Variation of the shape factor values of the crystals.

3.3.5. Thermal characteristic of the α -glycine crystals

The TG and thermogravimetric derivative (DTG) curves showing the thermal decomposition patterns of α -glycine crystals obtained in the presence of 250 ppm oleic acid at different heating rates are shown in Figure 3.24. As mentioned 3.1.5 part, thermal decomposition of α -glycine crystals obtained in pure media involved a two-stage thermal degradation process. In TG and DTG curves for the crystals obtained in 250 ppm oleic acid, the weight loss increased slightly. For instance, the total solid residue at 800 °C was 20.8% and 19.6% for crystals in the absence and presence of oleic acid, respectively.

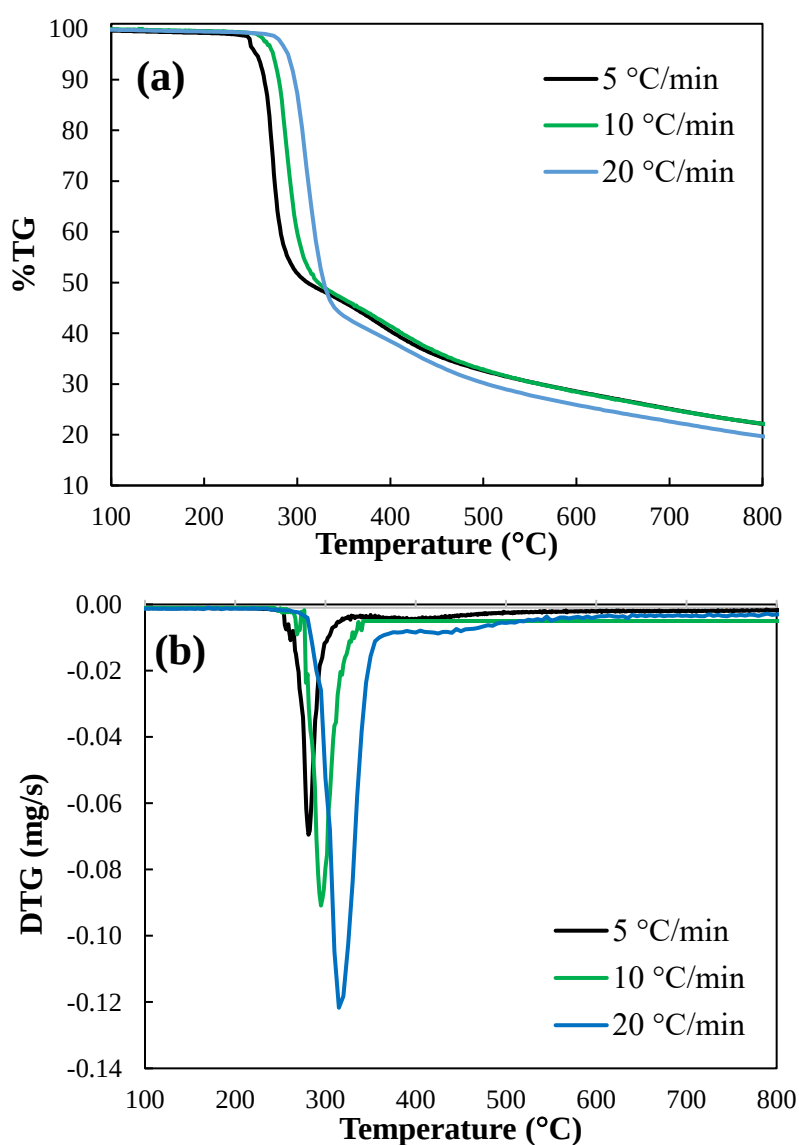


Figure 3.24. a) TG b) DTG curves of the crystals obtained in the presence of 250 ppm oleic acid at 5, 10 and 20 °C/min heating rate.

The higher total mass loss in additive media could be related to the oleic acid content of the samples. Comparing the DTG curves of the crystals obtained in the absence of additive, the maximum peak temperature increased in the presence of additive for each heating rate. Whereas the peak temperature was 286°C for pure media, this value was 294 °C due to the oleic acid adsorbed on the crystal surface.

3.3.6. Kinetic analysis

The kinetic parameter for the crystals obtained in pure and impure media was determined for the main decomposition region in the temperature range 245 to 340 °C and 260 to 353 °C, respectively. Figure 3.25 shows the activation energy values as a function of conversion between 0.1 and 0.9 with an interval 0.1 for the crystals obtained.

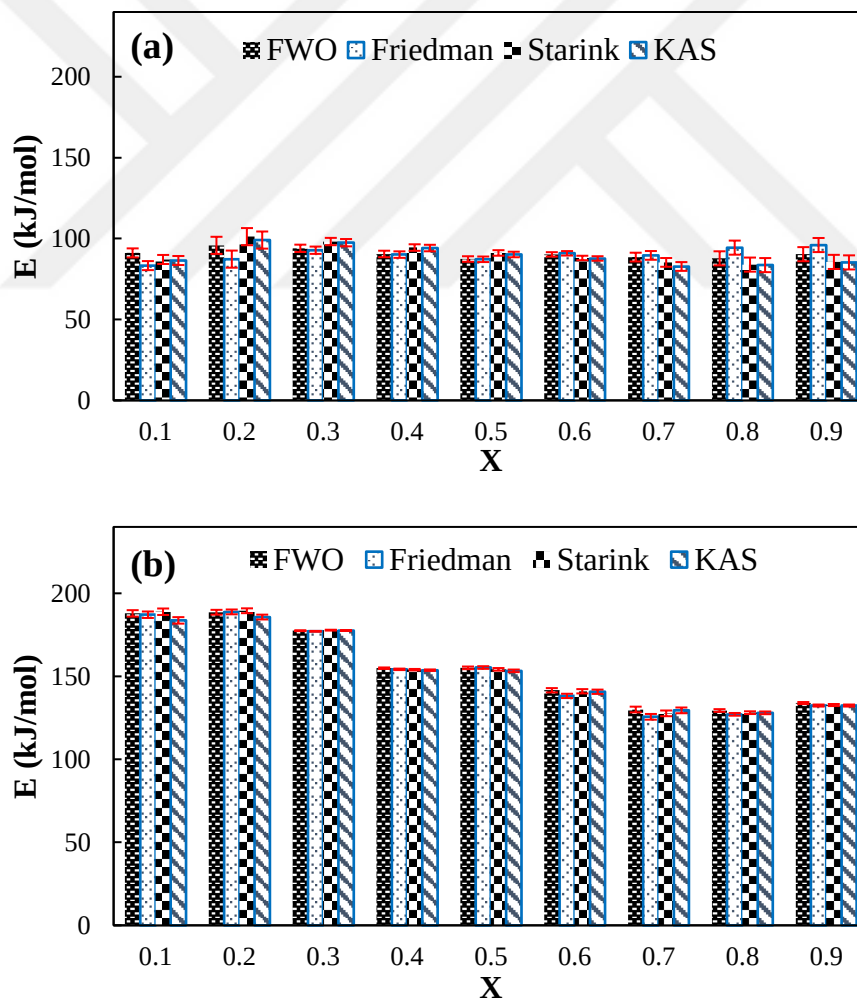


Figure 3.25. Activation energy distribution based on conversion for crystals obtained in pure media in the presence of 250 ppm oleic acid.

The calculated values of activation energy and correlation coefficient (R^2) in the conversion range between 0.1 and 0.9 with an interval 0.1 are given in Table 3.4. The calculated activation energy values as a function of conversion for the crystals obtained in pure media were very close each other, with high R^2 values. This result showed that decomposition of the crystals obtained in pure media had similar kinetic behavior for all conversion values, did not include complex reactions, and were attributable only to amino group decomposition. These calculated values were nearly the same for all models studied; this was an indication of the accuracy and reliability of the results.

Table 3.4. The activation energy (E, kJ/mol) and R^2 values of the crystals obtained with and without oleic acid using the FWO, Friedman, Starink, and KAS models.

Media	α	FWO		Friedman		Starink		KAS	
		E	R^2	E	R^2	E	R^2	E	R^2
Pure media	0.1	91.1	0.9963	83.3	0.9998	87.1	0.9956	86.4	0.9953
	0.2	95.8	0.9999	87.3	0.9911	101.2	0.9965	99.1	0.9976
	0.3	94.0	0.9963	92.8	0.9963	98.2	0.9955	97.5	0.9954
	0.4	90.5	0.9962	90.1	0.9988	94.5	0.9953	94.2	0.9953
	0.5	87.4	0.9965	87.2	0.9986	91.1	0.9957	90.2	0.9962
	0.6	90.2	0.9997	90.9	0.9999	88.0	0.9963	87.7	0.9963
	0.7	88.6	0.9986	89.6	0.9999	85.3	0.9969	82.8	0.9969
	0.8	87.8	0.9976	94.4	0.9957	83.9	0.9982	83.6	0.9982
	0.9	90.3	0.9971	96.0	0.9967	85.6	0.9996	85.3	0.9996
	Average	90.6		90.2		90.5		89.6	
Additive media	0.1	187.9	0.9894	187.1	0.9886	188.9	0.9885	183.7	0.9851
	0.2	188.6	0.9570	188.8	0.9593	189.5	0.9532	185.7	0.9586
	0.3	177.5	0.9595	177.1	0.9589	177.8	0.9548	177.6	0.9555
	0.4	154.9	0.9753	154.2	0.9783	154.0	0.9726	153.7	0.9725
	0.5	155.1	0.9586	155.3	0.9612	154.2	0.9530	153.3	0.9517
	0.6	141.6	0.9500	138.2	0.9544	141.0	0.9540	140.7	0.9537
	0.7	130.0	0.9594	125.6	0.9571	127.7	0.9526	129.5	0.9513
	0.8	129.4	0.9643	127.1	0.9529	128.1	0.9594	128.0	0.9592
	0.9	133.9	0.9830	132.4	0.9818	132.7	0.9805	132.4	0.9803
	Average	155.4	-	154.0	-	154.9	-	153.8	-

With the addition of the oleic acid to the media, the calculated activation energy values increased significantly. In other words, the minimum energy requirement of the crystals obtained in 250 ppm oleic acid for starting degradation was augmented. The average activation energy of the crystals obtained in additive media was 155.4, 154.0, 154.9, and 153.8 kJ/mol in the FWO, Friedman, Starink, and KAS models, respectively. As shown in Figure 3.25, while the calculated activation energy for pure media was almost same for whole conversion degree, this trend changed with different conversion value for additive media. The fluctuation observed in activation energy was attributable to the sample content and it showed that the reaction mechanism was not same. Compared to the pure media, the decomposition of the glycine crystals containing oleic acid was more difficult, and this process included a more complex interaction. This indicated that oleic acid affected the decomposition of the crystals and that oleic acid was adsorbed on the crystal surface. Furthermore, the results obtained by kinetic analysis were in good agreement with DTG results. The presence of oleic acid in the media resulted in a shift to higher temperature in the both maximum peak temperatures, and increased values of the calculated activation energy.

3.3.7. FTIR and elemental analysis

The functional groups of the crystals obtained in pure media and in the presence of 250 ppm oleic acid as determined by means of FTIR analysis; the spectra are shown in Figure 3.26.

Compared to FTIR spectra obtained in the pure media, the slight shifting behavior and an increase in intensity was observed. In addition, the specific peak at 1718 cm^{-1} peak indicating oleic acid was observed in the FTIR spectrum obtained in the additive media. The peak at 1285 cm^{-1} was also related to the C–O stretching of carboxylic group in oleic acid. Moreover, the C-H stretching vibration band in the double bond (C=C-H) at 3009 cm^{-1} indicated the presence of oleic acid [108]. These peaks indicated the presence of oleic acid adsorbed on the crystal surface.

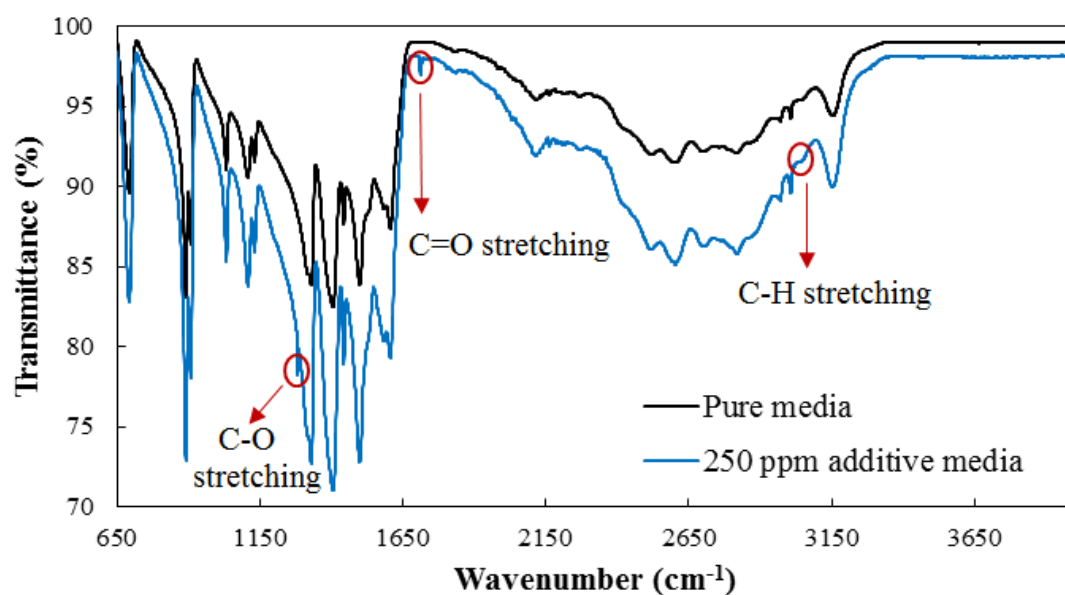


Figure 3.26. FTIR spectra of the crystals obtained in pure media (a) and impure media (b).

The crystals obtained were further characterized by elemental analysis. The elemental composition of the crystals obtained in pure media was 31.99% C, 6.69% H, and 18.55% N. When oleic acid was added to the media, this composition changed slightly. The crystals obtained in 250 ppm oleic acid consisted of 32.38% C, 6.73% H, and 18.47% N. The presence of the additive caused an increase in carbon and hydrogen content but a decrease in nitrogen content. In addition to the elemental analysis, the nitrogen quantification of the crystal end products were determined by Kjeldahl analysis using Gerhardt VAPODEST® 20. The nitrogen contents of crystals obtained in pure media and in the presence of additive media were 19.6% and 19.4%, respectively. This result was consistent with both elemental and FTIR analyses, confirming that oleic acid had adsorbed on the glycine crystal surface.

3.3.8. Filtration analysis

To detect the impact of oleic acid on the filtration characteristics of α -glycine, the filtration rates are measured in the absence and the presence of different concentrations of oleic acid. The specific cake resistance and the average cake porosity results are given in the Figure 3.27.

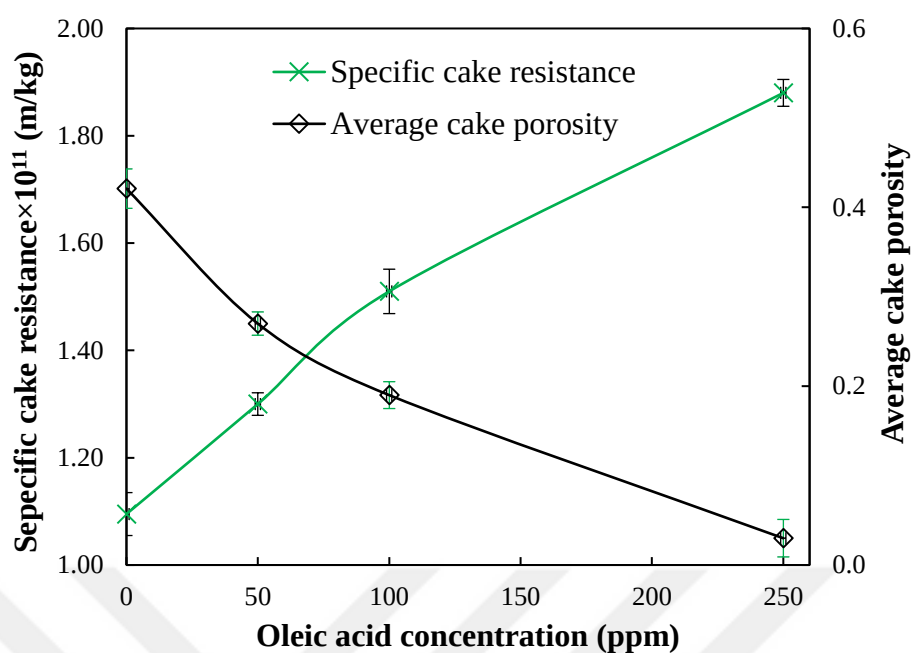


Figure 3.27. Variation of the specific cake resistance and average cake porosity values of the crystals obtained in the absence and presence various oleic acid concentrations.

As the concentration of oleic acid increased to 250 ppm, the specific cake resistance value increased to 1.88×10^{11} m/kg, while the average porosity value decreased to 0.03. This can be attributed to the morphological change and decrease in the average particle size of the crystals.

3.4. The Results of Myristic Acid Effects on Polymorphic Phase Transformation of Glycine*

3.4.1. Ultrasonic velocity measurement

The variation of the ultrasonic velocity over time during the phase transformation for the pure and myristic acid media is shown in Figure 3.28. As can be seen in Figure 3.28, the curves showed a similar tendency for both additive and non-additive media. As said before, the duration of the complete transformation process in pure media was 45 minutes. However, this time changed with the addition of the myristic acid in the crystallization media. The value for 50, 100 and 250 ppm myristic acid media was determined as 55, 60 and 66 minutes, respectively. This result showed that myristic acid had a retarding effect on the transformation process and increased the phase transformation time.

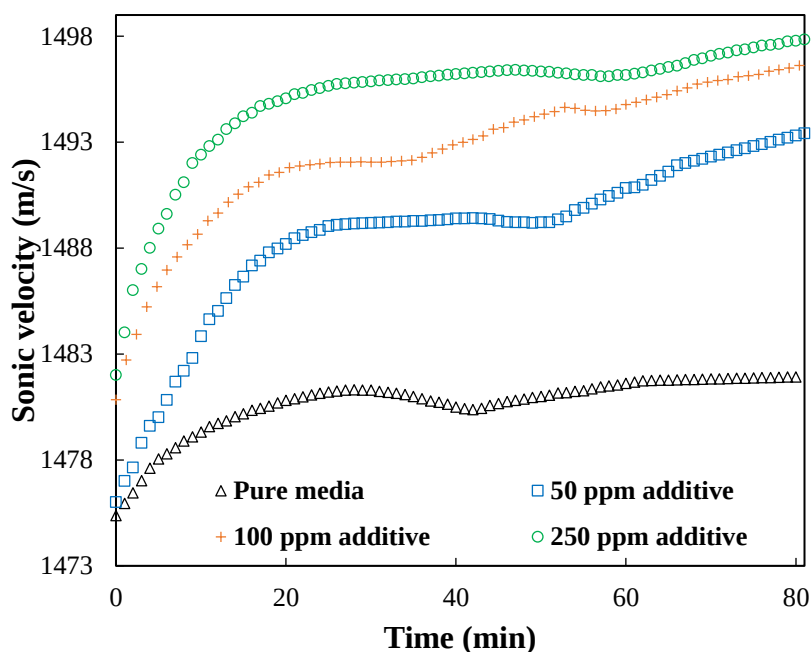


Figure 3.28. Changes in ultrasonic velocity over time for the crystals obtained in the absence and the presence of different myristic acid concentrations.

* Polat, S., Sayan P. (2018) Evaluation of myristic acid effect on polymorphic transformation of glycine. 25th International Workshop on Industrial Crystallization (BIWIC2018).

3.4.2. XRD analysis

The X-ray diffraction patterns of the crystals obtained by completion of transformation process in pure media and in the presence of different myristic acid concentrations are depicted in Figure 3.29.

As seen from the pattern of the crystals obtained in pure media, any characteristic peaks representing β -glycine form were detected. In other words, all peaks were regarded to the α -form and this result was coincided with the literature data [5]. After the addition of the myristic acid to media, the peaks obtained did not include any characteristic peaks related to the additive however there was a slight change in the diffraction pattern intensity.

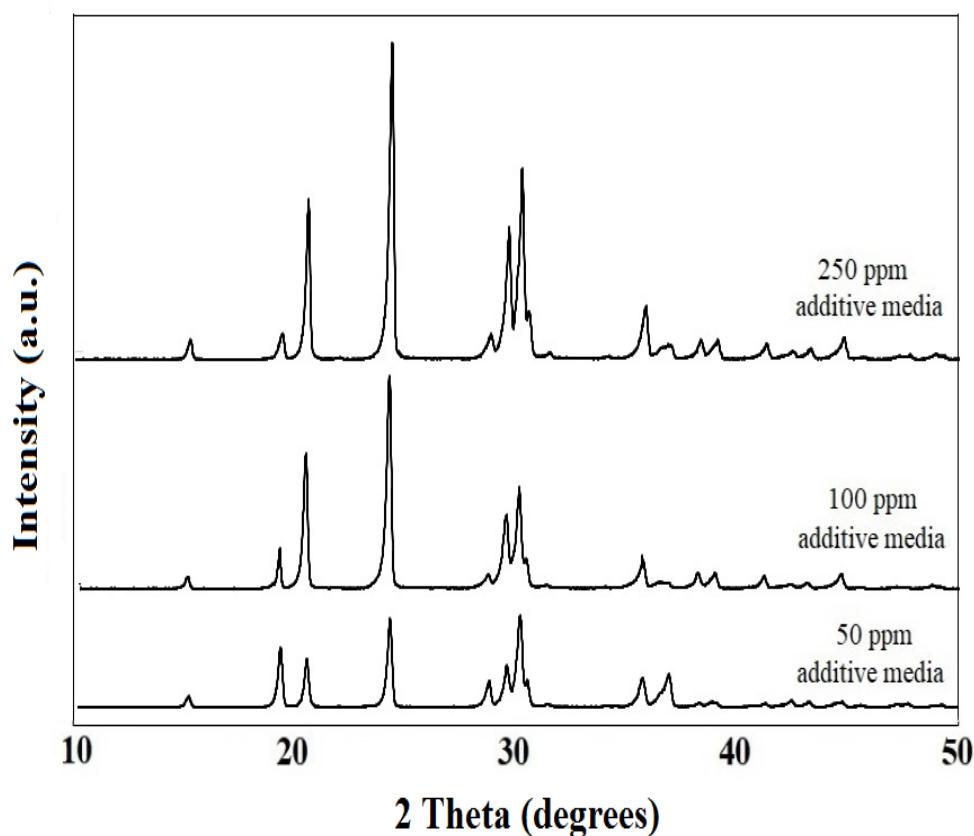


Figure 3.29. XRD results of the crystals obtained in the presence of different myristic acid concentrations.

3.4.3. SEM analysis

SEM analysis was performed to investigate the effects of myristic acid on crystal habit of glycine crystals. SEM images of α -glycine crystals obtained in pure media and in the presence of different myristic acid concentrations are given in Figure 3.30. The crystals obtained in pure media were long form and prismatic shape. In the presence of 50 ppm myristic acid, α -glycine crystals had a prismatic structure but had no distinct form. Multiple crystal formations were observed on the surfaces due to the crystal defects.

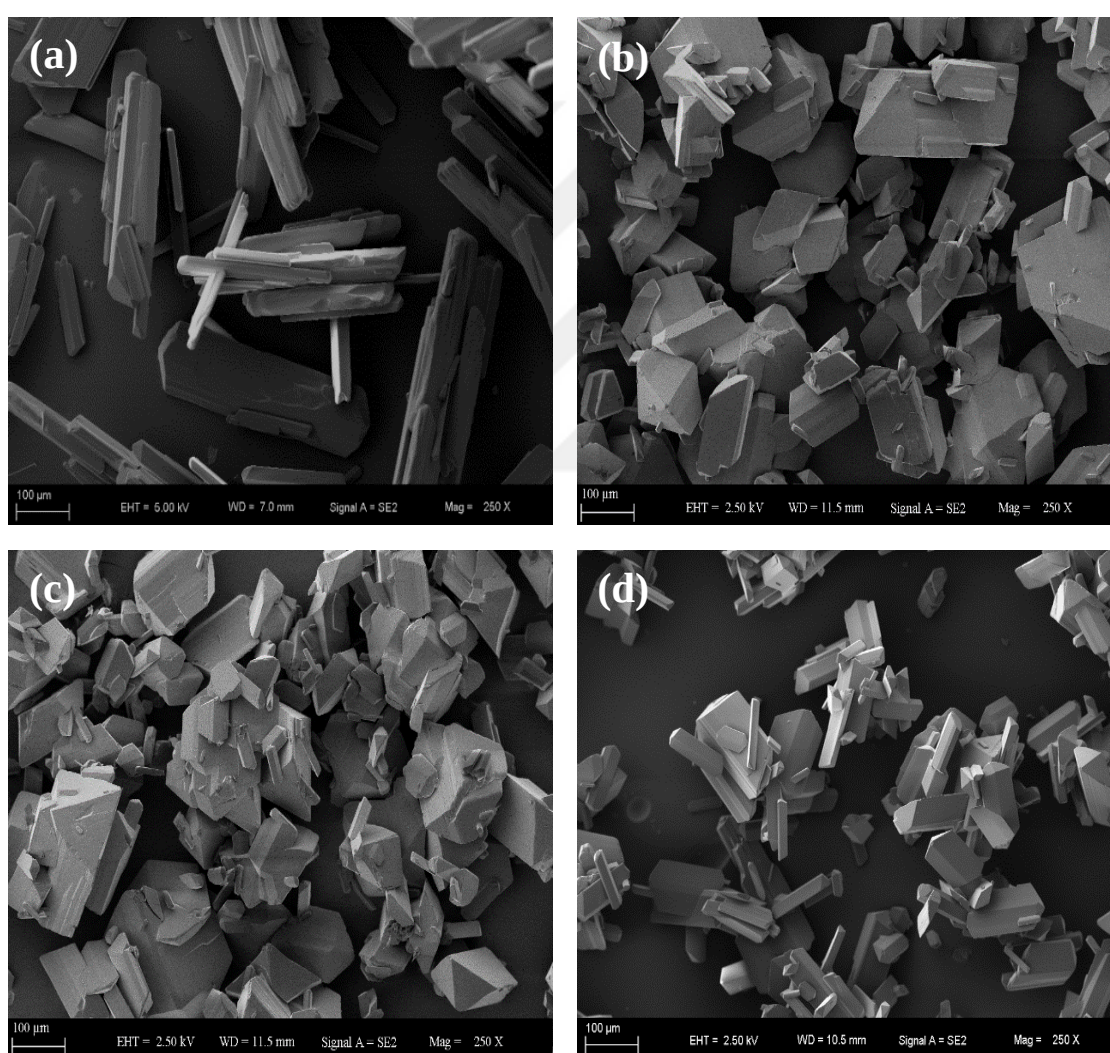


Figure 3.30. SEM images obtained a) in pure media b) in the presence of 50 ppm myristic acid c) in the presence of 100 ppm myristic acid d) in the presence of 250 ppm myristic acid.

Compared to pure media, the crystal widths increased whereas the lengths decreased. The aspect ratio of α -glycine crystals obtained in pure media was 0.483 whereas the aspect ratio was 0.514 for crystals obtained in the presence of 50 ppm myristic acid. As the concentration of myristic acid increased, the crystals obtained were shrunk, and the number of crystals with a smoother and more pronounced prismatic structure increased. Unlike the crystals obtained in the presence of 50 ppm myristic acid, the crystals in the form of rods also began to emerge. In other words, both prismatic and rod-shaped crystals coexisted. As the crystals grew on each other, agglomerates were formed. These agglomerates formed had an intact structure and were hardly affected by the hydrodynamic conditions of the media. In the detailed quantitative morphology analysis performed, the aspect ratio of the crystals obtained in the presence of 100 ppm additive was measured as 0.586 and average particle size of the crystals decreased from 85 μm to 71 μm . It was seen that there was a clear decrease in the average particle size compared to the crystals obtained in the presence of 50 ppm myristic acid. In the presence of 250 ppm myristic acid, the crystals were completely rod-shaped and their morphology was quite different from the crystals obtained in pure media and in the presence of 50 and 100 ppm additive media. The aspect ratio of the crystals was determined as 0.628 and the smallest particle size was obtained under these studied conditions. Agglomeration tendency was lower when compared with other additive concentrations studied. The crystals had a tendency to grow on each other, but because of their poor character, they could easily break due to the hydrodynamic conditions of the media. This, in turn, played an important role in the small particle size measured in this case.

3.4.4. Morphology analysis

Figure 3.31 shows the shape parameters such as elongation, circularity and convexity for α -glycine crystals grown in the absence and the presence of 250 ppm myristic acid.

The HS circularity value was 0.552 for pure media, while it was 0.705 for additive media. On the other hand, the addition of the myristic acid created a significant decrease in elongation value. While the elongation was 0.517 μm for pure media, this value was determined as 0.372 μm in additive media. This result was supported by SEM analysis. It was also detected that the convexity value was 0.979 for pure media and this value increased to 0.988 in the presence of myristic acid.

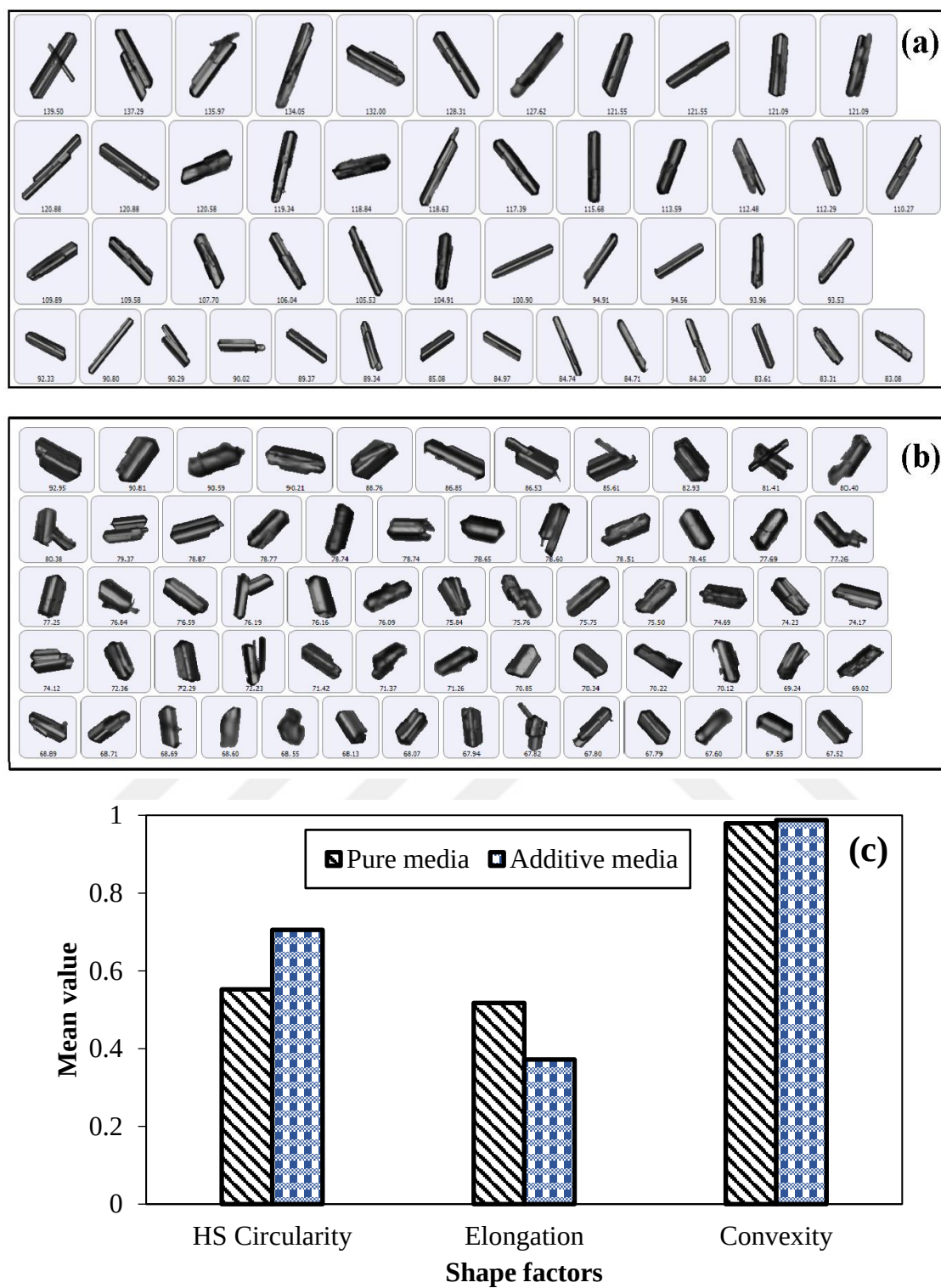


Figure 3.31. The shapes of the crystals obtained in (a) pure solution and (b) solution containing 250 ppm myristic acid. (c) Variation of the shape factor values of the crystals.

3.4.5. Thermal characteristic of the α -glycine crystals

The TG and thermogravimetric derivative (DTG) curves showing the thermal decomposition patterns of α -glycine crystals obtained in the presence of 250 ppm myristic acid at different heating rates are shown in Figure 3.32. In TG and DTG curves for the crystals obtained in 250 ppm myristic acid, the weight loss increased slightly. Moreover, the higher total mass loss was detected and the slight shifting in the maximum peak temperature was observed in myristic additive media.

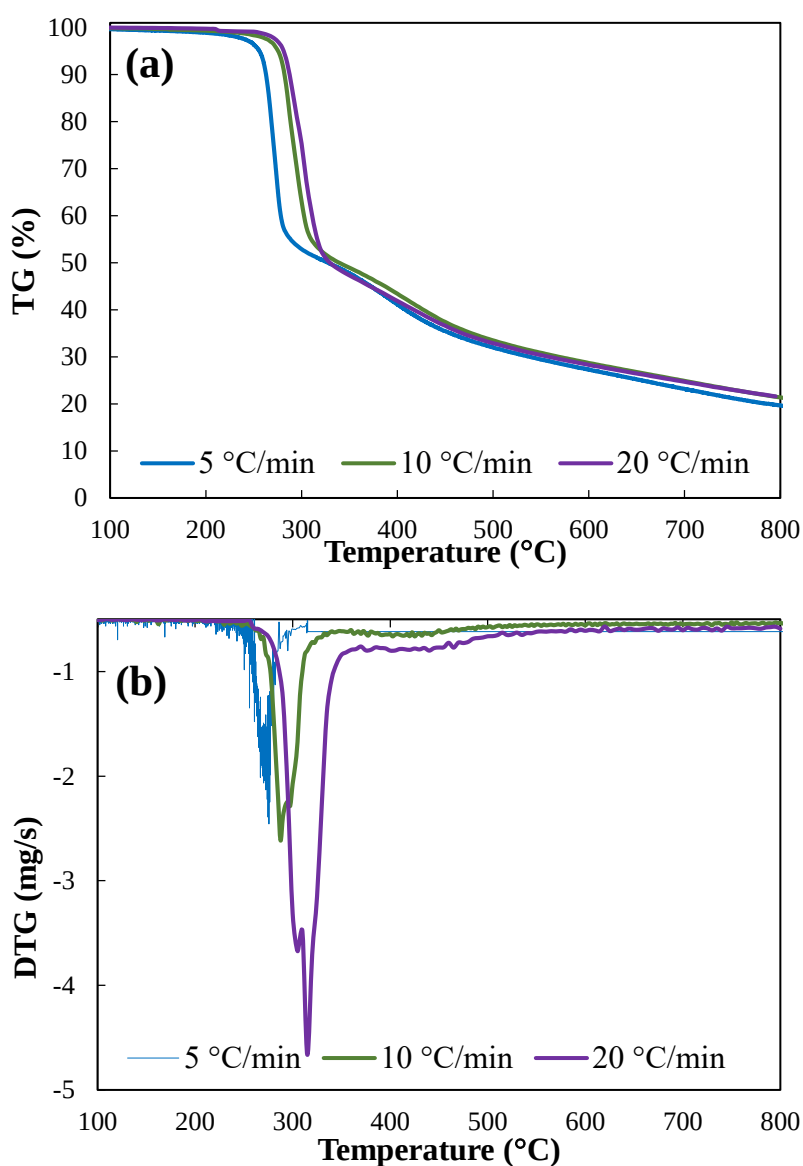


Figure 3.32. a) TG b) DTG curves of the crystals obtained in the presence of 250 ppm myristic acid at 5, 10 and 20 °C/min heating rate.

3.4.6. Kinetic analysis

The kinetic parameter for the crystals obtained in pure and myristic acid media was determined for the main decomposition region in the temperature range 245 to 340 °C and 265 to 365 °C, respectively. Figure 3.33 and Table 3.5 show the activation energy values as a function of conversion between 0.1 and 0.9 with an interval 0.1 for the crystals obtained.

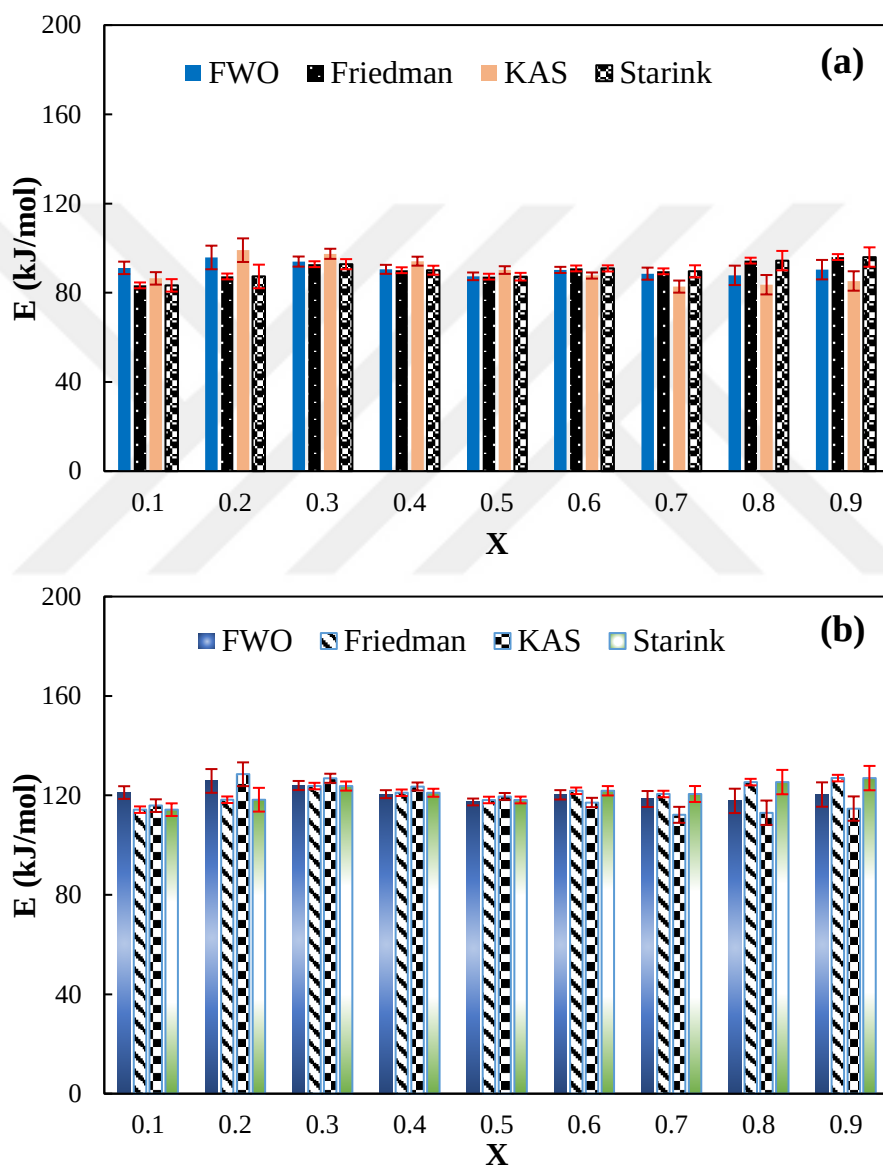


Figure 3.33. Variation of activation energy with respect to conversion degree for the crystals obtained a) in pure media and b) in the presence of 250 ppm myristic acid.

The average activation energy of the crystals obtained in 250 myristic acid media under the FWO, Friedman, Starink and KAS models was calculated as 120.6, 121.1, 120.3 and 119.1 kJ/mol, respectively. Although the activation energy calculated for the Friedman model was determined to be slightly higher than that of the other studied models, these values were nearly the same for all models studied, and they were in good agreement with each other. This situation indicates that the model equation fitted the experimental data well and the values obtained were reliable and accurate.

Table 3.5. The activation energy (E, kJ/mol) and R^2 values of the crystals obtained in the absence and in the presence of myristic acid using the FWO, Friedman, Starink, and KAS models.

Media	α	FWO		Friedman		Starink		KAS	
		E	R^2	E	R^2	E	R^2	E	R^2
Pure media	0.1	91.1	0.9963	83.3	0.9998	87.1	0.9956	86.4	0.9953
	0.2	95.8	0.9999	87.3	0.9911	101.2	0.9965	99.1	0.9976
	0.3	94.0	0.9963	92.8	0.9963	98.2	0.9955	97.5	0.9954
	0.4	90.5	0.9962	90.1	0.9988	94.5	0.9953	94.2	0.9953
	0.5	87.4	0.9965	87.2	0.9986	91.1	0.9957	90.2	0.9962
	0.6	90.2	0.9997	90.9	0.9999	88.0	0.9963	87.7	0.9963
	0.7	88.6	0.9986	89.6	0.9999	85.3	0.9969	82.8	0.9969
	0.8	87.8	0.9976	94.4	0.9957	83.9	0.9982	83.6	0.9982
	0.9	90.3	0.9971	96.0	0.9967	85.6	0.9996	85.3	0.9996
	Average	90.6		90.2		90.5		89.6	
Additive media	0.1	121.1	0.9816	114.3	0.9828	116.9	0.9883	115.9	0.9826
	0.2	125.8	0.9883	118.3	0.9944	131.0	0.9924	128.5	0.9883
	0.3	124.0	0.9991	123.8	0.9888	128.0	0.9878	126.9	0.9899
	0.4	120.5	0.9809	121.1	0.9923	124.3	0.9856	123.6	0.9906
	0.5	117.4	0.9874	118.2	0.9901	120.9	0.9900	120.0	0.9941
	0.6	120.2	0.9923	121.9	0.9984	117.8	0.9936	117.1	0.9996
	0.7	118.6	0.9949	120.6	0.9883	115.1	0.9946	112.2	0.9887
	0.8	117.8	0.9899	125.4	0.9994	113.7	0.9974	113.0	0.9896
	0.9	120.3	0.9958	127.0	0.9964	115.4	0.9904	114.7	0.9973
	Average	120.6		121.1		120.3		119.1	

As shown in Table 3.5, the addition of myristic acid significantly increases the activation energy of glycine crystal decomposition, showing a high linear correlation coefficient. The presence of myristic acid to the crystallization media causes a fluctuation in

activation energy. The α -glycine crystals with additive media required a higher activation energy value during thermal decomposition process due to the additive content. This could be consistent with the adsorption of the myristic acid to the crystal surface.

3.4.7. FTIR and elemental analysis

The FTIR spectra of the crystals obtained in pure and non-pure media were collected for the qualitative determination of their chemical structure and investigation of adsorption of myristic acid on the crystal surface. Figure 3.34 shows the FTIR spectra for the crystals obtained in pure media and in the presence of 250 ppm myristic acid.

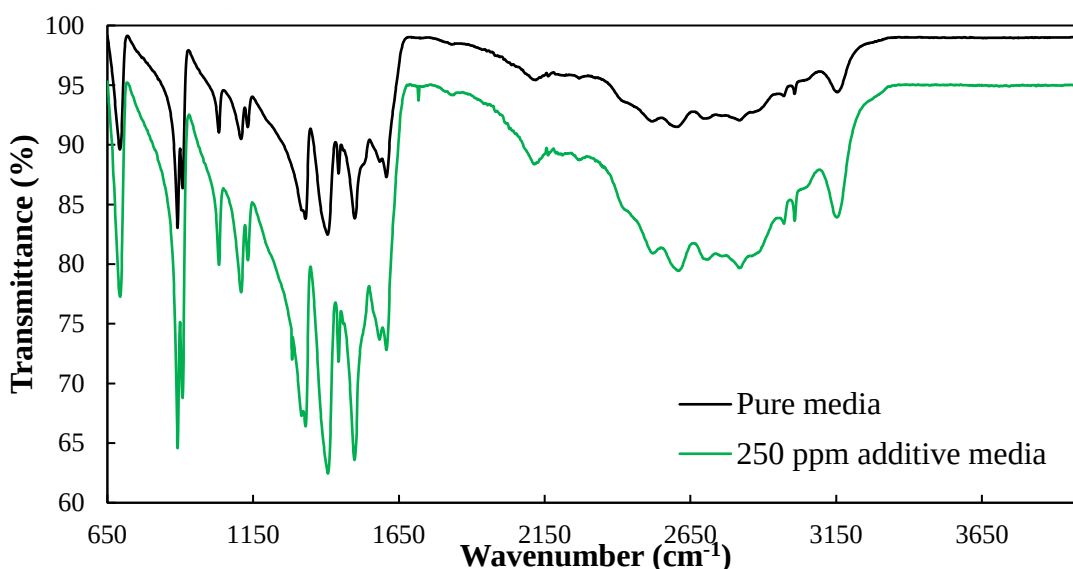


Figure 3.34. FTIR spectra of the crystals obtained in pure solution and solution containing 250 ppm myristic acid.

Compared to the pure media, the crystals grown in additive media displayed two different absorbance bands due to adsorption of myristic acid on the crystal surface. The bands located around at 1700 cm^{-1} and 1280 cm^{-1} were ascribed to C=O and C–O stretching vibration of the carboxylic group in myristic acid. This result indicated the presence of additive on the crystal. The elemental composition of the crystals obtained before and after myristic acid adsorption was determined and the variation of the compositions were examined to detect the influence of the additive on the crystals. The elemental composition of the pure α -glycine crystals contained 31.99% C, 6.69% H, and 18.55% N.

After 250 ppm myristic acid adsorption, % C, % H, and % N values of the crystals were determined as 32.14, 6.73 and 18.40, respectively. The result obtained from elemental analysis was that the content of the crystals were slightly changed. Both FTIR and elemental analysis results supported each other. In parallel with FTIR analysis, elemental analysis was another confirmation of the myristic acid binding on the crystal surface.

3.4.8. Filtration analysis

In order to determine the impact of myristic acid on the filtration characteristics of α -glycine, the filtration rates are measured in non-additive media and in the presence of different concentrations of myristic acid. The filtration rate measurements were evaluated and the specific cake resistance and the average cake porosity were calculated. The results are given in the Figure 3.35.

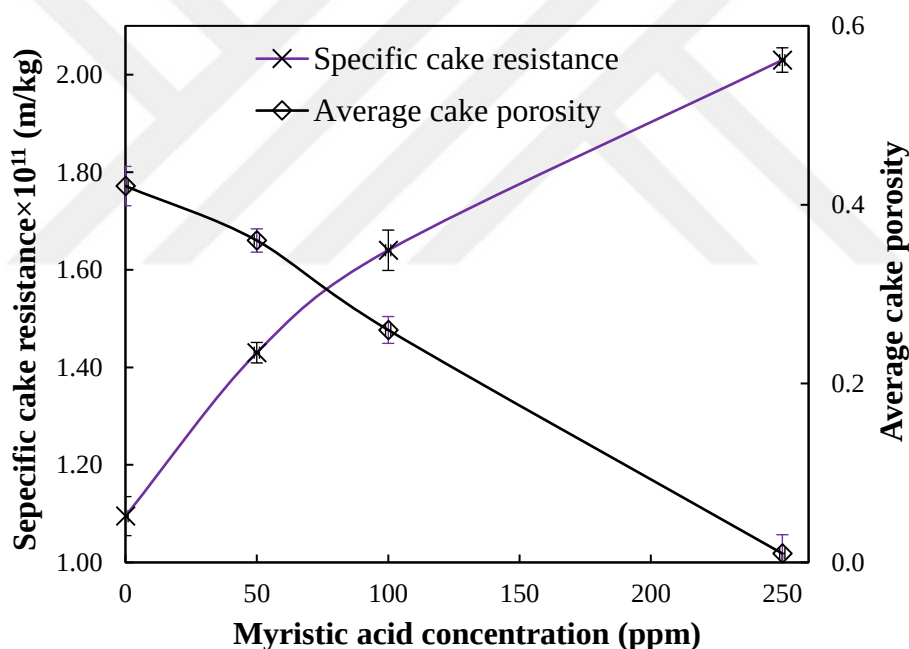


Figure 3.35. Variation of the specific cake resistance and average cake porosity values of the crystals obtained in the absence and presence various myristic acid concentrations.

As shown in Figure 3.35 when the concentration of myristic acid increased to 250 ppm, the specific cake resistance value increased to 2.03×10^{11} m/kg, while the average porosity value decreased to 0.01. This can be attributed to the morphological change and decrease in the average particle size of the crystals.

3.5. The Results of Various Carboxylic Acids Effects on Polymorphic Phase Transformation of Glycine*

3.5.1. Ultrasonic velocity measurement

The solution mediated phase transformation time from β -glycine to α -glycine obtained in the presence of three different carboxylic acid additives (acetic, tartaric and citric acid) was determined using an ultrasonic measuring technique at a constant temperature of 25 °C. The changes in the ultrasonic velocity over time during the phase transformation observed for the pure and non-pure media are shown in Figure 3.36.

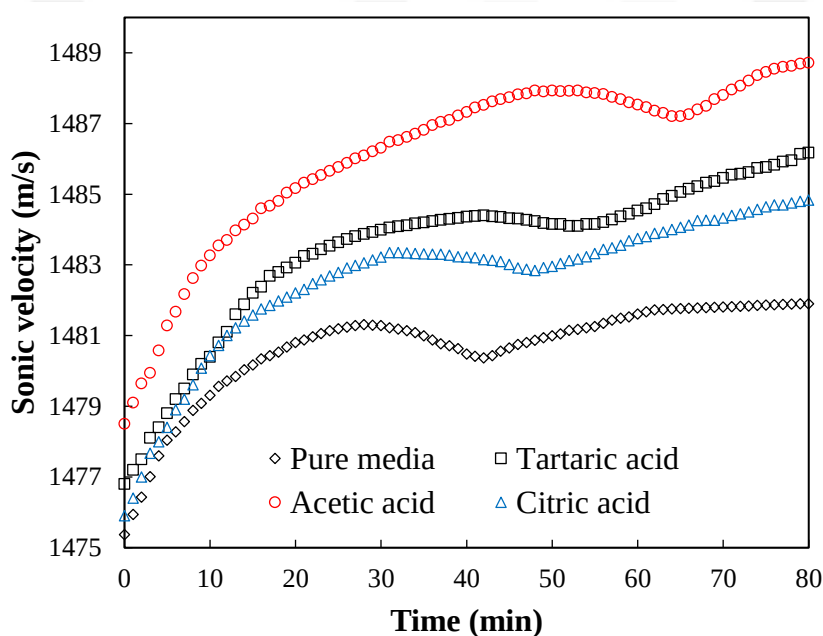


Figure 3.36. The variation in the ultrasonic velocity values versus time observed for the additive containing and non-additive crystallization media.

The curves in Figure 3.36 show a similar tendency for both the additive containing and non-additive media. As said before, this transformation process can be divided into three different steps. These are β -glycine dissolution, α -glycine nuclei formation and α -glycine crystal growth, respectively. The duration of the complete transformation of β -glycine to α -glycine crystals obtained in the pure solution was 45 min. However, this changed upon

* Submitted to Journal.

the addition of the carboxylic acid additives to the crystallization medium. The values obtained for the media containing acetic, tartaric and citric acid were determined to be 51, 58 and 69 min, respectively. These results show that the carboxyl acid additives have a retardation effect on the transformation process and increased the phase transformation time.

3.5.2. XRD analysis

The X-ray diffractograms recorded for the crystals obtained upon the completion of the transformation process in the different carboxylic acid additive containing and non-additive media are depicted in Figure 3.37.

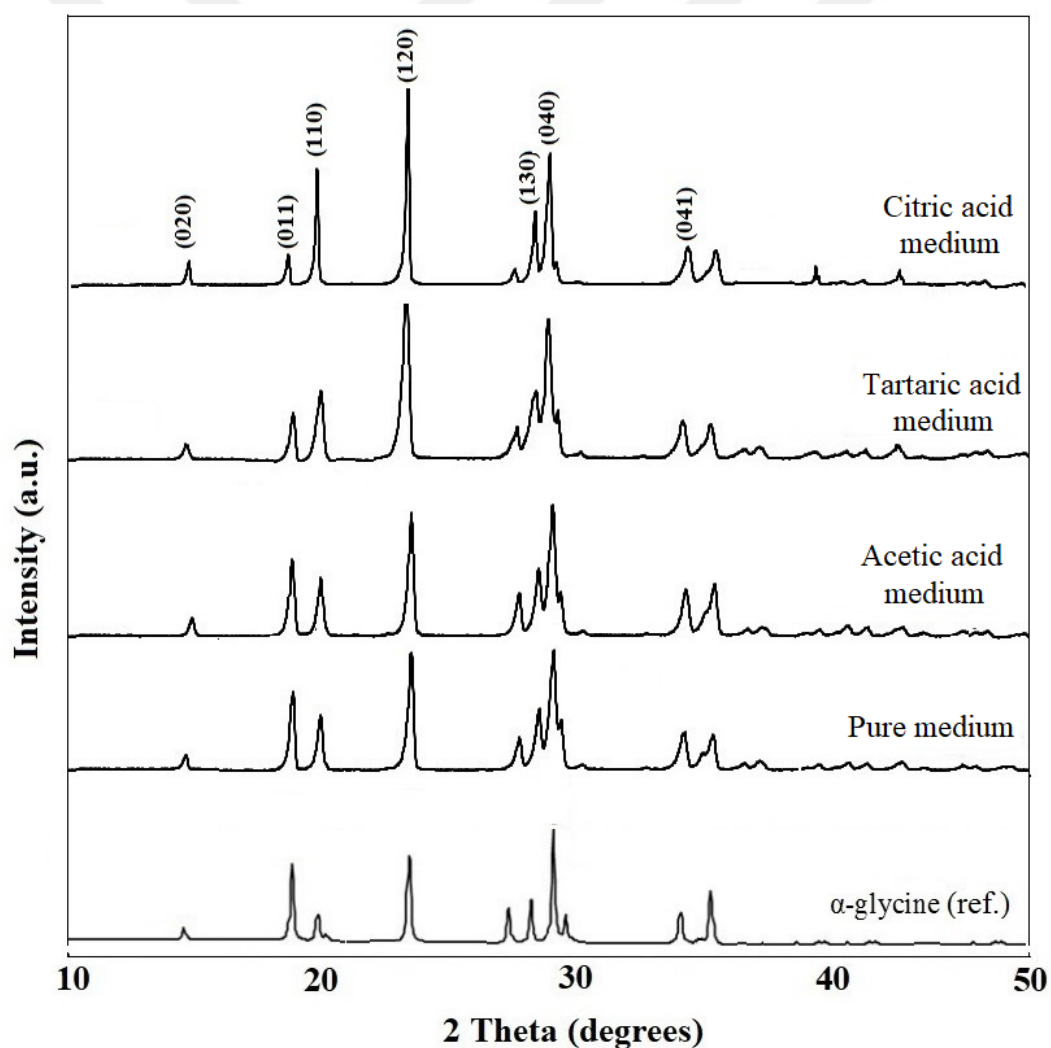


Figure 3.37. The XRD results recorded for the crystals obtained from the additive containing and non-additive media.

The characteristic peaks of the β -glycine form were not observed in the diffractograms recorded for the crystals acquired from the pure solution. In other words, all the peaks correspond to the α -glycine form and this result was in agreement with the literature [11]. Upon the addition of the carboxylic acid additives to the crystallization medium, the observed peaks did not include any characteristic peaks related to the carboxylic acid additives, however, there was a slight change in the peak intensity of the diffraction patterns.

The average crystallite size (ξ) of the crystals obtained from the additive containing and non-additive media was determined from the intensity of the strongest peak at $2\theta = 23.85^\circ(120)$ and calculated from the XRD patterns using the following equation [109].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3.1)$$

where k is a constant (0.94), λ is wavelength of the X-ray radiation (1.540598 Å), β is the full width at half maximum of the reference diffraction peak (measured in radians) and θ is the angle of diffraction. The calculated crystallite size of the crystals obtained from the non-additive, acetic acid, tartaric acid and citric acid containing media were found to be 31.89 nm, 37.07 nm, 35.06 nm and 32.36 nm, respectively. The values of the crystallite size for the crystals obtained from the additive-containing media were slightly higher than observed for the crystals obtained from the pure medium.

3.5.3. SEM and morphology analysis

SEM was used to investigate the surface characteristics and determine the carboxylic acid additive effects on the α -glycine crystals. Figure 3.38 demonstrates the SEM images of the crystals obtained upon the completion of the transformation process in the additive containing and non-additive media. The pure α -glycine crystals have a rod-like form and prismatic shape. Morphological analysis of the pure crystals revealed that the aspect ratio was 0.483. The crystals resembled each other and had a homogeneous appearance with smooth surface. The α -glycine crystals obtained from the crystallization medium containing acetic acid lost their rod-like form and gained a pyramidal appearance. The

aspect ratio of the α -glycine crystals was determined to be 0.521. When compared to the pure medium, the agglomeration tendency of the crystals increased in the acetic acid-containing crystallization medium. The agglomerates have a weak character and are in a form that could be broken by the hydrodynamic conditions of the medium, which is in agreement with the increase in the aspect ratio observed.

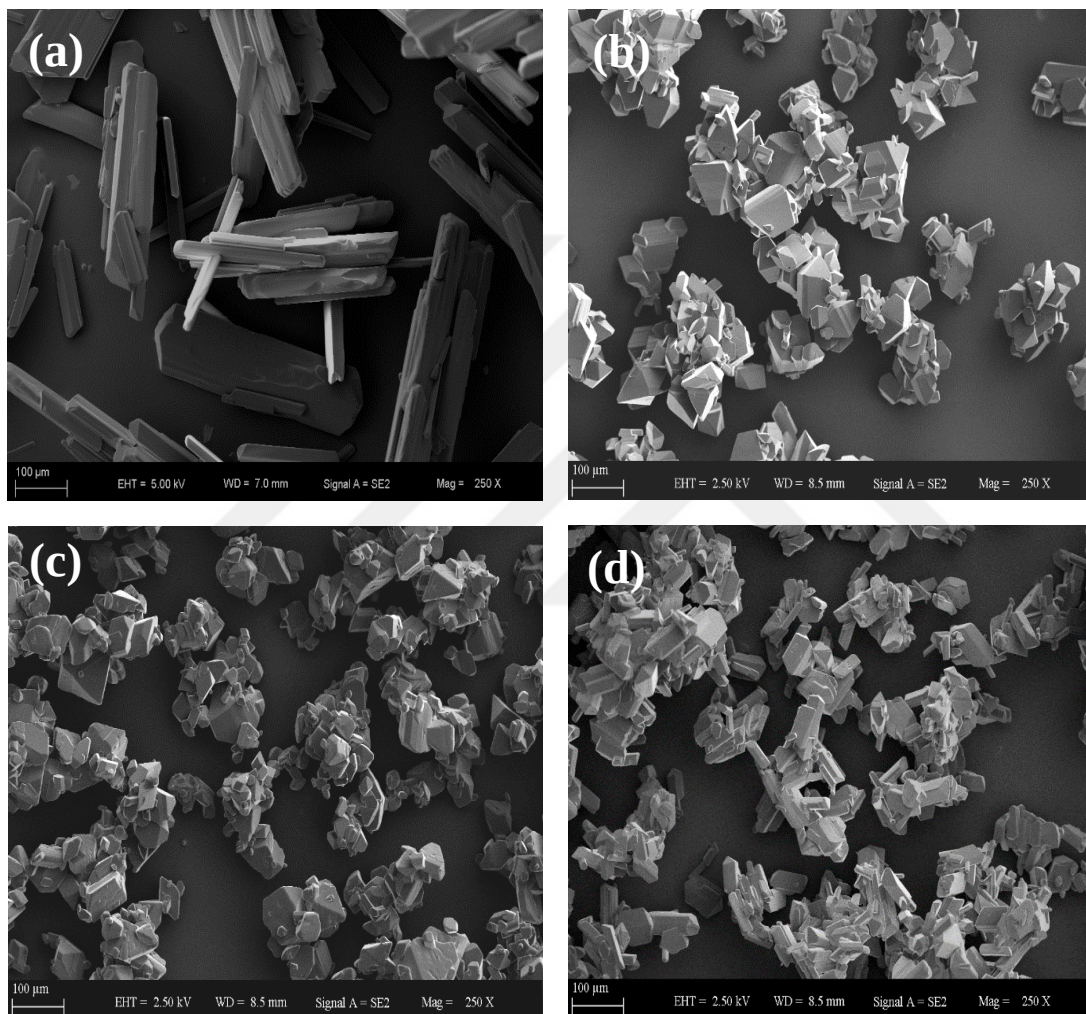


Figure 3.38. The SEM images of the crystals obtained for the crystals obtained from the (a) pure solution and the (b) acetic acid, (c) tartaric acid and (d) citric acid containing media.

However, it was seen that the sharp edges of the pyramidal crystals were rounded when compared to the crystals obtained in the solution containing citric acid. At the same time, the crystals were observed to form on top of each other and formed agglomerates with a more robust structure. Crystals that did not have a definite form were also observed due

to crystal defects. In the quantitative morphological analysis, the HS circularity value was found to be 0.552 for the pure medium, while it was 0.591 and 0.687 for the media containing acetic and tartaric acid, respectively. Moreover, the elongation (1-width/length) was also determined to be 0.479 and 0.413 for the media containing acetic and tartaric acid, respectively. That is, the elongation value of the crystals decreased upon the addition of the carboxylic acid additive to the crystallization medium. This result was also supported by the SEM analysis. The crystals obtained from the solution containing citric acid were not in a straight structure, but in a hexagonal form. Although they were morphologically similar to the pure glycine crystals, their aspect ratio was increased. This value was determined to be 0.508. This suggests that the crystals maintained their main crystal form and the values of the aspect ratio were similar. The crystal size of the α -glycine obtained from the citric acid-containing medium decreased and these crystals formed compact agglomerates. Intensely intercalated crystals were present and the number of crystals formed as a result of the growth due to crystal defects was considerably high. Thus, the SEM analysis results show that the carboxylic acid additives have a significant impact on the surface morphology and shape parameters of the glycine crystals.

Depending on the number of carboxyl groups in the carboxylic acid additive, the crystal morphology was affected negatively. Upon increasing the number of carboxyl groups in the carboxylic acid additive, the number of defects formed on the crystals surface increased and accordingly, the appearance of the crystals deteriorated. At the same time, the tendency to agglomerate increased and the aspect ratio increased from 0.483 to 0.587.

3.5.4. Thermal characteristic of the α -glycine crystals

The thermal stability of the glycine crystals was investigated using TGA. The TGA and DTG curves represent the weight loss rate observed for the crystals obtained from the additive containing and non-additive media (Figure 3.39).

As explained before, the thermal degradation of the glycine crystals showed two weight loss regions. The curves showed that the main degradation zone was in the temperature range of 280–340 °C at a heating rate of 20 °C/min. In this case, this first stage of weight loss corresponds to the decomposition of the amino groups in the glycine crystals and

indicates a weight loss of ~50%. The second stage was characterized by a weight loss of 30% due to the decomposition of carboxyl groups at 359–535 °C [102].

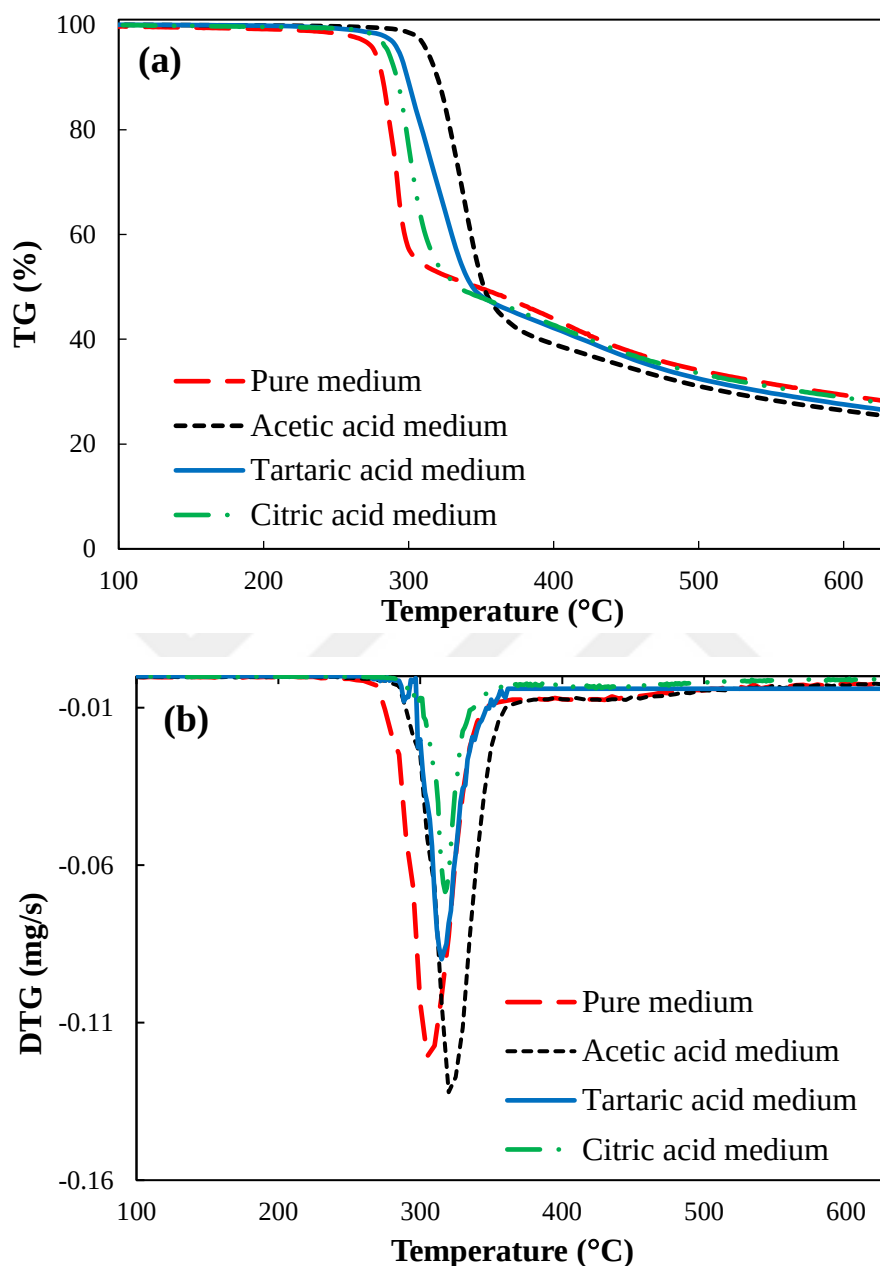


Figure 3.39. The (a) TGA and (b) DTG curves obtained for the crystals obtained from the additive containing and non-additive media at a heating rate of 20 °C/min.

Above this temperature, the weight loss became almost constant till the end of the decomposition process. The TGA and DTG curves recorded for the crystals obtained from the media containing acetic, tartaric and citric acid display similar decomposition

behavior. When compared to the pure medium, the maximum peak temperature showed a shift towards a higher temperature of $\sim 6^{\circ}\text{C}$ for all the carboxylic acid additives studied at the same heating rate. The glycine crystals obtained in the additive-containing media are thermally more stable when compared to those formed in the pure media due to the carboxylic acid content and therefore, the decomposition of the glycine crystals was more difficult and required a larger amount of energy.

3.5.5. Kinetic analysis

The activation energy (the minimum energy required to start a reaction) for the α -glycine crystals obtained from the additive containing and non-additive media was calculated using the DAEM method based on the main degradation region temperature between $245\text{--}340^{\circ}\text{C}$ and $260\text{--}350^{\circ}\text{C}$, respectively. The changes in the activation energy calculated from the individual slopes of the lines based upon the linear model equations for the conversion degree from 0.1 to 0.9. The correlation coefficient of these lines varied between 0.998 and 0.980. This shows the high reliability of the results obtained. The activation energy values calculated for every conversion degree are given in Figure 3.40.

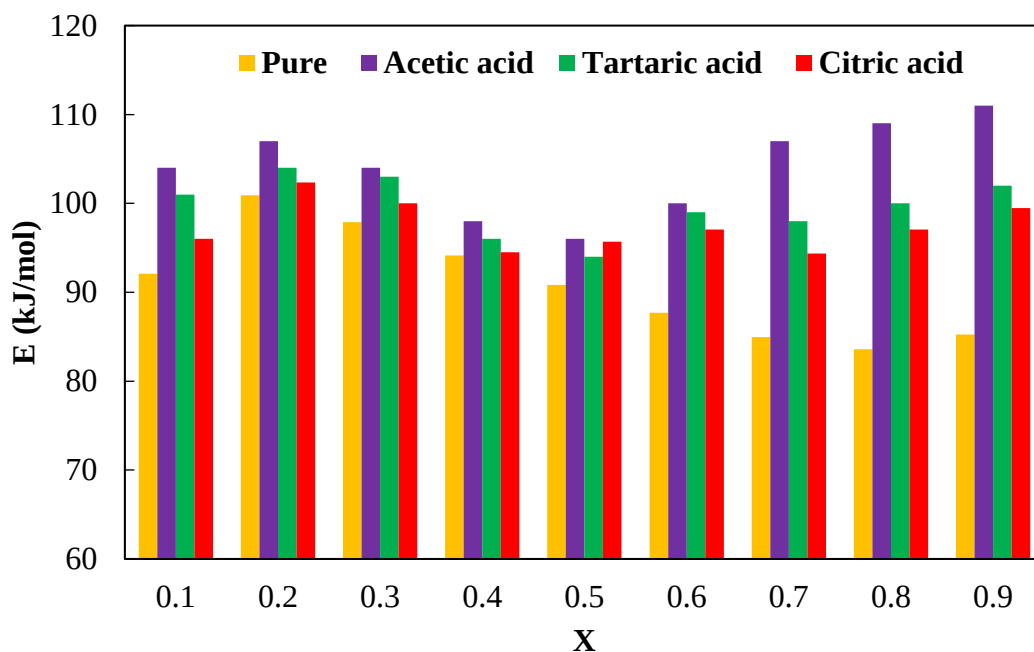


Figure 3.40. The change in the activation energies depending on the conversion degrees of the crystals obtained from the pure solution and acetic acid, tartaric acid and citric acid containing media.

The average activation energy for the as-obtained crystals was found to be 90.8, 104.0, 99.7 and 98.0 kJ/mol for the pure medium and acetic, tartaric and citric acid containing media, respectively. Examining the result obtained for the crystals obtained from the pure media, the values of the activation energy were nearly the same for each conversion degree and no fluctuations were observed. In the presence of the carboxylic acid containing media, the increasing activation energy and at the same time an irregular trend, differences and fluctuations were detected due to content of the crystals obtained from the non-pure media. When compared to the carboxylic acids used as the additive in itself, the average activation energy calculated on the basis of the increase in the number of carboxyl groups included in the additive decreased. Within the carboxylic acid additives studied, an increase of 15% was observed in the presence of acetic acid while this increase found to be around 10% for both the tartaric and citric acid containing media. Therefore, the highest increase in the average activation energy occurred in the medium containing acetic acid. This result confirmed the adsorption occurs on the crystal's surface and displays the thermal characteristics of the crystals.

3.5.6. TGA/FTIR and elemental analysis

The TGA/FTIR spectra of the crystals obtained from the additive containing and non-additive media were collected during the qualitative determination of their chemical structure to investigate the adsorption of the carboxylic acid additives onto the crystal surface as a function of time. Figure 3.41 shows the 3D FTIR spectra of the as-obtained crystals.

The FTIR spectrum showed that the crystals obtained from the pure solution contained all the characteristic peaks of α -glycine [110] and this spectrum was in consistent with the XRD results. When the FTIR spectra recorded for the glycine crystals obtained from solutions containing 500 ppm of the different carboxylic acid additives were examined, it was clearly observed that the crystals contained the typical peaks for both glycine and the carboxylic acid additive. When compared to the pure medium, the crystals grown in the additive containing media displayed two different absorbance bands due to adsorption of the carboxylic acid on the crystal's surface. The bands located at $\sim 1710\text{ cm}^{-1}$ and $\sim 1280\text{ cm}^{-1}$ were ascribed to the C=O and C–O stretching vibrations of the carboxylic groups in acetic, tartaric and citric acid. It was also observed that the additives containing different

numbers of carboxyl groups have different peak intensities. When the intensities of the peaks obtained at the maximum peak temperature were compared, the maximum value was reached in the presence of acetic acid, which has the lowest number of carbonyl groups. This result indicates the presence of the additive in the crystal.

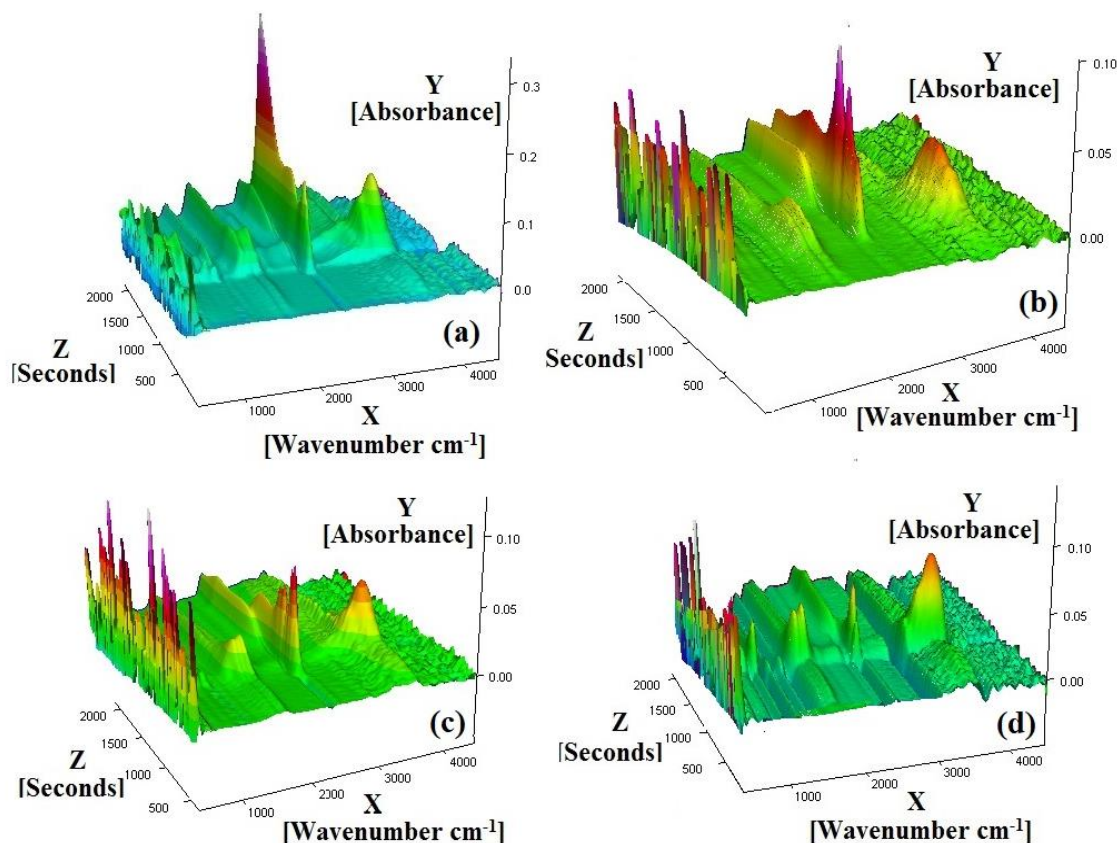


Figure 3.41. The 3D FTIR spectra of the crystals obtained from the (a) pure solution and (b) acetic acid, (c) tartaric acid and (d) citric acid containing media.

The elemental compositions of the crystals obtained before and after the adsorption of the carboxylic acid additive were determined and the variation in the compositions was examined to detect the influence of the carboxylic acid additives on the crystals. The elemental composition of pure glycine contains 31.99% C, 6.69% H and 18.55% N. After adsorption of the additive, the % C, % H and % N values of the crystals obtained in the media containing acetic, tartaric and citric acid were determined to be 32.23, 6.71 and 18.49; 32.00, 6.72 and 18.44; 32.26, 6.74 and 18.39, respectively. The results obtained

from the elemental analyses show that the content of the crystals was slightly changed and the N content decreased upon increasing the number of carboxyl groups in the carboxylic acid additive. Both the TGA/FTIR and elemental analyses support each other. In parallel with the FTIR analyses, the elemental analyses further confirm the carboxylic acid additives were bound onto the crystal's surface.

3.5.7. Adsorption study

To determine the amount of adsorbed carboxylic acid on the crystal's surface and to characterize the crystals quantitatively, the adsorption properties of the crystals were examined. Upon completion of the transformation process, the samples were collected, filtered and the filtrate analyzed for the residual carboxylic acid concentration using a UV spectrometer. The adsorption capacity (q_e , mg/g) was determined using the mass balance equation shown below:

$$q_e = \frac{(C_i - C_e) \times V}{W} \quad (3.2)$$

where C_i and C_e are the initial and equilibrium concentration of the carboxylic acid additive in the solution (mg/L), respectively, V is the volume of the solution (L) and W the mass of the adsorbent (g).

The dependence of the adsorption capacity value on the contact time of the crystals obtained from the different carboxylic acid additive containing media is given in Figure 3.42. Figure 3.42 shows the adsorption process for the additives was rapid during the initial stage and increased gradually until reaching equilibrium at 60 min. The q_e values obtained for acetic, tartaric and citric acid adsorption on the glycine crystals were 2.97, 2.38 and 1.72 mg/g, respectively. The adsorption capacities slightly decreased upon increasing the number of carboxyl groups in the carboxylic acid additive due to the fact that small molecule adsorption was easier.

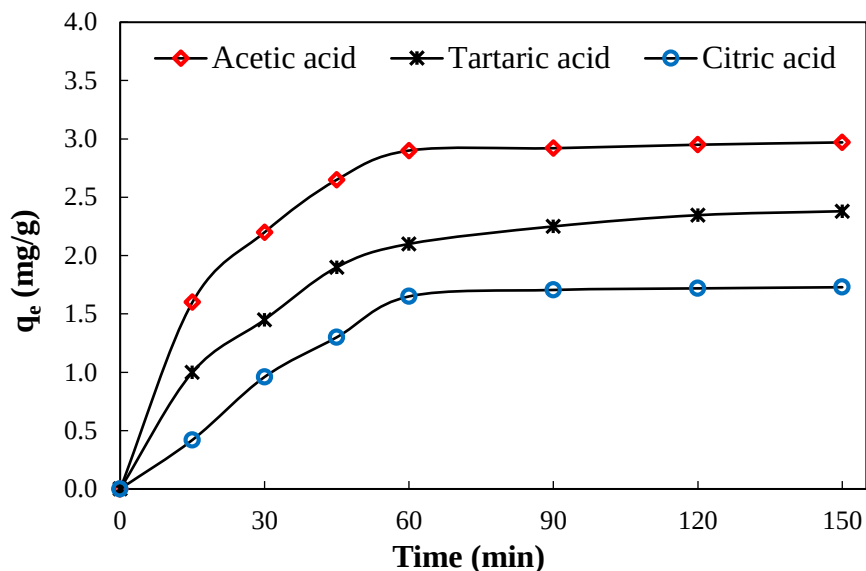


Figure 3.42. The variation of the adsorption capacity value with time observed for the crystals obtained from the acetic, tartaric and citric acid containing media.

3.5.8. Filtration analysis

To detect the effects of the carboxylic acid additives on the filtration properties of the glycine crystals, filtration rate measurements were performed and the average specific cake resistance and average cake porosity were calculated (Table 3.6).

Table 3.6. The results of the filtration analysis.

Media	Specific cake resistance	Average cake porosity
Pure media	1.100×10^{11}	0.4209
Acetic acid	1.403×10^{11}	0.1933
Tartaric acid	1.412×10^{11}	0.1856
Citric acid	1.540×10^{11}	0.1182

The average specific cake resistance and cake porosity of pure α -glycine were 1.100×10^{11} m/kg and 0.4209, respectively. When compared to the pure medium, the specific cake resistance showed a distinctive increase in the presence of all the carboxylic acid additives studied. The highest resistance was obtained for the citric acid containing medium. While an increase in the average specific cake resistance was approximately 30% in the 500 ppm acetic acid-containing medium, which increased to around 40% in the presence of citric acid. This result was consistent with images obtained during the SEM analysis. The change in the morphology of the crystals and the increase in agglomeration directly affected the filtration rate. Considering the average cake porosity results, as shown in Table 3.6, the values obtained from the solutions containing the additives were lower than the value obtained from the pure solution. For the medium containing acetic acid, the average cake porosity was 0.1933 and this value was determined to be 0.1856 and 0.1182 for the tartaric and citric acid containing solutions, respectively. The filtration results indicate that significant differences exist in the additive-containing media and it can be concluded that the carboxylic acid additives significantly affect the filtration properties of the glycine crystals.

3.6. The Results of Ultrasonic Irradiation Effects on Polymorphic Phase Transformation of Glycine*

The polymorphic phase transformation of β -glycine to α -glycine was analyzed in the absence and presence of three different intensities of ultrasonic irradiation in a batch system. The experiments were performed to explore the effects of ultrasonic irradiation and its intensity on phase transformation time, morphology, storage stability, and filtration characteristics.

3.6.1. XRD and DSC analysis

The transformation process of the crystals produced in the presence of an ultrasonic source was monitored through XRD analysis of the samples taken at certain time intervals. XRD results of crystals obtained at $t = 8$ min in the absence of an ultrasonic source and in the presence of three different intensities of ultrasonic irradiation are shown in Figure 3.43. The XRD results clearly revealed that the polymorph transformation time depended on the ultrasonic intensity applied. Increasing the intensity of ultrasonic irradiation shortened the transformation time. At $t = 8$ minutes, the crystals obtained in the absence of ultrasonic irradiation had a specific peak at $2\theta = 18^\circ$ showing the β form of glycine and the other peaks detected were also linked to β -glycine [94]. At low ultrasonic irradiation, while this specific peak was dominant, new peaks appeared at 20° and 29° , which were characteristic of α -glycine [11]. At 30 W ultrasonic irradiation, the intensities of these peaks changed. The characteristic β -glycine peak intensity decreased, whereas the intensities of α -glycine peaks increased. The Rietveld refinements applied for the crystals produced under an ultrasonic power of 20 W or 30 W at $t = 8$ min are given in Figure 3.44. This analysis method demonstrates the close fit of the peaks observed in the experimental patterns (i.e., the observed X-ray powder diffraction pattern of the sample) with their respective simulated patterns.

* Polat, S., Sayan P. (2018) Effect of ultrasonic irradiation on morphology and polymorphic transformation of glycine. *Ultrasonics Sonochemistry*, 47, 17-28

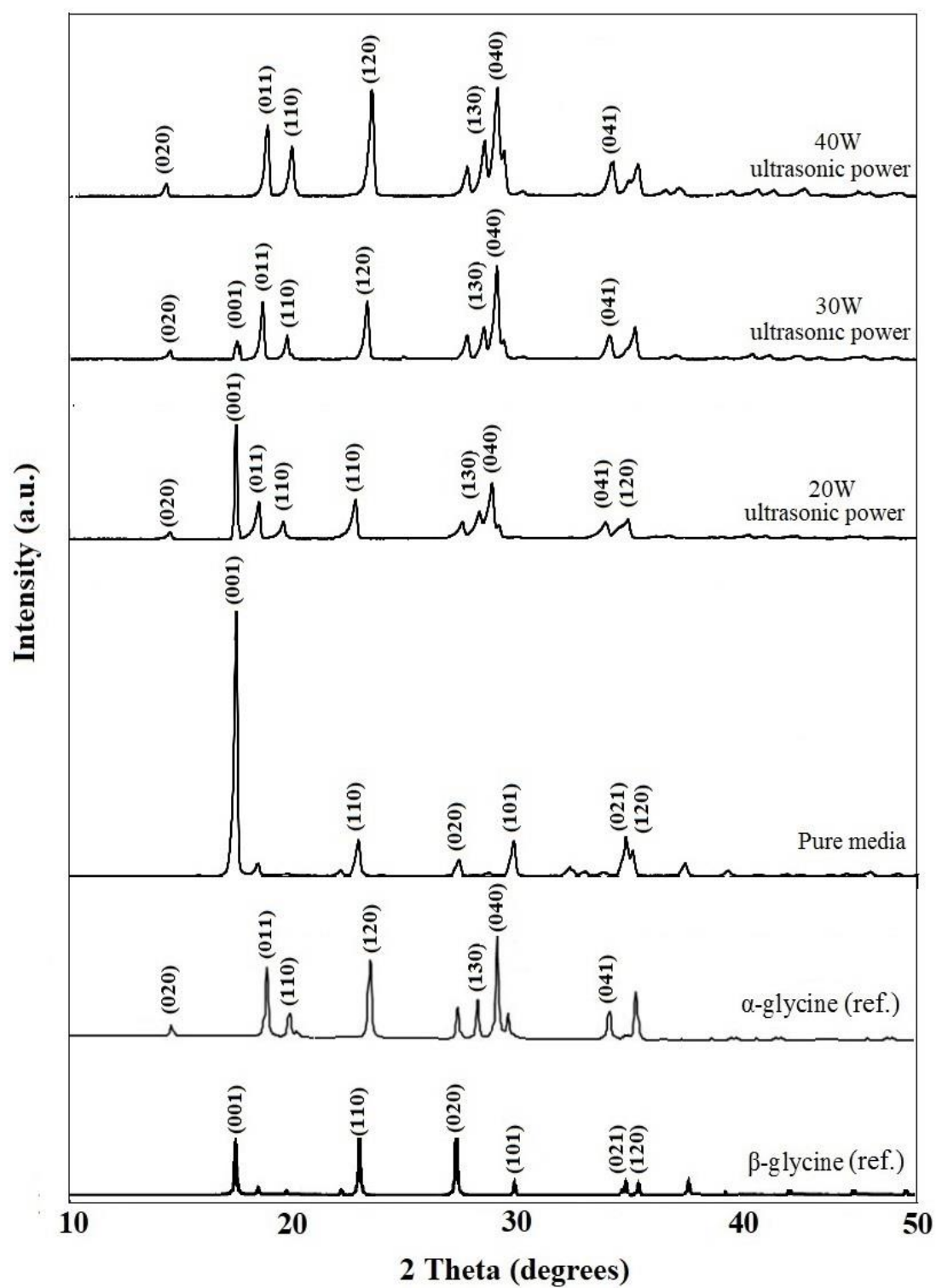


Figure 3.43. XRD results of the crystals obtained in the absence and presence of ultrasound at $t = 8$ min.

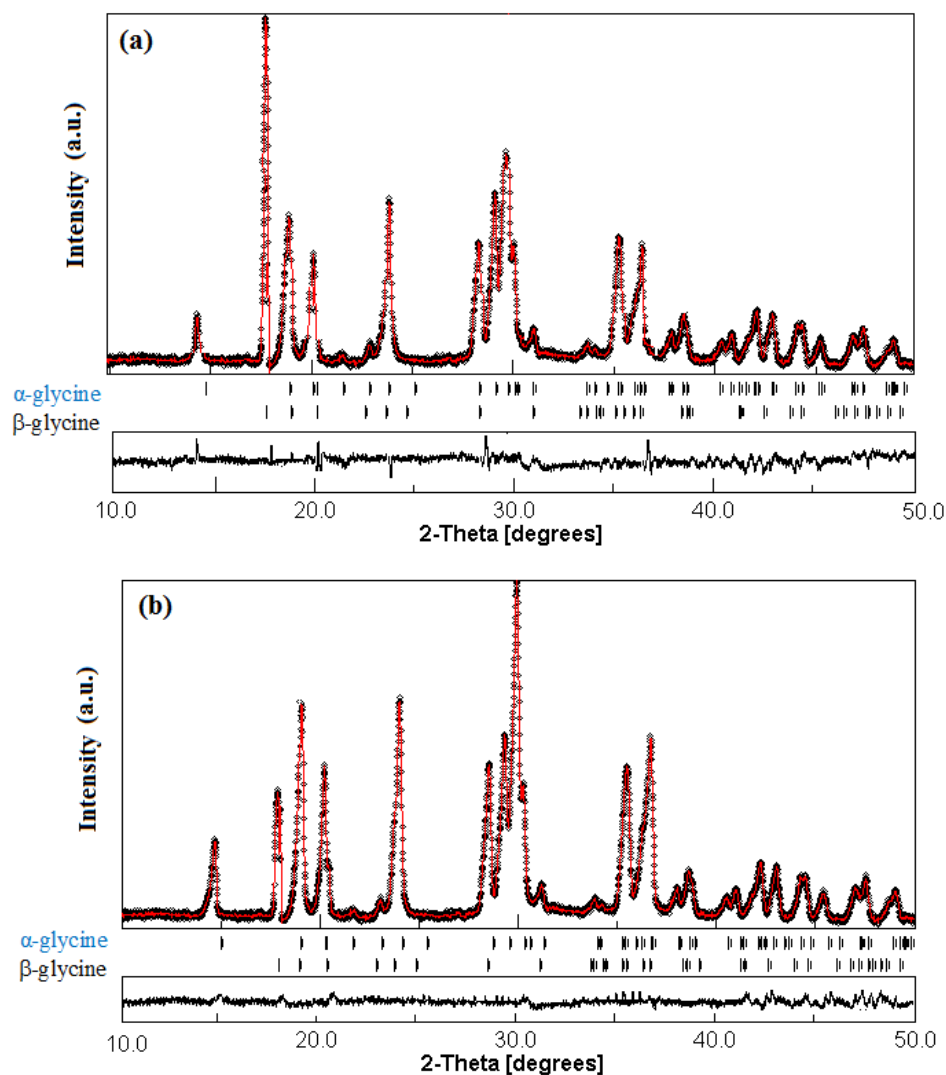


Figure 3.44. Structural Rietveld refinement for the glycine crystals obtained in the presence of 20 W (a), and 30 W (b) ultrasonic power at $t=8$ min.

The method reveals that the mass fraction of β -glycine was 49.71% after ultrasonic irradiation at 20 W, which decreased upon increasing the ultrasonic power to 30 W (mass fraction of β -glycine = 11.34%). The results indicate that the formation of α -glycine was more favorable under a higher ultrasonic irradiation power. At 40 W ultrasonic power, the peaks related to the β form disappeared; i.e., the glycine crystals obtained were completely in the α form. These results showed that there was a relationship between transformation time and ultrasonic irradiation. While the phase transformation completed

at $t = 45$ minutes for pure media, completion times of 25, 16, and 8 minutes were obtained for the crystals obtained at 20, 30, and 40 W ultrasonic power, respectively. It was noted that the transformation rate increased and the transformation time reduced with the increase of ultrasonic power applied.

XRD results of the end product obtained after the completion of the transformation process are shown in Figure 3.45. The results revealed that all the crystals obtained under sonication were in the α form and that their peak intensities were changed due to the ultrasonic effect. Peak intensity was augmented in parallel to the increase in the ultrasonic power. For example, the relative intensity of the peak at 20° was around 6,000 at 20 W ultrasonic power, and about 16,000 and 20,000 for the 30 W and 40 W power, respectively.

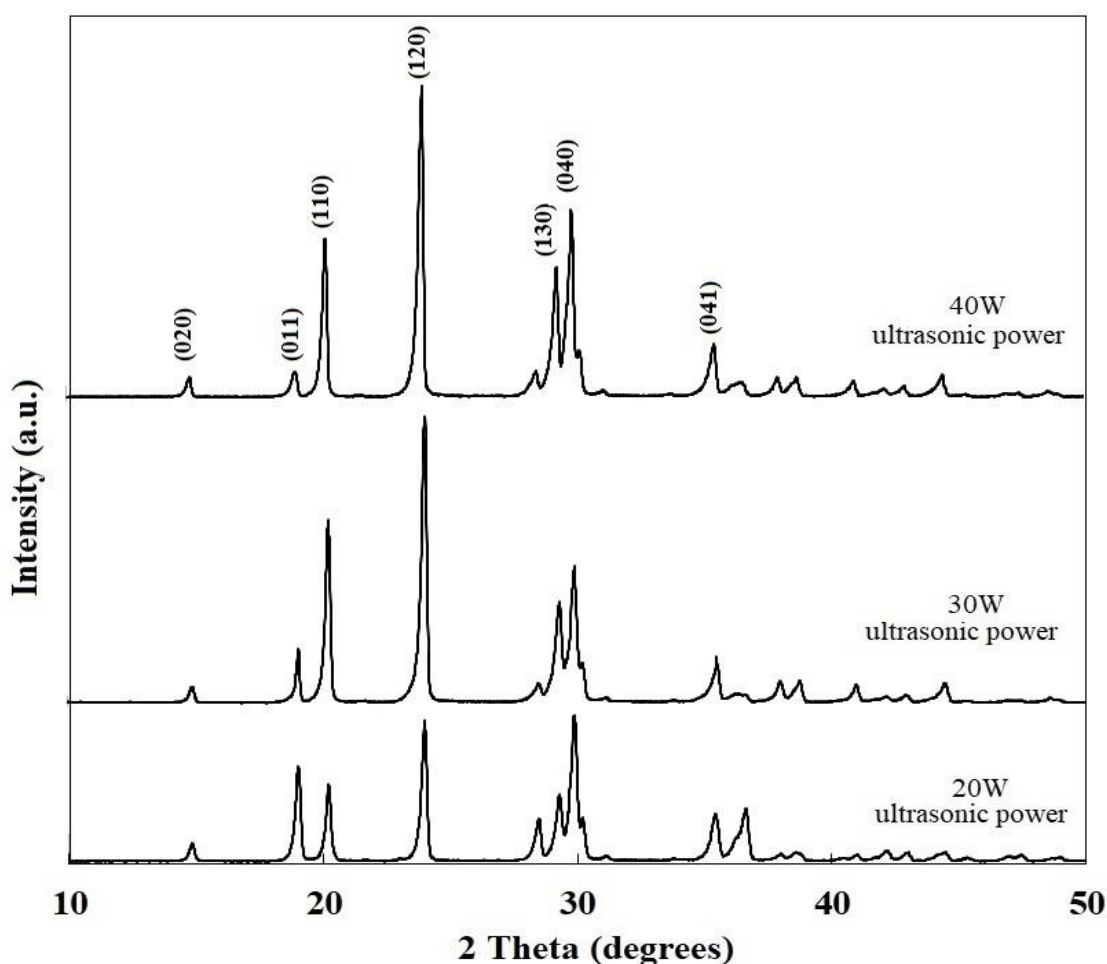


Figure 3.45. XRD results of the end products obtained under different ultrasonic irradiation.

The thermal characterization of α -glycine crystals obtained by completing the polymorphic phase transformation process with and without ultrasonic irradiation was performed by DSC analyzer and the results are given in Figure 3.46.

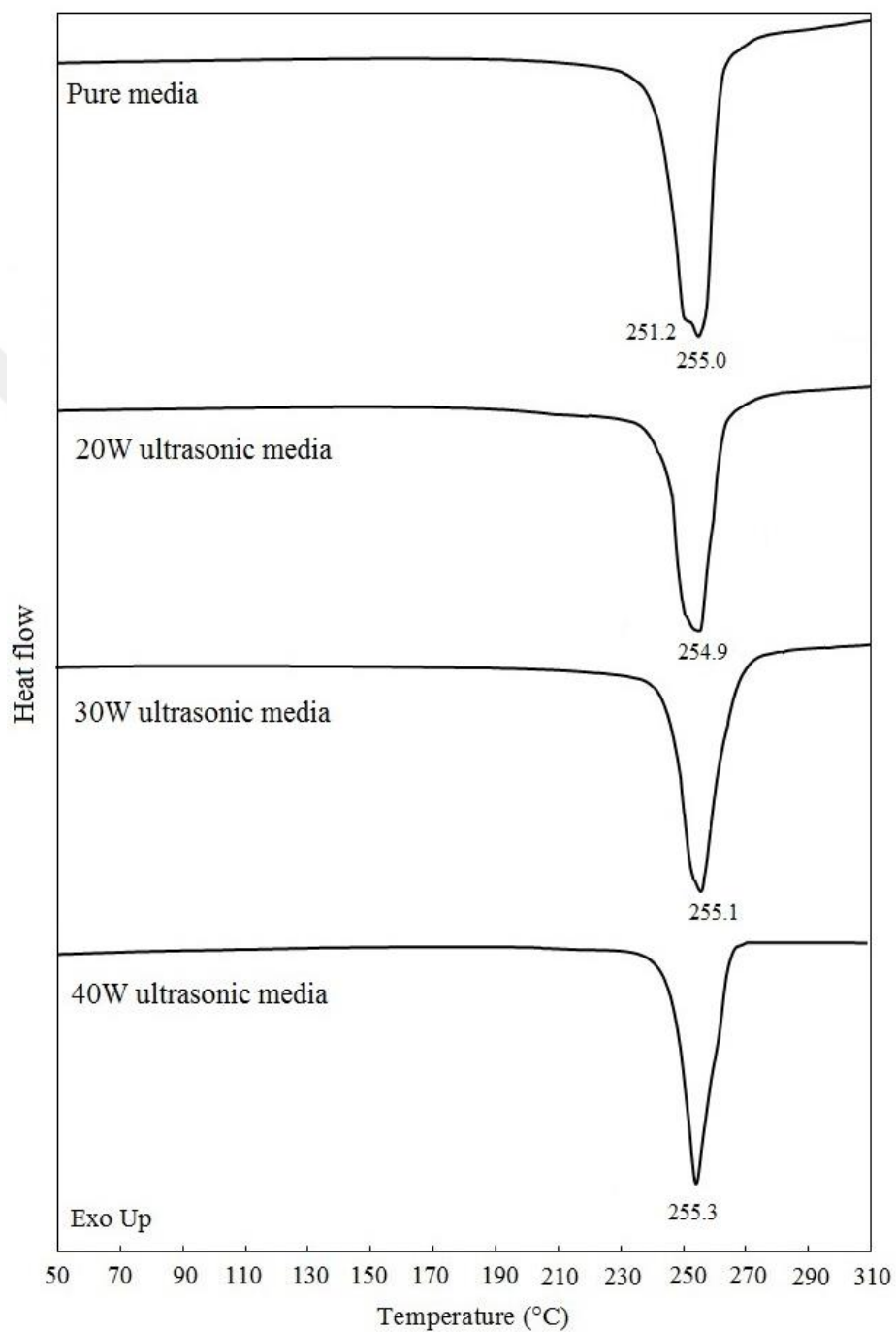


Figure 3.46. DSC results of the crystals obtained in the absence and presence of ultrasonic irradiation.

The DSC curve for the crystals obtained in pure media presented two peaks among which the first peak at around 250 °C belonged to the presence of trace amount of β polymorph in the crystal. The next peak at 255 °C was attributed to the melting point of the α -polymorph [99]. On the other hand, the crystals produced in the presence of the 20, 30 and 40 W ultrasonic power had only a peak at 254.9, 255.1 and 255.3 °C, respectively. These results showed that the crystals obtained did not include any amount of the β -form and all crystals were in α form.

3.6.2. SEM analysis

The SEM images of α -glycine crystals obtained by completing the polymorphic phase transformation process with and without ultrasonic irradiation are given in Figure 3.47.

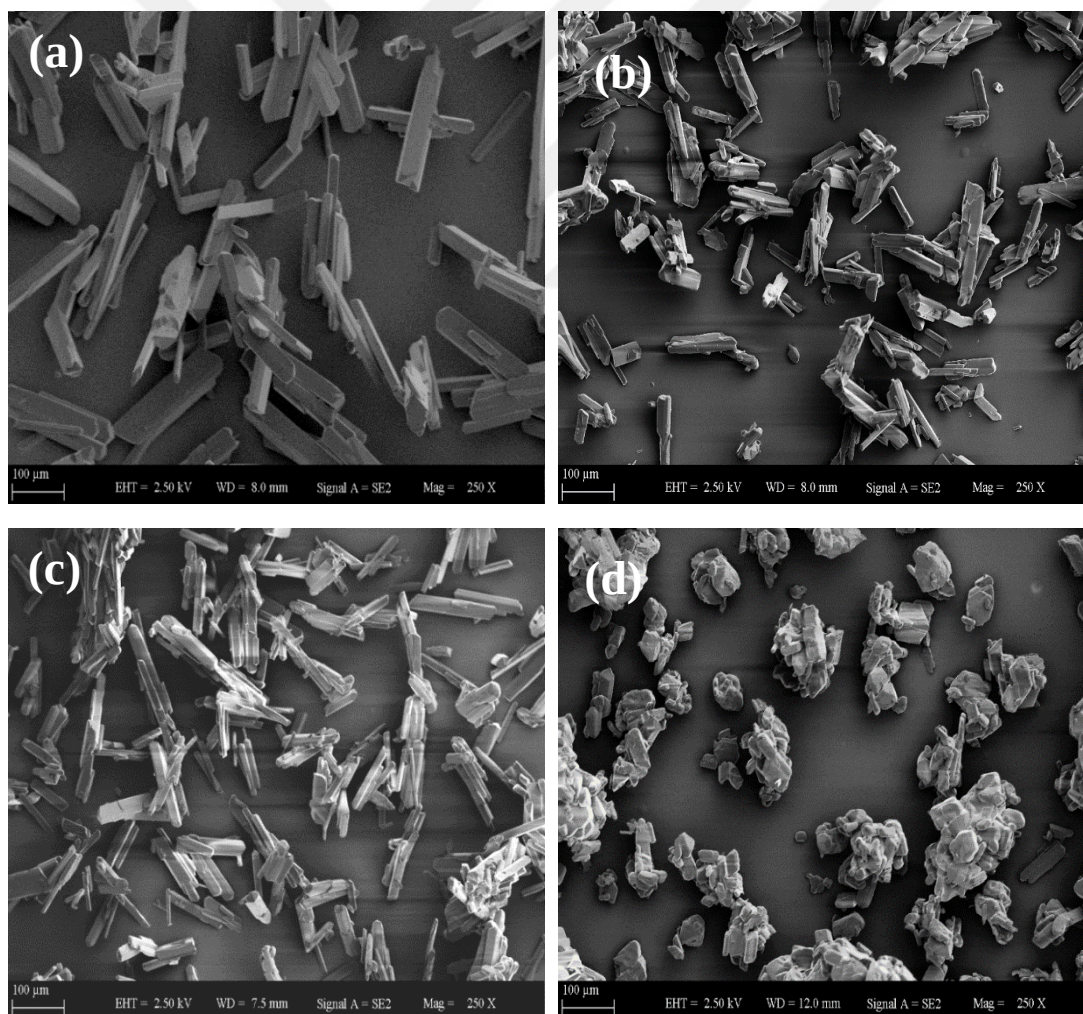


Figure 3.47. SEM images of the crystals obtained in the absence and presence of ultrasonic irradiation.

The crystals obtained in the absence of ultrasound were prismatic with a regular form and rod shape, which was consistent with previous studies [25,80]. These crystals were robust and did not undergo any breakage owing to the hydrodynamic conditions of the media. In the presence of low intensity ultrasound at 20 W, the α -glycine crystals showed successive growth behavior. Moreover, slight breakages were observed on the crystal surface due to the ultrasonic irradiation. The prismatic sharp ends of crystals tended to become round but they preserved their rod form. Furthermore, the particle size of the crystals was smaller compared to those prepared in the absence of ultrasonic irradiation. The crystals obtained with moderate ultrasound power of 30 W began to lose their apparent form. Deformations occurred on all crystal edges and surfaces and the amount of breakage increased significantly. Similar to the crystals obtained with 20 W ultrasonic power, the successive crystal growth behavior continued and the widths and lengths of the crystals reduced significantly. Moreover, glycine crystals obtained using 30 W ultrasonic power continued to undergo breakage. However, these effects scaled up with increasing ultrasonic intensity, with a higher effect yielded by the 30 W compared to the 20 W case. In the presence of the 40 W ultrasonic power, the crystal morphology changed entirely. The rod form was replaced by a shorter, partially rounded form, which can be attributed to the ultrasonic effect. In addition, the intensity of the ultrasonic irradiation applied caused deformations on the sharp edges of the crystals. The highest deformation, breakage, and morphological changes occurred under the 40 W ultrasonic power, and these crystals also showed intensive agglomeration. That is increase in ultrasonic power increased agglomeration.

3.6.3. Morphology analysis

The morphological characteristic, that is the size and shape, of the α -glycine crystals obtained by the completion of the transformation of β -glycine into α -glycine in non-sonicated and sonicated media were examined simultaneously in detail using a Morphologi G3 device from Malvern. In this context, the particle size distributions of glycine crystals obtained under the studied conditions as well as the shape factors, like circularity, elongation, and convexity values, were determined.

Circularity is the ratio of the perimeter of a circle with the same area as the particle divided by the perimeter to the actual particle image. Circularity values range from 0 to 1. The

circularity of a perfect circle is 1, while the circularity of a ‘spiky’ or irregular object is closer to 0. Both overall form and surface roughness can affect circularity. Therefore, the circularity approaches 1 as the shape becomes more round and smooth. The edge roughness of a particle is described by its convexity, which is calculated by dividing the convex hull perimeter by the actual particle perimeter. The convexity of a smooth shape is 1, while the convexity of a very ‘spiky’ or irregular object is closer to 0. Elongation is $[1 - \text{width}/\text{length}]$ and, as implied by its name, it is a measure of elongation; its values range from 0 to 1. The elongation value of a shape that is symmetrical in all axes, e.g. a circle or a square, is 0; elongation values of shapes with large aspect ratios are closer to 1 [100,106,107].

Figure 3.48 shows the plots of particle size distribution determined by considering the circle equivalent (CE) diameter, the diameter of a circle with the same area as the particle, of α -glycine crystals obtained by the completion of the phase transformation in the absence and presence of ultrasound. Particle size distribution curves showed normal distributions in all operating conditions, and bimodal distribution was not observed.

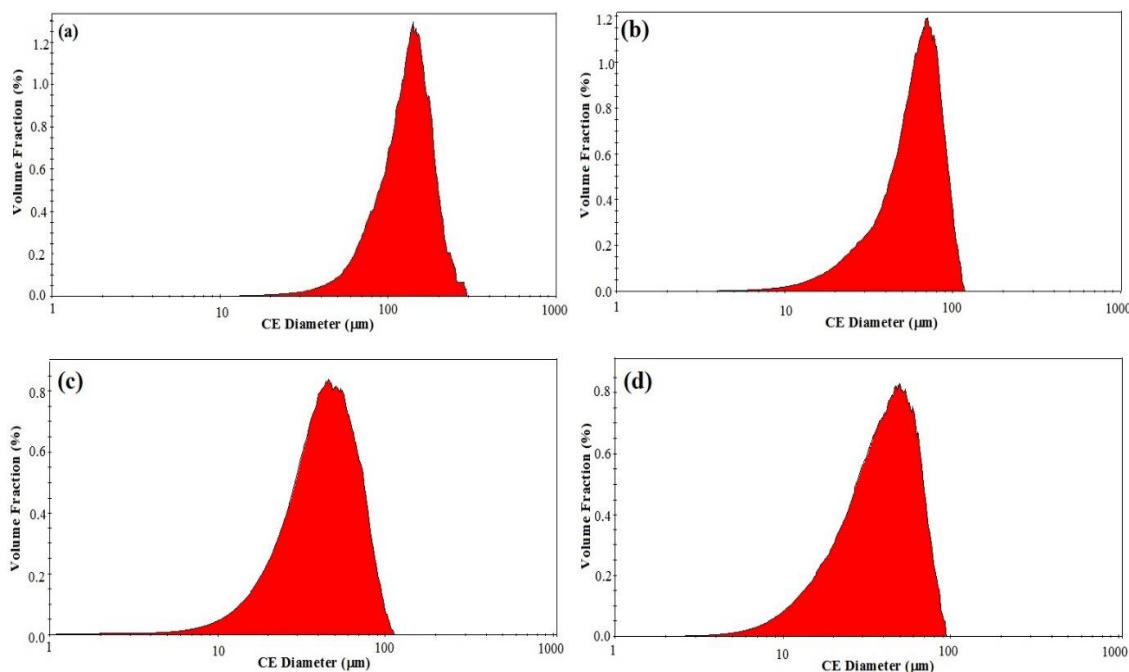


Figure 3.48. The particle size distribution of the glycine crystals obtained in the absence (a) and presence of 20 W (b), 30 W, (c) and 40 W (d) ultrasonic power.

Table 3.7 shows $D(v, 0.1)$, $D(v, 0.5)$, and $D(v, 0.9)$ values obtained by using such particle size distributions. $D(n, 0.5)$ is the size in micrometers at which 50% of the sample is smaller and 50% is larger, whereas $D(n, 0.1)$ and $D(n, 0.9)$ are the particle sizes below which 10% and 90% of the sample is distributed, respectively. The v in the expression shows that this refers to the volume distribution [94]. As can be clearly seen from Table 3.7, while the mean CE value was 131.6 μm in those prepared in the absence of ultrasonic irradiation, these values were measured as 60.93, 42.55, and 39.22 μm with increasing ultrasonic intensity.

Table 3.7. Values of CE diameter according to volume distribution and mean area.

Media	CE Diameter (μm)			Mean Area (μm) ²
	D (0.1)	D (0.5)	D (0.9)	
Without ultrasound	74.01	131.6	179.4	1939.18
20W ultrasonic power	27.95	60.93	84.64	205.92
30W ultrasonic power	19.63	42.55	70.93	103.37
40W ultrasonic power	16.35	39.22	64.55	27.16

Accordingly, the mean projected area values decreased with increasing ultrasonic intensity. In the evaluation of approximately 40000 crystals in the Morphologi G3 device, the length and width of the crystals were determined for non-sonicated and sonicated media. The results obtained are presented in Figures 3.49a and 3.49b, respectively. As can be seen in Figure 3.49, the length and width distributions of the crystals obtained in those prepared in the absence of ultrasonic irradiation were wide compared to the crystals obtained in ultrasonic media.

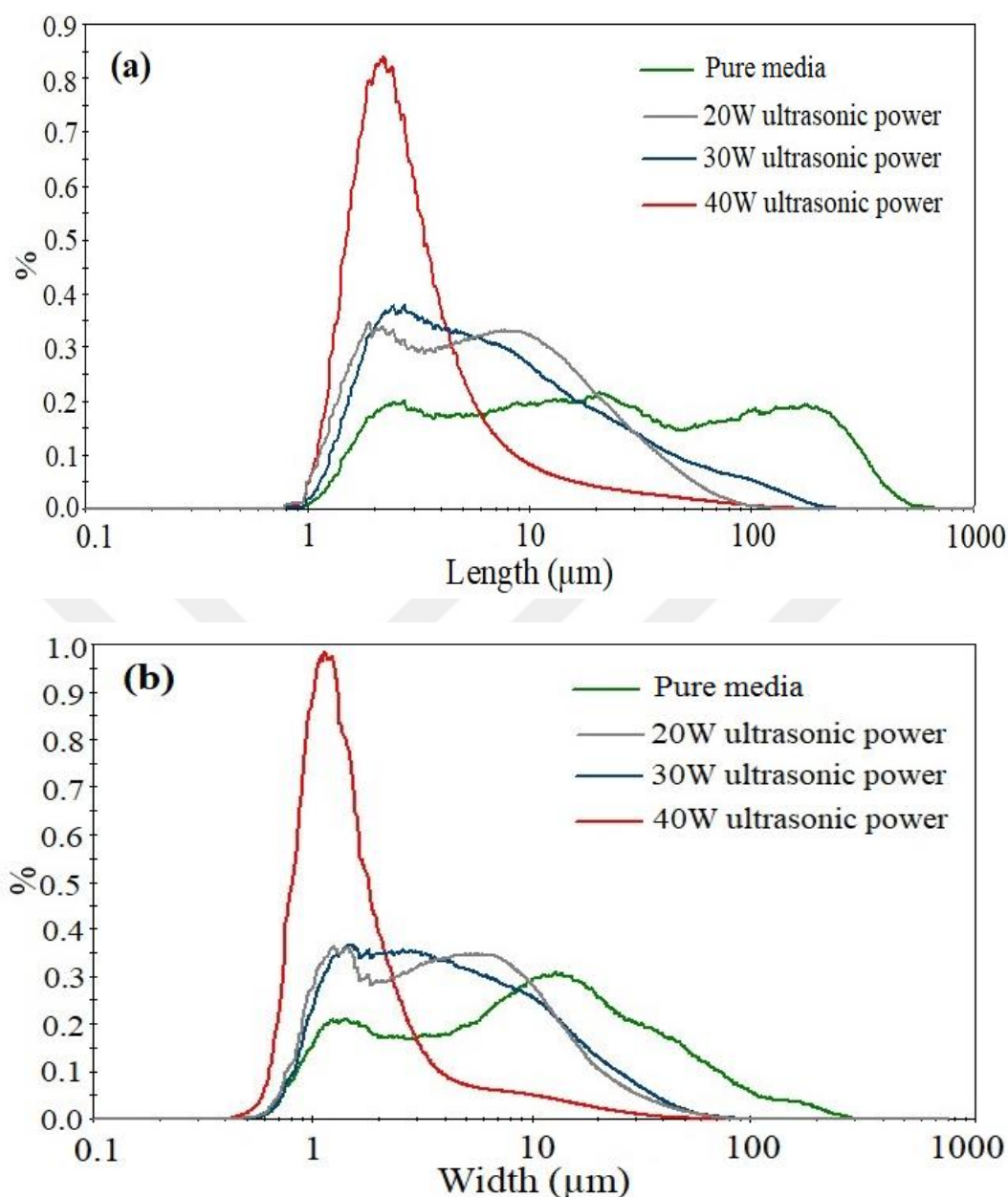


Figure 3.49. The crystal length (a) and width (b) distributions obtained in the absence and presence of ultrasonic irradiation.

The application of ultrasonic irradiation in crystallization media resulted in narrow distributions. Both the length and the width of the crystal distributions were narrower with increasing ultrasonic intensity. In other words, the ultrasound power was inversely proportional to the size distributions. The images of some of the crystals obtained using the Morphologi G3 are given in Figure 3.50. Glycine crystals obtained in those prepared in the absence of ultrasonic irradiation have smooth surface and rod shape.



Figure 3.50. The shapes of the crystals obtained in the absence (a) and the presence of 20 W (b), 30 W (c), and 40 W (d) ultrasonic power.

With the increase of applied ultrasonic intensity, the crystals lost their smooth surface and the crystals obtained were rough. Twinning was formed in the structures and irregularities increased accordingly. Sharp edges begun to round, and breaking and abrasions increased. The highest impact was observed at 40 W, where the highest ultrasonic intensity was applied. The morphology of the crystals obtained in the media where 40 W ultrasonic intensity was applied was completely changed compared to the crystals prepared without ultrasonic irradiation. The crystals completely lost their rod form and their edges gained a different appearance by rounding. When images obtained from the Morphologi G3 device, which analyzes morphologic structures systematically, and SEM analysis performed using lower amounts of sample are compared, similar morphological changes are observed. In other words, the Morphologi G3 and SEM results were in agreement with each other. Both analytical methods clearly showed that the crystals underwent morphological change with increasing ultrasonic intensity. Shape factors such as circularity, convexity, and elongation were examined to quantify the measured shape of the crystals. Figure 3.51 shows the variation of the calculated particle shape factor values of the crystals obtained in the absence and different ultrasonic media.

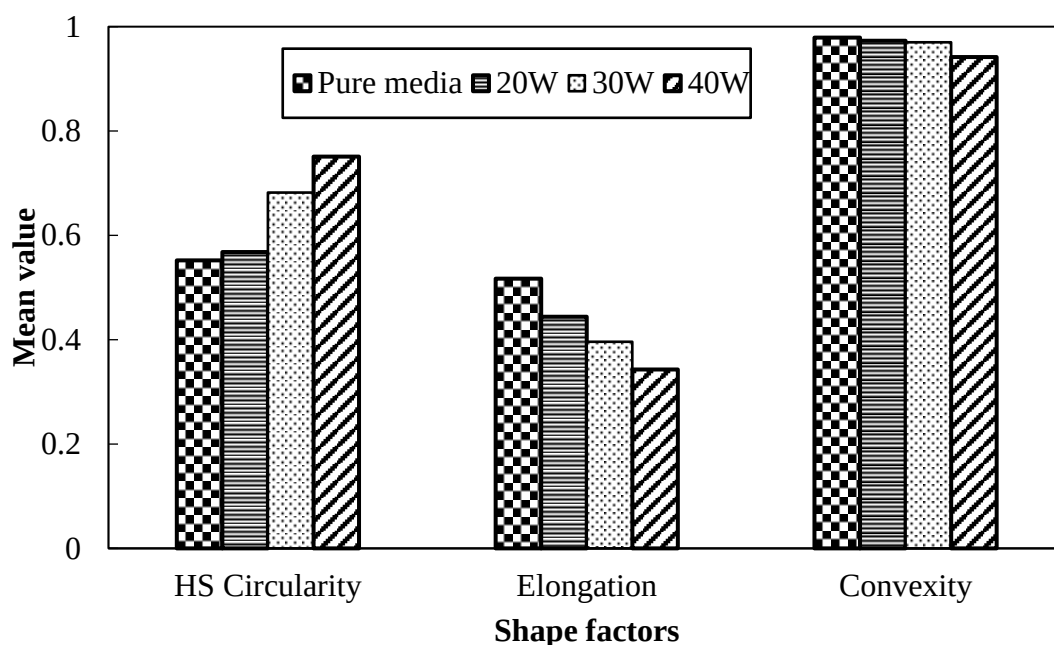


Figure 3.51. The shapes of the crystals obtained in the absence (a) and the presence of 20 W (b), 30 W (c), and 40 W (d) ultrasonic power.

As can be clearly seen from Figure 3.51 while the high sensitivity (HS) circularity value of the glycine crystals obtained by the completion of the phase transformation process in the absence of ultrasonic irradiation was 0.552, this value reached a maximum value of 0.751 with increasing ultrasonic intensity. It is expected that the circularity value is low because the crystals obtained without ultrasonic irradiation media have a rod-like structure. At the same time, the elongation value determined by considering the shapes of the crystals seems to have a higher value than the crystals produced in the ultrasonic media. The fact that the elongation value calculated for the crystals obtained without ultrasonication higher than the elongation value of the crystals produced in the ultrasonic media supports this result. As the ultrasonic impact increases, the circularity value increases while the elongation value decreases. On the other hand, it was determined that the convexity value, which characterizes the shape factor, was between 0.979 and 0.942, and it was independent from the ultrasonic impact. Aspect ratios obtained by dividing the width of the crystal by its length were calculated in order to determine the aggregation tendency in the working conditions. The aspect ratio value determined as 0.483 in the absence of ultrasonic irradiation increases to 0.657 with the ultrasonic power at 40 W. This is an indication that agglomeration of the crystals increases in terms of shape analysis. As a matter of fact, the images obtained from SEM and Morphologi G3 analysis support this view. Another parameter that can be used to characterize the morphology of the obtained crystals is solidity. Solidity is defined as the object area divided into areas enclosed by the convex hull area. Mean solidity value calculated for glycine crystals obtained in the absence of ultrasonic irradiation is determined as 0.910, while this value reaches to 1 with the increasing impact of ultrasonic intensity. At the same time, it is known that solidity values of morphologically very smooth rounded shapes are 1. The solidity results showed that the glycine crystals have more rounded surfaces with ultrasonic impact.

3.6.4. Storage stability

In this study, stability, an important physical property of polymorphic crystals, was investigated under different storage conditions. For this purpose, the stability of the glycine crystals obtained in pure media and in the presence of the 30 W ultrasonic power

was studied in the dry state and in the solution state for one month. The obtained crystals were analyzed by XRD and Morphologi G3 analyzer. Figure 3.52 shows the XRD analysis results for the end products obtained with and without ultrasound after 1 month of storage.

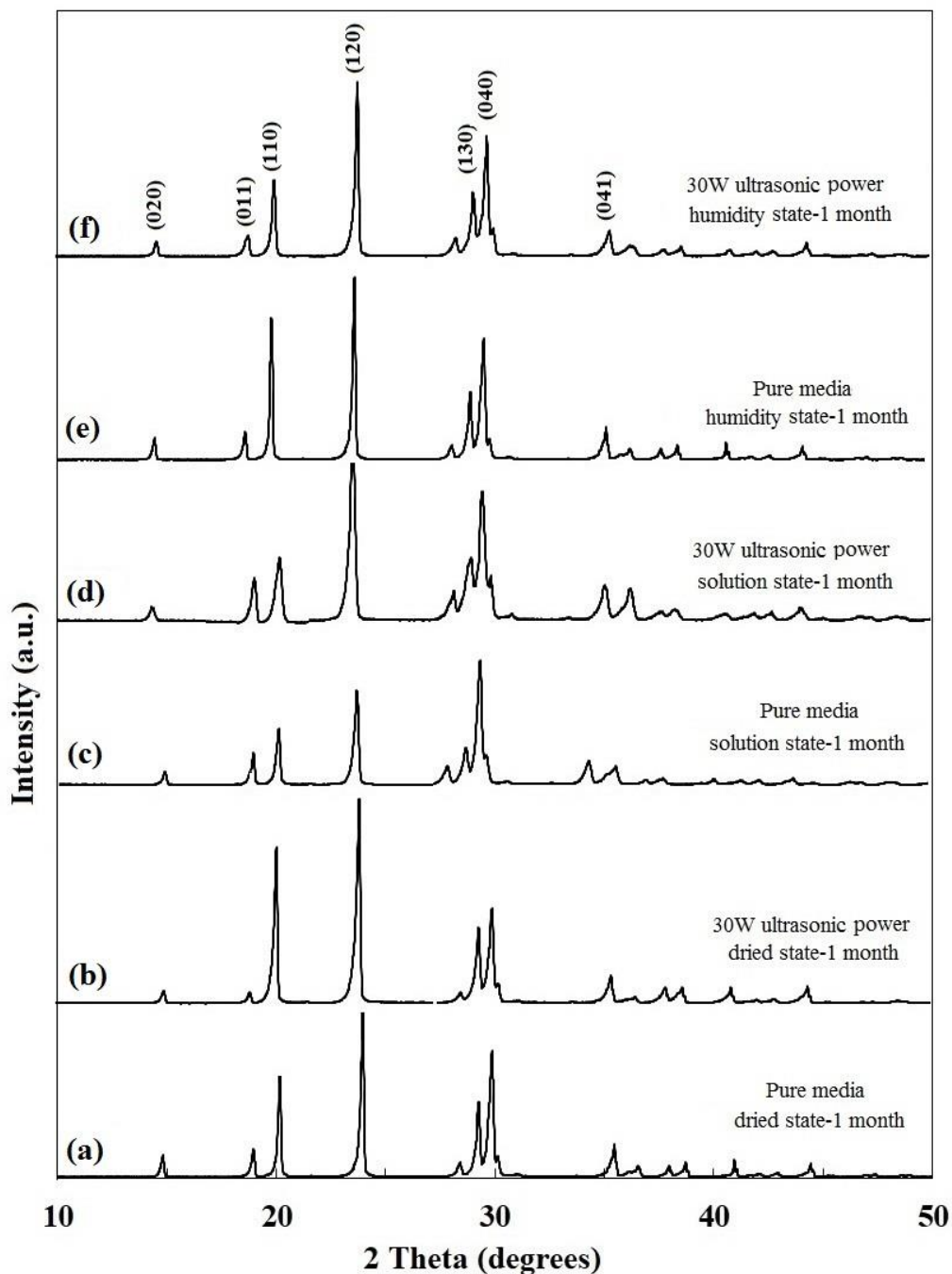


Figure 3.52. XRD results for the crystals obtained in the absence and presence of 30 W ultrasonic power under different storage conditions.

As can be clearly seen from the XRD results, in all conditions that were examined, glycine remained in the α form and there was no second phase formation. The images of some of the crystals obtained using the Morphologi G3 for dried state test conditions are given in Figure 3.53.

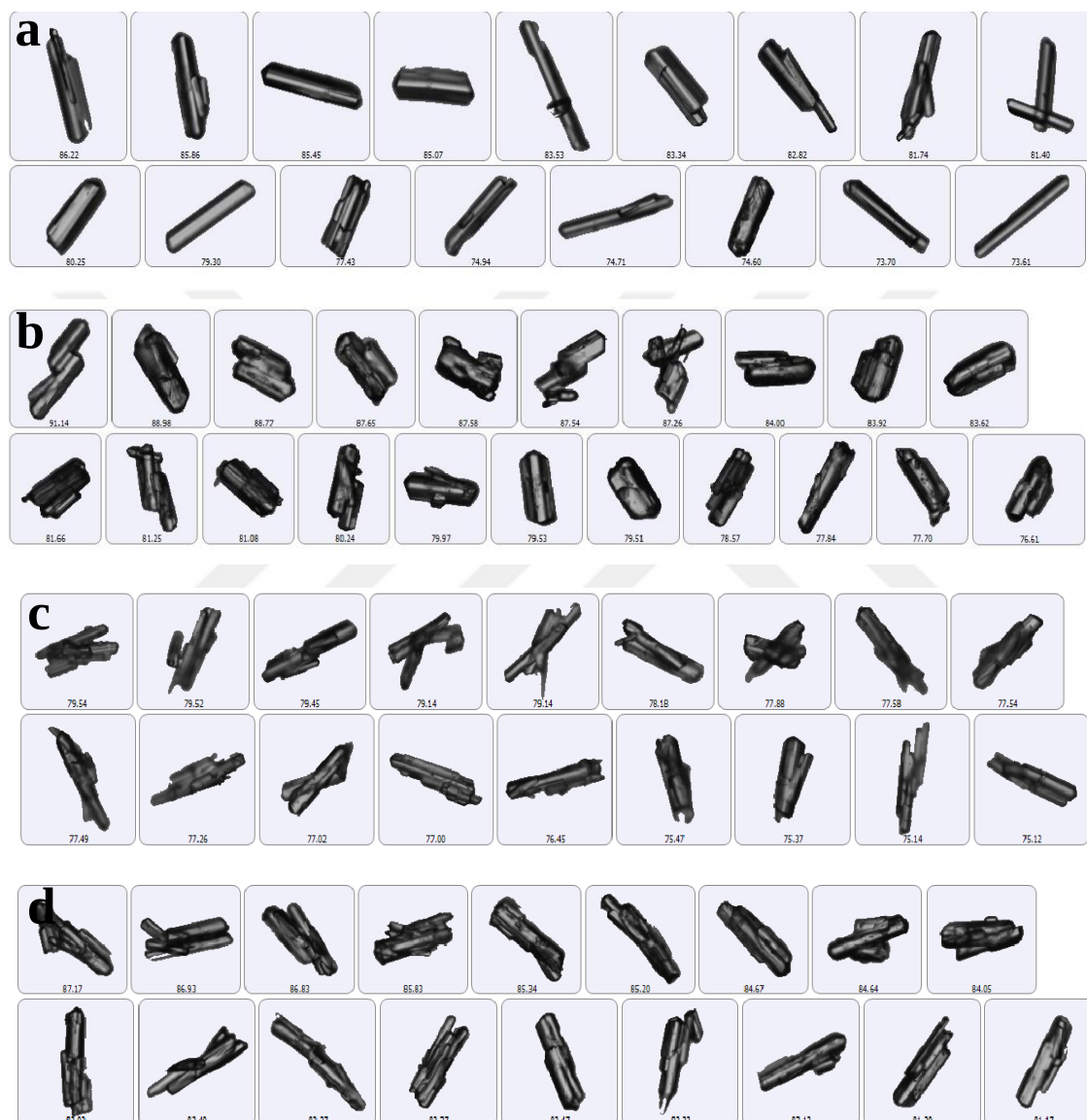


Figure 3.53. The shapes of the crystals obtained in (a) pure media and stored for 1 day, (b) pure media and stored for 1 month, (c) 30 W ultrasonic power and stored for 1 day, and (d) 30 W ultrasonic power and stored for 1 month under dried state conditions.

When the images of the crystals obtained in the absence of ultrasonic irradiation and stored for 1 day in the dried state were examined, the crystals had a smooth surface and were in a rod-like form. When the crystals stored for 1 month in the dried state were compared with the crystals stored for 1 day, it was seen that the crystals obtained were partially deformed and their smooth surfaces disappeared. At the same time, the aspect ratio of the crystals stored for 1 month was increased with respect to that for the crystals stored for 1 day, increasing from 0.485 to 0.529. The images of the crystals obtained with 30 W ultrasonic power and stored for 1 day and 1 month in the dried state are given in Figures 3.53c and 3.53d, respectively. When the images were examined, no significant change in crystal morphology could be seen. Similarly, the aspect ratios of the crystals obtained after 1 day and 1 month storage were determined as 0.657 and 0.654, respectively. In addition, as can be seen from Figure 3.54, the average particle size of the crystals obtained in the presence of 30 W ultrasonic power did not change. The 1-month stability studies carried out in the dried state conditions showed that the stability of the crystals obtained with ultrasonic irradiation was higher than that of the crystals obtained in pure media.

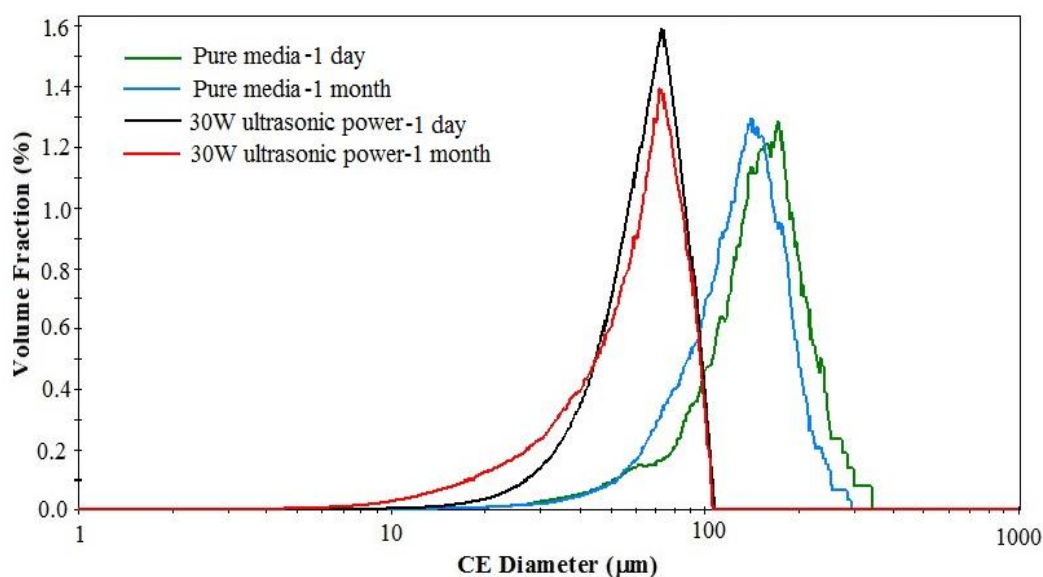


Figure 3.54. The particle size distribution of the glycine crystals obtained in the absence and presence of 30 W ultrasonic power under dried state conditions.

A similar stability study was also conducted in the solution state. The images of the crystals obtained using the Morphologi G3 are given in Figure 3.55. Similar to the dried state storage results, the crystals obtained in the pure media and stored in solution were slightly deformed at the end of 1 month of storage whereas no morphological change was observed for the crystals obtained in the ultrasonic media.

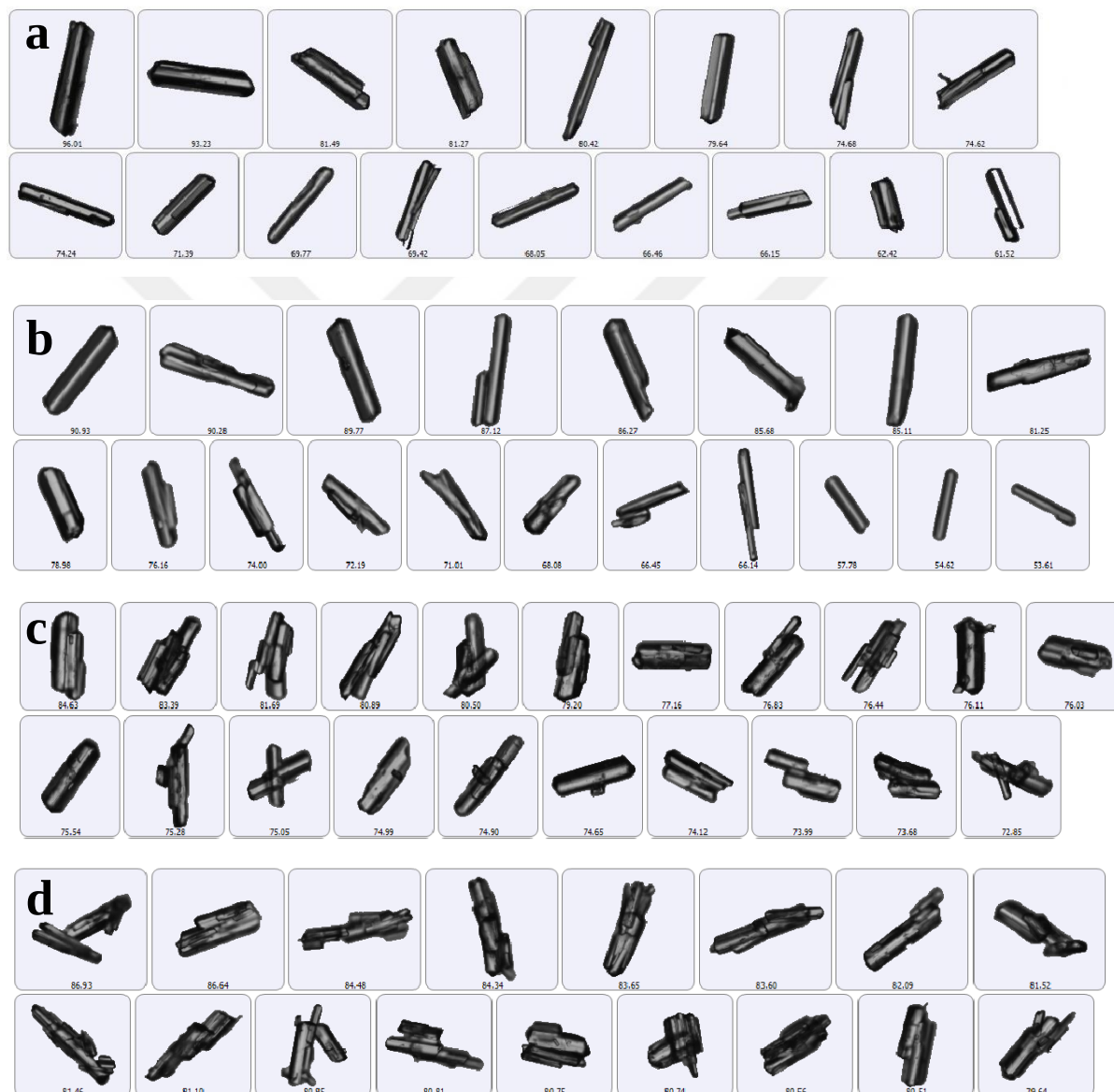


Figure 3.55. The shapes of the crystals obtained in (a) pure media and stored for 1 day, (b) pure media and stored for 1 month, (c) 30 W ultrasonic power and stored for 1 day, and (d) 30 W ultrasonic power and stored for 1 month under solution state conditions.

The aspect ratios of the crystals obtained in pure media and in the presence of ultrasound after 1 day of storage were 0.489 and 0.657, respectively, and 0.541 and 0.652 after 1 month of storage, respectively. This clearly indicates that the ultrasonic effect enhanced the stability of the glycine crystals. Moreover, the storage stability of α -glycine crystals was investigated under humid condition (40 °C, 75% RH). The images of the crystals are given in Figure 3.56. There was no significant change in the morphology and average particle size of the crystals obtained both without and with ultrasonic irradiation.

3.6.5. Filtration analysis

To investigate the influence of ultrasonic irradiation and its intensity on the filtration characteristics of the glycine crystals, the filtration rates of the crystals obtained under both pure and sonication conditions were measured; the dry cake mass and cake height were also determined. The specific cake resistance of the glycine produced without ultrasonic irradiation was calculated as 1.095×10^{11} m/kg. Under 20 W ultrasonic power, the filtration rate of the crystals decreased and the specific cake resistance was determined to be 2.146×10^{11} m/kg. Such an increase in the specific cake resistance may suggest morphological changes of crystals as well as breakage induced by the ultrasonic irradiation. Owing to the extended breakage in presence of 30 W ultrasonic power, the specific cake resistance increased similarly to the crystals obtained at 20 W ultrasonic power, and was calculated to be 3.055×10^{11} m/kg. However, this increasing tendency in specific cake resistance was not observed at 40 W ultrasonic power. The specific cake resistance of α -glycine crystals obtained at this power was determined as 8.023×10^{10} m/kg. Compared to both media without ultrasonication and the various ultrasonic powers studied, the observed decrease can be attributed to the change of the crystal habit. As shown in the SEM image of the crystals obtained at 40 W ultrasonic power, unlike the crystals obtained with 20 W and 30 W ultrasonic power, the crystals formed compact and stable aggregates. This type of aggregate directly affected the filtration characteristics of the crystals. The cake porosities of the crystals were identified in addition to the average specific cake resistance. The cake porosity was calculated according to the results of the filtration rate measurements conducted at 700 mbar. For the glycine crystals obtained in the absence of ultrasonic irradiation, this was calculated to be 0.421. The cake porosity decreased with increasing ultrasonic power. The average cake porosities were determined as 0.441 and 0.319 for the crystals obtained in the presence of 20 and 30 W ultrasonic

power. On the other hand, an approximately 5% increase was observed in the cake porosity in the presence of 40 W ultrasonic power compared to the media without sonication due to the morphologic differences of the crystals.

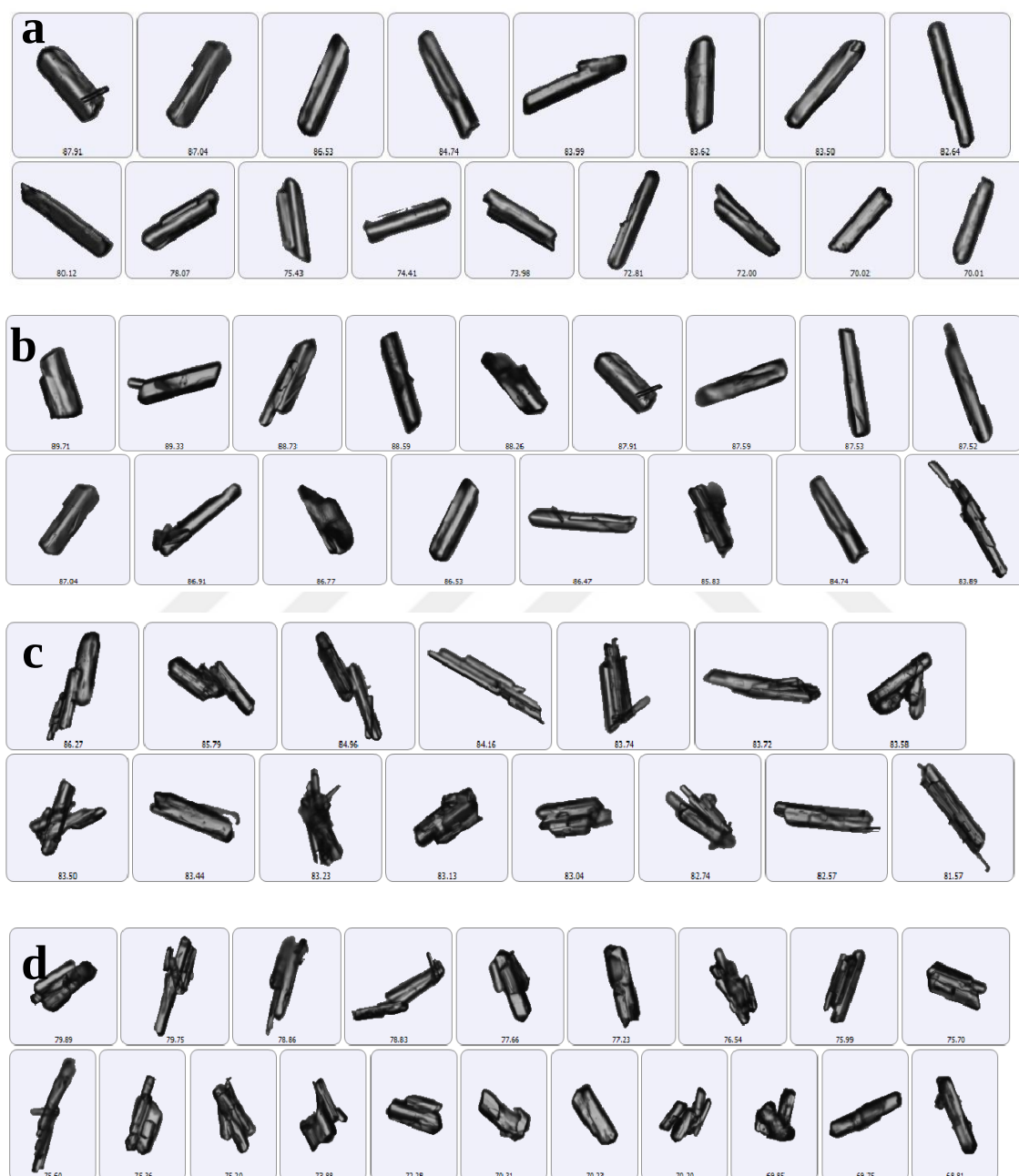


Figure 3.56. The shapes of the crystals obtained in (a) pure media and stored for 1 day, (b) pure media and stored for 1 month, (c) 30 W ultrasonic power and stored for 1 day, and (d) 30 W ultrasonic power and stored for 1 month under humid conditions.

3.7. The Results of UV Radiation Effects on Polymorphic Phase Transformation of Glycine*

The influence of UV radiation on the phase transformation of β glycine to α glycine was investigated at 25 °C in the absence and the presence of varying intensities of UV radiation. To further understand the role of UV radiation and its intensity on glycine phase transformation, these experiments were also performed in the presence of propane-1,2,3-tricarboxylic acid used as the additive.

3.7.1. Ultrasonic velocity measurement

The transformation process of β glycine to α glycine in pure media and in the presence of a UV source was followed by measuring the ultrasonic velocity of the suspension. The ultrasonic velocity curve obtained in pure media at 25 °C is given in Figure 3.57. As said before, this curve indicated that the transformation process had three different stages: the dissolution of the metastable form (β glycine), the nucleation of the stable form (α glycine) and growth of the α glycine. Firstly, ultrasonic velocity increased with time resulting from dissolution of the β glycine. Secondly, a distinct decrease in ultrasonic velocity represented the starting point of nucleation of the stable α glycine at 42 minutes. The final stage was related to the growth of α glycine crystals and the ultrasonic velocity started increasing slowly with time as a result of crystal growth of the α glycine. The ultrasonic velocity curves obtained in the presence of three different UV radiation intensities are shown in Figure 3.57a. It was determined that the transformation rate is dependent on the intensity of UV radiation. The UV radiation caused notable changes both in the ultrasonic velocity and the transformation rate, and these results are shown in Figure 3.57. The transformation rate increased due to the increasing UV radiation intensity. The duration of the phase transformation at 8W was around 31 minutes, whereas at 20W it decreased to around 18 minutes. To examine the effects of UV on the glycine phase transformation, the ultrasonic velocity was measured at 8W, 12W and 20W of UV radiation in the presence of a constant 500 ppm of additive. These results are shown in Figure 3.57b. By using the additive together with UV in the crystallization media, the phase transformation duration differed.

* Polat, S., Sayan P. (2018) Impacts of UV Radiation on the Polymorphic Transformation of β Glycine to α Glycine. *Crystal Research and Technology*, 53 (1), 1700103 (1-10).

The duration at 500 ppm of additive was about 55 minutes, while at 500 ppm of additive and 20W of UV radiation it decreased to 36 minutes.

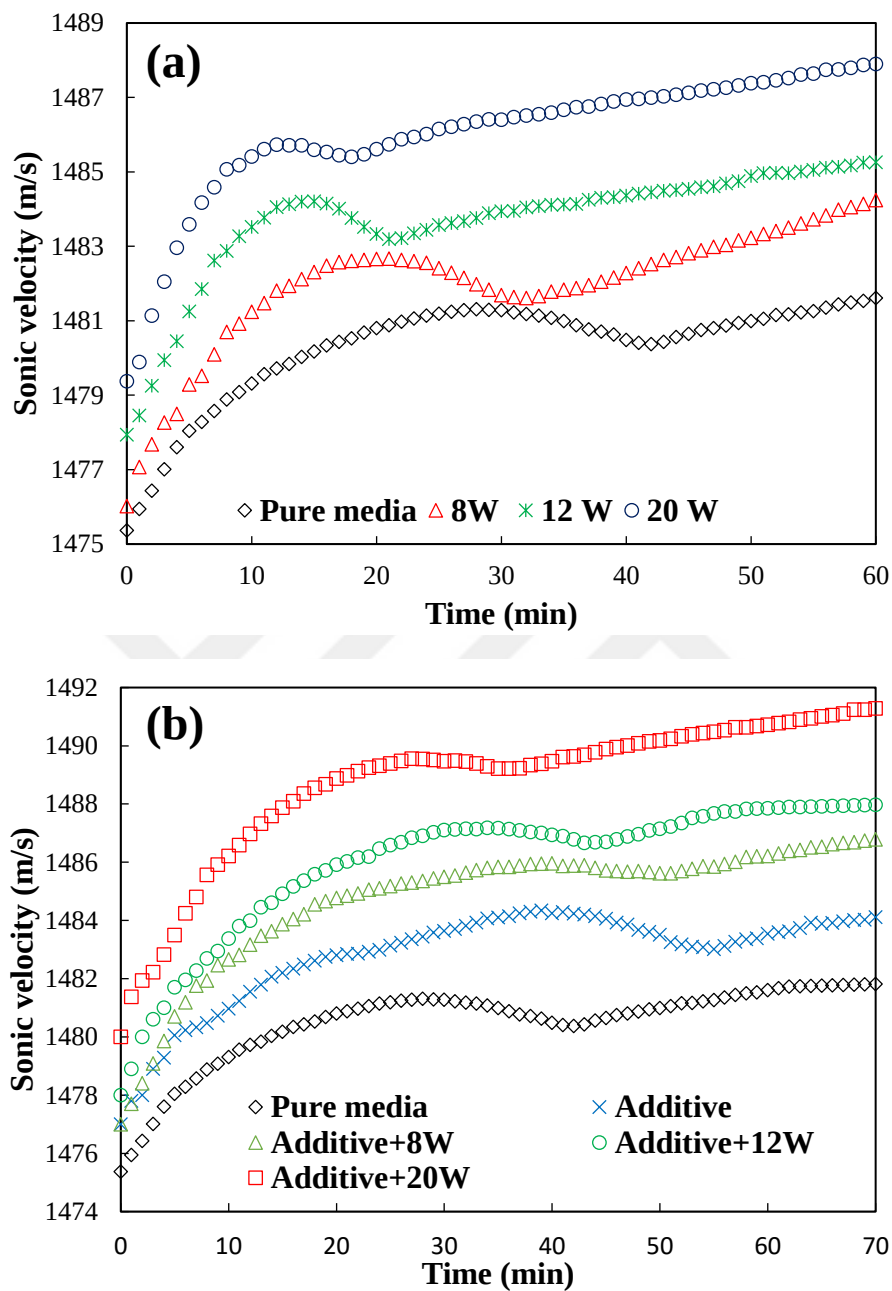


Figure 3.57. Variation of ultrasonic velocity of the suspension versus time a) in pure media and in the presence of varying UV radiation sources b) in the presence of the additive and the presence of the additive and varying UV radiation sources together.

The comparison with pure media suggests the additive causes an increase in the transformation period, although the presence of UV radiation tended to decrease the

transformation time. Thanks to the experimental results, it can be concluded that the phase transformation rate of β glycine to α glycine increases with rising UV radiation.

3.7.2. XRD analysis

The XRD patterns for the glycine phase transformation process at 25°C in pure media as a function of transformation time – where the XRD patterns were used to identify the crystals – are shown in Figure 3.58a. At $t = 0$ minutes, the characteristic β glycine peak was detected at 18° and all peaks related to the β glycine were found to be similar to the descriptions by other researchers in previous works [94,110]. The starting precursor was the β form, transforming into the α form as the reaction proceeded. After $t = 20$ min, two new peaks at 20° and 29° began to appear, which were taken to be the characteristic α glycine peaks in the X-ray diffraction pattern. While the intensity of these two peaks increased with reaction time, the β glycine peak intensities decreased gradually. The phase transformation finished at $t = 45$ minutes, at which time all the diffraction peaks related to β glycine disappeared and the peaks resembled typical α glycine peaks. It could be clearly concluded that phase transformation from β glycine to α glycine was finished at $t = 45$ minutes.

Figure 3.58b shows the X-ray diffraction patterns of the crystals obtained after completion of the transformation in the presence of different UV radiation intensities. All the peaks characterizing α glycine were detected in the XRD analysis; however, the peak intensities increased with the intensity of UV radiation. For instance, while the relative intensity of the peak at 20° was around 11,000 for the 20W UV lamp, it was about 9,500 and 4,400 for the 12W and 8W UV lamps, respectively.

In order to demonstrate the effects of UV on the transformation process of glycine, the experiments were performed in the presence of both a constant 500 ppm of additive and different UV lamps with varying intensities. The XRD results are shown in Figure 3.59. No different peak characterizing carboxylic acid was encountered in the presence of 500 ppm of propane-1,2,3-tricarboxylic acid when used as an additive, although a leftward shifting behavior with increasing intensities was observed in the XRD peaks in the presence of propane-1,2,3-tricarboxylic acid when compared to those in pure media. This can be explained by the incorporation of additive molecules within the crystal lattice. In this situation, structural imperfections and internal strains take place in the individual

lattice symmetry. As a result, shifts and changes occur when the additive is present in comparison to media with no additives [97].

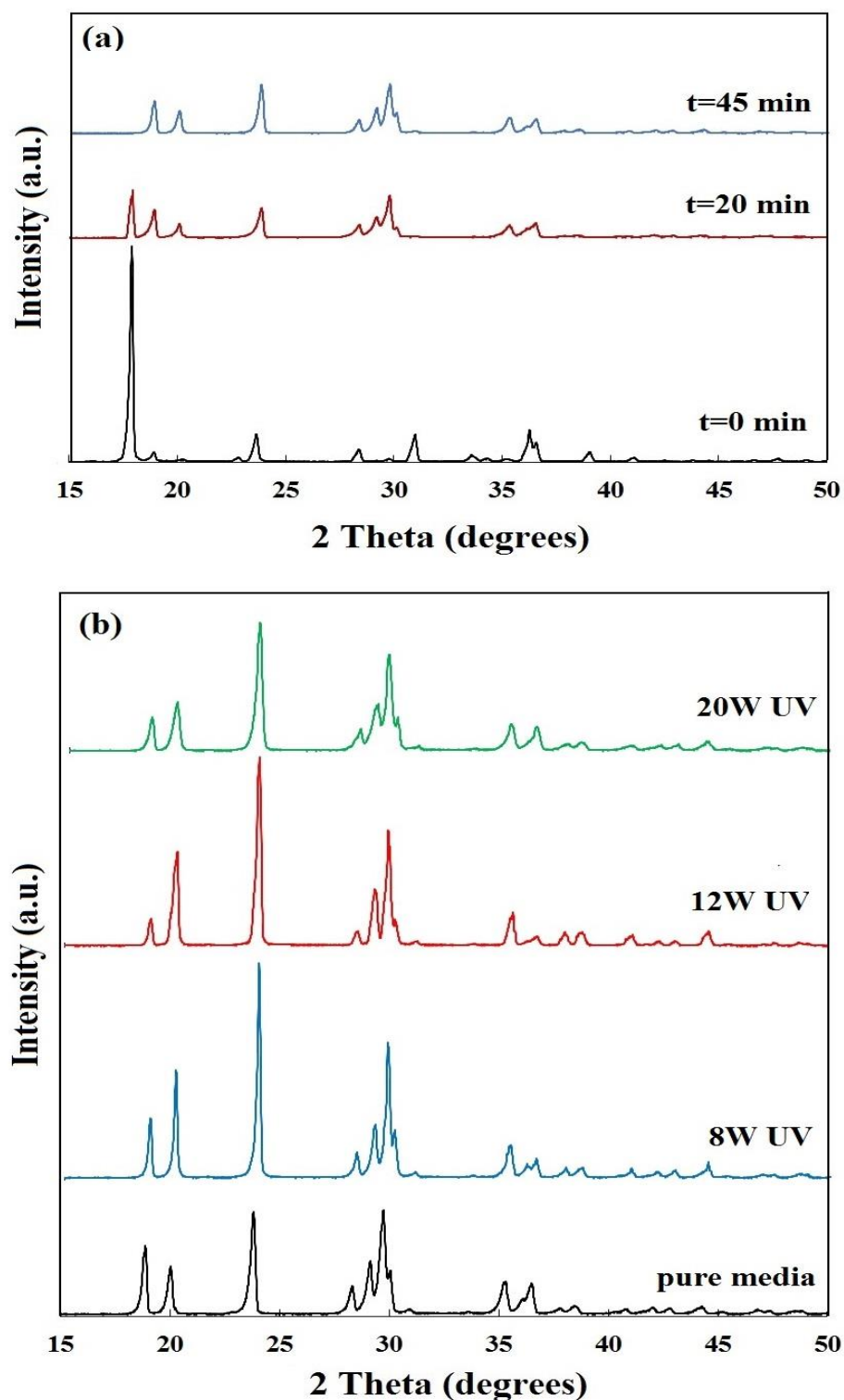


Figure 3.58. The X-ray diffraction patterns of the crystals a) obtained at different times for pure media b) obtained with different UV sources.

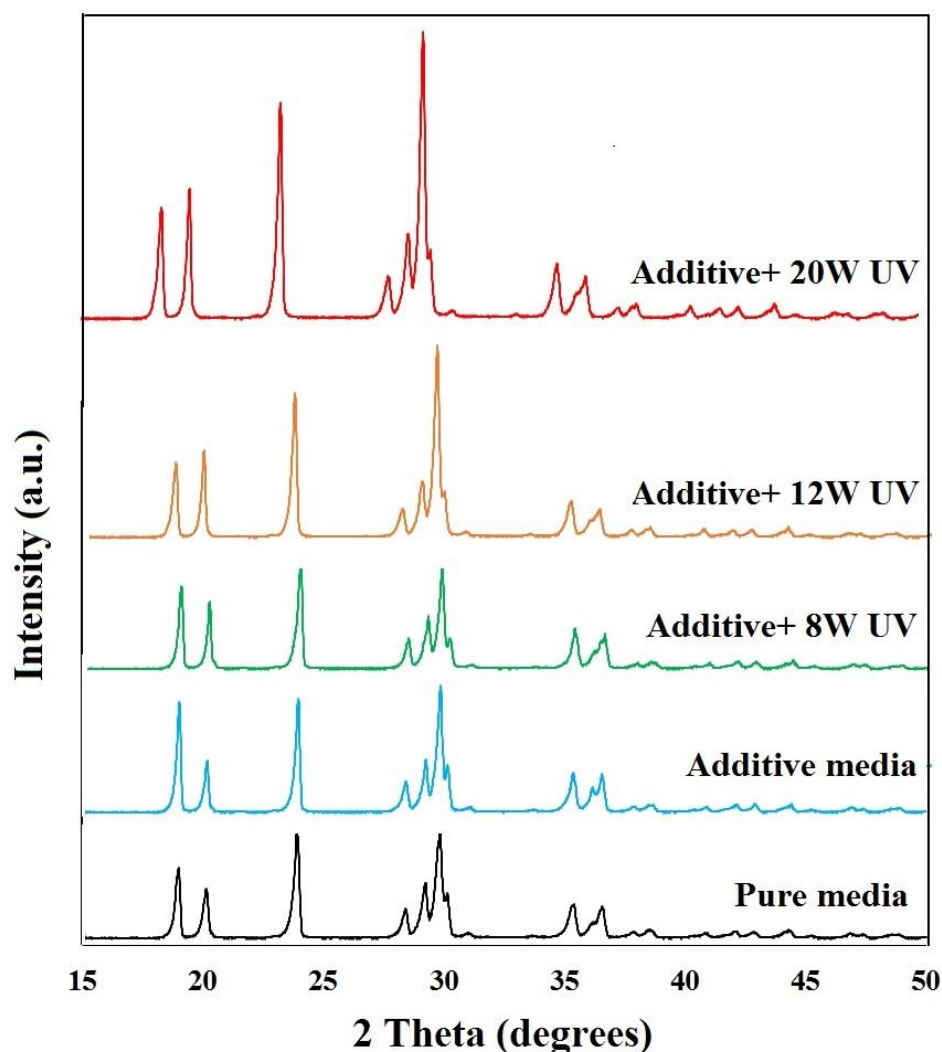


Figure 3.59. The X-ray diffraction patterns of the crystals in the presence of additive, and the presence of additive with varying UV sources.

It can be stated that the peak intensities were nearly the same with an 8W UV lamp for the combined additive–UV effects compared to XRD results for only the media with additive; however, with increasing UV intensity the peak intensities increased distinctively. The result indicates that the UV radiation had a small effect on XRD peaks at low intensity, but at higher intensity the UV radiation tended to increase the peak intensities both in pure media and in additive media. It could be explained that the internal strains occurred due to additive effect became higher with increasing UV intensity and that this situation caused the rise in the peak intensity.

3.7.3. SEM analysis

The crystals illustrated in Figure 3.60 were formed in pure media and, being of uniform prismatic form, they also had a sharp-cornered structure. The crystals are grown by intertwining. The crystals obtained are strong and subject to disruption by the hydrodynamic conditions of the media only at a low rate.

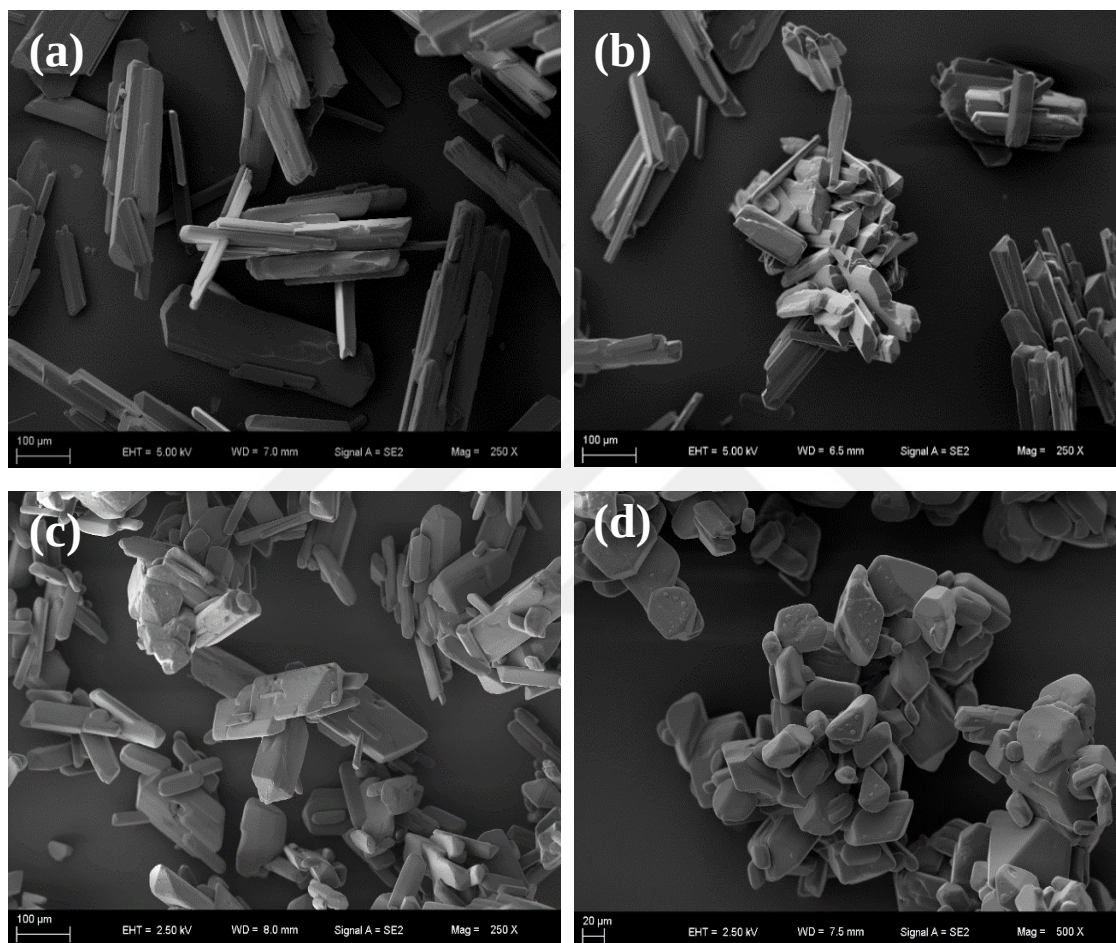


Figure 3.60. The SEM images obtained a) in pure media b) in the presence of an 8W UV radiation source c) in the presence of a 12W UV radiation source d) in the presence of a 20W UV radiation source.

The general morphology of the crystals obtained in the crystallization media with an 8W UV radiation source differs from those in pure media. By comparing them with the pure media, the crystal lengths were shortened and the sharp corners were slightly rounded in the crystals that formed. The crystals obtained were short and blunt, and found to be grown by intertwining, similar to pure media. Additionally, deformation is seen to begin

appearing on the crystal surfaces. The crystal lengths were reasonably shortened and rounding of the sharp corners began to be obvious for crystals produced by the experiments performed in the presence of a 12W UV radiation source. The crystals produced had a more homogeneous morphology and were in short rod forms. The surface deformation observed at 8W was also seen at 12W. At 20W the crystals obtained had lost their sharp corners completely. Their lengths were shortened and grew in the form of the short rods when observed at 12W, resulting with agglomerate crystals. Because the nuclei occurring on crystal's surfaces is growing, highly deformed and non-obviously shaped crystals are seen. Hence, the crystals produced in pure media were seen to be undergoing obvious morphological changes due to the increasing intensity of the UV radiation source. While the average size of the crystals acquired in pure media was 85 μm , it was measured to be 70 μm , 65 μm and 58 μm respectively in the presence of 8W, 12W and 20W UV radiation sources. The particle size distribution curves of the crystals obtained are given in Figure 3.61.

In order to detect the effects of UV radiation on morphology within non-pure media, experiments were performed in the same conditions as pure media in the presence of propane-1, 2, 3-tricarboxylic acid – chosen as model matter. The images of the crystals produced solely with the 500 ppm of the additive without a UV radiation source are shown in Figure 3.62.

In comparison to pure media, it was found that crystals obtained via the presence of the additive have a pyramidal shape and a sharp-edged structure. Surface nucleation and growth defects were observed on the crystal surfaces. As seen on Figure 3.62, the average particle sizes of crystals obtained by the presence of the additive were decreased significantly and measured to be 64 μm . When the SEM images were examined, it was seen that surface nucleation of the crystals produced by 500 ppm of the additive and 8W of UV radiation was increased. Because defects in the crystal lattices increased, the shape of the crystals began to deteriorate. Few sharp corners were rounded off when comparing against the crystals produced by the media with additive. The average particle size of crystals was measured to be 60 μm . Crystals lost their sharp corners to a much greater extent with an increase in UV radiation intensity.

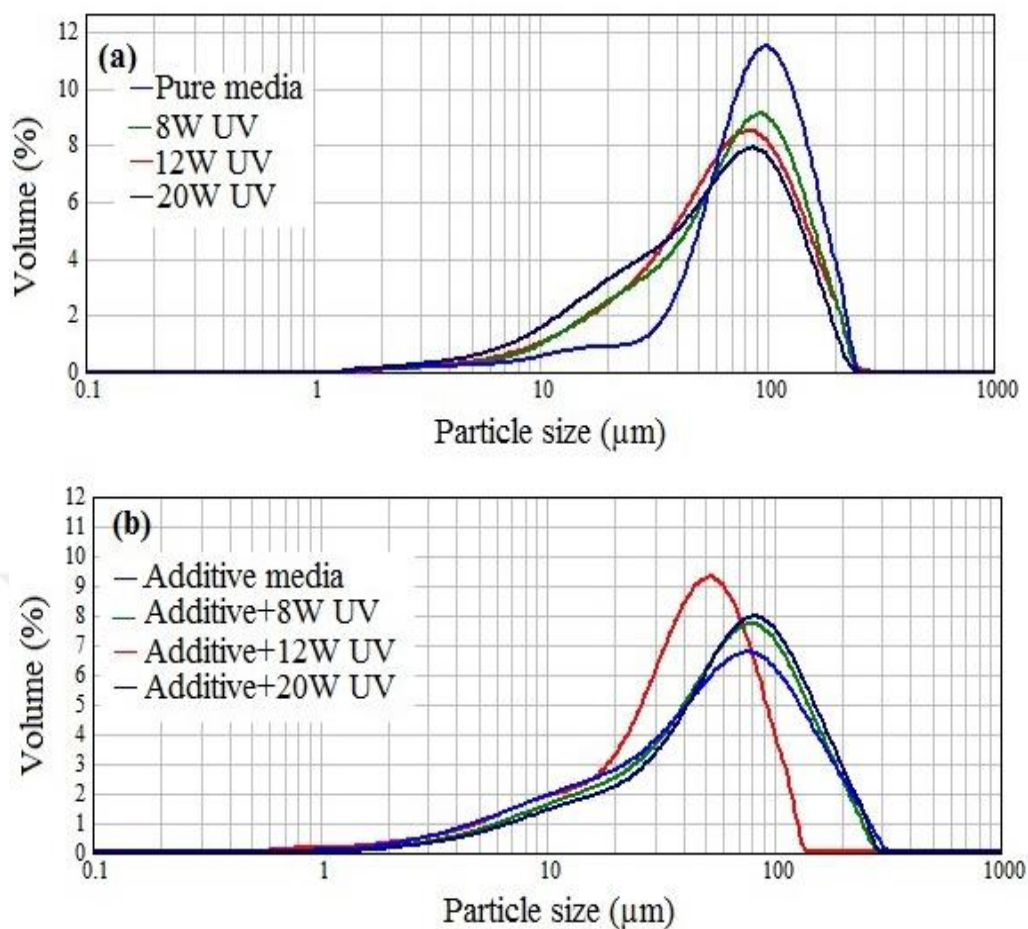


Figure 3.61. The particle size distribution of the crystals obtained a) in pure media and in the presence of varying UV radiation sources b) in the presence of the additive and the presence of the additive and varying UV radiation sources together.

Both surface nucleation and defects were increased within the surfaces of crystals obtained with 12W UV radiation, and the crystals lost their usual appearance. The average particle size of crystals produced by the presence of 12W of UV radiation was measured to be 56 μm. All the edges and corners of crystals produced in the presence of 20W of UV radiation were rounded, the lengths were shortened and the crystals grew by intertwining. The crystal morphology exhibited deformation and did not have a distinct shape. Their dimensions were decreased and measured to be 41 μm. The results obtained within both pure and additive media illustrated that UV radiation had an influence on crystal morphology. With rising UV radiation intensity within both the media mentioned, significant morphological changes were revealed, and the average particle size decreased.

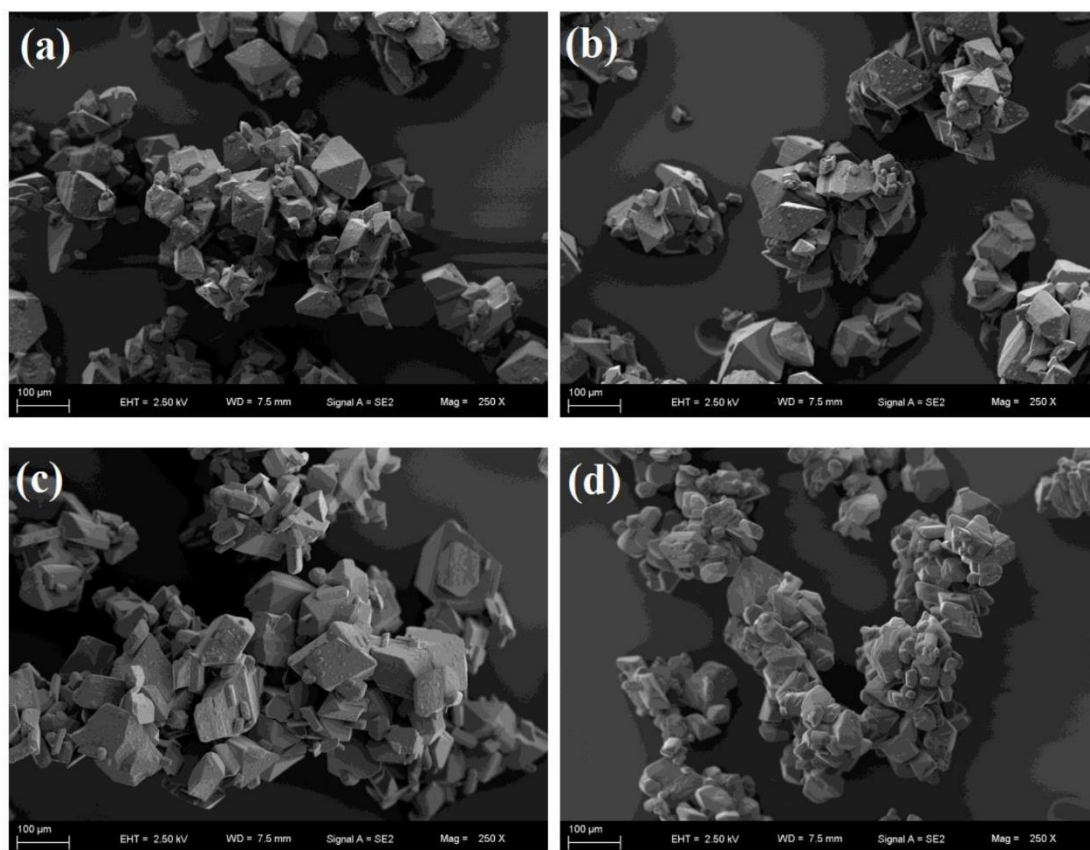


Figure 3.62. The SEM images obtained in the presence of a) additive b) additive with 8W UV radiation source c) additive with 12W UV radiation source d) additive with 20W UV radiation source.

3.7.4. TGA/MS/ATR-FTIR

Figure 3.63 shows the TGA and thermogravimetric derivative (DTG) curves for the crystals obtained in pure media, those obtained in the presence of 500 ppm of additive and those obtained in the presence of 500 ppm of additive with a 12W UV radiation source during thermal decomposition in a nitrogen atmosphere.

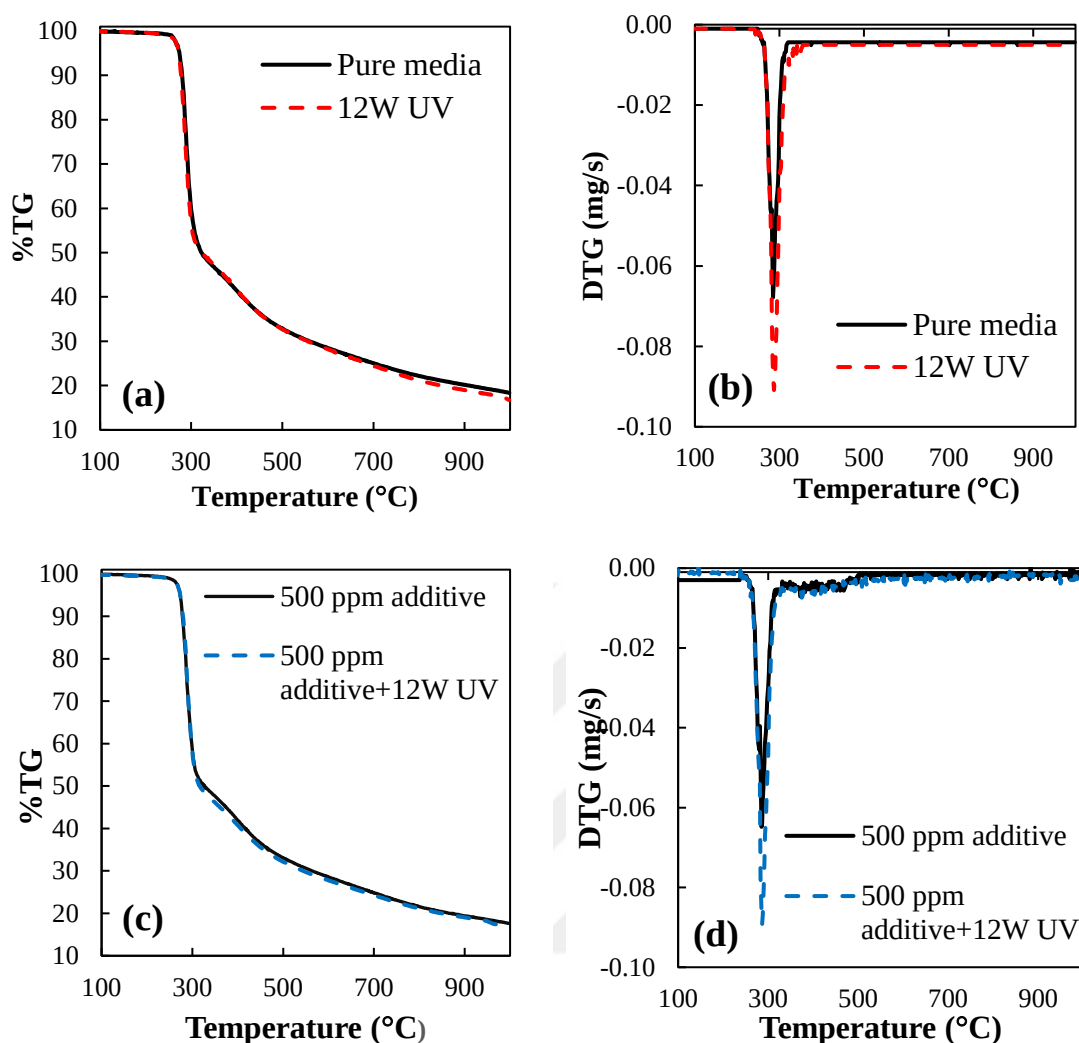


Figure 3.63. a) TGA curves and b) DTG curves of glycine obtained in pure media and in the presence of 12W UV radiation source c) TGA curves and d) DTG curves of glycine obtained in the presence of 500 ppm of additive and in the presence of 500 ppm additive with a 12W UV radiation source.

For the crystals obtained in pure media, their thermal decomposition could be separated into two stages. As said before, the first stage of weight loss corresponded to the decomposition of the amino group in the glycine molecule within the temperature range from 253 to 326°C. The recorded weight loss was approximately 50% at this stage. This situation showed that the decomposition of the amino group accounted for most of the weight loss during the process. A further weight loss of about 30% of the total weight was observed in the temperature range from 326 to 520°C. This was attributed to the decomposition of the carboxyl group from the glycine molecule. The total weight residue

was 18.35%. This result was similar to the values that have been stated in published literature for glycine [102]. Thermal decomposition behaviors of the other three crystal samples followed the same routes, and the TGA curves had the same shapes; however, it was observed that the weight loss of the crystals changed. The thermograms for the crystals obtained in the presence of 12W UV radiation source and in the presence of 500 ppm additive with a 12W UV radiation source showed that the weight loss of the samples was 83.28% and 83.66% respectively. It was also observed that the weight loss trend increased in the presence of a UV radiation source. The highest weight loss existed in the case of 500 ppm of additive with a 12W UV radiation source, which could be an indicator of the organic molecules owing to the UV radiation source.

In addition to the TGA–DTG results, the ATR–FTIR analyses were performed on both to identify the functional groups of the crystals and determine the possible effects of UV radiation on the glycine crystals. Figure 3.64a presents the Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectrums of the crystals obtained in pure media and in the presence of a 12W UV radiation source. The spectrum of crystals obtained in pure media and α glycine is in agreement with work reported in published literature [103,110].

All expected peaks that characterize α glycine were observed for the crystals produced in pure media and they were shown in Figure 3.64a. The broad intense absorption bands between 2200 and 3300 cm^{-1} shows N–H stretching of the NH_3^+ group that is hydrogen bonded with COO^- in the crystal lattice of the amino acid [94]. The peak at 3153 cm^{-1} could be attributed to asymmetric stretching of the NH_3^+ group. The absorption bands observed at 1599 and 1406 cm^{-1} were related to asymmetric and symmetric stretching vibrations of the COO^- group respectively. The bands at 1499 cm^{-1} were ascribed to symmetric stretching of the NH_3^+ group. The band at 1444 cm^{-1} corresponded to CH_2 bending vibrations as well as the other peak seen at 1327 cm^{-1} was attributed to CH_2 twisting mode. Moreover, the absorbance peaks at 1032 and 1109 cm^{-1} were related to the CN stretching vibration and NH_3^+ rocking, respectively. The bands seen at 891 and 693 cm^{-1} were associated with C–C symmetric stretching and O–C=O bending vibrations, respectively. The FTIR spectrum for the crystals obtained in the presence of a 12W UV radiation source is given in Figure 3.64a. The spectra showed identical patterns to the

pure media. However, when compared to pure media, decreasing intensity behavior was observed in the spectrum bands in the presence of UV radiation.

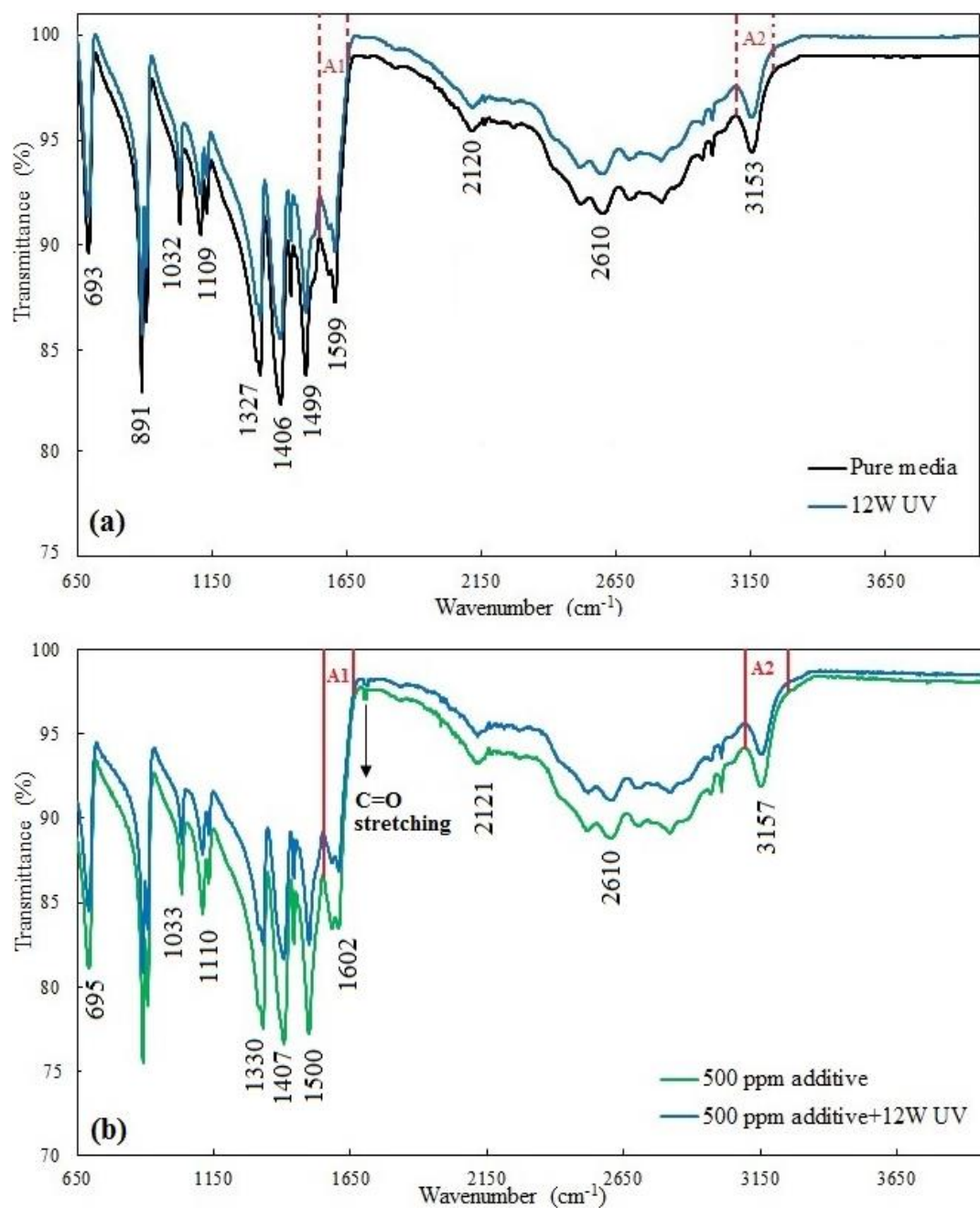


Figure 3.64. ATR-FTIR spectrums of the crystals obtained a) in pure media and in the presence of a 12W UV radiation source b) in the presence of additive and in the presence of additive with a 12W UV radiation source.

In order to show the effects of UV radiation on glycine, two areas of the FTIR spectrum should be examined carefully. The areas between 1557 and 1623 cm^{-1} (A1), 3126 and

3180 cm^{-1} (A2) were associated with the COO^- groups and NH_3^+ respectively. After exposing them to UV radiation, the absorption intensity in both areas decreased. The decreased intensity of the bands may be caused by the destruction of glycine under UV radiation, and this result agreed with previous work in published literature [111].

Figure 3.64b shows the ATR-FTIR spectrums of the crystals obtained in the presence of 500 ppm of propane-1,2,3-tricarboxylic acid, and in the presence of propane-1,2,3-tricarboxylic acid with a 12W UV radiation source, respectively. When the spectrum was examined for the crystals obtained in the presence of the additive, the peaks that characterize α glycine were detected using ATR-FTIR analysis. Apart from the spectrum obtained in pure media, it included a distinctive peak at 1710 cm^{-1} that is associated with the presence of C=O stretching vibrations due to carboxylic acids. The appearance of this peak confirmed the presence of propane-1,2,3-tricarboxylic acid and it also showed that the additive could be adsorbed onto the crystal surface. In the presence of both the additive and the UV source, a similar spectrum was obtained and the appearance of a new peak at 1708 cm^{-1} was attributed to the presence of the carbonyl group as a consequence of the adsorption of the additive into the crystal lattice. When the results were compared to pure media, the peak intensities increased in the additive media; nevertheless, a noticeable decrease was observed in the peak intensities in the presence of both the additive and the UV radiation sources. The peak intensity is in direct proportion to the relative concentration and it was observed that the presence of UV radiation in the phase transformation media caused noticeable reductions in the peak intensity as a result of deformation of organic molecules. The main difference between the two figures was the lower intensity and lower yields obtained in the presence of UV radiation. If the areas under the curves on Figure 3.64b are compared, this effect could be clearly seen.

In addition to the ATR-FTIR analysis, the TGA-MS technique was utilized to determine possible interactions and changes induced by propane-1,2,3-tricarboxylic acid on the glycine phase transformation process by providing sensitive, real time, non-destructive and simultaneous measurements. Using MS spectra, the chemical nature of the gases produced during thermal decomposition was evaluated by comparing the intensity of the peaks belonging to the different mass-to-charge (m/z) ratios. Figure 3.65 shows the TGA-MS spectrograms for glycine crystals produced in the presence of propane-1,2,3-tricarboxylic acid, and then in the presence of propane-1,2,3-tricarboxylic acid and a UV

radiation source together. According to the data from the MS spectra examining the molecular and ion components of propane-1,2,3-tricarboxylic acid, characteristic peaks corresponding to the propane-1,2,3-tricarboxylic acid are given by m/z values of 45, 58, 86 and 112. When the propane-1,2,3-tricarboxylic acid profile is investigated as a function of temperature, the intensive signal of the species appeared mainly in a temperature range from 230 to 392°C for both samples.

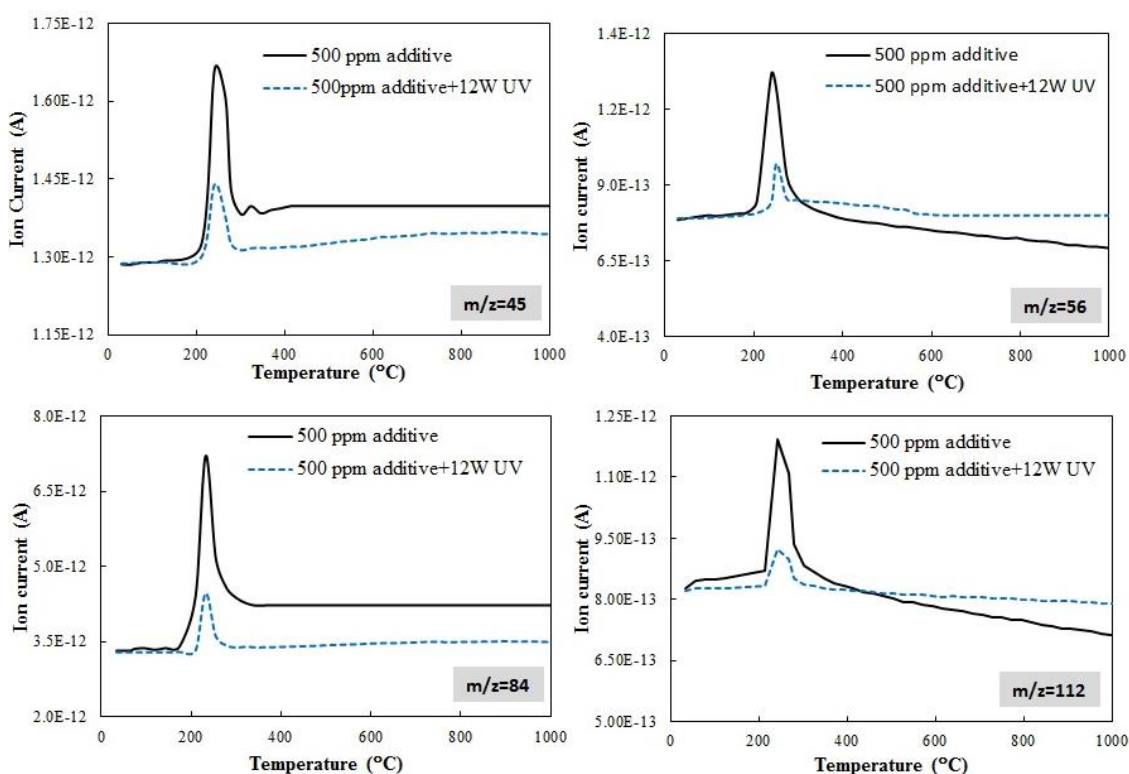


Figure 3.65. TGA–MS spectrograms of glycine crystals obtained in the presence of 500 ppm of additive and in the presence of 500 ppm of additive with a 12W UV radiation source.

According to Figure 3.65, it seems that the effect of UV radiation results in a decrease of the yield of this carboxylic acid groups. In other words, the peak absorbance intensities of these groups are found to be relatively low compared to the peaks of crystals obtained in the presence of only the additive. It can be obviously stated that the propane-1,2,3-tricarboxylic acid peaks showed a similar trend to the FTIR spectrum. Thus, the results obtained using the TGA–MS method support the conclusions derived from the ATR–FTIR analysis.

3.8. The Results of Tricarballic Acid Effects on Phase Transformation of Calcium Sulfate Hemihydrate to the Dihydrate Form*

In this part, phase transformation of calcium sulfate hemihydrate to calcium sulfate dihydrate was performed in a batch-type crystallizer in the absence and then the presence of tricarballic acid (propane-1,2,3-tricarboxylic acid). Three different tricarballic concentrations 250 ppm, 1000 ppm and 2500 ppm were used throughout the experiments. The influence of tricarballic acid used as an additive on the phase transformation was explored detailed.

3.8.1. Conductivity measurements

The transformation process of calcium sulfate hemihydrate to dihydrate in pure media and in presence of an additive was followed by measuring the conductivity of the suspension. The conductivity curve obtained in pure media is given in Figure 3.66.

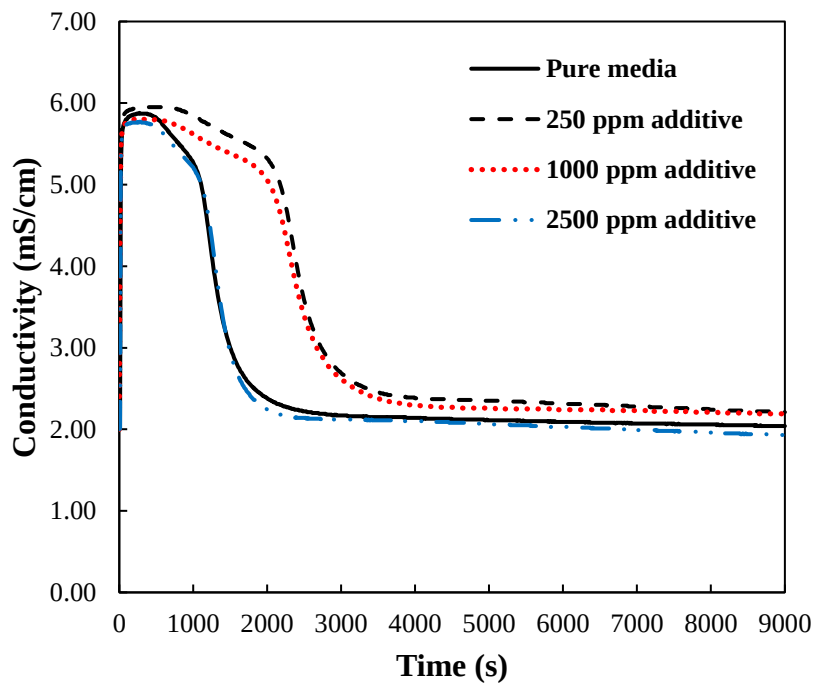


Figure 3.66. Variation of conductivity versus time in pure media and in the presence of varied tricarballic acid concentrations.

* Polat, S., Sayan P. (2017) Effects of tricarballic acid on phase transformation of calcium sulfate hemihydrate to the dihydrate form. *Crystal Research and Technology*, 52 (5), 1600395 (1-10).

This curve indicated that the transformation process included three different stages: dissolution of the hemihydrate; nucleation of the dihydrate; and growth of the dihydrate. This curve agreed with existing reports in the literature [92]. In the first stage, the conductivity showed a sharp increase resulting from dissolution of the hemihydrate. Figure 3.66 shows that this stage was completed within about 1.5 minutes under the studied conditions. Nucleation of the calcium sulfate dihydrate occurred in the second stage; no distinctive change was observed in the conductivity. The third stage was related to growth of the dihydrate crystals arising from the heterogeneous nucleation onto the hemihydrate particles. The curve obtained in pure media showed that the conductivity decreased until the conversion process was complete. The decrease in conductivity resulted from variation of calcium ions concentration during the transformation of hemihydrate to dihydrate. At $t=2.5$ h, the transformation process was complete, and the conductivity had reached a fixed value. The conductivity curves obtained in the presence of three different additive concentrations are also shown in Figure 3.66. Whereas the conductivity of saturated solution used in pure media was measured to be 2 mS/cm, the conductivity values of the saturated solution in the presence of 250, 1000, and 2500 ppm tricarballic acid were 2.09 mS/cm, 2.16 mS/cm, and 2.34 mS/cm respectively. The additive caused both notable changes in conductivity and different transformation rates; the results are shown in Figure 3.66. It was noted that at high concentration the additive had almost no influence on transformation time, whereas at lower concentrations, the additive tended to extend the transformation time. Unlike published results for other carboxylic acids, the present study found that the retarding effect of tricarballic acid on transformation of hemihydrate to dihydrate decreased with increase of carboxylic acid concentration [42].

3.8.2. SEM analysis

The SEM images taken at different times during the transformation process of calcium sulfate hemihydrate to dihydrate in pure media are shown in Figure 3.67: the calcium sulfate hemihydrate crystals had no distinct shape, yet they consisted of plate-like, layered, and porous structures at $t=0$ min. With the beginning of the transformation process, the porous structure decreased significantly, and the crystals started to grow to the needle-like form. This process was a relatively rapid transformation process,

completed within 15 minutes. Whereas some crystals kept essentially the same needle-like form, a significant part of the crystals transformed into the plate-like form. It was also observed that during this transformation process the increase that occurred in the volume of the pores was caused by incorporation of water into the pores causing the crystals to break into smaller crystals. These broken crystals revealed a complicated structure that consisted of mixtures needle and plate structures. With the completion of the transformation, the pores closed entirely, and almost all crystals had been transformed into the plate-like structure. With the completion of the transformation, the pores closed entirely, and almost all crystals had been transformed into the plate-like structure.

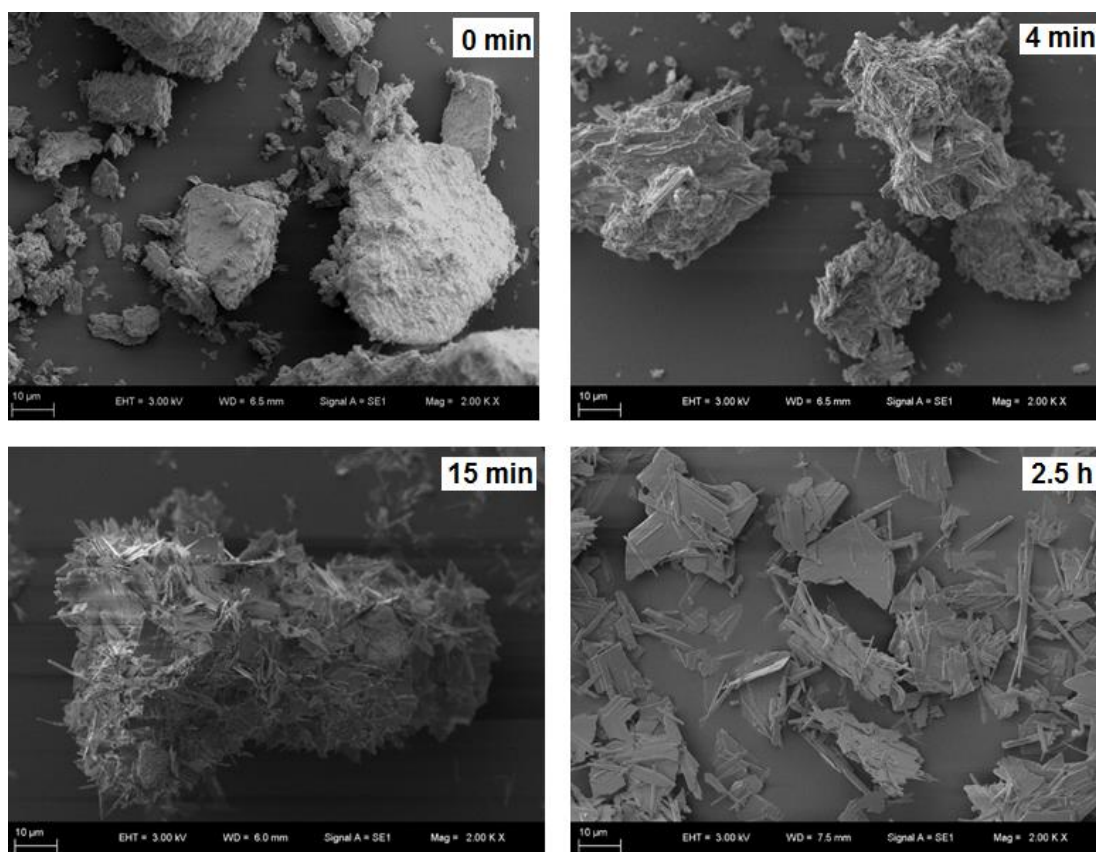


Figure 3.67. The SEM images taken at different times in pure media.

The SEM images presented in Figure 3.68 for the crystals obtained in the presence of 2500 ppm tricarballylic acid show that the carboxylic acid used as additive in the media drastically affected both crystal growth and the crystal morphology during the transformation process.

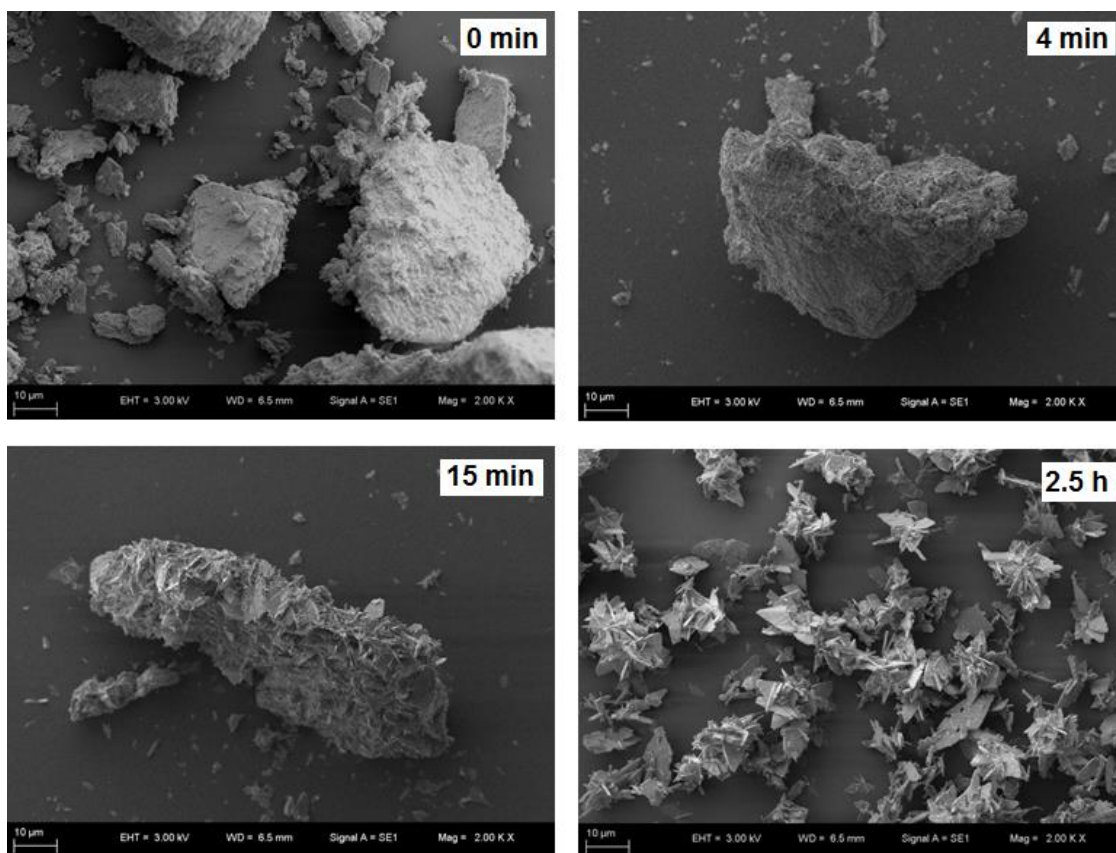


Figure 3.68. The SEM images taken at different times in the presence of 2500 ppm tricarballic acid.

It could be hypothesized that tricarballic acid was adsorbed on active growth sites of the crystals, and that this situation caused the change the growth behavior of crystals in terms of crystal shape and size. The growth-surfaces partially changed crystals had developed as the plate-like form, and the needle-like form of crystals was not observed at $t=15$ min. During the transformation process from hemihydrate to dihydrate, this type of crystals could be broken easily by the hydrodynamic conditions of the media because of the mechanical effects resulting from the increase in crystal volume. The crystals formed in the presence of 2500 ppm tricarballic acid were of similar plate-like structures but growing in an interlaced manner. However, the particle size of the crystals decreased considerably compared with the crystals obtained in the pure media. To determine the variation in particle size, the average particle size as measured through a laser diffraction particle size analyzer changed depending on the phase transformation time. At $t=0$ min the average particle size of calcium sulfate hemihydrate was 45 µm. Whereas the average

particle size of the crystals obtained in pure media was 36 μm , the particle size of crystals obtained in the presence of 2500 ppm tricarballic acid was 16 μm at $t=2.5$ h. The variations of particle size in pure media had markedly more or less similar values; however, these variations were substantially different in the presence of carboxylic acid. Furthermore, filtration rate measurements were carried out to detect the filtration characteristics of the crystals obtained. It was determined that the specific cake resistance showed a significant change in the presence of the additive. While the specific cake resistance of the crystals obtained in pure media was 2.23×10^{11} kg/m, this value was calculated as 7.247×10^{11} kg/m for the crystals obtained with a concentration of 2500 ppm of tricarballic acid at 20 °C. As clearly seen in the SEM images, this increase in specific cake resistance can be explained by the decrease in the size and morphological change of the crystals.

3.8.3. XRD analysis

The X-ray diffraction patterns of original samples for calcium sulfate anhydrite, hemihydrate and dihydrate are presented in Figure 3.69. The characteristic peaks of anhydrite phase were at 25.5° and 38.5°. While XRD patterns exhibited strong diffraction peaks at 14.72°, 25.67°, 29.69° and 54.14° for calcium sulfate hemihydrate, the XRD patterns exhibited strong diffraction peaks at 11.59°, 20.72°, 23.40° and 29.11° for calcium sulfate dihydrate. The X-ray diffraction patterns of the crystals obtained in pure media depending on the phase transformation time are shown in Figure 3.70. All peaks related to the calcium sulfate hemihydrate existed at $t=0$ min; this was consistent with reference patterns and previous studies [112,113]. With the beginning of the transformation process, the characteristic diffraction peaks of calcium sulfate dihydrate began to appear at $t=4$ min. The calcium sulfate hemihydrate coexisted with the dihydrate form, and the pattern of the dihydrate showed different characteristic peaks compared with the peaks of the hemihydrate phase. While these peaks intensities gradually increased, the hemihydrate peaks started to disappear at $t=15$ min.

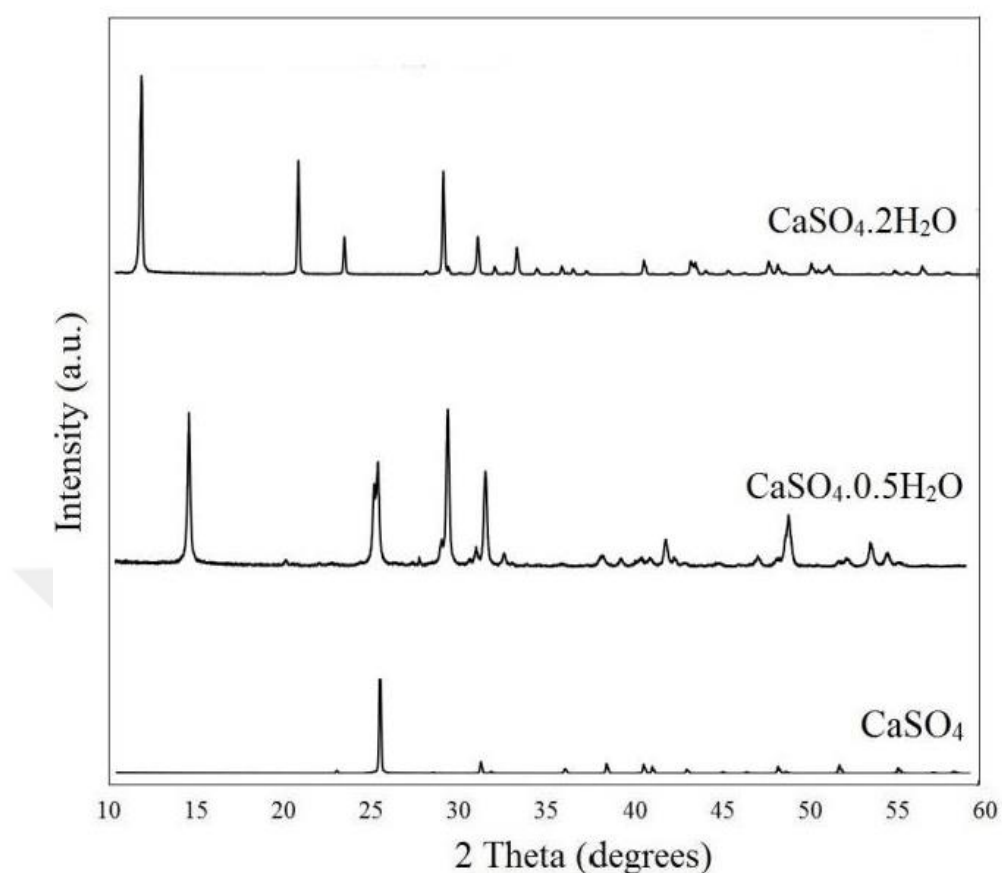


Figure 3.69. The X-ray diffraction patterns of the reference crystals.

The phase transformation finished at $t=150$ minutes, at which time the diffraction peaks resembled typical calcium sulfate dihydrate peaks. These results showed clearly that calcium sulfate hemihydrate was completely transformed to calcium sulfate dihydrate. Figure 3.70 also shows the X-ray diffraction patterns of the crystals obtained in the presence of 2500 ppm tricarballic acid at $t=150$ min. Figure 3.70 shows a rightward shifting with decreasing intensities observed in the XRD peaks in the presence of carboxylic acid as compared with those in pure media. This situation could be explained by incorporation of additive molecules with the crystal lattice. Thus, structural imperfection and internal strains occur in the individual lattice symmetry. As a result of this, the shifting and changing in peaks occur in the presence of additive compared with pure media [97].

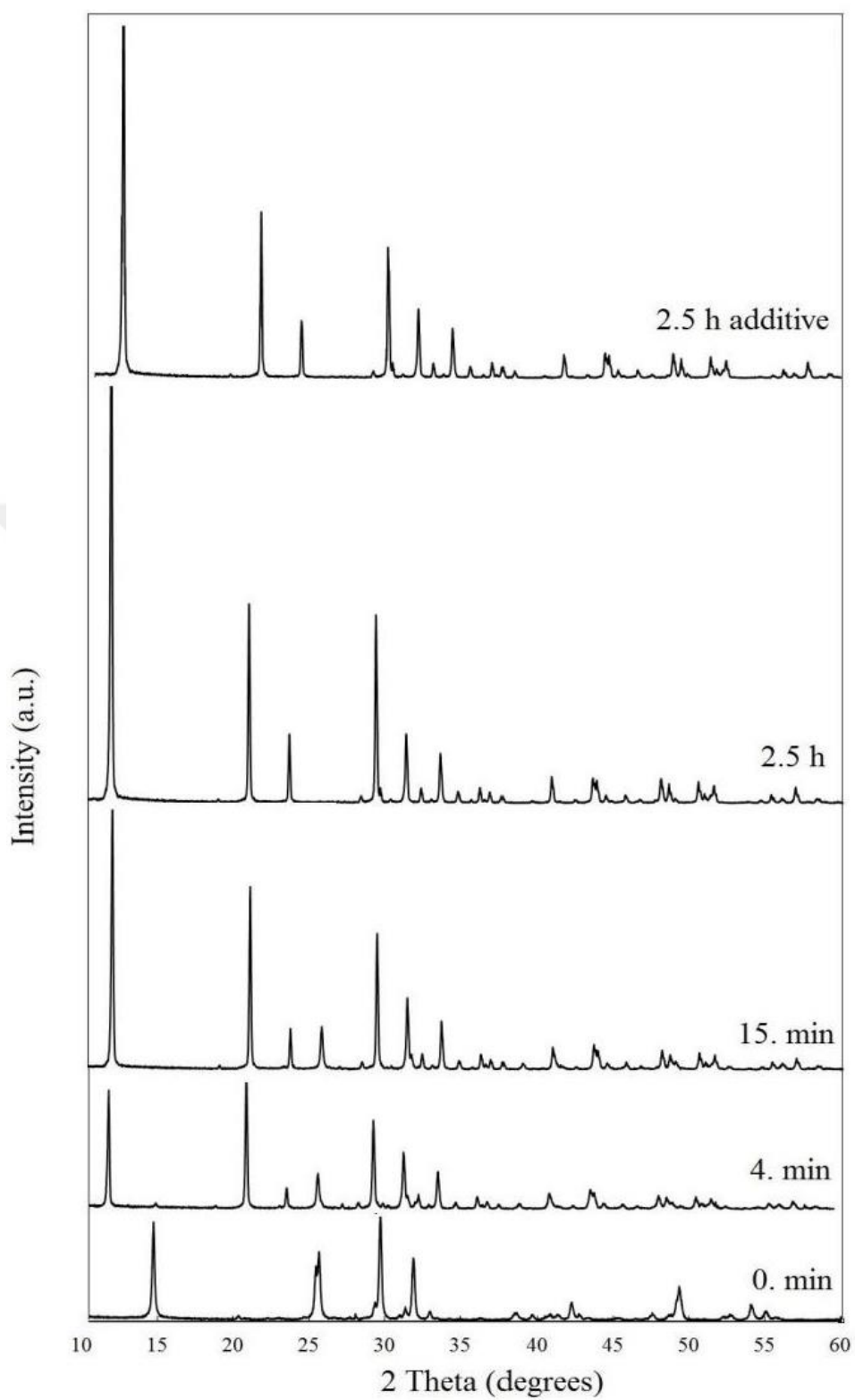


Figure 3.70. The X-ray diffraction patterns of the crystals obtained at different times.

3.8.4. TGA analysis

Thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere from 30 to 500 °C at 10 °C/min to determine the variation of crystal water loss depending on phase transformation time. Figure 3.71 shows the thermograms obtained at different times during the transformation of hemihydrate to dihydrate in pure media.

The thermogram obtained at $t=0$ min, showed that the weight loss of the sample was 5.82%, which corresponded to loss of crystal water (0.5 water molecule per crystal) of calcium sulfate hemihydrate. As the conversion proceeded, the weight loss increased. The total weight loss was determined to be 16.81 and 19.90% at $t=4$ min and $t=15$ min respectively. Based on TGA curves obtained at $t=2.5$ h, the weight loss was found to be 21.25%. This loss was agreement with the literature [114]; it resulted from the removal of 2.0 water molecules of calcium sulfate dihydrate. When compared to this gradual increase, it was obvious that calcium sulfate hemihydrate was transformed into calcium sulfate dihydrate; this result is consistent with the XRD patterns.

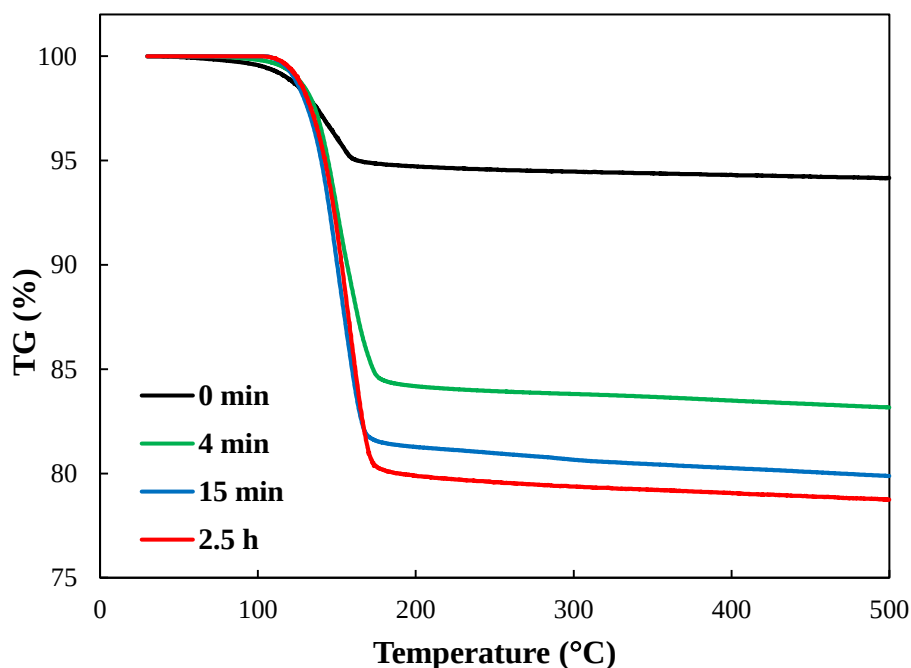


Figure 3.71. The thermograms of the crystals obtained in pure media at different times.

3.8.5. ATR-FTIR analysis

The FTIR measurements play a great role when providing direct information on changes that occur in the chemical compositions and functional groups of the crystals. Taking these situations under consideration, the FTIR analysis of the samples taken at $t=0$ min and $t=2.5$ h in the absence and presence of 2500 ppm tricarballic acid were done using FTIR. FTIR spectra of the samples obtained at $t=0$ min, $t=2.5$ h in pure media and the reference FTIR spectra of calcium sulfate hemihydrate and dihydrate are given in Figure 3.72.

As consistent with the reference calcium sulfate hemihydrate FTIR spectra, the sample was completely composed of calcium sulfate hemihydrate at the initial stage of transformation process. The absorbance peaks at 3604 and 3606 cm^{-1} represented O-H stretching vibrations, which were indicative of water. The absorption peak at 1618 cm^{-1} was also attributed to bending vibrations of water molecules. The absorbance peaks in the region of 1030–1150 cm^{-1} were associated with S-O stretching, and the peak at 659 cm^{-1} was representative of SO_4 bending vibrations. At completion of the transformation process, all peaks were related to the calcium sulfate dihydrate. The presence of water in calcium sulfate dihydrate were evidenced by the absorption peaks at 3396 and 3524 cm^{-1} arising from the O–H stretching vibration and by the 1618 and 1681 cm^{-1} peaks of O–H bending vibrations.

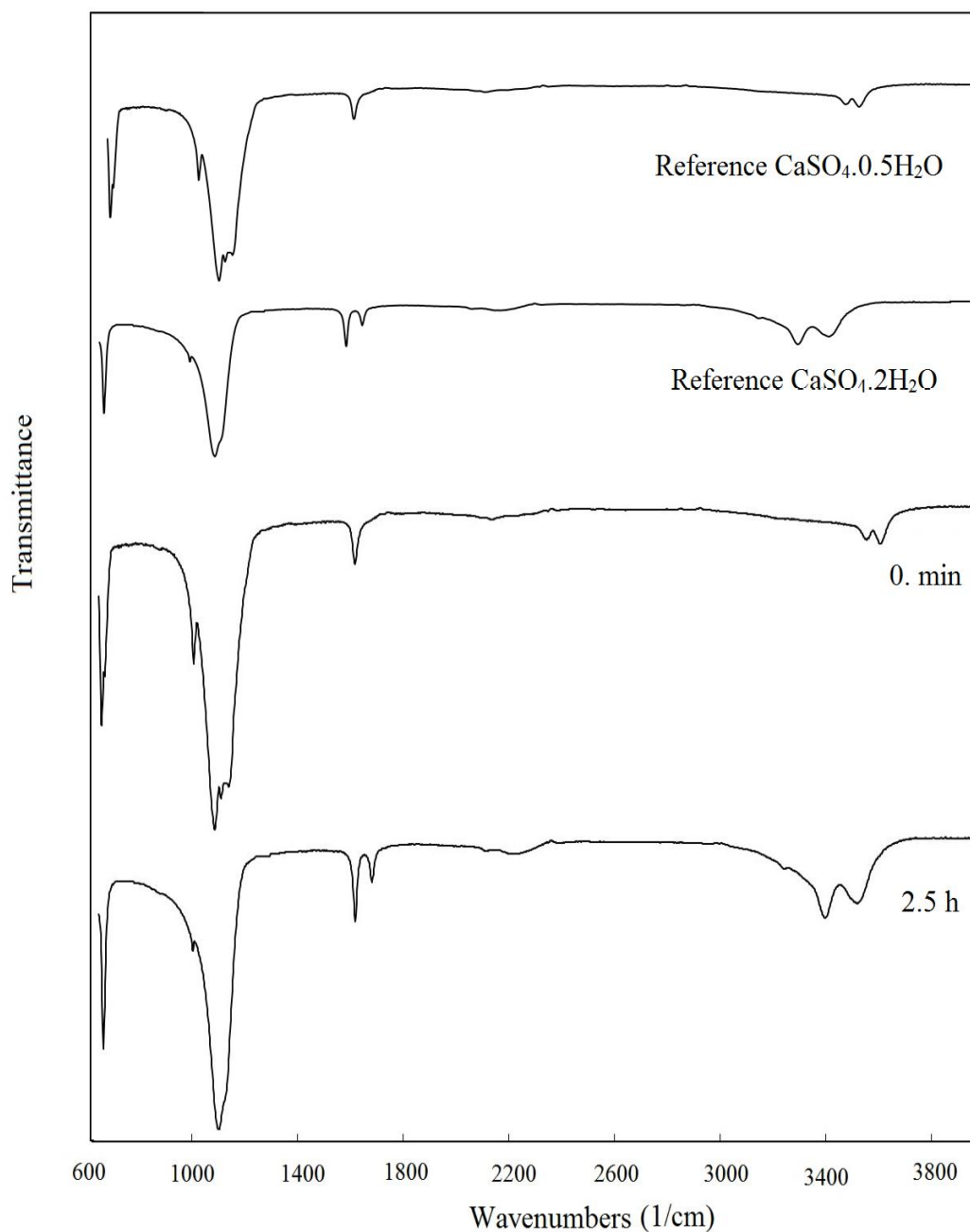


Figure 3.72. FTIR spectra of the crystals taken at $t=0$ min and $t=2.5$ h in pure media.

Although calcium sulfate hemihydrate included only one bending vibration peak at 1618 cm^{-1} , calcium sulfate dihydrate contained two stronger and sharper peaks at 1618 and 1681 cm^{-1} because of the presence of two types of water molecules. Furthermore, the position of the O-H stretching vibration changed during the transformation process: the peaks at 3604 and 3606 cm^{-1} in the hemihydrate shifted to 3396 and 3524 cm^{-1} in the dihydrate due to hydrogen bonding vibrations [115,116].

3.8.6. TGA/FTIR/MS analysis

The more powerful and sensitive method, namely TGA-FTIR and TGA-MS, were used instead of ATR-FTIR to identify incorporation of carboxylic acid with crystal surface during the transformation process. Figure 3.73 illustrates the three-dimensional FTIR spectrum of the samples obtained in the presence of 2500 ppm tricarballic acid for the change of individual functional groups with respect to time. Although some similarities with the samples obtained in pure media were observed, significant differences were seen in the presence of carboxylic acid. It is obvious from Figure 3.73a that the most intense absorbance peaks between the temperatures of 121 and 280 °C related to C=O stretching vibrations.

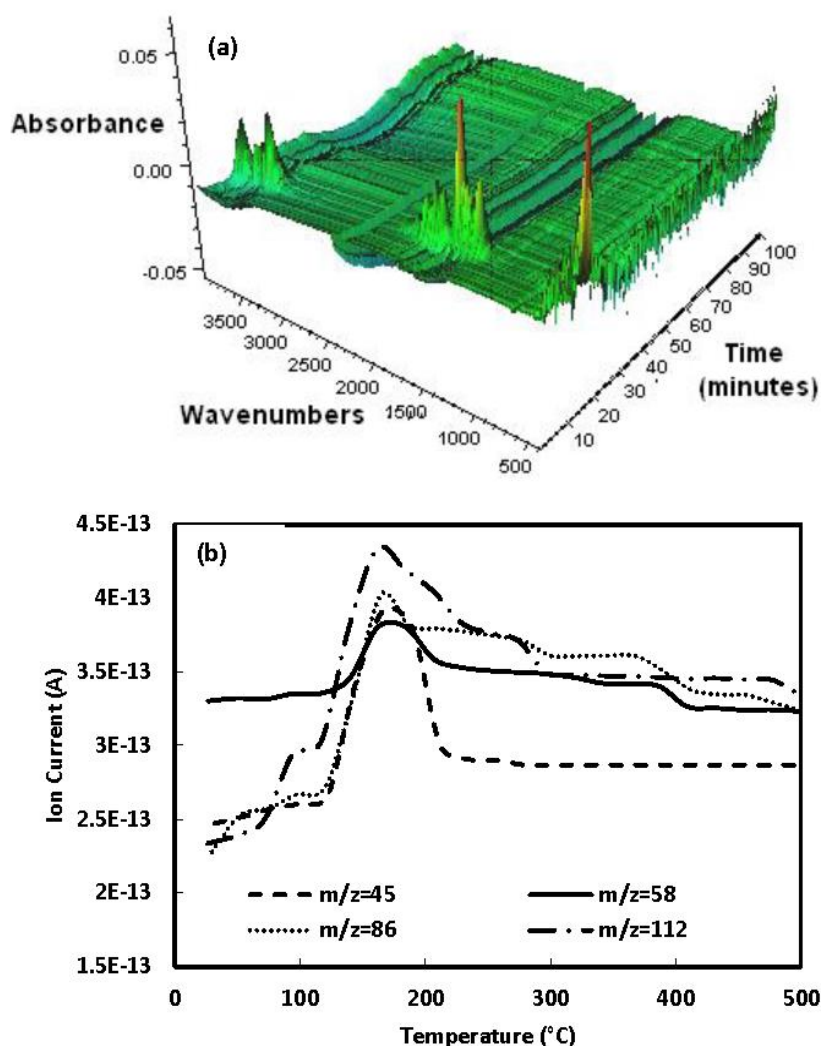


Figure 3.73. (a) 3D FTIR spectrum and (b) TGA-MS spectrograms of the calcium sulfate dihydrate crystals produced in the presence of 2500 ppm tricarballic acid.

When carboxylic acid content is included, the bands seen at 1738 cm^{-1} are attributable to carbonyl stretching vibrations. Moreover, the presence of carboxylic acid was proven by other bands that appeared at 1315 cm^{-1} and 1140 cm^{-1} , related to C-O stretching and O-H bending.

For further characterization of the samples obtained in the presence of 2500 ppm tricarballic acid, TGA-MS was applied simultaneously. Figure 3.73b shows the TGA-MS spectrograms. The primary mass-to-charge ratios (m/z) were identified as 45, 58, 86, and 112. These m/z values characterize tricarballic acid, and the most intense signals appeared within the temperature range 139 to $234\text{ }^{\circ}\text{C}$. Thus, result obtained using TGA-MS method was compatible with the result of TGA-FTIR analysis. Furthermore, these results showed that the carboxylic acid used in this study adsorbed on the crystal surface.

3.8.7. Kinetic analysis

Friedman, FWO, and KAS models were used to determine activation energy, showing the minimum energy requirement in this study. Furthermore, the activation energy of the samples obtained at $t=0\text{ min}$, $t=2.5\text{ h}$ in pure media and at $t=2.5\text{ h}$ in the presence of 2500 ppm additive concentration was determined to understand the interaction mechanism of calcium sulfate dihydrate and tricarballic acid during the phase transformation.

Figure 3.74 shows the plotted lines of the Friedman, FWO, and KAS models, respectively, for the sample obtained at $t=2.5\text{ h}$ in the presence of 2500 ppm tricarballic acid. Nine conversion values were utilized varying from 0.1 to 0.9 to examine the correlation between E and α . In Figure 3.74, all lines showed an acceptable degree of linearity with the selected models; each line was nearly parallel to the others, which was attributed to the similar activation energies at different conversions.

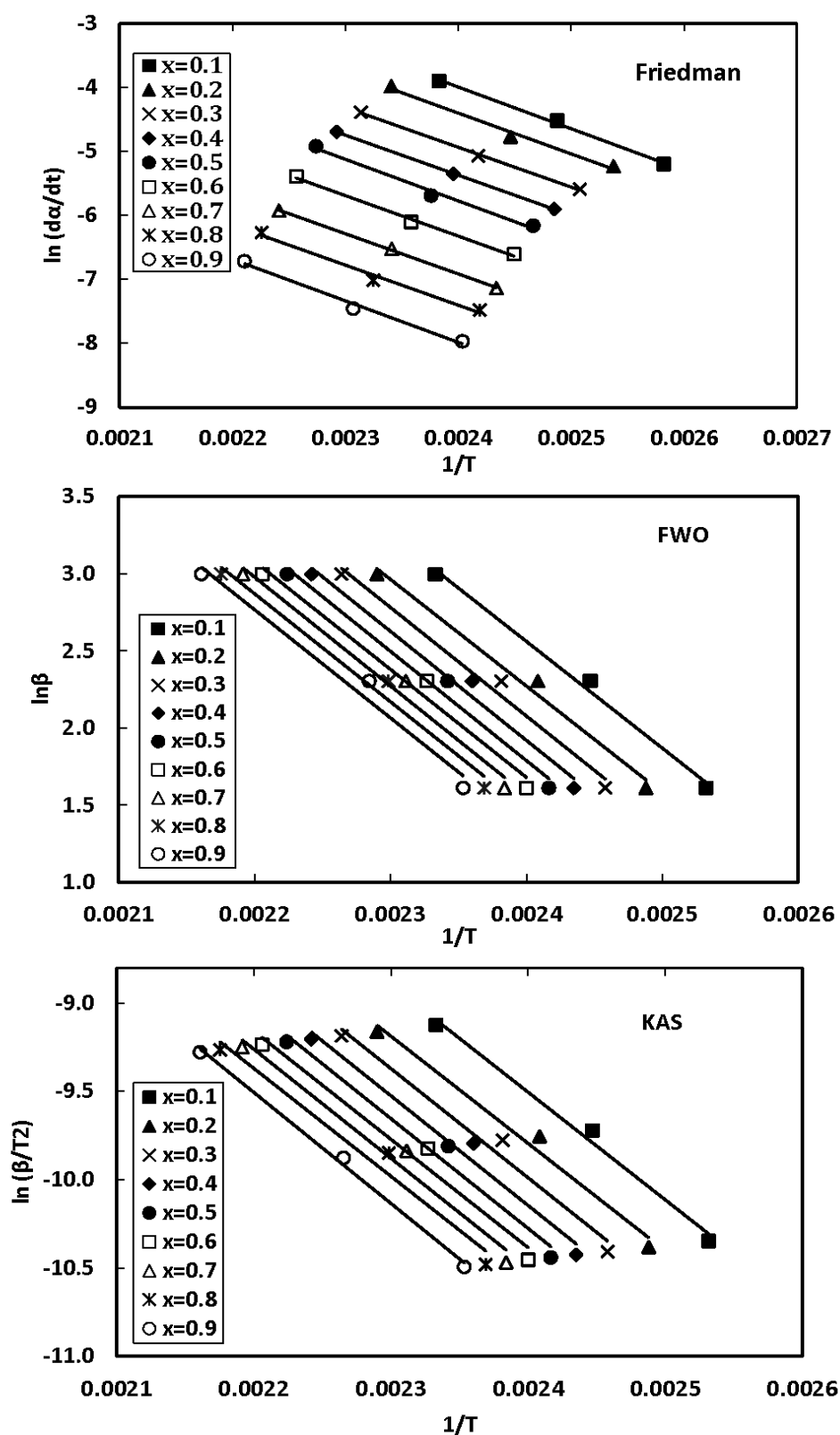


Figure 3.74. The typical plots of Friedman, FWO, and KAS models for the calcium sulfate dihydrate crystals in the presence of 2500 ppm tricarballylic acid.

Figure 3.75 shows the activation energy change in accordance with conversion calculated by the Friedman, FWO, and KAS models for the samples taken at $t=0$ min and $t=2.5$ h in the absence and presence of 2500 ppm tricarballylic acid.

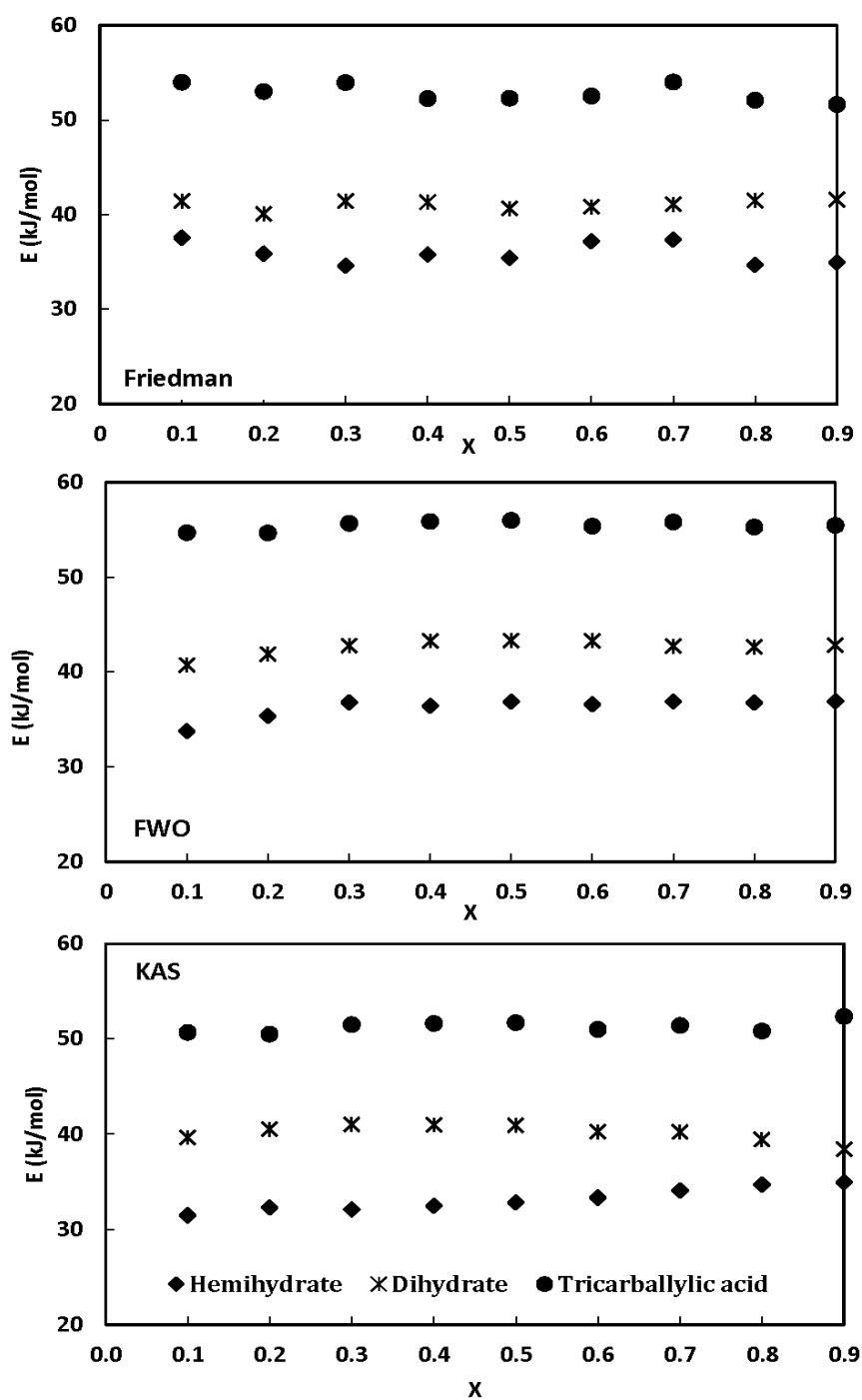


Figure 3.75. Activation energies calculated by Friedman, FWO, and KAS models at different conversion degrees.

The samples taken at $t=0$ min had one main stage in thermal dehydration process related to the loss of $0.5\text{H}_2\text{O}$ mole. During the dehydration process water must be released from the hydrate, requiring the rupture of hydrogen bonds and possibly coordination links. The magnitude of E can be related to the rupture of these links in the samples [117]. The average activation energy of the initial sample for this dehydration step was 35.93, 36.24, and 34.12 kJ/mol for the Friedman, FWO, and KAS models, respectively. These values were close to each other; it could be said that the calculated activation energy from each model showed well-fitting with each other. With the completion of the transformation process, the obtained average activation energy in pure media determined for two dehydration step corresponded to the transformation of calcium sulfate dihydrate to hemihydrate and to anhydrite was 41.10, 42.58, and 40.15 kJ/mol for Friedman, FWO, and KAS models, respectively. The activation energy in all conversions was almost the same value. With the addition of tricarballic acid to the media, the calculated activation energy using Friedman, FWO, and KAS models increased to 52.84, 55.40, and 51.28 kJ/mol, respectively, compared to the activation energy of the samples obtained in pure media. The implication is that this carboxylic acid used as an additive had a significant influence on the increase of activation energy, meaning that the energy requirement was higher than that for the pure media. It could be said that this additive may bind to the surface of the crystals and/or change the energies of different surfaces of the crystal. Furthermore, the increase of average activation energy value in the presence of additive can be related to the excess energy required to break additive-water bonds in the sample. Therefore, detailed adsorption study was carried out to determine whether adsorbed this carboxylic acid was bonded to the crystal surface or not.

3.8.8. Adsorption characteristics

3.8.8.1. Effect of additive concentration, contact time and temperature on adsorption process

The impact of tricarballic acid concentration, and contact time on the adsorption process were determined as a function of temperatures ranging from 20 °C to 40 °C. The results are given in Figure 3.76.

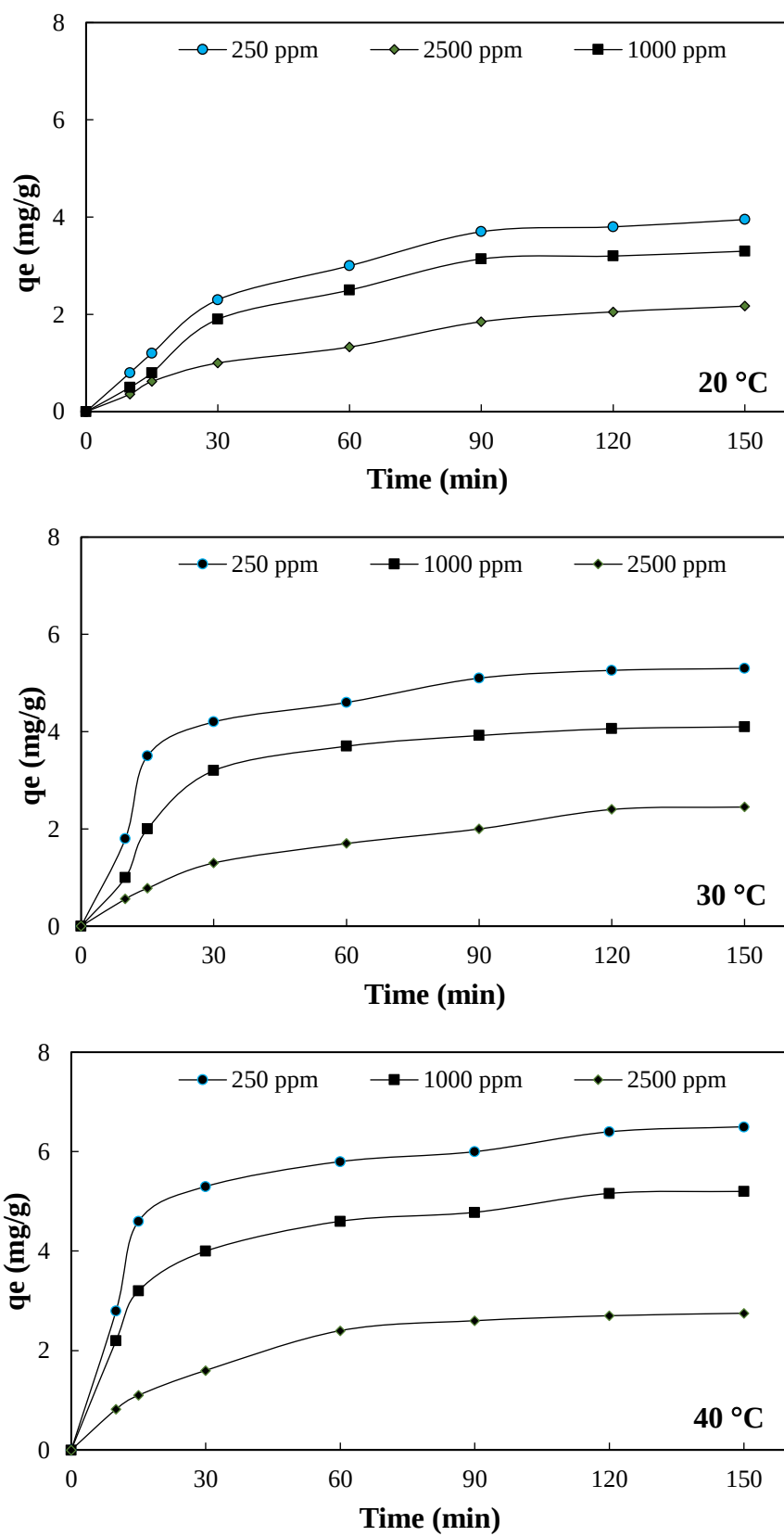


Figure 3.76. Effects of initial additive concentration, and contact time on the adsorption process at different temperatures.

When the results were examined, it was determined that the amount of tricarballic acid adsorption increased as the contact time increased at lower additive concentrations. The adsorption of tricarballic acid was also investigated as a function of temperature. The change in temperature affected the equilibrium capacity of the adsorbent for specific sorbates. In the presence of all additive concentrations, the adsorption efficiency increased when the temperature increased, the results of which can be explained by the increase that occurs in the molecular diffusion rate and in the active sites on the surface at higher temperatures [118]. This situation also revealed that the adsorption process was endothermic. The maximum adsorption capacities were determined as 3.95, 5.3 and 6.5 mg/g for the crystals obtained in the presence of 250 ppm tricarballic concentrations at 20, 30, and 40 °C temperature, respectively.

3.8.8.2. Adsorption equilibrium isotherms

Table 3.8 shows the calculated adsorption equilibrium isotherm model parameters. The maximum adsorption capacity obtained from the Langmuir isotherm was calculated as 4.0900, 5.9952, and 5.5127 mg/g at 20, 30 and 40 °C, respectively. In other words, in consistent with the results shown in Figure 3.76, the amount of tricarballic acid adsorbed increased with the increase in the temperature.

Table 3.8 also shows the calculated correlation coefficient (R^2) values for all the studied models. The low R^2 values reveal that these models are inappropriate for the characterization and explanation of the experimental data. When the relative coefficients were considered, it was determined that out of all the models studied, the Langmuir model was the best for characterizing the results.

3.8.8.3. Adsorption kinetics

The adsorption kinetics results are shown in Table 3.9 at a significance level $\alpha = 0.05$. The best fit model was determined based on the correlation coefficient R^2 because R^2 shows the relationship between calculated and experimental values.

Table 3.8. Adsorption isotherm constants at different temperatures.

Parameters			
Isotherms	20 °C	30 °C	40 °C
Langmuir			
q_m (mg/g)	4.0900	5.9952	5.5127
K_L (L/mg)	0.0039	0.0023	0.0006
R_L	0.7219	0.8116	0.6401
R^2	0.9998	0.9986	0.9988
Freundlich			
$K_F ((\text{mg/g})(\text{L/mg})^{1/n})$	0.4134	0.2679	0.6493
n	3.4855	2.6015	3.6311
R^2	0.9722	0.9851	0.9079
Temkin			
K_T (L/mg)	0.7586	1.2552	1.0172
B	0.0594	0.0248	0.0820
R^2	0.9907	0.9899	0.9249

It can be seen from Table 3.9, the pseudo-second order kinetic model was seen to be a better model to statistically characterize the experimental data. Therefore, it is clear that the kinetics of tricarballic acid adsorption on the calcium sulfate dihydrate conformed to the pseudo-second order rate expression showing that the adsorption rate depended on chemisorption [119,120].

3.8.8.4. Adsorption thermodynamics

The thermodynamic parameters values were calculated, and their results are given in Table 3.10.

Table 3.9. Calculated kinetic parameters at different temperatures.

Kinetic Model	20 °C	30 °C	40 °C
Pseudo-first order			
q_e (mg/g)	199.53	193.53	184.84
k_1 (1/min)	0.0001	0.00013	0.0002
R^2	0.7840	0.9790	0.9530
Pseudo-second order			
q_e (mg/g)	10.787	9.2166	8.8574
k_2 (g/mg.min)	0.0418	0.0193	0.0037
R^2	0.9996	0.9843	0.9889
Elovich			
α (mg/g.min)	0.0699	0.0931	0.1292
B (g/mg)	1.4607	0.9479	1.2360
R^2	0.9344	0.895	0.8375
Intra-particle diffusion			
k_p (mg/g.min ^{1/2})	0.2946	0.2380	0.1505
C	8.2669	1.7460	1.1044
R^2	0.8563	0.6760	0.9836

Table 3.10. Calculated thermodynamic parameters at different temperatures.

T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
20	14.72		
30	14.08	33.77	64.98
40	13.42		

As can be seen from Table 3.10, the ΔH° value was positive. The positive value for the enthalpy change confirmed that adsorption of tricarballic acid occurred endothermically. Moreover, the positive value of ΔS is an indication of the increased disorderliness at the solid/solution interface during the adsorption of the additive by the adsorbent.

3.9. The Results of Glutamic Acid Effects on Phase Transformation of Calcium Sulfate Hemihydrate to the Dihydrate Form*

3.9.1. Conductivity measurements

The transformation process of calcium sulfate hemihydrate to dihydrate in the absence and the presence of glutamic acid as additive was followed by a measurement of the conductivity of the suspension. The conductivity curve obtained in the pure media is given in Figure 3.77a. In agreement with the existing reports in the literature [92] this curve shows that the transformation process consisted of three different stages: dissolution of the hemihydrate; nucleation of the dihydrate; and growth of the dihydrate.

As stated before, in the first stage, the conductivity showed a sharp increase, which resulted from dissolution of the hemihydrate. Figure 3.77a shows that this stage was completed within about 1.5 minutes under the given conditions. Nucleation of the calcium sulfate dihydrate occurred in the second stage; no distinctive change was observed in the conductivity. The third stage was related to growth of the dihydrate crystals arising from the heterogeneous nucleation onto the hemihydrate particles. The curve obtained in the pure media shows that the conductivity decreased until the conversion process was complete. The decrease in conductivity resulted from the variation in the concentration of the calcium ions during the transformation of hemihydrate to dihydrate. At $t=2.5$ h, the transformation process was complete, and the conductivity had reached a fixed value. The conductivity curves obtained in the presence of three different additive concentrations are also shown in Figure 3.77a. Whereas the conductivity of the saturated solution used in pure media was measured to be 2×10^3 $\mu\text{S/cm}$, the conductivity values of the saturated solution in the presence of 250, 1000, and 2500 ppm glutamic acid were 2.10×10^3 $\mu\text{S/cm}$, 2.17×10^3 $\mu\text{S/cm}$, and 2.24×10^3 $\mu\text{S/cm}$, respectively. As shown in Figure 3.77a, the additive caused notable changes in conductivity and differences in transformation rates. The transformation rate decreased with the increase of additive concentration. From the results above, it could be concluded that the effect of glutamic acid on the phase transformation process depends

* Polat, S., Sayan P. (2017) Impact of glutamic acid on the transformation of calcium sulfate hemihydrate to dihydrate: Characterization, equilibrium, kinetics, and thermodynamics. Chemical Engineering Communications, 204(11), 1318-1331.

on the concentration. It was observed that at low concentrations, the additive had almost no influence on transformation time, whereas at higher concentrations, the additive tended to prolong the transformation time. In other words, the retarding effect of glutamic acid on the transformation of hemihydrate to dihydrate increased with an increase of its concentration.

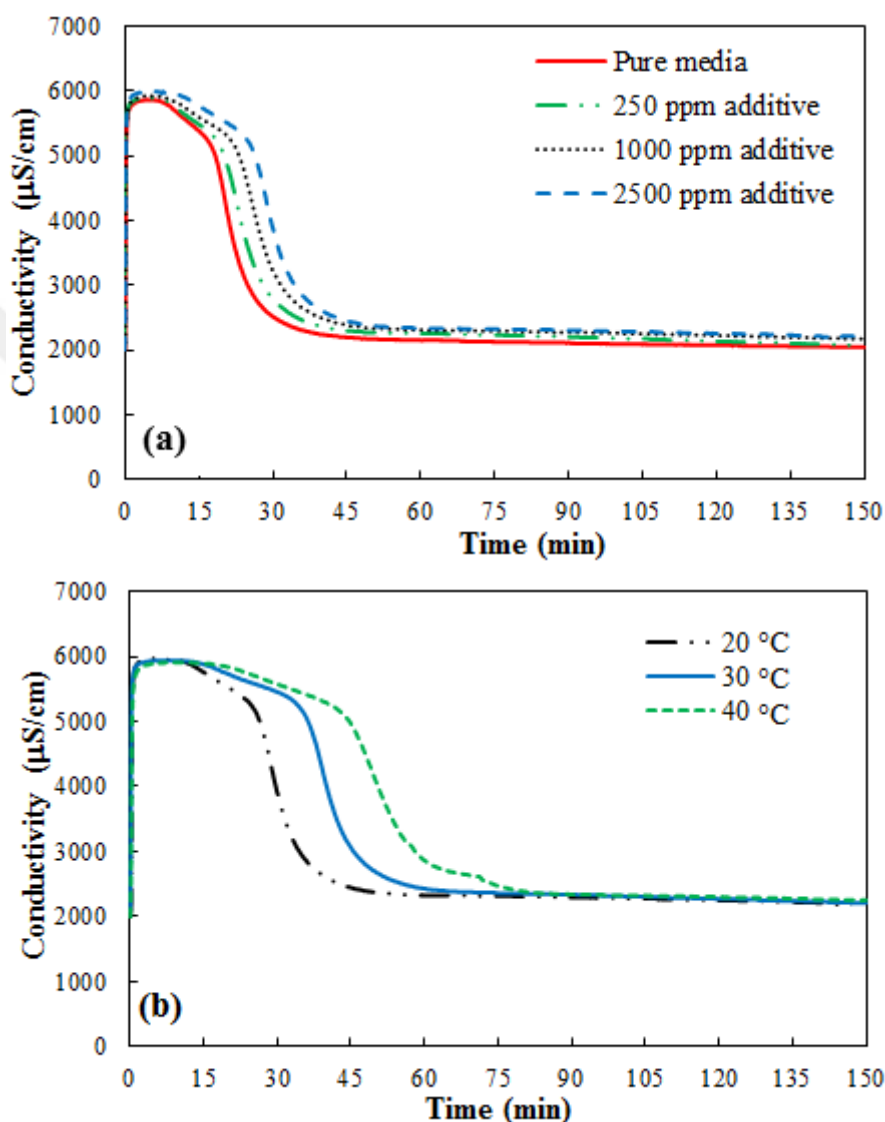


Figure 3.77 Variation of conductivity in terms of time (a) in pure media and in the presence of varied glutamic acid concentrations at 20 °C (b) in the presence of 2500 ppm glutamic acid at three different temperatures.

The variation of conductivity in terms of time in the presence of 2500 ppm of glutamic acid at three different temperatures is given in Figure 3.77b. It is clear from Figure 3.77b that the retarding effect in the transformation time is highly sensitive to temperature. With

the presence of 2500 ppm glutamic acid content, the transformation rate decreased with the increase of temperature. Here it is important to note that the increase in temperature led to a shift, in conductivity curves, towards higher transformation time, which could be an indicator of an increase in the amount of adsorbed glutamic acid due to higher temperature. From these conductivity curves, it can be seen that the effect of glutamic acid on the phase transformation process is heavily dependent on the glutamic acid concentration and temperature.

3.9.2. SEM and TEM analysis

The SEM image of calcium sulfate hemihydrate is given in Figure 3.78, where it can be seen that calcium sulfate hemihydrate crystals had no distinct shape, but rather consisted of sponge-like, porous and layered structures. Since these crystals have weak and frail layers, these kinds of structures could be easily broken by the hydrodynamic conditions of the media. In the beginning of the transformation process, the crystals started to grow into the needle-like form. At $t=15$ min, needle-like and plate-like structures were formed together. With the completion of the transformation process of calcium sulfate hemihydrate to dihydrate in pure media at 20 °C, the crystals transformed into plate-like structures. As seen in Figure 3.78, the plates that formed were relatively thin and as a result, broke under the influence of hydrodynamic conditions. The crystals that had broken away from the fundamental crystal had a disordered rod-shaped crystal structure.

The SEM images of the crystals obtained in the presence of 2500 ppm glutamic acid concentration at 2.5h and at three different temperatures (20, 30 and 40 °C) are shown in Figure 3.78. The crystals formed at 20 °C had a completely plate-like form with a weak structure. It was determined that the thickness of the plates increased with the increase of the temperature. The crystals formed at 30 °C were composed of plates more durable, with higher resistance to breakage than the plates in crystals formed at 20 °C. The most compact plate-like structured crystals were obtained at 40 °C, and the breakage tendency of the crystals decreased with the increase of the temperature. Furthermore, it was found that agglomeration tended to occur for the crystals formed at 40 °C. These outcomes that occurred in the presence of glutamic acid resulted from the increase in the amount of adsorbed glutamic acid to the surface of the crystal. The thickness of the crystals also

increased significantly as the thin and weak layered structure transformed into a thick and compact plate-like structure. These results can be clearly observed in the SEM images, where the thicknesses of the crystals measured by means of SEM analyses were determined as 0.73 μm , 1.05 μm and 1.57 μm at 20, 30 and 40 $^{\circ}\text{C}$, respectively.

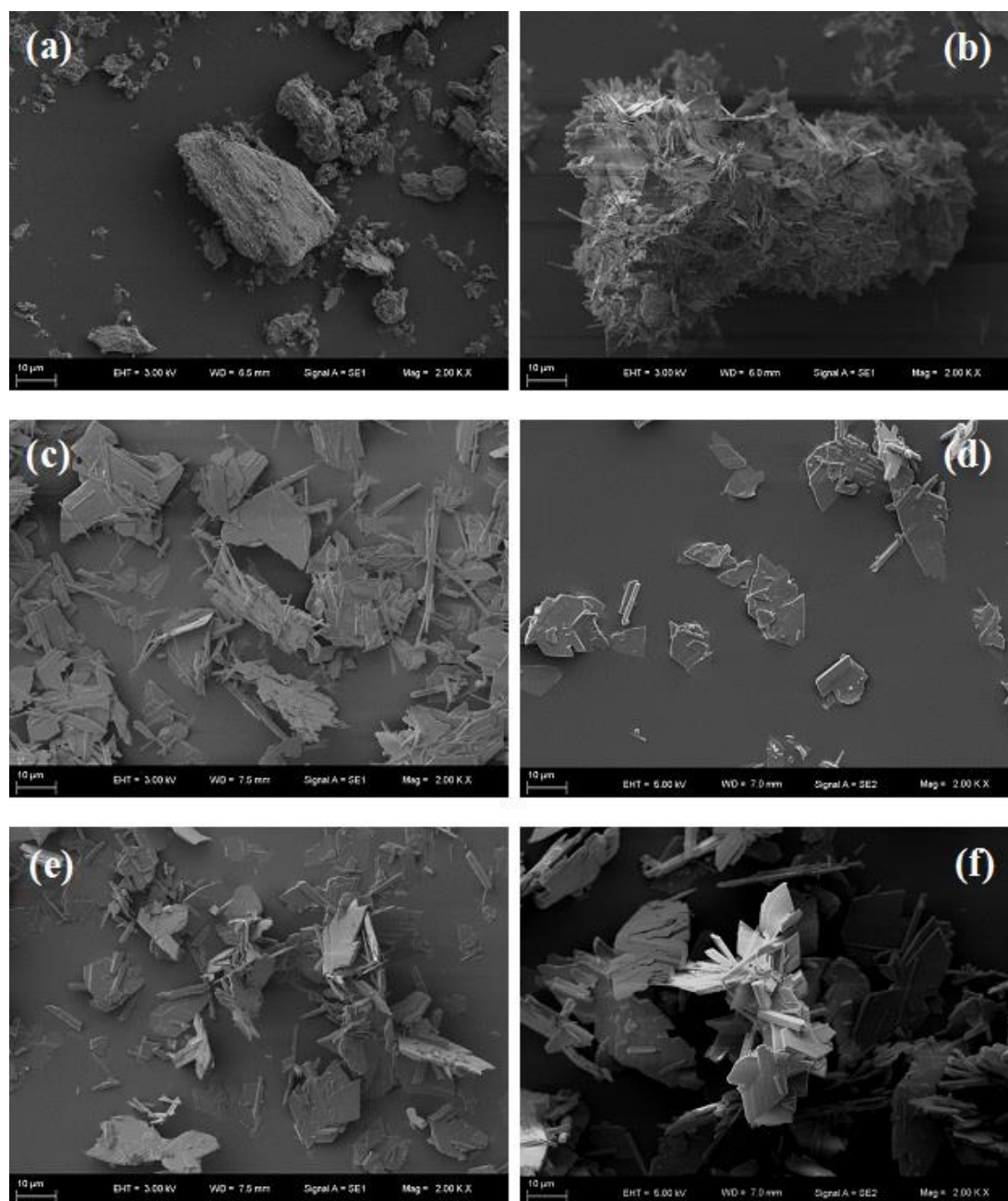


Figure 3.78. The SEM images taken at different times in pure media at 20 $^{\circ}\text{C}$ [a) $t=0$ min b) $t=15$ min c) $t=2.5$ h] and at different temperatures in the presence of 2500 ppm glutamic acid concentrations [d) $T=20$ $^{\circ}\text{C}$, e) $T=30$ $^{\circ}\text{C}$, f) $T=40$ $^{\circ}\text{C}$].

In addition to SEM analysis, the TEM analysis was performed for the crystals before and after glutamic acid adsorption at three different temperatures (20, 30 and 40 °C) to gain more information about crystal morphology. Figure 3.79 shows the TEM images of the crystals obtained in pure and impure media. As consistent with the SEM results, the TEM images indicated that the surface was smoothed and the thickness of the crystals increased due to surface coverage with glutamic acid.

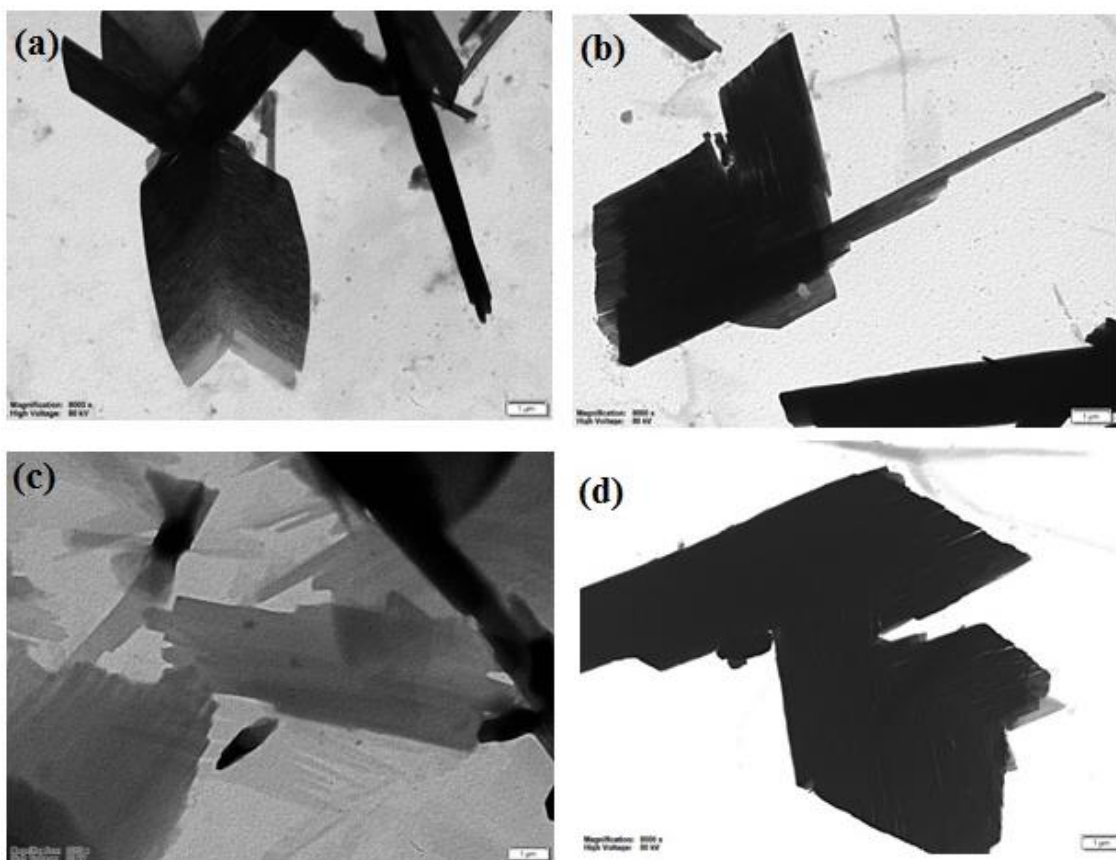


Figure 3.79. The TEM images taken at $t=2.5\text{h}$ in pure media at 20 °C (a) and in the presence of 2500 ppm glutamic acid concentrations at different temperatures [(b) $T=20\text{ °C}$, (c) $T=30\text{ °C}$, d) $T=40\text{ °C}$].

The average particle size also increased compared with the crystals produced in the pure media. To determine the variation in particle size, the average particle size, as measured through a laser diffraction particle size analyzer, changed according to the temperature.

The particle size distribution curves of the calcium sulfate dihydrate crystals obtained in pure and impure media are given in Figure 3.80.

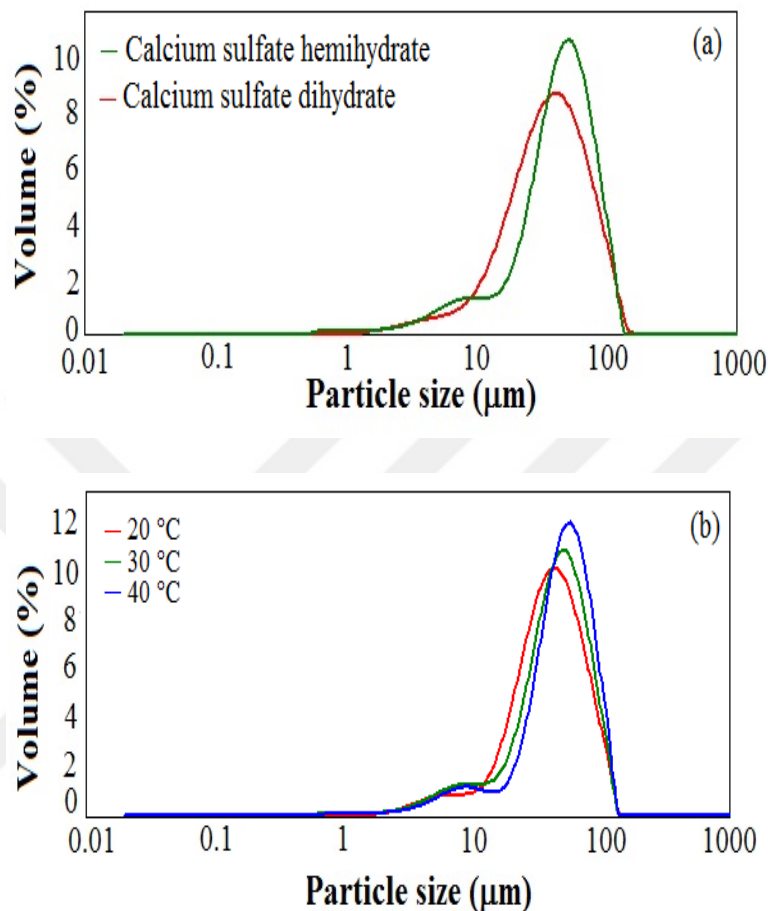


Figure 3.80. The particle size distribution of the crystals in pure media at $T=20\text{ }^{\circ}\text{C}$ (a) and in the presence of 2500 ppm glutamic acid concentrations at different temperatures (b).

At $t=0$ min, the average particle size of calcium sulfate hemihydrate was $45\text{ }\mu\text{m}$. Whereas the average particle size of the crystals obtained in pure media was $36\text{ }\mu\text{m}$, the average particle size of the crystals obtained in the presence of 2500 ppm glutamic acid was $40\text{ }\mu\text{m}$ respectively at $t=2.5$ h and at $20\text{ }^{\circ}\text{C}$. The average particle size of the crystals obtained in pure media showed a distinct increase as the temperature increased. The particle sizes of crystals obtained in the presence of 2500 ppm glutamic acid at 30 and $40\text{ }^{\circ}\text{C}$ were 45 and $52\text{ }\mu\text{m}$, respectively. These increases in the average particle size were related to a morphological change of the obtained crystals. In addition to particle size analysis,

filtration analysis was carried out. As seen on Figure 3.81, the specific cake resistance increased as the glutamic acid concentration increased. While the specific cake resistance of the crystals obtained in pure media was 1.20×10^{11} kg/m, this value was calculated as 3.21×10^{11} kg/m for the crystals obtained with a concentration of 2500 ppm of glutamic acid at 40 °C. As clearly seen in the SEM images, this increase in specific cake resistance resulted from breaks in the crystals and reduction of the average particle size.

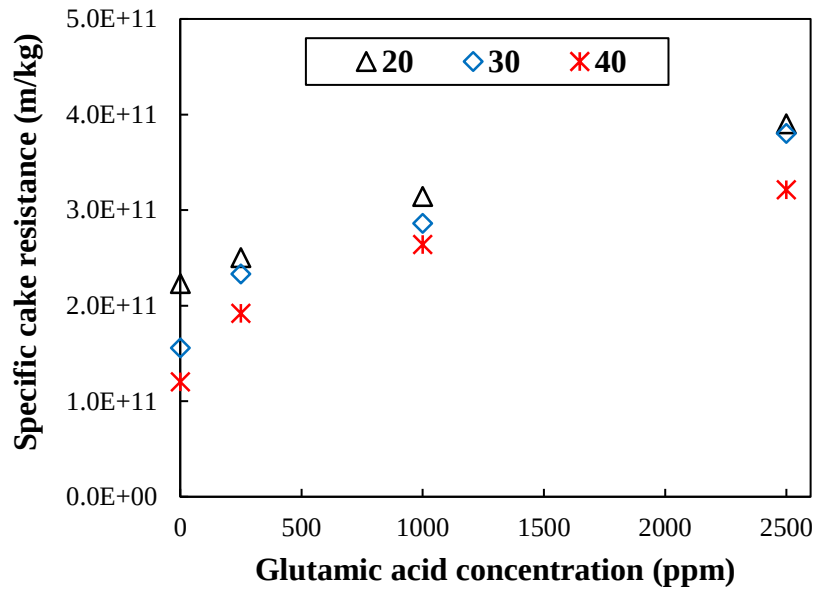


Figure 3.81. The influence of glutamic acid concentration and temperature on the specific cake resistance of the crystals.

In addition to particle size analysis, BET analysis was performed to both characterize the crystals and determine the effect of additive on the surface area of the calcium sulfate dihydrate. The porous characteristics of the calcium sulfate hemihydrate crystals were confirmed by BET analysis and its surface area was found to be 5.05 m²/g. With the completion of the transformation process, the BET surface area decreased distinctively and its value was 2.95 m²/g for the calcium sulfate dihydrate crystals obtained in pure media at 20 °C. This showed that the pores got smaller and more compact structure obtained. Addition of the glutamic acid to the media caused a significant decrease in the BET surface area and the surface area of the crystals produced in the presence of 2500 ppm glutamic acid at 20 °C was measured as 1.04 m²/g. It was also determined that the surface area values were decreased when the temperature increased. While BET surface

area of the crystals obtained in the presence of 2500 ppm glutamic acid at 30 °C was 0.99 m²/g, this value was determined as 0.54 m²/g for the crystals obtained at 40 °C. These results revealed that glutamic acid had a significant effect on surface area of the crystals and they supported the SEM results.

3.9.3. XRD analysis

Figure 3.82 shows the X-ray diffraction patterns of the calcium sulfate dihydrate produced in pure media and in the presence of 2500 ppm glutamic acid concentration at different temperatures. As said before, the strong peaks at 11.59°, 20.72°, 23.40°, 29.11°, 31.14° and 33.34° were observed which was assigned to the calcium sulfate dihydrate for crystals obtained in pure media at 20 °C. These peaks obtained were compatible with calcium sulfate dihydrate peaks reported in the literature. When the XRD peaks of the crystals obtained in the presence of 2500 ppm glutamic acid and the XRD peaks of the crystals obtained in pure media at 20 °C were compared, the peak intensity values measured increased. As clearly shown in Figure 3.82, the peak intensities also increased with the increase in temperature. The highest increase in the peak intensity of calcium sulfate dihydrate crystals occurred at 40 °C. These changes appeared in the presence of additive may indicate that glutamic acid adsorbed on the calcium sulfate dihydrate surfaces.

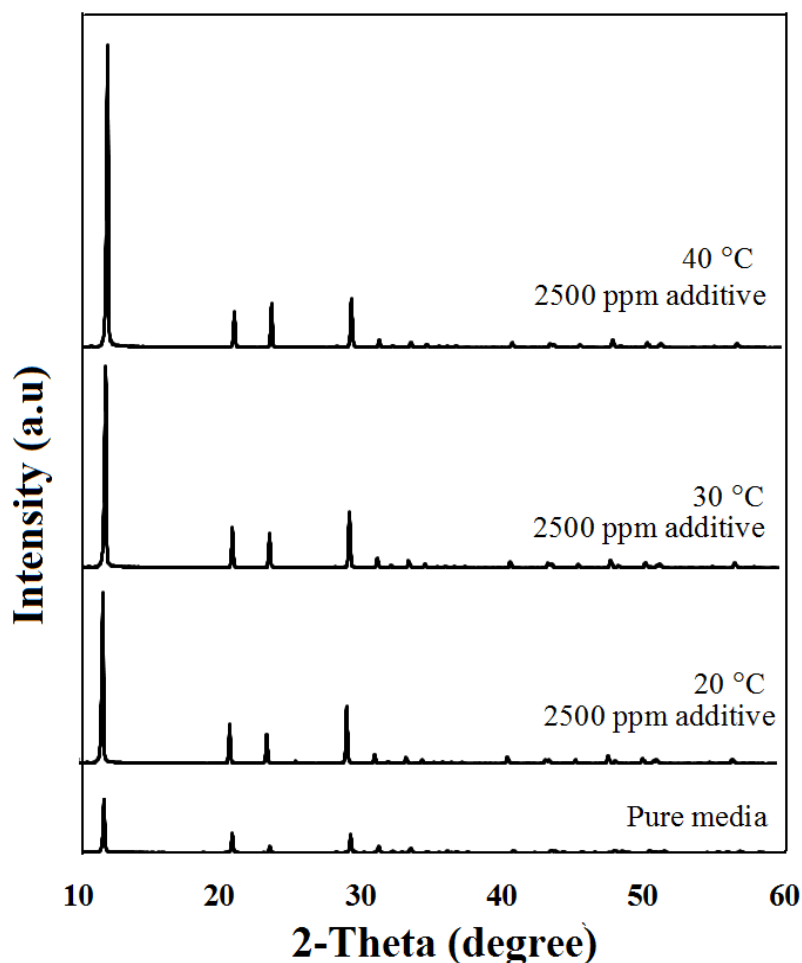


Figure 3.82. XRD results of calcium sulfate dihydrate in pure and impure media.

3.9.4. TGA analysis

Figure 3.83 shows the TGA/DTA curves for calcium sulfate dihydrate obtained both in the absence and in the presence of 2500 ppm glutamic acid at $T=20\text{ }^{\circ}\text{C}$. The TGA and DTA curves indicated that these two samples presented similar curves, and, as stated in previous publications [121] the weight losses occurred in two steps that followed each other very closely. Based on TGA curves, the average weight losses for two samples were found to be approximately 20%. As shown by DTA curves obtained in the presence of 2500 ppm glutamic acid, the peaks were shifted to a lower temperature owing to the effect of additive. The initial and final temperatures were shifted to lower temperatures from $142\text{ }^{\circ}\text{C}$ to $134\text{ }^{\circ}\text{C}$ and $155\text{ }^{\circ}\text{C}$ to $148\text{ }^{\circ}\text{C}$, respectively. The shifting that occurred in the may could be caused by the addition of the additives in transformation media.

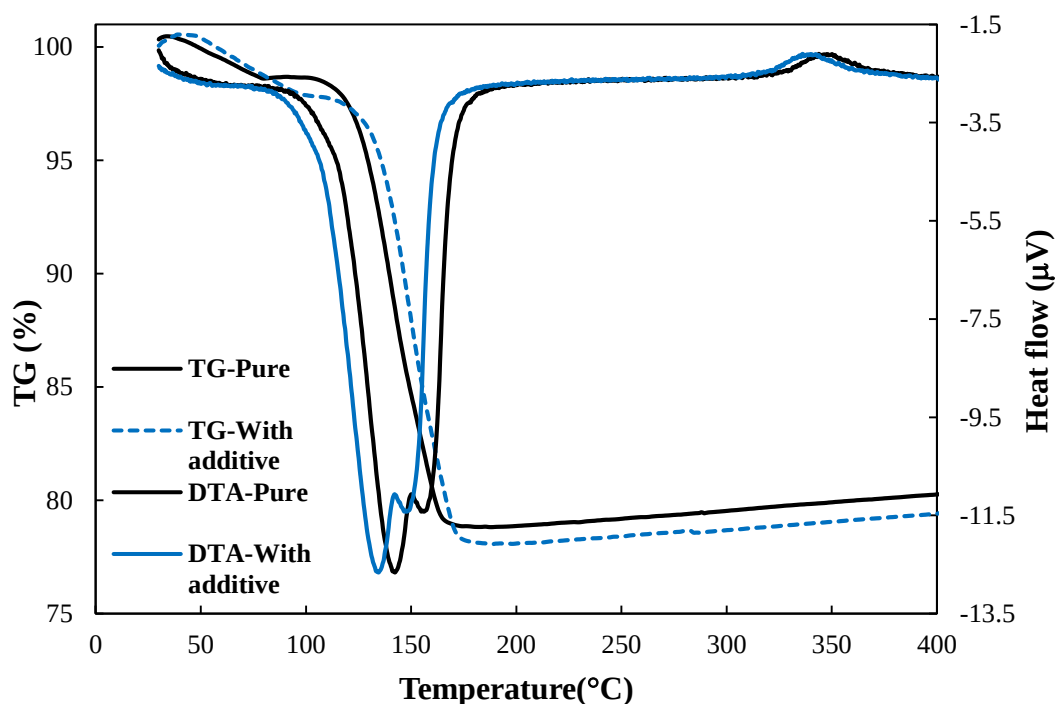


Figure 3.83. TGA and DTA curves of calcium sulfate dihydrate obtained in the absence and the presence of 2500 ppm glutamic acid at 20 °C.

3.9.5. ATR-FTIR analysis

The FTIR spectra, which provides direct information about the chemical compositions and the functional groups of the samples, taken in pure media at 20 °C at the initial stage and at the completion of the transformation process, are given in Figure 3.84. Figure 3.84 also shows the FTIR spectrum of the samples produced in the presence of 2500 ppm glutamic acid, at 20 °C, 30 °C and 40 °C, to determine whether the glutamic acid bonded with the crystal structure during the transformation process. When examining the FTIR spectra of the samples obtained in the presence of glutamic acid, two distinctive peaks, one at 3267 cm^{-1} , and one at 1724 cm^{-1} , were detected for all of the temperatures studied. These two peaks were attributed to N-H stretching and C=O (carboxyl) stretching, the results of which confirm the presence of glutamic acid [65]. When the FTIR spectra obtained at different temperatures were compared, it was detected that the intensities of obtained peaks increased with the temperature. These results confirmed the mechanism of glutamic acid adsorption during the transformation process of calcium sulfate hemihydrate to dihydrate.

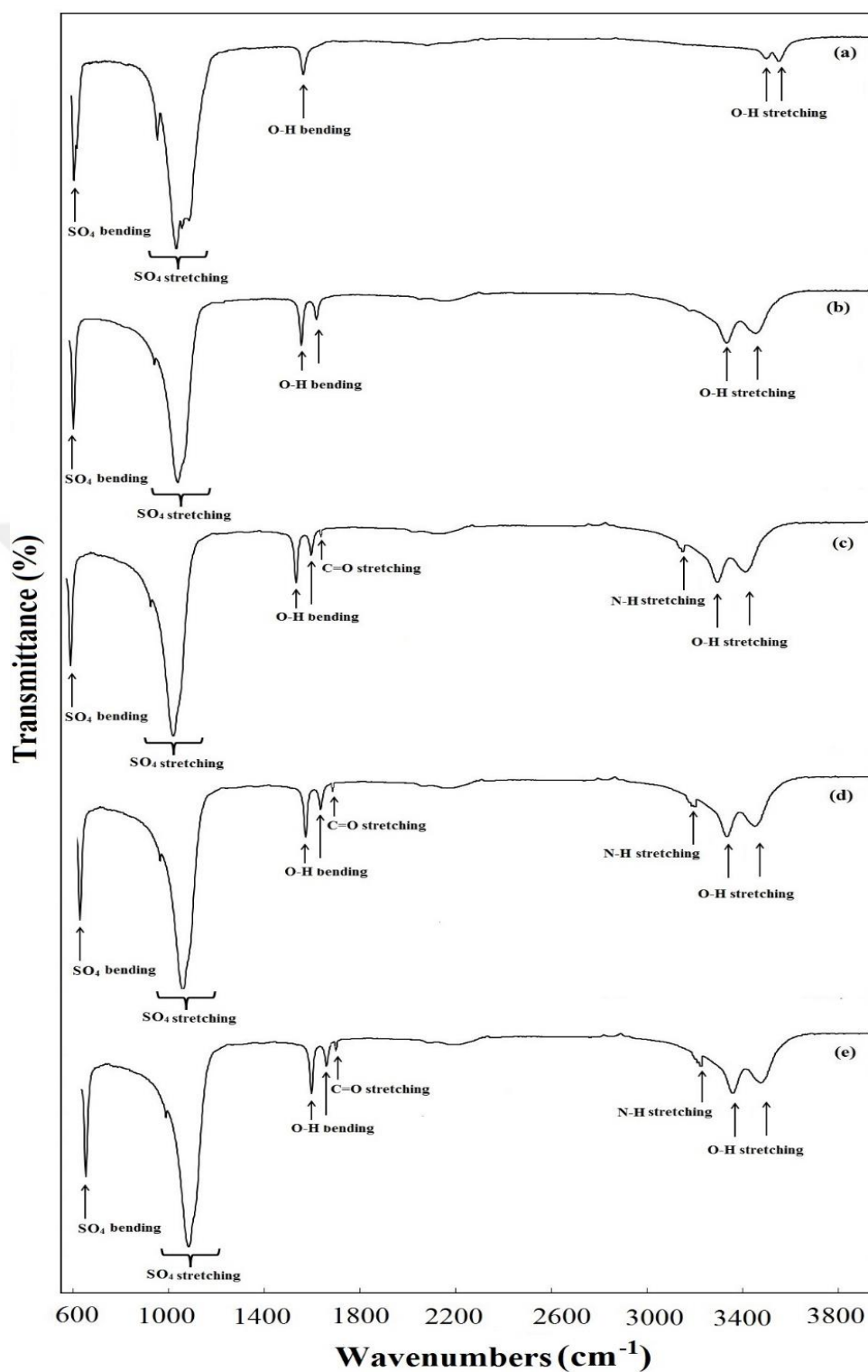


Figure 3.84. FTIR spectra of the crystals taken at different times and different temperatures a) $t=0$ min and $T=20$ °C, b) $t=2.5$ h and $T=20$ °C c) With additive $t=2.5$ h and $T=20$ °C, d) With additive $t=2.5$ h and $T=30$ °C, e) With additive $t=2.5$ h and $T=40$ °C.

3.9.6. TGA/FTIR/MS analysis

Figure 3.85 shows the three-dimensional FTIR spectrum of the samples obtained in the presence of 2500 ppm glutamic acid for the change of individual functional groups with respect to time. In addition to the TGA/FTIR analysis, gases that evolved were simultaneously analyzed by TGA/MS. Figure 3.85 shows the TGA/MS spectrograms of calcium sulfate dihydrate crystals produced in the presence of 2500 ppm glutamic acid at $T=20\text{ }^{\circ}\text{C}$. The primary mass-to-charge ratios (m/z) were identified as 41, 45, 56, 73, 75 and 84 which characterize glutamic acid. Both results may confirm the glutamic acid adsorption during the transformation process of calcium sulfate hemihydrate to dihydrate.

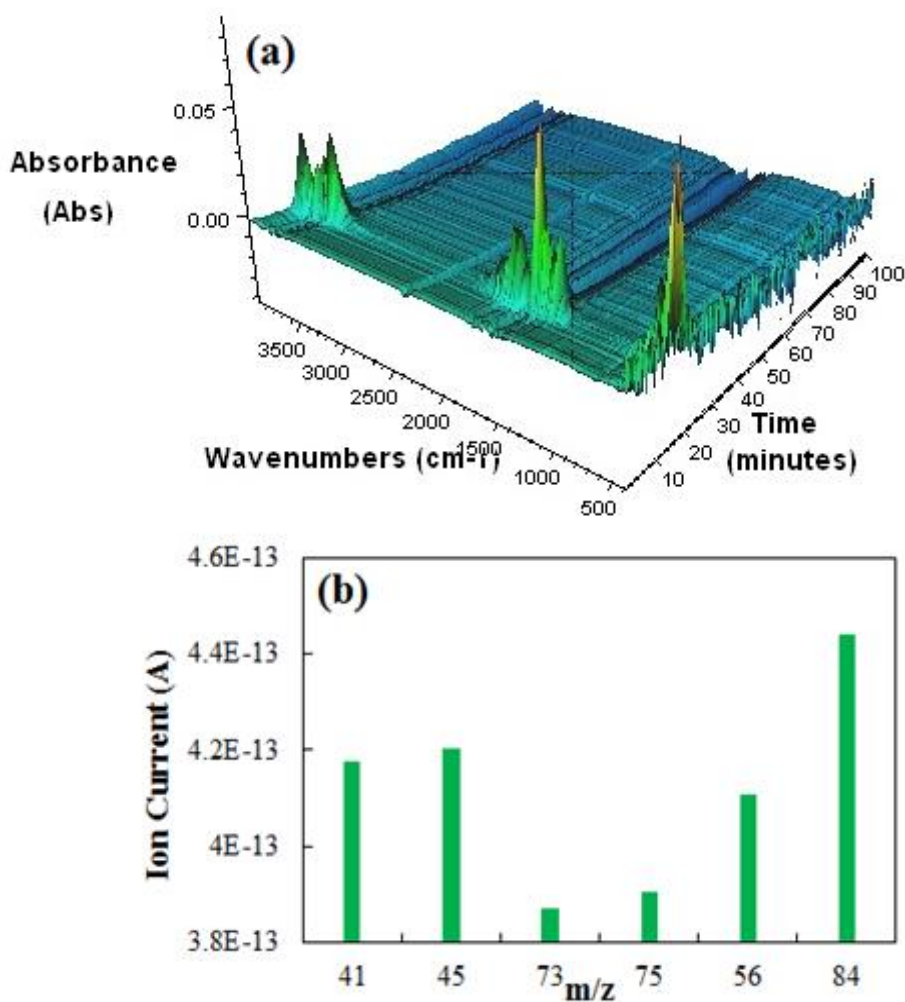


Figure 3.85. (a) 3D FTIR spectrum and (b) TGA-MS spectrograms of the calcium sulfate dihydrate crystals produced in the presence of 2500 ppm glutamic acid.

3.9.7. Adsorption characteristics

3.9.7.1. Effect of additive concentration, contact time and temperature on adsorption process

In this part, where the adsorption characteristics of glutamic acid on the transformation of calcium sulfate hemihydrate to dihydrate was studied in a batch type crystallizer, the influence of additive concentration, and contact time on the adsorption process were determined as a function of temperatures ranging from 20 °C to 40 °C. The results are given in Figure 3.86.

When the results were examined, it was detected that the amount of glutamic acid adsorption increased as the contact time and additive concentration increased. For all the different concentrations used, this increase occurred sharply in the first 30 min, before the adsorption of glutamic acid reached an equilibrium at 120 min. After this time, no distinctive increase or decrease was observed in the amount of adsorbed glutamic acid per unit mass of adsorbent. The initial rapid adsorption rate may have occurred due to the availability of a large number of vacant sites and the absence of internal diffusion resistance. After this time, the very low increase in additive uptake that was observed can be attributed to the low number of surface-active sites on adsorbent [119]. The adsorption of glutamic acid was also examined as a function of temperature. The change in temperature affected the equilibrium capacity of the adsorbent for specific sorbates. In the presence of all additive concentrations, the adsorption efficiency increased when the temperature increased, the results of which can be explained by the increase that occurs in the molecular diffusion rate and in the active sites on the surface at higher temperatures [118]. This situation also revealed that the adsorption process was endothermic. The maximum adsorption capacities were determined as 6.32, 7.99 and 12.24 mg/g for the crystals obtained in the presence of 2500 ppm additive concentrations at 20, 30, and 40 °C temperature, respectively.

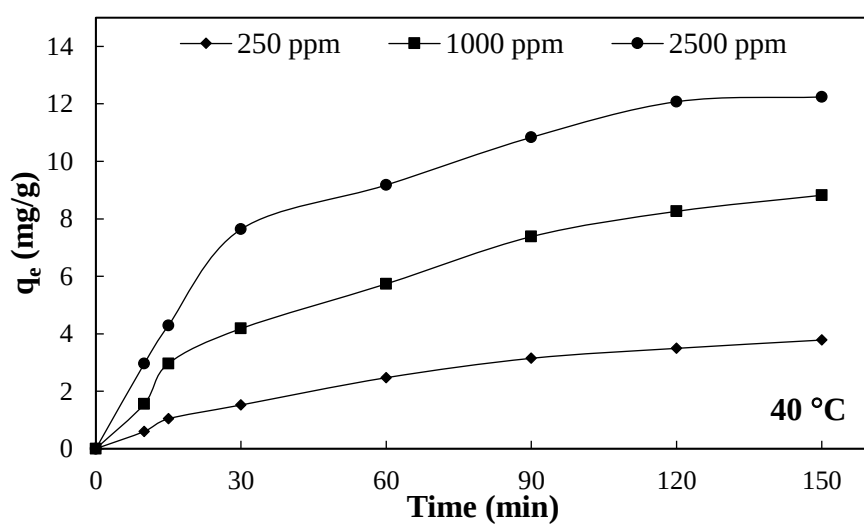
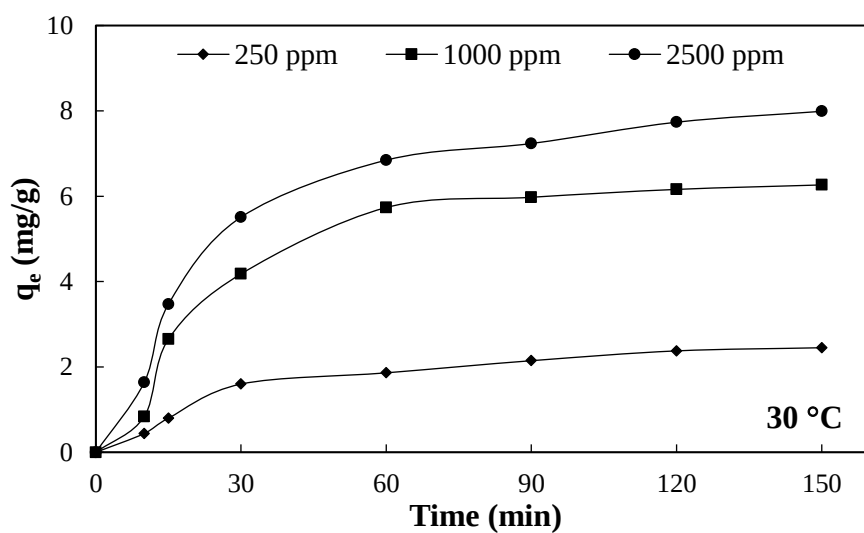
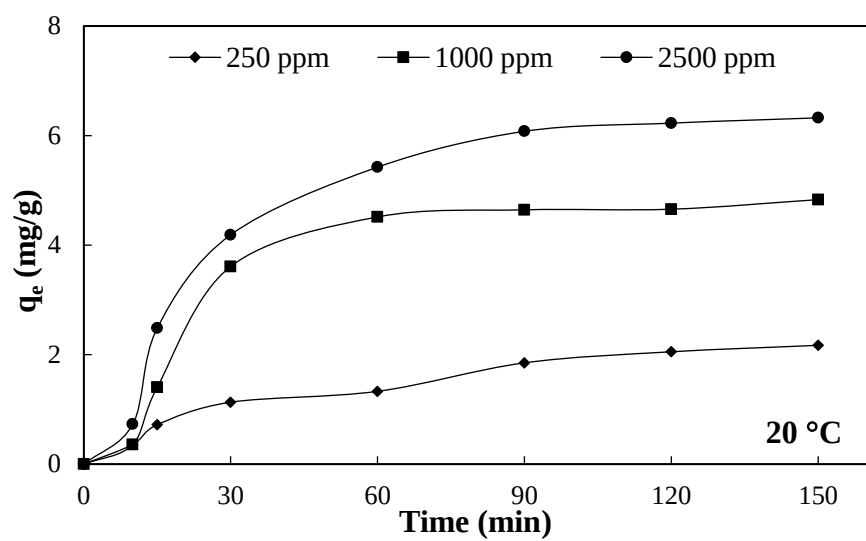


Figure 3.86. Effects of initial additive concentration, and contact time on the adsorption process at different temperatures.

3.9.7.2. Adsorption equilibrium isotherms

Table 3.11 presents the calculated adsorption equilibrium isotherm model parameters. The maximum adsorption capacity obtained from the Langmuir isotherm was calculated as 68.027, 109.89, and 169.49 mg/g at 20, 30 and 40 °C, respectively. In other words, in agreement with the results shown in Figure 3.86 the amount of glutamic acid adsorbed increased with the increase in the temperature.

Table 3.11. Adsorption isotherm constants at different temperatures.

Parameters			
Isotherms	20 °C	30 °C	40 °C
Langmuir			
q_m (mg/g)	68.027	109.89	169.49
K_L (L/mg)	0.0056	0.0019	0.0021
R_L	0.6429	0.8420	0.8215
R^2	0.9853	0.9966	0.9957
Freundlich			
$K_F ((\text{mg/g})(\text{L/mg})^{1/n})$	2.0401	2.1604	3.5289
n	2.1436	2.0292	2.0272
R^2	0.9761	0.9457	0.9352
Temkin			
K_T (L/mg)	0.0199	0.0169	0.0168
B	19.520	24.991	38.085
R^2	0.9777	0.9838	0.9953

In the Langmuir isotherm model, the R_L values obtained at different temperatures were between 0.6429 and 0.8420, which indicates favourable adsorption of glutamic acid by calcium sulfate dihydrate. This situation was also supported by the Freundlich model results. The (n) value in the Freundlich model ranged from 2.0272 and 2.1436, which means the adsorption of glutamic acid on crystals was favorable. Table 3.11 also shows the calculated correlation coefficient (R^2) values for all the studied models.

The low R^2 values reveal that these models are inappropriate for the characterization and explanation of the experimental data. When the relative coefficients were considered, it was determined that out of all the models studied, the Langmuir model was the best for characterizing the results. In addition, for all of the studied models, a non-linear regression analysis was conducted for the modeling of adsorption isotherms. The experimental isotherm fitting was plotted on the basis of non-linear equations. The plot is given in Figure 3.87.

Data obtained through the linear and non-linear methods were similar, and they supported each other. The Langmuir model should be selected as the most appropriate isotherm model for describing the adsorption equilibrium behavior of glutamic acid on calcium sulfate dihydrate. This result also showed that the adsorption of glutamic acid on calcium sulfate dihydrate had a homogenous distribution of active sites and a monolayer sorption of adsorbate on the outer surface [122].

3.9.7.3. Adsorption kinetics

The adsorption kinetics results from the parameters and correlation coefficients are given in Table 3.12 at a significance level $\alpha = 0.05$. The best fit model was determined based on the correlation coefficient R^2 because R^2 shows the relationship between calculated and experimental values.

From an examination of Table 3.12, it can be seen that the pseudo-first order model was not suitable for characterizing the experimental data had a low R^2 value. Rather, the pseudo-second order kinetic model was seen to be a better model to statistically characterize the experimental data. Therefore, it is clear that the kinetics of glutamic acid adsorption on the calcium sulfate dihydrate conformed to the pseudo-second order rate expression showing that the adsorption rate depended on chemisorption [119,120].

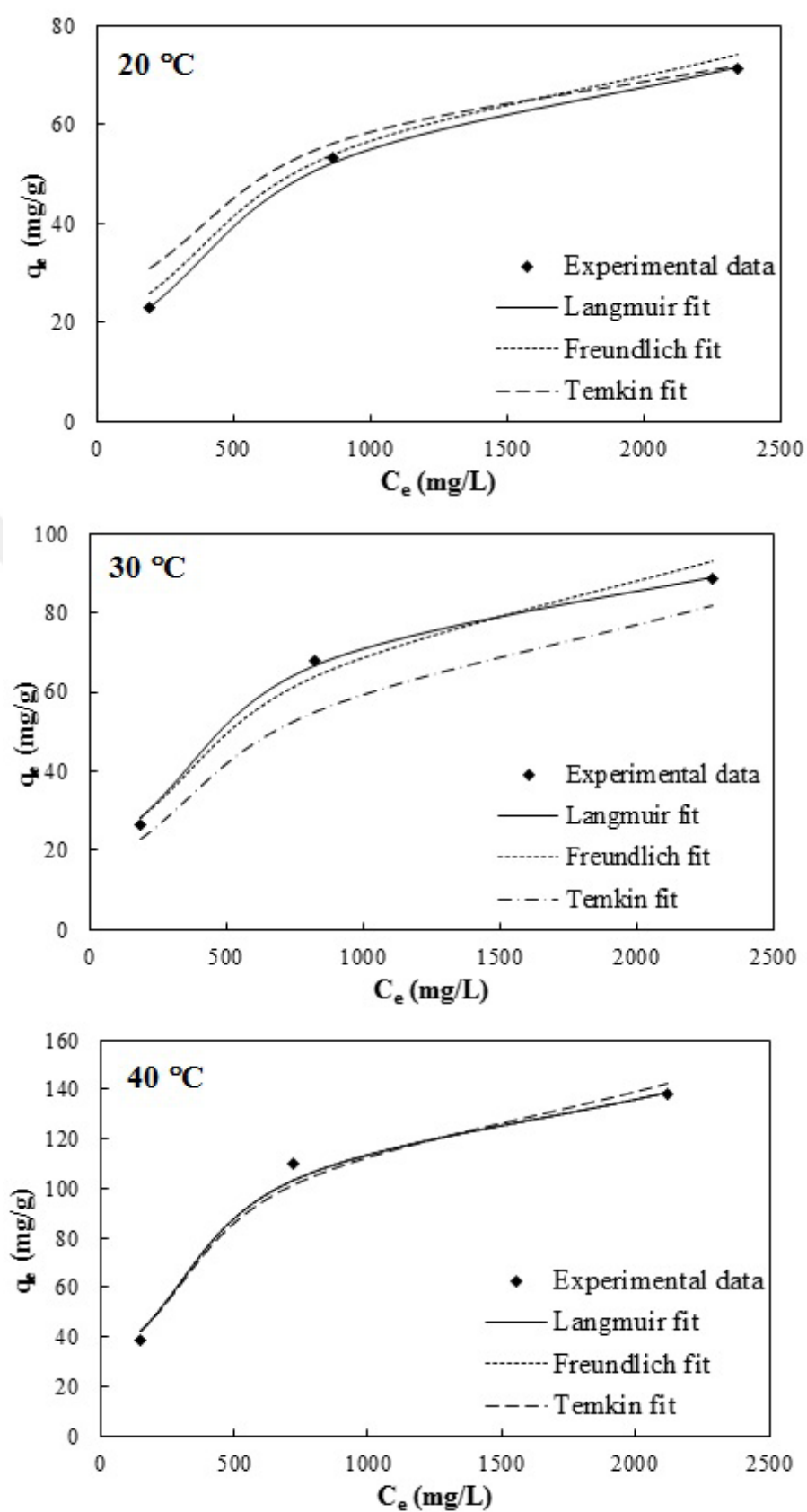


Figure 3.87. Fit of adsorption isotherm models by non-linear procedure.

Table 3.12. Calculated kinetic parameters at different temperatures.

Kinetic Model	20 °C	30 °C	40 °C
Pseudo-first order			
q_e (mg/g)	7.244	7.088	25.29
k_1 (1/min)	0.041	0.032	0.053
R^2	0.791	0.893	0.814
Pseudo-second order			
q_e (mg/g)	9.310	8.865	12.66
k_2 (g/mg.min)	0.002	0.006	1.921
R^2	0.906	0.975	0.986
Elovich			
α (mg/g.min)	0.403	0.578	0.277
B (g/mg)	0.392	0.350	0.838
R^2	0.907	0.763	0.980
Intra-particle diffusion			
k_p (mg/g.min ^{1/2})	0.709	0.835	1.193
C	0.263	0.290	0.100
R^2	0.901	0.940	0.947

The modelling of adsorption kinetics was also studied through non-linear forms of kinetic models. The best fit of kinetic data were obtained by the pseudo-second order model, and the plot for which is shown in Figure 3.88. Data obtained through the linear method were compatible with the data results of the non-linear method.

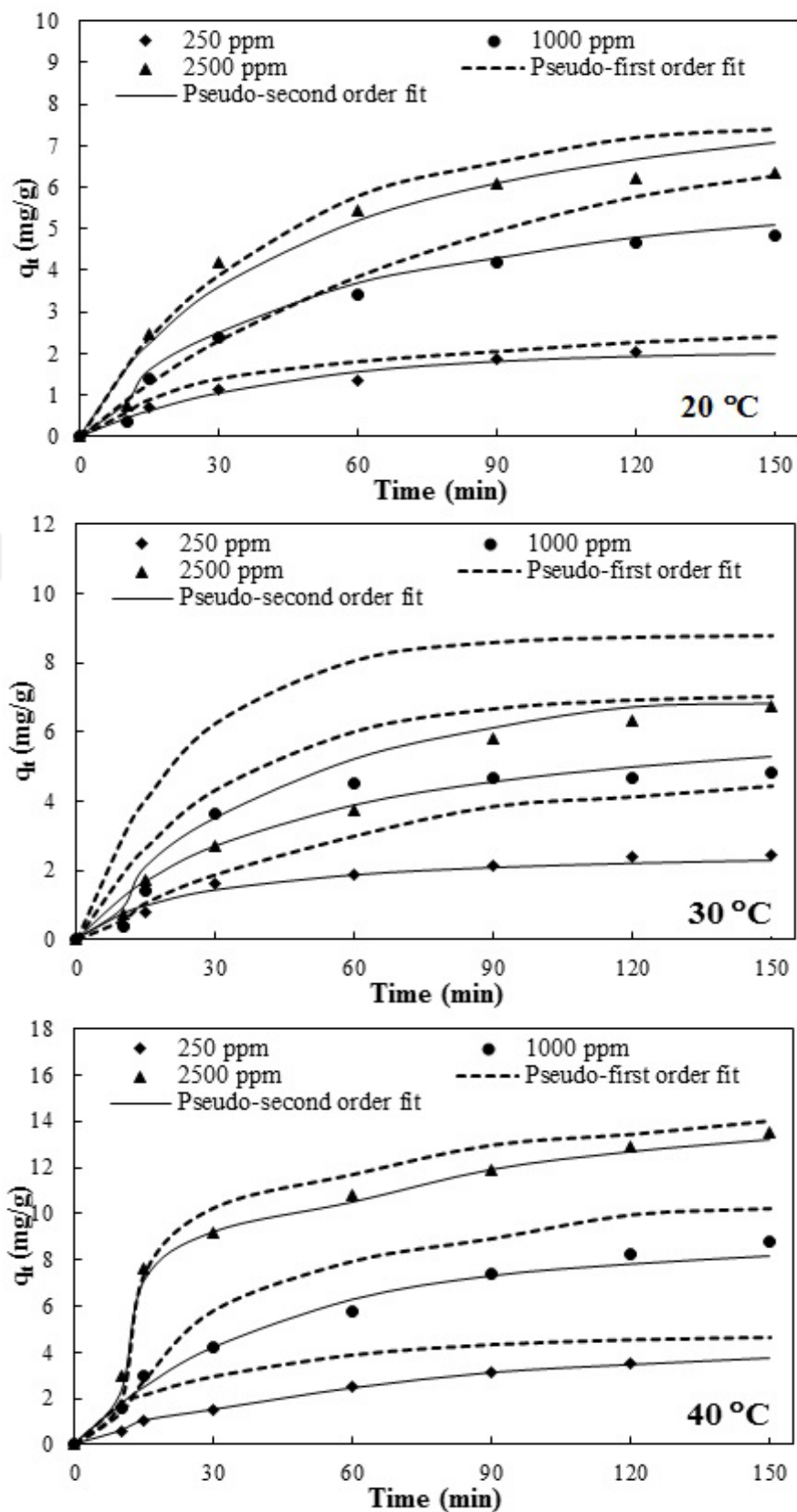


Figure 3.88. Fit of adsorption kinetics models by non-linear procedure.

3.9.7.4. Adsorption thermodynamics

The standard Gibbs free energy change values were calculated, and their results are presented in Table 3.13.

Table 3.13. Calculated thermodynamic parameters at different temperatures.

T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
20	-10.71	30.13	139.3
30	-12.10		
40	-13.49		

According to the results, the negative ΔG° values showed that the adsorption of glutamic acid on calcium sulfate dihydrate is spontaneous and that a chemical process was involved in glutamic acid adsorption. Furthermore, it was seen that the absolute ΔG° values increased with the increase of the temperature, suggesting that a rise in temperature is conducive to the adsorption process for all studied concentrations. The enthalpy (ΔH°) values of the adsorption process were also calculated. It was determined that the enthalpy changed 30.13 kJ/mol at 1000 ppm additive concentration. The positive ΔH° values showed that in addition to the adsorption process being endothermic, there was an increase in the adsorption capacity value of the adsorbent as the temperature increased, the findings of which were in agreement with the results shown in Figure 3.86. The positive value of ΔS is an indication of the increased disorderliness at the solid/solution interface during the adsorption of glutamic acid by the adsorbent.

3.10. The Results of Propionic Acid Effects on Phase Transformation of Calcium Sulfate Hemihydrate to the Dihydrate Form*

3.10.1. Conductivity measurements

Transformation of the calcium sulfate hemihydrate into the thermodynamically stable calcium sulfate dihydrate was monitored by in-situ measurement of conductivity in the crystallizer via conductometry. From the in-situ measurement of the conductivity values, the conductivity curves for the crystals were obtained, in the absence and presence of various additive concentrations at 20 °C, and their results are shown in Figure 3.89a. As stated before, the transformation process had three different stages: dissolution of the hemihydrate, nucleation and then the growth of the dihydrate crystals, respectively. It can be observed that the conductivity value increased rapidly at the initial step. After calcium sulfate hemihydrate was dissolved completely, the nucleation of the dihydrate crystals occurred. During this stage no significant change in the conductivity value occurred. When the calcium sulfate dihydrate crystals grew, conductivity against time was significantly reduced and the transformation process was complete at 150 minutes. In this time the conductivity value reached a fixed value. Figure 3.89a also shows the dependence of the conductivity values versus time at different propionic acid concentrations. The curves obtained had the same trend in additive media; however, the transformation rate increased as more propionic acid was introduced to the media. Figure 3.89b provides information about the conductivity changes of the crystals obtained in the presence of concentration of 2500 ppm of the additive during the transformation process at different temperatures. It was noted that the transformation rate was significantly affected by the temperature. The results in Figure 3.89b show that the rate increased with increasing temperature.

* Polat, S., Sayan P. (2018) Assessment of propionic acid adsorption performance on the phase transformation of calcium sulfate hemihydrate to dihydrate. Separation Science and Technology, 53 (13), 1966-1978.

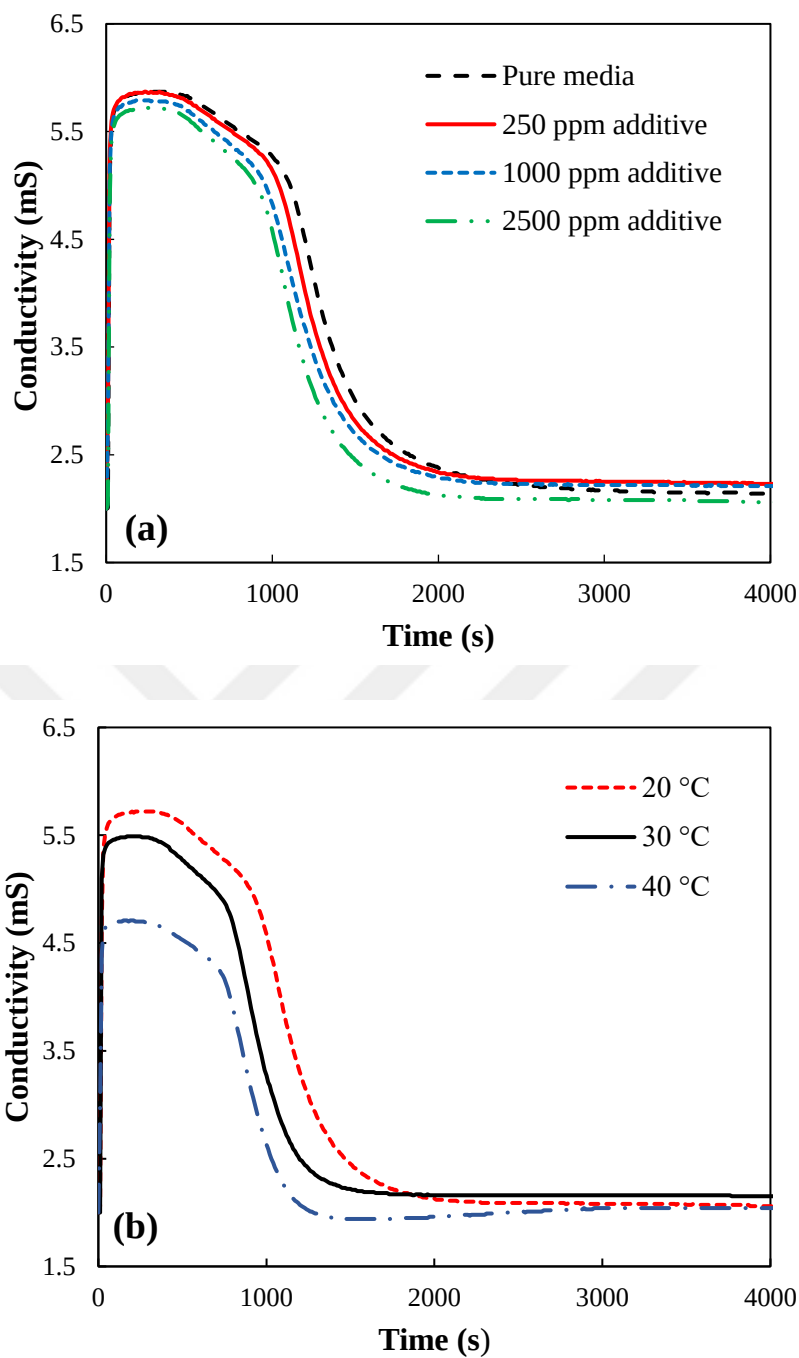


Figure 3.89. The change in conductivity as a function of time during the transformation process (a) in pure media and in the presence of varied propionic acid concentrations at 20 °C (b) in the presence of 2500 ppm of propionic acid at three different temperatures.

3.10.2. SEM analysis

Figure 3.90 shows SEM images of the crystals obtained as a result of the transformation of calcium sulfate hemihydrate into dihydrate in pure media and at 20°C. Calcium sulfate hemihydrate crystals were poor, compact, formless and with a porous structure. They were broken easily and split into smaller particles due to their poor structure. The porous characteristics of the calcium sulfate hemihydrate crystals were shown by BET analysis, and their surface area was determined to be 5.05 m²/g. As can be seen in Figure 3.90, the crystals obtained in pure media at 20°C had an overlapping plated structure, leaf-like and of poor character. The crystals with a poor, plated structure were easily broken by the effect of the hydrodynamic conditions of the media. Accordingly, both the average particle size of the crystals became smaller and the crystals lost their apparent shapes. Furthermore, as shown in the SEM images, the pores became smaller and the BET surface area decreased distinctively to a value of 2.95 m²/g for the calcium sulfate dihydrate crystals without an additive at 20°C. Calcium sulfate dihydrate crystals obtained in the presence of 2500 ppm of propionic acid at 20°C were composed of very thin plates and they could easily be broken under ambient conditions. As can be seen clearly in SEM images, the crystals obtained had no apparent shape. However, rod-shaped crystals were formed by plates breaking. This situation caused the average particle size to reduce. At the same time, compared to the pure media, the BET surface area of the crystals also decreased in the presence of additive. This value was determined to be 2.04 m²/g for crystals in the presence of 2500 ppm of propionic acid. This result revealed that propionic acid had a significant effect on the surface area of the crystals. When SEM images taken at different temperatures and in the presence of 2500 ppm of propionic acid were examined, the crystals were observed to be thickened by the temperature increase. It was observed that there was an increase in plate thicknesses for crystals obtained at 30°C compared to those obtained at 20°C. An increase was also seen in the number of rod-shaped crystals splitting from the main crystal structure as a result of breaking because of plate thickening. When the ends of the rod-shaped crystals were examined, it was clear that they were particles splitting from the main crystal. With the increase in temperature, the formation of rod-shaped crystals at 40°C occurred in a similar way to the formation of rod-shaped crystals at 30°C. However, it was seen that the crystals thickened and

increased in volume. In the particle size measurements, it was determined that the average particle size increased with rising temperature.

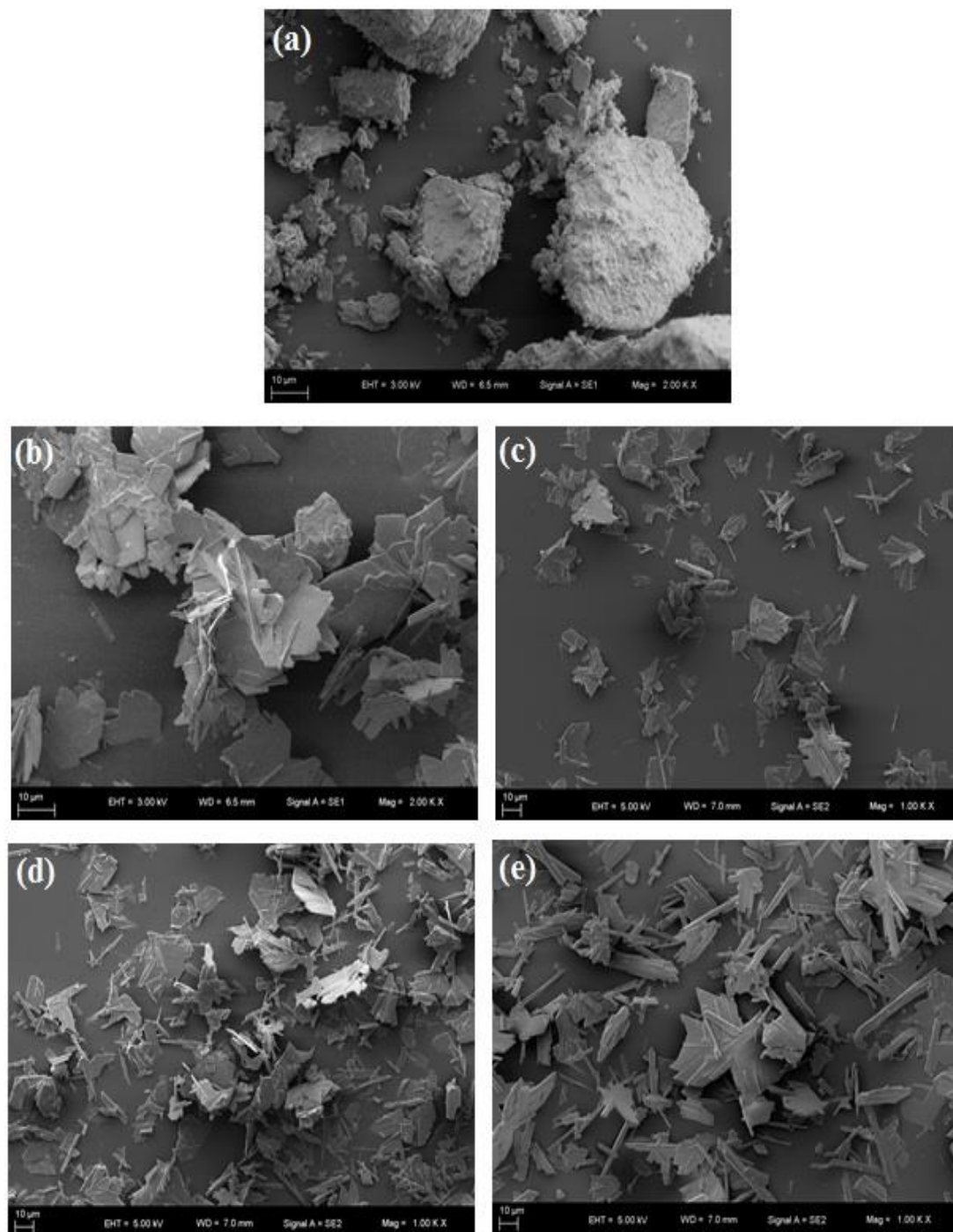


Figure 3.90. SEM photos of calcium sulfate hemihydrate crystals (a), calcium sulfate dihydrate crystals without additive at 20°C (b), with 2500 ppm additive at 20°C (c), 30°C (d), 40°C (e).

3.10.3. XRD analysis

X-ray diffraction (XRD) is an effective technique both to detect the crystal structure and to monitor the phase transformation process. Figure 3.91 shows X-ray diffraction patterns of calcium sulfate hemihydrate, and calcium sulfate dihydrate produced in pure media and in the presence of a concentration of 2500 ppm of propionic acid at different temperatures.

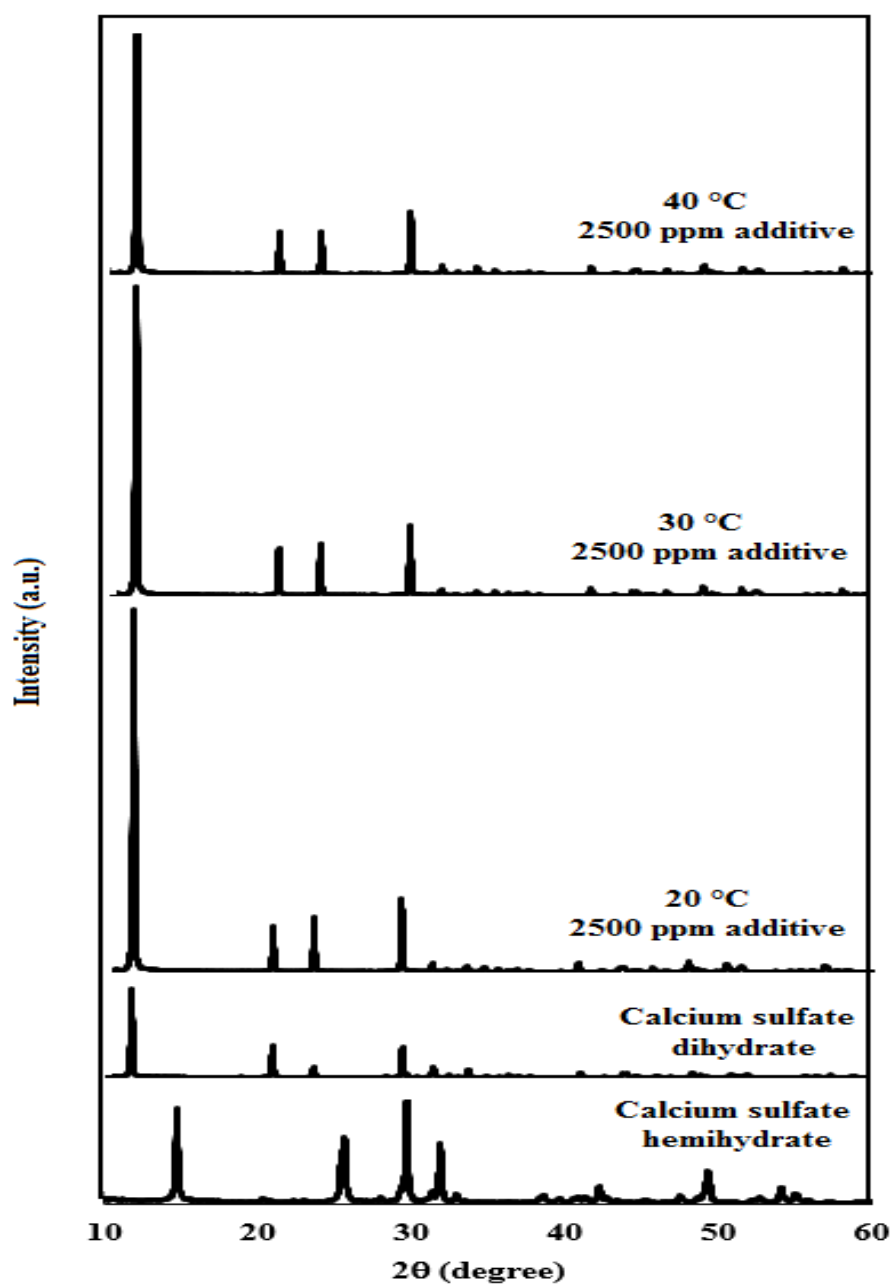


Figure 3.91. X-ray diffraction spectra.

At $t=0$ minutes, four characteristic calcium sulfate hemihydrate XRD peaks were determined at $2\theta = 14.72^\circ$, 25.67° , 29.69° and 54.14° . The crystals formed in pure media after 2.5 hours had strong peaks at 11.59° , 20.72° , 23.40° , 29.11° , 31.14° and 33.34° , which were attributed to the calcium sulfate dihydrate. No second phase, the formation of an amorphous structure, or any impurities of contamination were detected. This result showed that the initial material consisted of the pure hemihydrate form, and the crystals obtained at the completion of the transformation in pure media were in the form of the dihydrate. The peaks obtained were compatible with the calcium sulfate hemihydrate and dihydrate peaks reported in published literature [17,89]. When examining the XRD peaks of calcium sulfate dihydrate obtained in the presence of 2500 ppm of propionic acid, it was determined that the measured peak intensity values decreased in comparison to pure media. It was also determined that the peak intensities of the crystals decreased when the temperature increased. In published literature, the change in the peak intensity of the crystals produced in the presence of additives is explained by the adsorption of the additives onto the crystal surfaces [97]. Thus, the change in peak intensity may indicate that propionic acid is adsorbed onto the calcium sulfate dihydrate surface.

3.10.4. Particle size and filtration analysis

The average particle size of the crystals obtained in the absence and in the presence of different additive concentrations (250 ppm, 1000 ppm and 2500 ppm) at three different temperatures was measured and the change in the average size of the crystals is shown in Figure 3.92. The average particle size of the calcium sulfate hemihydrate crystals was $45\text{ }\mu\text{m}$, whereas the average particle size of the crystals obtained in pure media at $20\text{ }^\circ\text{C}$ – after the transformation – was determined to be $36\text{ }\mu\text{m}$. By the addition of propionic acid to the media, the particle size was reduced remarkably. As seen in Figure 3.92, the average particle size of the crystals obtained for a concentration of 2500 ppm of additive at $20\text{ }^\circ\text{C}$ was measured to be $25\text{ }\mu\text{m}$. This situation can be explained by the propionic acid potentially blocking the active sites of the crystals, reducing the crystal growth and consequently reducing the average size of crystals.

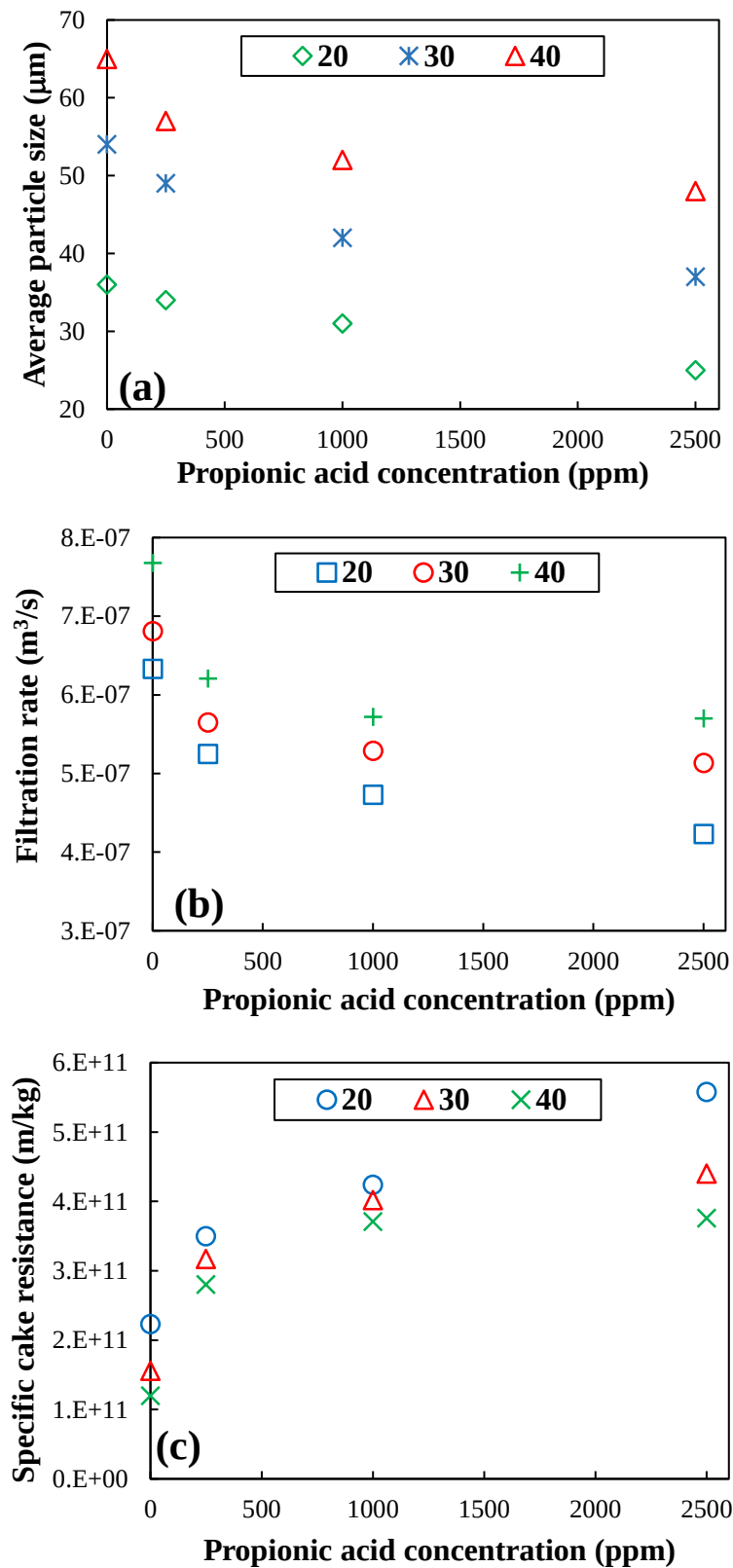


Figure 3.92. The influence of propionic acid concentration and temperature on the average particle size (a) filtration rate (b) and the specific cake resistance (c) of the crystals.

Figure 3.92 also shows how the particle size is significantly affected by the temperature. The average particle size of the crystals obtained without additive media increased with an increase in temperature. The crystals produced at 40 °C are significantly bigger than the crystals produced at 20 °C. The average particle size of the crystals were measured to be 36, 54 and 65 μm for 20, 30 and 40 °C, respectively in pure media. It was also detected that the particle size was reduced when the propionic acid concentration increased at all temperatures studied. At a constant 2500 ppm of propionic acid, the average particle size of the crystals was determined to be 25, 37, and 48 μm at 20, 30 and 40° C, respectively.

The filtration rate analysis of the crystals, obtained as a function of temperature and additive concentrations, was performed at a constant pressure of 700 mm Hg. The results for the filtration rate measurements and the specific cake resistance, which were calculated according to the results of the filtration rate measurements of the crystals produced in the presence of different additive concentrations, are given in Figure 3.92. It was determined that the filtration rate decreased in the presence of propionic acid at constant temperature. It was also detected that filtration rate showed a significant change when the temperature increased. As seen on Figure 3.92, the specific cake resistance increased as the propionic acid concentration increased. While the specific cake resistance of the crystals obtained in pure media was 2.23×10^{11} kg/m, this value was calculated as 5.58×10^{11} kg/m for the crystals obtained with a concentration of 2500 ppm of propionic acid at 20 °C. As clearly seen in the SEM images, this increase in specific cake resistance resulted from breaks in the crystals and reduction of the average particle size. In experiments conducted at different temperatures, and at constant additive concentrations, the specific cake resistance decreased as temperature increased. This effect can be explained by the increase in the size and the thickness of the calcium sulfate dihydrate crystals. Both particle size analysis and specific cake resistance results were compatible with the SEM analysis.

3.10.5. TGA/FTIR/MS analysis

The thermogravimetric data (TGA) curves, as well as the derivative thermogravimetric data (DTG) curves of the calcium sulfate dihydrate produced in pure media and in the presence of 2500 ppm of propionic acid concentration at 20 °C, are shown in Figure 3.93. As presented in Figure 3.93, the decomposition process of the pure calcium sulfate

dihydrate could be divided into two consecutive stages: the dihydrate form was transformed into the hemihydrate form between 80 to 150 °C and the anhydrite formed between 150 and 175 °C, respectively.

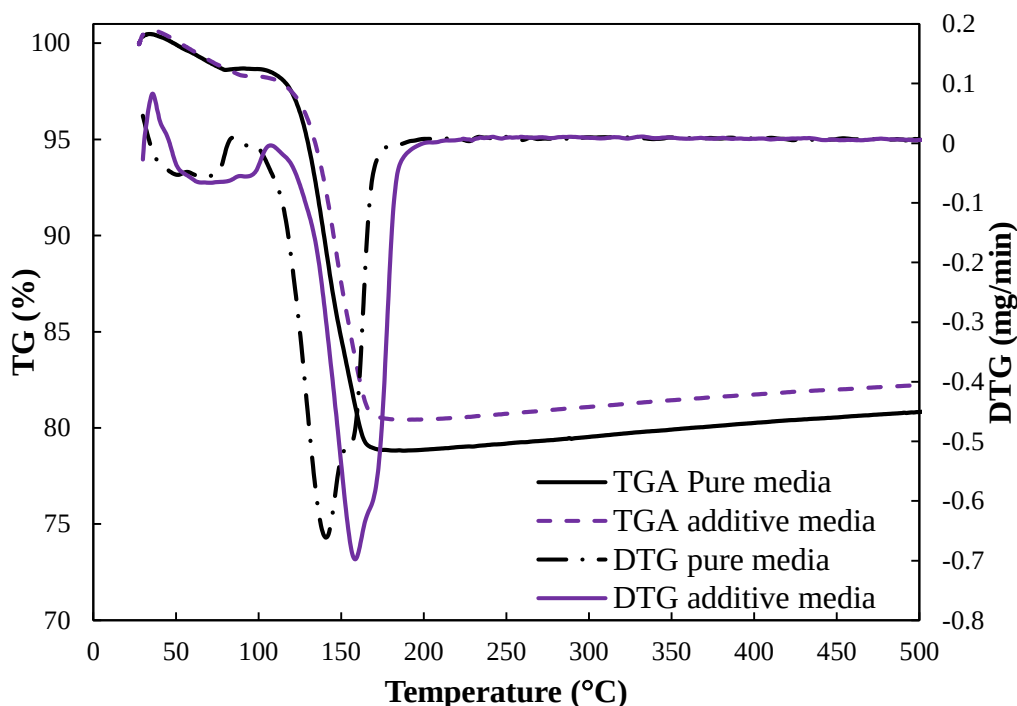


Figure 3.93. TGA and DTG curves of the crystals without additive (a) and with 2500 ppm of propionic acid.

As stated before, the mass loss was approximately 11% in the first stage, and it was caused by the dehydration of 3/2 mol of water. The second stage accounted for approximately 9% mass loss and this loss was related to the dehydration of 1/2 mol of water in the calcium sulfate dihydrate. As can be clearly seen in the TGA and DTG curves of crystals produced in impure media, it showed similar behavior in terms of thermal decomposition, and the dehydration process took place over two steps accompanied by about an 18% mass loss. But, a shifting behavior was detected in the maximum peak temperature; the temperature of the beginning and the end of the dehydration reaction was also shifted. While the maximum peak temperature was 141 °C in pure media, the value in this case was determined to be 158 °C. This situation can be the result of the adsorption of propionic acid onto the crystal surface. Both to understand the binding of the additive on

the crystal and to detect the chemical composition of the volatile products during the thermal decomposition process, the crystals produced in both pure and impure media were analyzed via online MS coupled to TGA. The mass spectra of the various species are shown in Figure 3.94.

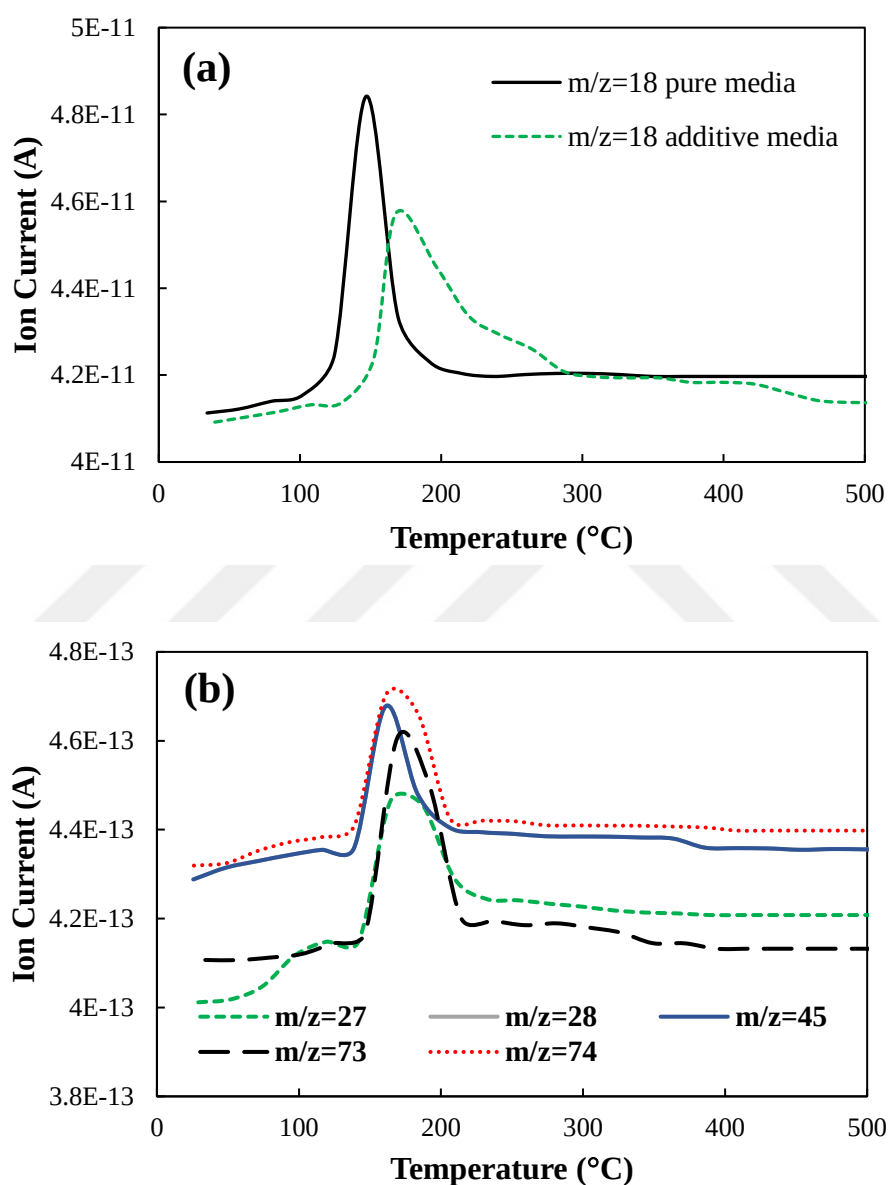


Figure 3.94. Single ion current curves obtained during the transformation process in pure media (a) and in the presence of 2500 ppm propionic acid (b).

During the thermal decomposition of pure calcium sulfate dihydrate crystals, the main product water, characterized by the release of molecular ion fragments with $m/z = 18$, occurred in the temperature range from 124 to 191 °C. Additionally, the evolved gas reached a maximum value at 147°C. Although small time delays occurred because of the transportation of volatile components from TGA to MS, these results were found to be consistent with DTG results. The results obtained from the measurements taken from 30 to 500°C and the mass/charge ratios (m/z) from 1 to 300 are also given in Figure 3.94 for the crystals obtained in 2500 ppm of propionic acid. Unlike the peak at $m/z = 18$, several new peaks at $m/z = 27, 28, 45, 73$ and 74 were detected in the temperature range from 133 to 206°C. These mass/charge ratios characterize propionic acid as mentioned in published literature [123]. When the peak intensities were examined, the most intense peak of the crystals belonged to the characteristic peak of water vibration. Compared to the water peak, the intensities of propionic acid peaks were determined to be low. These results suggested that the evolved gas crystals obtained in impure media contained mostly of water but with small amounts of propionic acid.

TGA/FTIR analysis was also performed to characterize the structure of the crystal and to gain information about functional groups of the evolved gases during thermal decomposition of calcium sulfate dihydrate produced in the presence of 2500 ppm of propionic acid. Figure 3.95 presents the Gram–Schmidt curve and 3D FTIR spectrum obtained at a 10 °C/min heating rate for the crystals produced in the presence of additive. The Gram–Schmidt curve, that indicates how the concentration of the evolved gases varies with time during thermal decomposition had one sharp peak at about 14.3 minutes, which is similar to the DTG and TGA/MS results.

The FTIR spectrum of the standard reference calcium sulfate dihydrate characterizes O-H stretching vibrations at $3600\text{--}3400\text{ cm}^{-1}$ and H-O-H bending at 1680 cm^{-1} and 1620 cm^{-1} . The bands seen at 663 cm^{-1} and 594 cm^{-1} result from SO_4 bending vibrations in the structure of calcium sulfate dihydrate [116]. When the 3D FTIR spectrum showing the change of spectral intensity as a function of wavelength and time was examined, the crystals had various functional groups. C=O vibration bands were seen at $1760\text{--}1690\text{ cm}^{-1}$ indicating the presence of propionic acid, as well as the characteristics peaks of calcium sulfate dihydrate crystals. It was clear that the propionic acid bound to the crystal

surface and the maximum adsorption occurred in a temperature range from 140 to 192°C. These results obtained from TGA/FTIR were in agreement with the TGA/MS results.

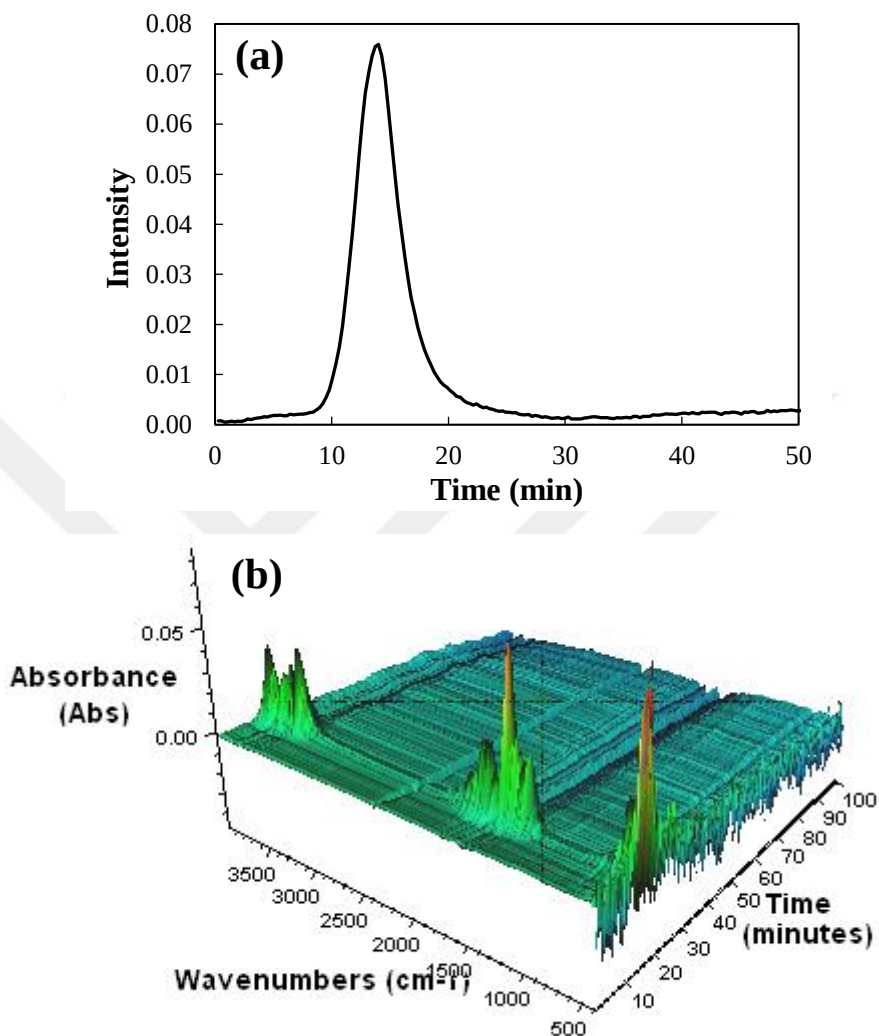


Figure 3.95. Gram–Schmidt curve (a) and 3D FTIR spectrum (b) of the crystals obtained with a concentration of 2500 ppm of propionic acid.

3.10.6. Adsorption studies

3.10.6.1. Influence of concentration, temperature and contact time

The effects of additive concentration and contact time on adsorption were examined at a concentration of 250 to 2500 mg/L of propionic acid over a 20 to 40°C temperature range. Figure 3.96 shows the dependence of adsorption capacity values versus contact time at different temperatures.

According to these results, it was determined that the adsorption capacity (q_e) increased by increasing the concentration from 250 to 2500 mg/L, and the amount of additive adsorbed onto the dihydrate crystals decreased with increasing temperature. The maximum adsorption capacities were determined to be 10.4, 8.5 and 7.2 mg/g at 20, 30 and 40°C, respectively. This showed the exothermic nature of the adsorption process. The contact time is also another important parameter affecting propionic acid adsorption onto the calcium sulfate dihydrate. It was determined that at the initial stage, the adsorption process was fast, and a large amount of propionic acid adsorbed onto the crystal surface in the first 60 minutes. Then, it reached equilibrium within 90 minutes and after this time, no significant change was observed. The explanation of this phenomenon may be due to the fact that the number of available adsorption sites decreases as time passes because of the interaction between adsorbent and the additive.

3.10.6.2. Adsorption equilibrium isotherms

The adsorption isotherm parameters obtained from the Langmuir, Freundlich, and Temkin models at different temperatures were calculated with the help of the linear expressions, and their respective results are given in Table 3.14. At the same time, the compatibility of the isotherm models used in this study with experimental data is also shown in Table 3.14. Increasing the correlation coefficients (R^2) value towards 1 indicates that there was a large correlation between values obtained experimentally and those predicted by the model.

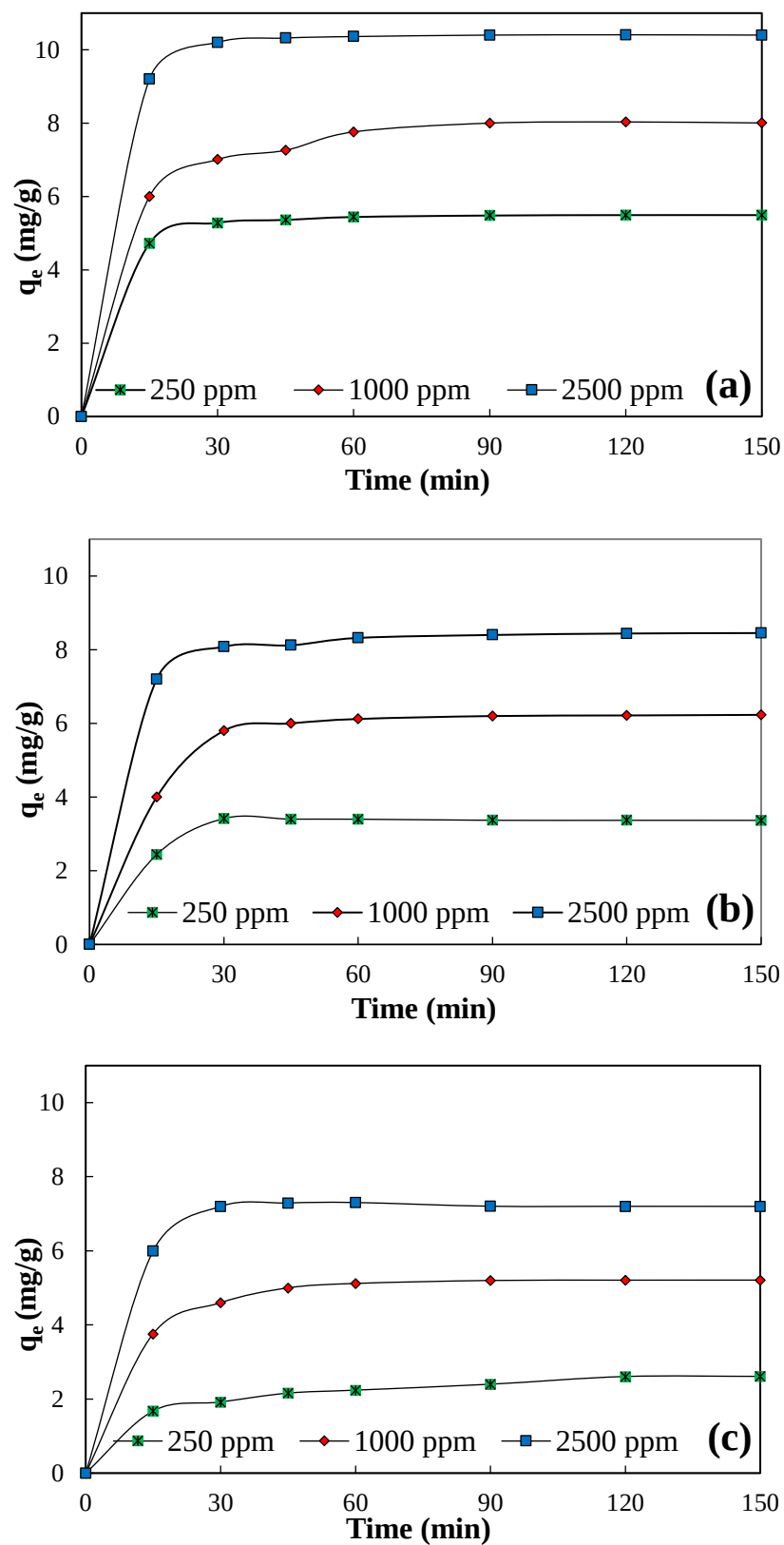


Figure 3.96. Effects of propionic acid concentration, time and temperature on the adsorption process.

As can be seen in the R^2 values given in Table 3.14, the Freundlich model was found to be more compatible with the experimental data than the other models. In Freundlich isotherm models, K_F (mg/g)(L/mg) $^{1/n}$ and n are the constants indicating the relative adsorption capacity and intensity of adsorption, respectively. The values of n and $1/n$ give information regarding the favorability of adsorption and heterogeneity factor, respectively. In general, $n > 1$ shows that the type of adsorption isotherm is favorable and that greater n values are associated with higher adsorption intensities. The expression $0 < (1/n) < 1$ is an indication of the adsorption intensity of the surface heterogeneity, and as the $1/n$ value approaches zero, the heterogeneity of the surfaces increase [124].

Table 3.14. Isotherm constant results for propionic acid adsorption onto calcium sulfate dihydrate at 20°C, 30°C and 40°C.

Isotherm models	20 °C	30 °C	40 °C
Langmuir model			
q_m (mg/g)	11.097	9.9108	8.8496
K_L (L/mg)	0.0057	0.0025	0.0018
R^2	0.9888	0.9886	0.9886
Freundlich model			
n	4.5977	2.8003	2.2472
K_F ((mg/g) (mg/L) $^{-1/n}$)	1.9489	0.5477	0.2387
R^2	0.9954	0.9920	0.9970
Temkin model			
B	1.6416	1.9541	1.9115
K_T (L/mg)	0.2326	0.0322	0.0182
R^2	0.9890	0.9110	0.9290

In this study, the n values were 4.5977, 2.8003 and 2.2472 for 20, 30 and 40°C, respectively. These results showed that propionic acid adsorbed onto the crystal surface in a favorable and multilayer manner under experimental conditions and its adsorbent surfaces were heterogeneous.

3.10.6.3. Adsorption kinetics

Pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion model parameters for different temperatures and their respective correlation coefficients are given in Table 3.15. When examining Table 3.15, it was seen that the relative coefficients determined for the pseudo-second order adsorption kinetic model were higher than values calculated for the other models used. This result indicated that the pseudo-second-order model was more compatible with the experimental data, and the adsorption of propionic acid onto calcium sulfate dihydrate occurred via chemical sorption.

Table 3.15. Kinetic parameter results.

Kinetic Model	20 °C	30 °C	40 °C
Pseudo-first order			
q_e (mg/g)	108.37	163.30	188.50
k_1 (1/min)	0.00014	0.00012	0.00007
R^2	0.7845	0.6852	0.8601
Pseudo-second order			
q_e (mg/g)	5.7110	3.8506	2.5517
k_2 (g/mg.min)	0.0608	0.0394	0.0459
R^2	0.9998	0.9974	0.9978
Elovich			
α (mg/g.min)	344.31	1.9164	1.5088
B (g/mg)	1.9227	1.4245	2.3929
R^2	0.9167	0.7630	0.9859
Intra-particle diffusion			
k_p (mg/g.min ^{1/2})	0.2521	0.3000	0.3950
C	8.2669	0.7010	0.8709
R^2	0.9747	0.9420	0.9031

The intra-particle diffusion rate constants, k_p , for propionic acid adsorption onto the calcium sulfate dihydrate at different temperatures are also given in Table 3.15. These values were determined as 0.2946, 0.2380 and 0.1505 $\text{mg/g.min}^{1/2}$ at 20 °C, 30 °C and 40 °C, respectively. The obtained k_p values decreased with increasing temperature. Depending on the temperature, the mobility of the adsorbate decreased due to the nature of the exothermic properties of the adsorption. Moreover, the intra-particle diffusion model was plotted and the plots of the model – dependent on temperature – did not pass through the origin. This result indicated that the intra-particle diffusion was not the rate-limiting step for the adsorption process of propionic acid onto calcium sulfate dihydrate crystals.

3.10.6.4. Adsorption thermodynamics

Table 3.16 shows thermodynamic parameters (ΔG° , ΔH° and ΔS°) calculated for propionic acid adsorption. The Gibbs free energy change values were found to be 12.576, 15.069, 16.426 kJ/mol for 20, 30 and 40°C, respectively.

Table 3.16. The thermodynamic parameters.

T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
20	12.576		
30	15.069	-44.010	-193.733
40	16.426		

As can be seen from Table 3.16, the ΔH° value was negative. The negative value for the enthalpy change confirmed that adsorption of propionic acid occurred exothermically at temperatures between 20 to 40°C. Moreover, the negative values for entropy revealed the decrease in the degree of freedom of the system.

4. CONCLUSIONS

The purpose of this study was to examine the behavior of polymorph and pseudo-polymorph in the presence of various additives. Firstly, the phase transformation of β -glycine to α -glycine in a water/ethanol media was investigated in terms of its polymorphism in the presence of various additives. In the next step, the pseudo-polymorphic phase transformation of calcium sulfate hemihydrate to dihydrate was examined in the presence of tricarballic, glutamic and propionic acids. The main conclusions obtained from this study are summarized as follows:

- First of all, the transformation of glycine β into α form was investigated in the absence and in the presence of lauric acid. The addition of lauric acid to media caused changes not only the phase transformation time but also to the transformation rate. Additionally, the presence of the additive had a direct impact on the crystal morphology. The results obtained from the SEM and morphology analyses revealed that the elongation value was lower when using the additive. However, both the yield of rounded shaped-crystals and the agglomeration tendency increased with a high concentration of lauric acid. Regarding the thermal decomposition of the crystals within additive free media, the activation energy calculated from FWO, Friedman, Starink and KAS kinetic models was 90.6, 90.2, 90.5, and 89.6 kJ/mol, respectively. Compared to pure media, higher activation energy was obtained for the crystals produced in the presence of lauric acid. Furthermore, the characterization of the crystals obtained in pure and impure media were performed by elemental and FTIR analyses, where the results showed that the crystals obtained in either medium were consistent with each other, indicating that lauric acid adsorbed on the crystal surface.
- Secondly, the effects of butyric acid on the polymorphic phase transformation of glycine were investigated in the current study. The ultrasonic velocity measurement results show that butyric acid led to an extension of the transformation time. The duration was 45 ± 1 minutes for pure media. The presence of 250 ppm butyric acid significantly increased the transformation time to 75 ± 1 minutes. This is consistent with the XRD analysis. The SEM analysis shows that the morphology of the crystals was affected by the additive. The prismatic type crystals transformed into smaller rounded crystals with a tendency to aggregate in the presence of butyric acid. The additive media caused a change

in the elongation, convexity, and circularity of the crystals shape parameters. The elongation value decreased from 0.517 ± 0.13 to 0.287 ± 0.10 with the addition of 250 ppm additive. The variations in morphology of the crystals affected the crystal filtration characteristics. The results of the filtration rate measurements reveal that an increase in the amount of the additive in the crystallization media leads to an increase in the specific cake resistance and decrease in the porosity value. Significant changes in the FTIR spectrum of the crystals obtained in pure media were observed because of adsorption of butyric acid. The elemental analysis results indicate the butyric acid adsorption on the crystal surface. An increase in butyric acid content in glycine shifted the thermal decomposition temperature to a higher value. The results of the thermal decomposition kinetics of the crystals with and without additive reveal that an addition of butyric acid to crystallization media increases the average activation energy of the decomposition process. The calculated value increased from about 90 to 118 kJ/mol for the crystals obtained in 250 ppm butyric acid.

- The present study also revealed that oleic acid used as an additive had significant effects on the polymorphic phase transformation of glycine from the β to the α form. The presence of oleic acid in crystallization media decreased the transformation rate, and a higher additive concentration tended to extend the transformation time. Compared to pure media, the existence of oleic acid affected the crystal morphology in terms of both shapes and sizes of the crystals. Changes to the length and width of the crystals occurred in the presence of oleic acid: this additive enhanced the narrow crystal-size distribution. From the morphological point of view, the crystals obtained in pure media had a more elongated shape. In comparison, the circularity value of the crystals with the presence of oleic acid increased from 0.552 to 0.678 as the additive concentration increased. When the crystals were characterized by TG/DTG analysis, the value of the activation energy calculated using KAS, FWO, Starink, and Tang kinetic models for crystals obtained in pure media was lower than that for crystals obtained in oleic acid media. The increase in activation energy was attributed to the adsorption of additive on the crystal surface. The existence of oleic acid on the crystal was proven by FTIR, elemental, and Kjeldahl analyses.
- This study demonstrated that myristic acid can be used as the additive materials for the variation of the phase transformation behavior of β to α -glycine. The XRD results showed that the crystals obtained were completely in α form under all studied conditions.

SEM analysis results indicated that α -glycine crystals, which had a rod-like in pure media, experienced habit change in the presence of myristic acids. In addition, changes to the length and width of the crystals occurred in the presence of the additive. Both TGA-FTIR and elemental analysis results were confirmed that the additive adsorbed on the crystal surface during the phase transformation process.

- The present study also shows that carboxylic acids, namely acetic, tartaric and citric acid, can be used as an additive to control the phase transformation behavior from β -glycine to α -glycine. The XRD results indicate that the crystals are formed solely in α -form under all the additive conditions studied. The SEM analysis results show that the α -glycine crystals, which have a rod-like form in the pure solution, experience a change in the presence of the carboxylic acid additives. In addition, the variation in the shape parameters, especially the HS circularity, occurred in the presence of all the carboxylic acid additives. The filtration results show that the cake resistance value increased from 1.100×10^{11} to 1.540×10^{11} m/kg in the presence of the citric acid containing media. A simplified DAEM method was applied to the TGA data for the calculation of average activation energy of the crystals acquired in the additive containing and non-additive media. The TGA resulted in the decomposition of pure glycine at 280–530 °C and the crystals obtained in the presence of the carboxylic acid additives were difficult to decompose because the weight loss occurred over a wide temperature range (150–600 °C). Simultaneous FTIR analysis was performed to detect the functional groups and whether the additive was adsorbed or not. The carbonyl functional groups on the glycine crystals confirmed the adsorption of the carboxylic additives on the crystals during the phase transformation process. The amount of adsorbed acetic, tartaric and citric acid was 2.97, 2.38 and 1.72 mg/g, respectively.

- Another scope of this study was to investigate the impact of ultrasonic irradiation on the phase transformation process of glycine from the β to the α form. The phase transformation time was shortened with increasing ultrasonic irradiation. SEM analysis showed that the morphology of the glycine crystals was affected by ultrasonic irradiation and fairly large differences were observed in the shapes and sizes of the crystals obtained with different power. Glycine crystals obtained in media without the application of ultrasonic irradiation were prismatic and rod forms, but the crystals were transformed into the shorter partially rounded form in the presence of ultrasound. Moreover, deformation,

breakage, and agglomeration occurred under ultrasonic irradiation. The results of morphology analysis showed that the mean projected area, width, and length of the crystals decreased with increasing ultrasound power. The circularity value also increased while the elongation value decreased as the ultrasonic power increased. The changes in particle shape parameters and morphology characteristics seen in the presence of ultrasonic irradiation directly affected the filtration characteristics of glycine crystals. While the specific cake resistance of the glycine obtained in the absence of ultrasonic irradiation was calculated as 1.095×10^{11} m/kg, these values varied from 8.023×10^{10} to 3.055×10^{11} m/kg for crystals produced under ultrasonic irradiation.

- The other objective of this study was to examine the influence of UV radiation on the phase transformation of β glycine to α glycine. The ultrasonic velocity results showed that the transformation rate of β glycine to α glycine showed a progressive increase with the increase in the intensity of the UV radiation. On the other hand, the addition of propane-1,2,3-tricarboxylic acid to media caused to change the phase transformation time and the transformation rate was slowed. As revealed by the SEM images, the crystal morphology was affected UV radiation. After UV radiation, it was determined that the deformation occurring on the crystal surface, and the shortened lengths of the crystals, were caused by increasing UV intensities from 8W to 20W. Furthermore, the additive had a significant effect on the crystal morphology. The results obtained from the SEM and particle size analyses revealed that the average particle size of the crystals was lower when using the additive. Whereas the average particle size of the crystals obtained in pure media was 85 μm , this value was 64 μm for the crystals obtained in the presence of propane-1, 2, 3-tricarboxylic acid. The presence of the additive together with UV in the crystallization media resulted much smaller crystal size. According to the TGA–MS and ATR-FTIR results, significant changes were observed in the absorption peak intensities and the release of gases produced during thermal decomposition of glycine obtained in the presence of UV radiation reduced, which can be considered a degradation of the glycine. Based on these results, this study will be beneficial to understand the actual role of UV radiation on the phase transformation of β glycine to α glycine.

- This study also dealt with the transformation behaviour of calcium sulfate hemihydrate to calcium sulfate dihydrate in pure media and in the presence of

tricarballic acid. Experimental results indicate that tricarballic acid had a significant effect on the retention time and at low concentration tricarballic acid tended to extend the transformation time. It was also found that the average particle size and crystal morphology were affected by the additive. Consistent with the SEM images, the average particle size of the samples obtained in the pure media showed a distinct decrease in the presence of tricarballic acid. During the transformation process, the average activation energies of the crystals obtained at $t=2.5$ h in pure and impure media were calculated from Friedman, FWO, and KAS models; these results showed well-fitting with each other. By incorporating an additive to the media, the average activation energy of the crystals increased significantly compared to the crystals obtained in the pure media. Consistent data obtained simultaneously from TGA-FTIR and TGA-MS confirmed that tricarballic acid adsorbed on the crystal surface.

- The effects and adsorption characteristics of glutamic acid on the transformation process of calcium sulfate hemihydrate to calcium sulfate dihydrate have been explored in this paper. The conductivity results showed that the transformation rate of calcium sulfate hemihydrate to dihydrate tended to fall with the increase of both glutamic acid concentration and temperature. The experiment results indicated that additive concentration and temperature had important roles on the adsorption process and that glutamic acid adsorption increased with the increase in the temperature. As revealed from the SEM and TEM images, crystal morphology was affected by the glutamic acid. Whereas calcium sulfate hemihydrate had a sponge-like morphology, following the adsorption process, there were no pores observed and agglomeration tended to occur. As it is consistent with the SEM images, the average particle size of the samples obtained in the pure media showed an increase in the presence of glutamic acid. As compared with the sample obtained in pure media, significant changes in the FT-IR spectrum acquired in the presence of the additive were seen as result of the bonding of the glutamic acid with the calcium sulfate dihydrate. The Langmuir isotherm model better represented the adsorption isotherms with the highest correlation coefficient for describing glutamic acid adsorption. The adsorption kinetics were best fitted by the pseudo-second order rate expression. Thermodynamic parameters calculated using isotherm data showed that glutamic acid adsorption on calcium sulfate dihydrate was spontaneous and endothermic reaction.

- Finally, the transformation of calcium sulfate hemihydrate into dihydrate was investigated with and without propionic acid. In the first part of the study, the crystals were characterized, and these results showed that propionic acid significantly affected the transformation rate, the average particle size, the filtration characteristic, the morphology and the surface area of the crystals. The transformation rate was considerably increased at high propionic acid concentrations. It was determined that the completion of transformation process was accelerated about 10 % in the presence of additive media. While the average particle size decreased, the specific cake resistance increased in the presence of additive. The addition of propionic acid to media caused morphological changes and led to a decrease in the BET surface area. In the second part of the study, the experimentally obtained data for the adsorption of propionic acid onto the calcium sulfate dihydrate was modeled in terms of isotherms, kinetics and thermodynamics. The Freundlich isotherm model and pseudo-second-order kinetic model were the most suitable models to describe propionic acid adsorption during the transformation process. The thermodynamic data revealed the exothermic and chemical nature of the adsorption process. The results suggested that propionic acid can be utilized as an accelerator for the transformation process of calcium sulfate hemihydrate to dihydrate. The experimental results indicated that morphology, phase transformation time, stability, filtration, thermal and adsorption characteristics of glycine (polymorph) and calcium sulfate hemihydrate (pseudo-polymorph) could be changed in the presence of various additives used. Therefore, this study provides beneficial information for industrial applications and scientific studies.

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LIST OF PUBLICATIONS ABOUT THE THESIS SUBJECT BEING PREPARED

1. Papers Published on Science Citation Index and Science Citation Index Expanded Journals

1. **S. Polat**, P. Sayan (2018). The Characterization and Polymorphism of α -Glycine in the Presence of Butyric Acid. *Advanced Powder Technology*, 29(9), 1968-1976. Doi:10.1016/j.appt.2018.02.035
2. **S. Polat**, P. Sayan (2018). Effect of ultrasonic irradiation on morphology and polymorphic transformation of glycine. *Ultrasonics Sonochemistry*, 47, 17-28. Doi: 10.1016/j.ultsonch.2018.04.013
3. **S. Polat**, P. Sayan (2018). Assessment of propionic acid adsorption performance on the phase transformation of calcium sulfate hemihydrate to dihydrate. *Separation Science and Technology*, 53 (13), 1966-1978. Doi: 10.1080/01496395.2018.1442862
4. **S. Polat**, P. Sayan (2018). Evaluation of solvent-mediated phase transformation of glycine using oleic acid: Morphology and characterization study. *Chinese Journal of Chemical Engineering*, In press. Doi: 10.1016/j.cjche.2017.11.013
5. **S. Polat**, P. Sayan (2018). Kinetic analysis and polymorphic phase transformation of glycine in the presence of lauric acid. *Journal of Crystal Growth*, 481, 71-79. Doi: 10.1016/j.jcrysgro.2017.10.037
6. **S. Polat**, P. Sayan (2018). Impacts of UV Radiation on the Polymorphic Transformation of β Glycine to α Glycine. *Crystal Research and Technology*, 53(1), 1700103 (1-10). Doi: 10.1002/crat.201700103
7. **S. Polat**, P. Sayan (2017). Impact of glutamic acid on the transformation of calcium sulfate hemihydrate to dihydrate: Characterization, equilibrium, kinetics, and thermodynamics. *Chemical Engineering Communications*, 204(11), 1318-1331. Doi: 10.1080/00986445.2017.1364241
8. **S. Polat**, P. Sayan (2017). Effects of tricarballic acid on phase transformation of calcium sulfate hemihydrate to the dihydrate form. *Crystal Research and Technology*, 52 (5), 1600395 (1-10). Doi: 10.1002/crat.201600395

9. **S. Polat**, P. Sayan (2018). An experimental investigation and kinetic modeling study of the phase transformation behavior of glycine in various carboxylic acids. Asia-Pacific Journal of Chemical Engineering, Under Review.

2. Presented Announcements

1. **S. Polat**, P. Sayan (2017). The Characterization and Polymorphism of α -Glycine in the Presence of Butyric Acid. The Porous and Powder Materials Symposium and Exhibitions PPM 2017, Aydın-Turkey. (Oral presentation).

2. **S. Polat**, P. Sayan (2017). Assessment of Acetic Acid Effect on Glycine Phase Transformation. 3rd International Conference on Advances on Mechanical Engineering: ICAME 2017, Istanbul-Turkey. (Oral presentation).

3. **S. Polat**, P. Sayan (2017). Influence of propionic acid adsorption on phase transformation of calcium sulfate hemihydrate to the dihydrate. 24th International Workshop on Industrial Crystallization (BIWIC2017), Dortmund-Germany. (Poster presentation).

4. **S. Polat**, P. Sayan (2018). Evaluation of myristic acid effect on polymorphic transformation of glycine. 25th International Workshop on Industrial Crystallization (BIWIC2018), Rouen-France. (Poster presentation).

5. **S. Polat**, P. Sayan (2018). Influence of Tartaric Acid on Phase Transformation Behavior of Glycine. 1st International Eurasian Conference on Biological and Chemical Sciences (EurasianBioChem 2018), Ankara-Turkey. (Oral presentation).

6. **S. Polat**, P. Sayan (2018). Glisinin Polimorfik Faz Dönüşümünün İncelenmesi, 6. Ulusal Biyomühendislik Öğrenci Kongresi, İstanbul-Turkey. (Poster presentation).

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EDUCATION

PhD: Chemical Engineering, Marmara University, Turkey, 21/07/2014-31/08/2018.

MS: Chemical Engineering, Anadolu University, Turkey, 16/09/2011-29/01/2014.

BS: Chemical Engineering, Anadolu University, Turkey, 07/09/2006-11/06/2011.

RESEARCH INTERESTS

-Crystallization and polymorphism

-Polymorphic phase transformation

-Thermal decomposition kinetics

-Adsorption

-Material characterization

PROFESSIONAL EXPERIENCE

Teaching and Research Assistant (20/02/2014 - Present), Marmara University,
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