INVESTIGATION OF REACTION MECHANISM OF EPOXY RESINS WITH AMIDE FUNCTIONAL GROUPS

by

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Dedicated to my family

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ABSTRACT

INVESTIGATION OF REACTION MECHANISM OF EPOXY RESINS WITH AMIDE FUNCTIONAL GROUPS

Epoxy resins are used for many applications due to their noteworthy properties such as low creep, reasonable elevated temperature performance, chemical resistance and good adhesion to various substrate, etc. Epoxy resins gain such characteristics even at moderate level of crosslinking often referred as curings. There are various types of hardeners that initiate curing reaction, which all bring some characteristics to the material depending on their chemical and physical features. The information we have up to now, amides as hardener are not used as much as other kinds of curing agents like amines, anhydrides and acids, etc. Interestingly there are only a few reports on the reaction of epoxides with amides in general. Furthermore, in these limited studies done with amide and epoxy resins, there is little information about the effect of amide or the epoxide structure on these reactions, since the cured product analyses were mostly limited to FTIR analyses due to the solubility issues. Here, synthesis of soluble samples and their further spectroscopic analyses were aimed. Thus depending on these results about the structure of product, the idea about probable reaction pathway was developed. Also, temperature and heating time were adjusted to carry out the reaction under suitable conditions. Monomeric amide sources were used to avoid from complete crosslinked structure and provide solubility. Aromatic group containing amide and epoxy were used as well for comparison of effect of aromaticity and aliphaticity on reaction. In addition to FTIR and DSC, ^{1}H-NMR and LS-MS analysis were realized for soluble samples.

ÖZET

EPOKSİ REÇİNELERİN AMİT FONKSİYONEL GRUPLARI İLE GERÇEKLEŞEN REAKSİYON MEKANİZMASININ İNCELENMESİ

Epoksi reçineler düşük soyulma, uygun yüksek sıcaklık performansı, kimyasal dayanıklılık ve çeşitli yüzeylere olan yapışma özellikleri nedeniyle birçok uygulamada kullanılmaktadır. Epoksi reçineler bu özelliklerini kürleşme reaksiyonu ile kazandığı belli seviyedeki çapraz bağlanma yoğunluğu ile sağlarlar. Kimyasal ve fiziksel özelliklerine bağlı olarak malzemeye karekteristik özellikler katan birçok sertleştirici mevcuttur. Elimizdeki bilgilere göre sertleştirici olarak amitler; amin, anhidrit ve asitler gibi diğer sertleştiricilere göre daha az kullanılmaktadır. İlginçtir ki, epoksitlerin genel olarak amitlerle reaksiyonu hakkında sadece birkaç rapor vardır. Dahası, amit ve epoksi reçineler ile gerçekleştirilen sınırlı sayıdaki bu çalışmalarda amit ve epoksi reçinelerin bu reaksiyonlara olan etkisi hakkındaki bilgi ise kürlenmiş ürün analizlerinin çözünürlük sorunu nedeni ile FTIR ile sınırlı kalmasından dolayı kısıtlıdır. Bu çalışmada çözünebilir madde sentezi ve onların çeşitli spektroskopik analizleri hedeflenmiş olup oluşan molekülün yapısı hakkındaki bu sonuçlara dayanarak muhtemel reaksiyon mekanizması hakkında fikir geliştirilmiştir. Ayrıca reaksiyonun uygun koşullarda gerçekleşmesi için sıcaklık ve ısıtma süresi belirlenmiştir. Tam çapraz bağlı yapı oluşumundan kaçınmak ve çözünürlüğü sağlamak için monomerik amit molekülleri kullanılmıştır. Aromatik ve alifatik yapı etkisini araştırmak için aromatik gurup içeren amit ve epoksi moleküllerinden de fadalanılmıştır. Ayrıca FTIR ve DSC'ye ek olarak, çözünürlüğü olan örneklerin ^{1}H-NMR ve LC-MS analizleri de gerçekleştirilmiştir.

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LIST OF ACRONYMS/ABBREVIATIONS

$CDCl_3$	Deuterated Chloroform
DCM	Dichloromethane
DGBEA	Bisphenol A diglycidyl ether
DMSO-d_6	Deuterated Dimethyl Sulfoxide
DSC	Differential Scanning Calorimetry
EPP	Bis (2,3-epoxypropyl)phthalate
EWW	Epoxide Equivalent Weight
EX-313	Glycerol Polyglycidyl ether
FTIR	Fouirer Fransform Infrared Spectroscopy
H	Hydrogen
M_n	Number average molecular weight
M_w	Weight average molecular weight
NMR	Nuclear Magnetic Resonance
T_g	Glass transition temperature
THF	Tetrahydrofuran

1. INTRODUCTION

1.1. Thermoplastic and Thermosetting Polymers

Linear and branched polymers are defined as thermoplastics and they can soften and harden depending on the temperature. This provides some advantage for thermoplastics, they easily undergo fabrication process such as injection, extrusion molding, etc. Thanks to secondary forces between chains such polymers are rigid at low temperature while they can flow at high temperature due to destruction of these forces [1].



Figure 1. 1. Schematic represantation of a)Linear, b)Branced, c)Cross-Linked, d)Network [2].

Termosetting polymers are obtained by the formation of a polymeric network through crosslinking reactions that take place between functional polymer chains. Generally thermosetting resins are first partially polymerized where they become a prepolymer, then they undergo curing reaction and form crosslinked networks. Examples of common commercial thermosetting resins are phenolic resins, amino resins, epoxy resins, the alkyds and unsaturated polyester resins [1].

Curing proccess can be defined as formation of crosslink networks between uncross-linked resins with the help of suitable chemistry [1].

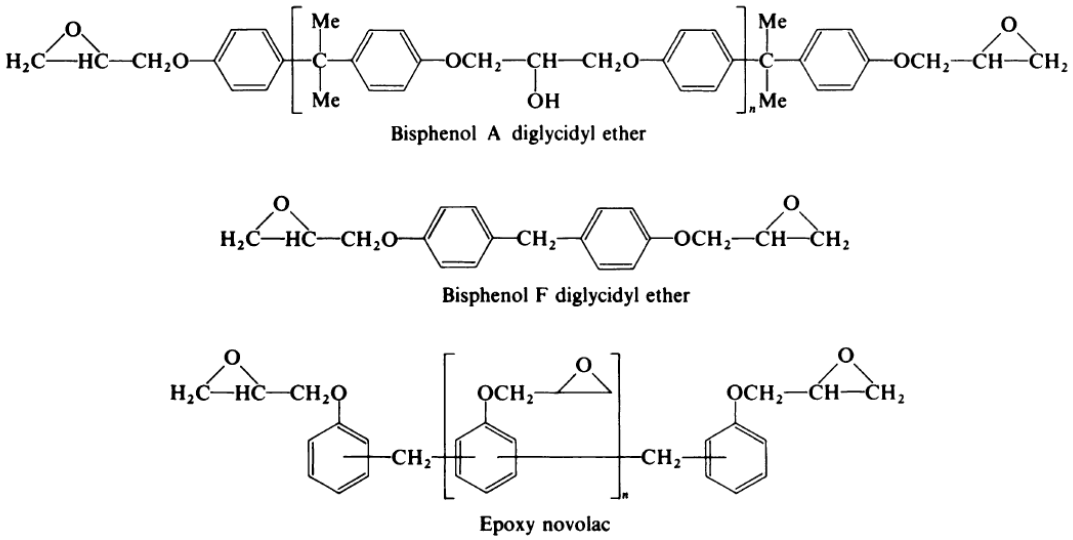


Figure 1. 2. Examples of thermosetting resins [3].

1.1.1. Epoxy Resin

Epoxy resins are an important class of polymeric materials which contain two or more oxirane ring or epoxy groups within their structure (Figure 1.4). Epoxy resins can undergo curing process *via* these epoxide groups by reacting with what is called hardeners. Similar to other thermosets, once cured, they form a cross-linked structure. They can be cured with a wide range of curing agents such as amines, anhydrides, thiols, etc. [4].

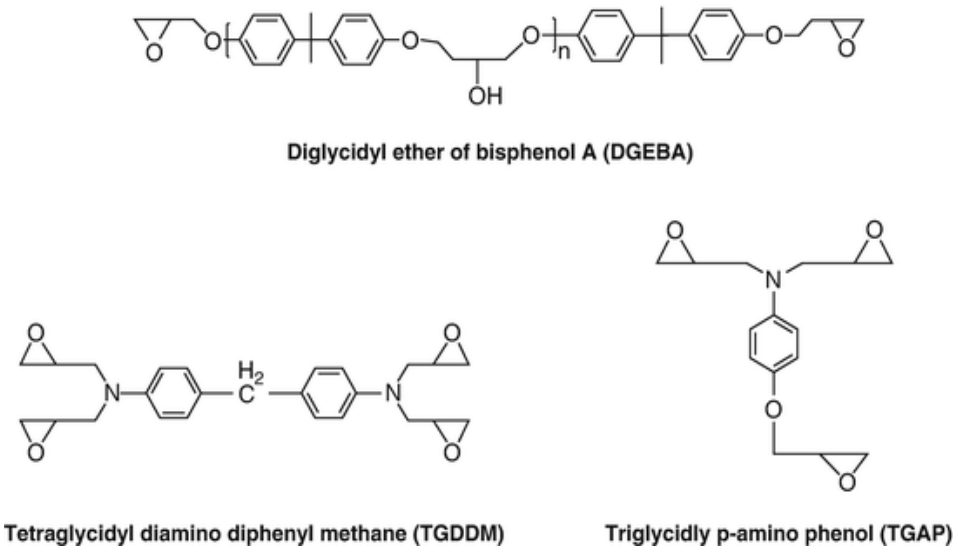


Figure 1. 3. Chemical structure of difunctional and multifunctional epoxies [5].

Depending on the synthesis process epoxy resins can be sorted as glycidyl epoxy and nonglycidyl epoxy resins. Glycidyl epoxy resins are produced by the condensation reaction between bisphenol A and epichlorohydrin (Figure 1.4.), while nonglycidyl epoxy resins are prepared by peroxidation reaction of olefinic double bonds [4].

Even though the first products that would now be called epoxy resins were synthesized as early as 1891[6,7], the first commercial attempt for epoxy resins were realized after the pioneering work carried out almost simultaneously and independently by Pierre Castan in Switzerland and by Sylvan Greenlee in the Unites States in the 1940s [4]. The earliest epoxy resins marketed were produced *via* reaction of bisphenol A with epichlorohydrin and today this is still the main route for the manufacturing of many epoxy resins (Figure 1.5.) [8].

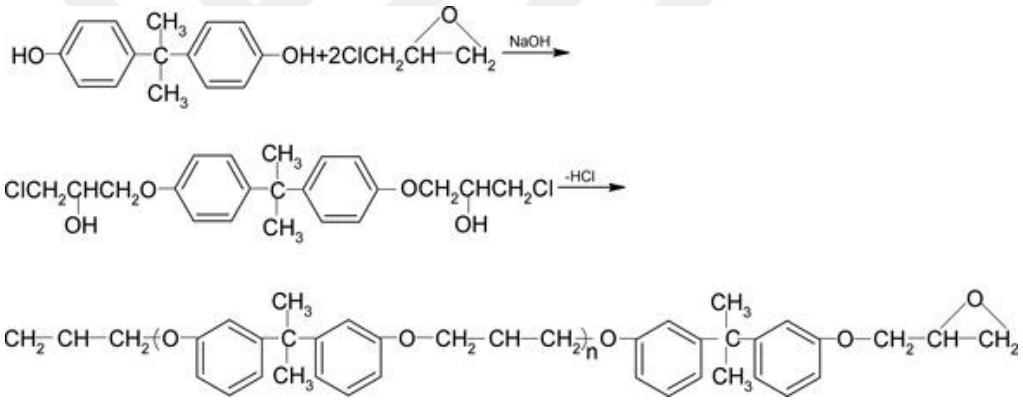


Figure 1. 4. General synthetic route for epoxy resins [9]

As thermosetting polymers, epoxy resins have a very large range of application area such as surface coating, casting, adhesives, encapsulation of electronic components, aerospace industry since they provide noteworthy characteristics, including [10]:

- ease-of-processing;
- low cost;
- very low shrinkage during and after cure;
- good mechanical strength;
- excellent adhesion to many substrates;
- wide range of curing conditions which can be adoptable to a given application [11][12].

Epoxide ring which is the major characteristic of the epoxy resins can be attacked by nucleophiles such as amine where epoxy pre-polymer forms a three-dimensional network. At the end of the curing process, there are several irreversible physical and chemical changes that take place. Final features of the cured material depend on the chemical structure and molecular weight of the epoxy resin and the curing agent. For example, cured resins containing aromatic rings or heterocyclic rings exhibit better thermal resistance than those constituted of aliphatic chains [12][13].

Despite being preferable thermosetting resins for the industry from many aspects, low toughness, poor weatherability and poor brittle resistance caused by the densely cross-linked structure are the main inconveniences of the epoxy resins [11][14]. Several attempts have been done to solve these problems. Some methods include introducing a new phase, usage of flexible curing agents and constituting interpenetrating networks with thermoplastics [13]. Moreover, designing epoxies with proper molecular structure and synthesis of flexible curing agents to toughen epoxy resins can be mentioned as other significant approaches [14].

All in all, it is apparently understood that choose of suitable starting reagents for curing process plays a key role to obtain a targeted result.

1.1.2. Epoxide Equivalent Weight (EWW)

Epoxide equivalent weight, EWW, is the weight of resin (in grams) that is considered to have one equivalent of epoxy group [15]. EEW is related to concentration of epoxy which is important to determine the amount of curing agents to cure epoxy resin [16].

Calculation of EEW of pure Bisphenol A diglycidyl ether (340g/mole) containing two active epoxy groups can be given as an example [15]:

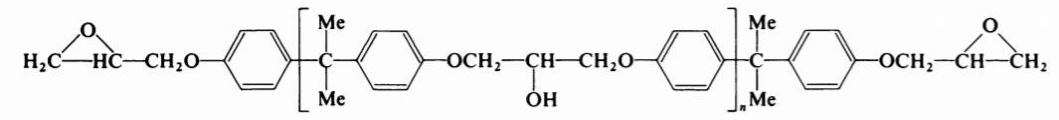


Figure 1. 5. Bisphenol A Diglycidyl Ether [3].

$$EWW = \frac{\text{Molecular Weight of DGEBA}}{\text{Number of Active Epoxide Group}}$$

$$EWW = \frac{340\ g/mol}{2equivalent/mol}$$

$$EWW = 170\ \text{g/equivalent}$$

1.2. Curing Chemistry of Epoxy Resins

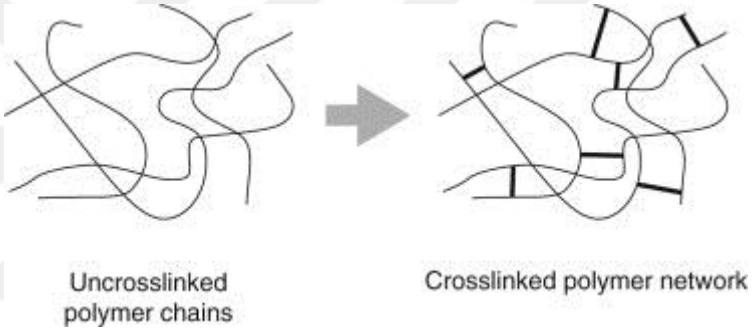


Figure 1. 6. Schematic representation of uncrosslinked and crosslinked polymer chains [17].

The epoxy resins can undergo the transformation called as curing or hardening with different curing agents or with themselves (through a catalyst), where they become mostly a solid crosslinked material (Figure 1.6.). Depending on the final properties targeted and manufacturing conditions, the selection of the resin and the curing agent can substantially vary. For example, curing may be fulfilled either at ambient temperature or with the application of an external energy sources like heat, ultraviolet or electron beam energy depending on the nature of the ingredients [16].

Epoxy curing reaction contains two primary types of mechanism:

1. Polyaddition Reaction
2. Homopolymerization Reaction

Both polyaddition and homopolymerization reactions give rise to increase in the molecular weight and crosslink density with no by-product. However, the curing reactions are exothermic and elevated temperature increases the rate of the reaction, in some cases bubble formation and thermal degradation are inevitable at high temperature curing process [16].

1.2.1. Polyaddition Reactions

Curing reaction between epoxy molecule and the other kinds of reactive molecule in the presence of a catalyst or without catalyst is known as an addition reaction. The epoxy resin molecules chemically bond to the curing agent and produce the new structure defined as heteropolymer [16].

Curing agent or hardener that reacts with epoxy resin and becomes a part of final cured product is an important ingredient of the formulation. Due to the incorporation into the cured material, the type and the concentration of the curing agent must be taken into account while formulating the desired product [16].

Polyamines, polyacids, polymercaptans and polyphenols can be assumed as the most commonly used curing agents [18] (Figure 1.7.). The stoichiometric amount of hardener makes up several percent to over 50 percent by weight of the epoxy formulation [16].

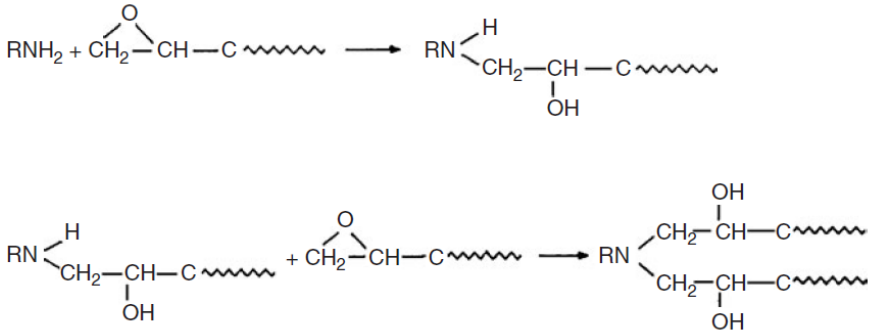


Figure 1. 7. Polyaddition reaction of epoxy resin [16].

However, in addition reaction, sometimes homopolymerization of the epoxide or other side reactions can be unavoidable. In order to prevent this problem, certain catalyst can be used [18].

1.2.2. Homopolymerization Reactions

In homopolymerization mechanism, the reaction happens between only the epoxy resins (Figure 1.8). In this case, the initiating compound, often referred as catalyst, only initiates the reaction and usually does not become a part of the polymeric network. So, the final properties of such cured materials only depend on the type of the resin [16].

Tertiary amines, Lewis acids and bases and dicyandiamides are commonly preferred as catalytic curing agents (Figure 1.9.). They are often employed in low concentrations (0 to 5 %-w/w) in a formulation [16].

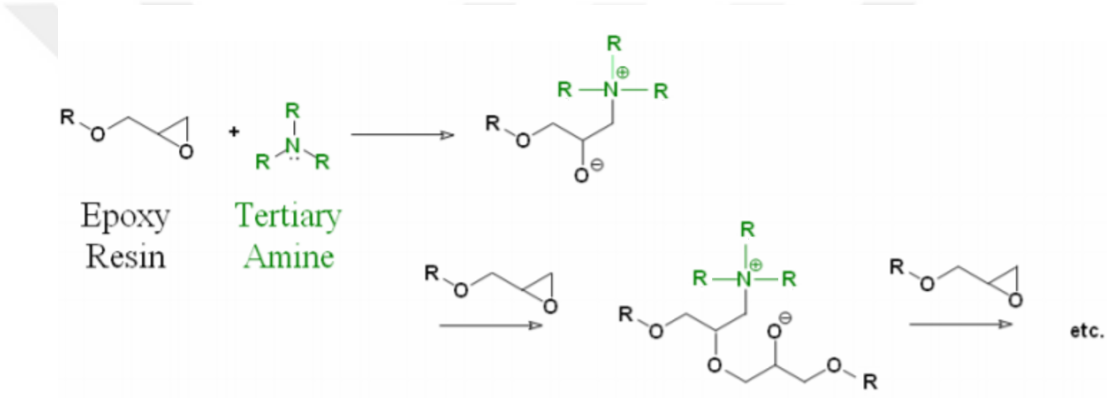


Figure 1. 8. Epoxy resin homopolymerization catalysed by tertiary amine [19].

In fact, the curing mechanism of epoxy resins with either curing agent or catalysts is much more complicated than it seems. Because there are many side reactions possible which take place at different rates and reaction sequences depending on the types of ingredients [16].

1.2.3. Epoxy Curing Kinetics

Despite providing adequate features, room temperature curing process cannot unfortunately produce high enough degree of crosslinking compared to curing at elevated temperatures. At high temperatures, epoxy resin and hardener are able to move better, and they have higher chance to react each other (Figure 1.9) [16].

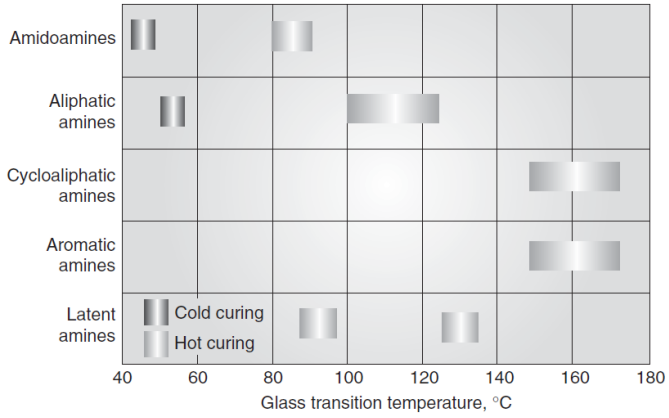


Figure 1. 9. Comparison of glass transition temperature of cured epoxy systems at room temperature and elevated temperature [16].

Also, there is another type of process defined as post curing where the epoxy resin and hardener first are reacted at room temperature and then at an elevated temperature. This kind of process ensures moderately higher crosslinking and thus a polymeric network with a higher Tg in some systems [16].

In case of incomplete reactions, there could be some reactive polar groups left that are able to uptake moisture and small molecules. As a consequence, long term durability of these materials may be influenced negatively. Therefore, curing should be arranged considering the desired properties at fully reacted conditions [16].

1.3. Curing Agents and Catalysts for Epoxy Resins

Curing agent, is one of the important element of the formulation and is responsible for initiating the chemical reaction and the formation of a crosslinked networks in epoxy resins [16]. The choice of curing agent depends on the desired properties and application. Polysulphide curing agents improve flexibility while rigid systems are obtained by aliphatic amines such as diethylene triamine (DETA), triethyl amine [11]. Epoxy resins may be cured with a wide variety of hardeners. These may be amines, carboxylic acids, anhydrides or amide-amines (Figure 1.10.) [20].

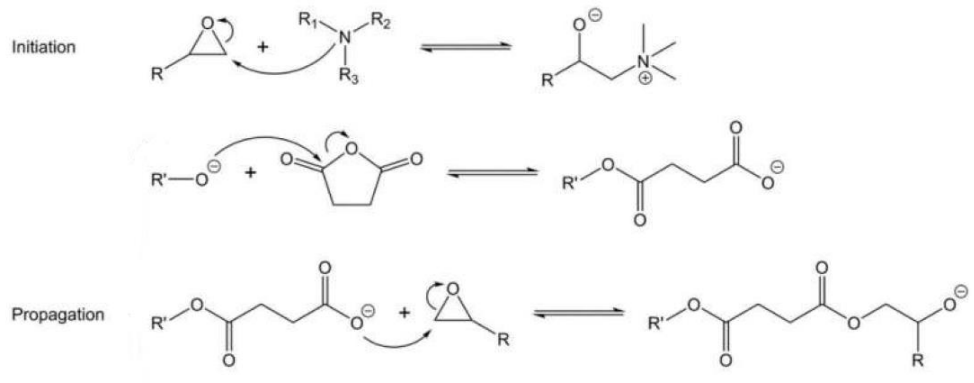


Figure 1. 10. Curing reaction mechanism of epoxide with anhydride initiated by tertiary amine [21].

Catalyts also react with epoxy resins. Different from the hardeners, they stay unchanged after curing reaction and only small amount of catalyst is enough to provide effective curing process. Tuning the curing agent concentration has an huge effect on curing as over- or undercatalysed resin gives rise to poor bond strength [16].

1.3.1. Polyamides as Hardeners

Polyamides are not preferred as a curing agent due to its low reactivity towards epoxides. A shown in Figure 1.11., polyamide hardener contains not only amide groups but also primary and secondary amine groups that participate in cross-linking reactions with the epoxy [8].

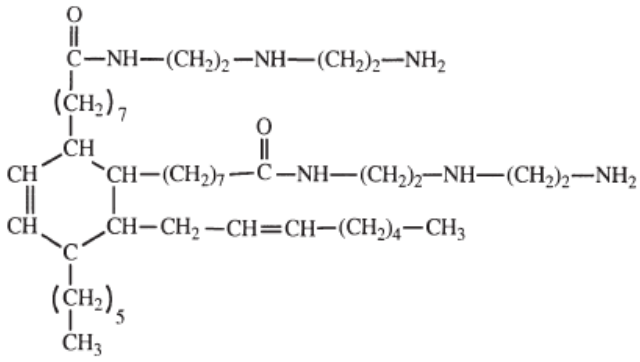


Figure 1. 11. Structure of a typical polyamide hardener [8].

Having relatively high molecular weight, the amide functional groups provide the flexibility to the cured structure. Polyamides are superior to other types of curing agents in

some ways like releasing low odors, providing good shear strength, thermal stability, environmental resistance, improved flexibility and longer pot life [16].

Even though, increasing amount of polyamide in cross-linked structure favors the flexibility, it lessens heat distortion temperature and chemical resistance [16].

Guo and Zhong studied cure kinetics of nylon/epoxy resin reactive blends and found that there were two type of reaction in the system. First of all, amide nitrogen acts as a nucleophile and attack to oxirane ring when the amide content is in excess (Figure 1.12) [22].

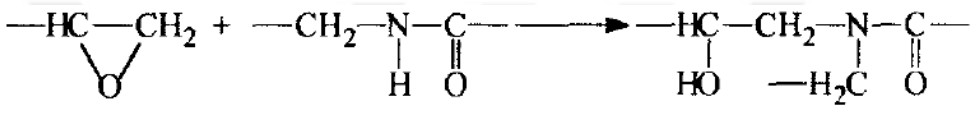


Figure 1. 12. Nucleophilic attack on oxirane ring by amide [22].

However, high epoxy concentration and high temperatures favors another mechanism which requires higher activation energy (Figure 1.13.) [22].



Figure 1. 13. Nucleophilic attack on oxirane ring by hydroxyl group [22].

In addition, Kim *and alias* reported the curing reaction based on nucleophilic attack on the oxirane ring by the amide nitrogen of the nylon-6 as shown Fig 1.14 [23].

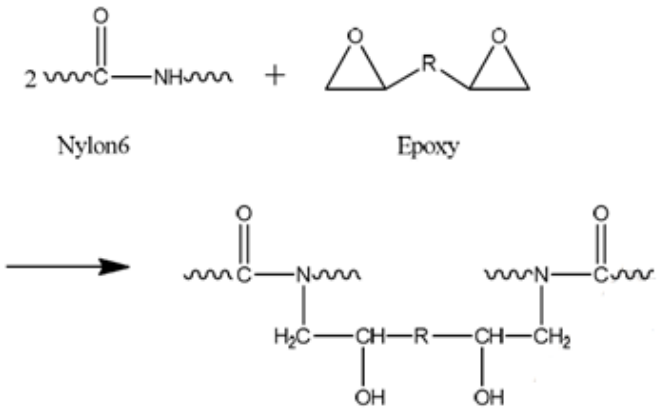


Figure 1. 14. Reaction mechanism of nylon6/epoxy [23].

There is another approach by Kamarova and his colleagues where amides react with oxirane ring and this mechanism was based on insertion reaction pathway (Fig 1.15) [24].

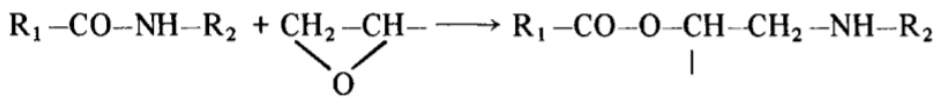


Figure 1. 15. Insertion reaction between amide and epoxy ring [24].

1.4. Parameters Influencing Resin Systems

1.4.1. Viscosity

Viscosity is a measure of the resistance to flow caused by chain entanglement, high intermolecular forces, the presence of reinforcing agents, and cross-links. Some functional groups that quite related to the flexibility affect viscosity of the polymer. For example, groups like methylene and ethylene oxides, dimethyl siloxanes give rise to chain motion, while stiffening groups such as 1,4-phenylene, carboxyl and sulfone decrease flexibility [16]. Moreover, temperature, molecular weight, glass transition temperature affects the viscosity of the resin as well. Higher molecular weight combined with elevated glass transition temperature will increase the melt viscosity of the polymer [25].

1.4.2. Molecular Weight

There are two important parameters of average molecular of a resin. One of them is the number of average molecular weight (Mn) which is responsible for physical properties and the other one is the mass average molecular weight (Mw) that affects resin melt viscosity [25].

1.4.3. Stoichiometry

The ratio of epoxy resin and curing agent have a huge effect on the characteristic of final product. While low degrees of crosslinking are needed for the toughness, highly cross-linked epoxy resins have better thermal resistance [16]. However, too high degrees of crosslinking results in poor crack and impact resistance [13].Calculating the stoichiometric

mixing ratio, functionality of the epoxy resin (EWW) and the curing agents must be taking into account [16].

There is a calculation for determining the necessary stoichiometric quantity of amine curing agent [26]:

$$Equivalent\ Weight\ of\ Amine = \frac{\text{Molecular Weight of Amine}}{\text{Number of active Hydrogen Atoms of Amine}}$$

Finally, stoichiometric ratio of amine that cure the epoxy resin is calculated by:

$$= \frac{\text{Equivalent Weight of Amine}}{\text{Equivalent Weight of Epoxy}}\ x\ 100$$

1.4.4. Effect of Crosslink Density

Crosslink density is related to the number of crosslink points per unit volume. The crosslink density has a huge effect on both physical and chemical properties of the cured product. The number of reactive sites and their locations and chain mobility between the functional sites involved in reactions is linked to the crosslink density (Figure 1.16.) [16].

Polymers that have a high crosslink density, are infusible, insoluble and dimensionally stable under high load while polymers possessing lower density resist better to stress, impact and cold [16].

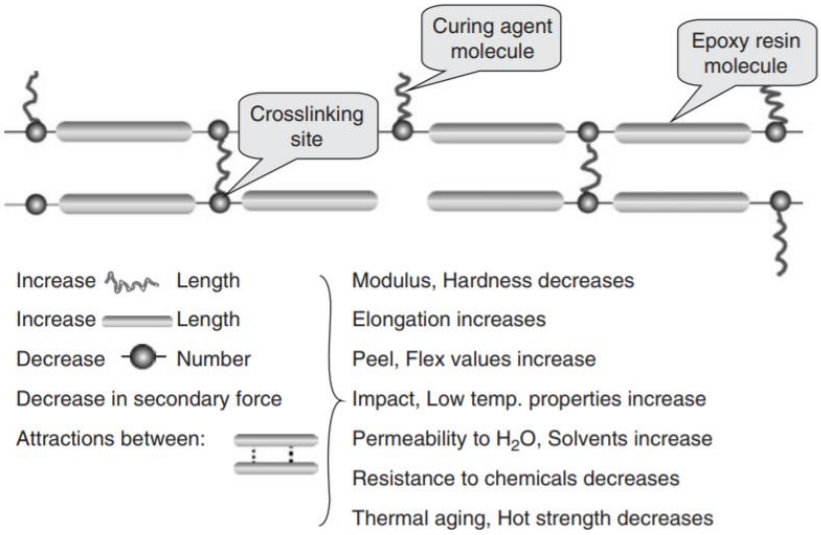


Figure 1. 16. Physical properties of epoxy cured molecule [16].

1.4.5. Glass Transition Temperature

Glass transition temperature is the temperature range at which local or segmental mobility begins. The presence of flexible main chain groups, nonpolar groups, dissymmetry causes lower Tg; on the other hand, existence of bulky pendent groups, chain symmetry, polar groups, crosslinking and formation of the macromolecules and polymer networks increase the Tg. The importance of the Tg is that it gives information about polymers' chemical and physical features. Amorphous plastics perform best below Tg but elastomers must be used above the brittle point, Tg, or they will act as a glass and be brittle and break when bent [16][20].

1.4.6. Structure of Resin

The structure of the epoxy resin is responsible for its physical and chemical properties. For example, while the aliphatic parts between ether linkages provide flexibility, aromatic rings are responsible for high heat and chemical resistance. Moreover, secondary hydroxyl groups existing along the structure contribute to adhesion forces. Depending on the molecular weight and chemistry, resins can be low-viscosity liquids or hard solids [16].

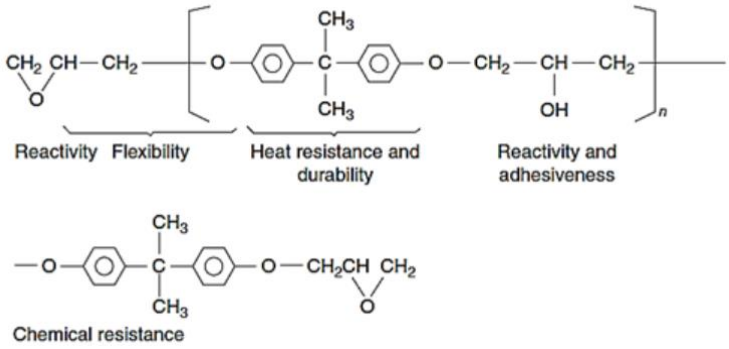


Figure 1. 17. Relationship between structure and characteristics [16].

2. AIM OF THE STUDY

The aim of this study is to investigate the reaction between epoxide and amide functional groups. According to the literature, these reactions should follow either an insertion/rearrangement or addition mechanism. However, these studies were carried out with polymeric systems and samples were mostly analyzed by FTIR. In this study, further structure analysis with 1H-NMR was aimed via synthesis of soluble small molecules. Glycerol polyglycidyl ether (EX-313) as an aliphatic epoxy resin and diglycidyl phthalate (bis (2,3-epoxypropyl)phthalate, EPP) as an aromatic ester epoxide were used. Moreover, in order to obtain soluble products for 1H-NMR and LC-MS analysis and avoid forming fully crosslinked structure, acetamide and benzamide as monofunctional small molecule amides were preferred. The products were analyzed by FTIR, 1H-NMR, LC-MS and DSC analysis whenever it was possible.

3. EXPERIMENTAL

3.1. Methods and Materials

Bis(2,3-epoxypropyl)phthalate (EPP) and Glycerol polyglycidyl ether (Ex-313) (EWW: 141g/eq) were obtained from KORDSA. Acetamide, benzoyl chloride and 37% ammonia were purchased from Merck, Aldrich. Polyacrylamide was obtained from Uras Kimya.

3.2. Instrumentation

Exstar SII DSC 7020 instrument was used for thermal analysis. As a method starting temperature was set to -20℃ and maximum temperature was 130℃. The rate was set to 20℃/min. Varian Gemini 400 MHz spectrometer was used in $CDCl_3$, DMSO-d_6 for ^{1}H-NMR analysis. Nicolet 380 FT-IR spectrometer was used for analysis. Waters Acquity Arc with QDa Detector was used for LC-MS measurements. Samples were prepared by dissolving 2 mg of samples in 2 mL acetonitrile.

3.3. Experiments

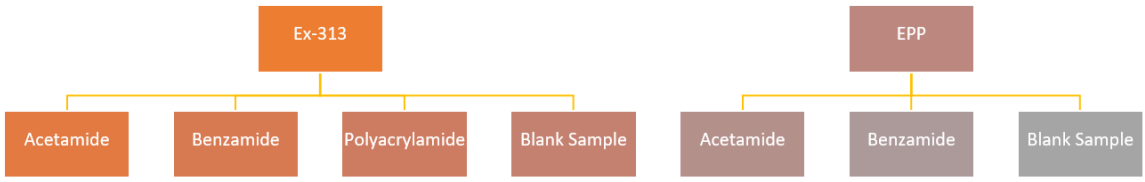


Figure 3. 1. General scheme of samples in this study.

As shown in Figure 3.1. Ex-313 and EPP underwent reaction between acetamide and benzamide at different temperatures in oven and glycerol bath and samples were taken periodically to check the reaction. To investigate self-reaction of epoxide monomers, EPP and Ex-313 were heated alone as a blank. Different from EPP, Ex-313 and polyacrylamide mixture were studied. All prepared samples and reaction conditions were given below.

3.3.1. Synthesis of Benzamide

16 mL of 37% NH3 and 25 mL of THF were placed in a 250 mL round bottom flask in ice bath and stirred. Then, 1.1mL benzoyl chloride (0.947 mmole) was added in small portions to the solution. The obtained white precipitate was filtered, washed with cold water, and recrystallized from hot water. The peaks observed at 3361cm-1, 3165cm-1, 1654cm-1, 1622cm-1 corresponds to the N-H symmetric and asymmetric stretching, C=O stretching (amide I band) and NH2 bending (amide II band), respectively. The FTIR data is consistent with literature [27].

3.3.2. Blank Experiments Carried Out with the Epoxides

3.3.2.1. Ex-313 under Curing Conditions. 4 g of Ex-313 was placed in a vial, stirred continuously and heated from 25℃ up to 175℃ in 4 hours.

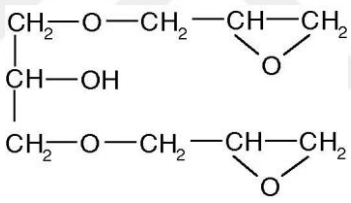


Figure 3. 2. Glycerol polyglycidyl ether (Ex-313).

3.3.2.2. EPP under Curing Conditions. 4 g of EPP was placed in a vial, stirred continuously and heated from 25℃ up to 175℃ in 4 hours.

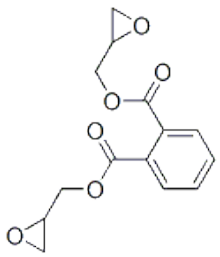


Figure 3. 3. Diglycidyl Phthalate (EPP).

3.3.3. Studies on the Reaction of Ex-313 with Various Amides

3.3.3.1. Reaction with Polyacrylamide. Ex-313 was mixed with polyacrylamide in 1:1 mole ratio (0.0281 mole, 3.967g Ex313; 0.0281 mole, 5.01g PAA) in aluminum pan. The mixture was heated in oven at different temperatures. Samples were taken periodically to check the process by FTIR.

3.3.3.2. Reaction with Acetamide. Ex-313 was mixed with acetamide in 1:1 mole ratio (0.0489 mole, 6.89g EX-313; 0.0489 mole, 2.89g AA) in an aluminum pan. The pans were put in the oven and heat at different temperatures. Samples were taken periodically to check the process by FTIR.

Additionally, EX-313 and Acetamide was mixed in a vial with same mole ratio, continuously stirred and heated on hot plate from 25℃ up to 175℃ in 4 hours. Then the sample was cooled to room temperature and 5 mL of DCM was added in order to disperse the sample and stirred. In order to dissolve the sample, some solvents were used like chloroform, THF, DMSO, N-Methyl pyrrolidone and DCM. Although none of these solvents provided efficiently dissolution, the sample dispersed in DCM better. Then, the mixture was extracted with 5 mL of distilled water to remove residual acetamide and Ex-313. After extraction, organic phase was centrifuged and filtered to collect gel-like particles and DCM was evaporated in vacuum oven.

3.3.3.3. Reaction with Benzamide. Ex-313 was mixed with benzamide in 1:1 mole ratio (0.0165 mole, 2.33g Ex313; 0.0165 mole, 2.01g BA), continuously stirred and heated at 25℃ from to 175℃ in 4 hours under sealed condition. Then the sample was cooled to room temperature and 5 mL of DCM was added in order to dissolve the sample and stirred. Then, the mixture was extracted with 5 ml of distilled water to remove residual benzamide and Ex-313. After extraction, organic phase was separated, and DCM was evaporated with rotary evaporator.

3.3.4. Studies on the Reaction of EPP with Various Amides

3.3.4.1. Reaction with Acetamide. EPP was mixed with acetamide in 1:1 mole ratio (0.053 mole, 15.016 g EPP; 0.053 mole, 3.184g AA) in an aluminum pan and stirred. The pan was put in oven and heat at different temperatures. Samples were taken periodically to check the

process by FTIR. Furthermore, one more sample was studied with the same process but this time heated directly at 170 ℃ for 20 minutes to investigate the initial temperature effect.

Additionally, EPP and acetamide mixture with the same mole ratio as previous samples was placed in a vial, continuously stirred and heated from 25℃ up to 175℃ in 4 hours under sealed condition. Then the sample was cooled to room temperature and 10 mL of DCM was added in order to dissolve the sample and stirred. Then, the mixture was extracted with 10 mL of distilled water to remove residual acetamide and EPP. After extraction, organic phase was separated, and DCM was evaporated in rotary evaporator.

3.3.4.2. Reaction with Benzamide. EPP was mixed with Benzamide in 1:1 mole ratio (0.016 mole, 4.599 g EPP; 0.016 mole, 2.03g BA) in a vial, continuously stirred and heated from 25℃ up to 170℃ in 4 hours under sealed condition.

4. RESULTS AND DISCUSSION

In the present manuscript, in the most general sense, the reaction between epoxy and amide functional groups was investigated. The work carried out can be divided into two main stages:

i. To begin with, the epoxy starting materials, glycerol polyglycidyl ether (Ex-313 Figure 4. 1.) and bis (2,3-epoxypropyl)phthalate (EPP, Figure 4. 2.) were heated, as blank samples, to check whether or not these epoxies would undergo any reaction on their own under the target curing conditions.
ii. Next, reactions of the epoxides with various amides were studied. Two classes of amides were investigated; polymeric amides (polyacrylamides), and monofunctional small molecule amides, acetamide and benzamide. As will be presented later, the polymeric amides, however, were abandoned at the very early stages of this study.

Reactions were carried out both in aluminum pans at open air in the oven, and in sealed vials in oil bath. Different temperature rates and time scale were tested to find the best reaction conditions. The results will be presented in the following sections following the above order.

4.1. Blank Experiments Carried out with The Epoxides

4.1.1. EX-313 under the Curing Conditions

These experiments were carried out to check if any structural change might happen in the epoxides under the curing conditions that would be applied. The most suspected reaction was the homopoymerization of the epoxides through ring opening reactions. Hence, 4.0 g of Ex-313 was heated at 170℃ for 4 hours. No structural change on the Ex-313 was observed based on the comparison of FTIR spectra of the samples taken before and after curing (Figure 4. 1).

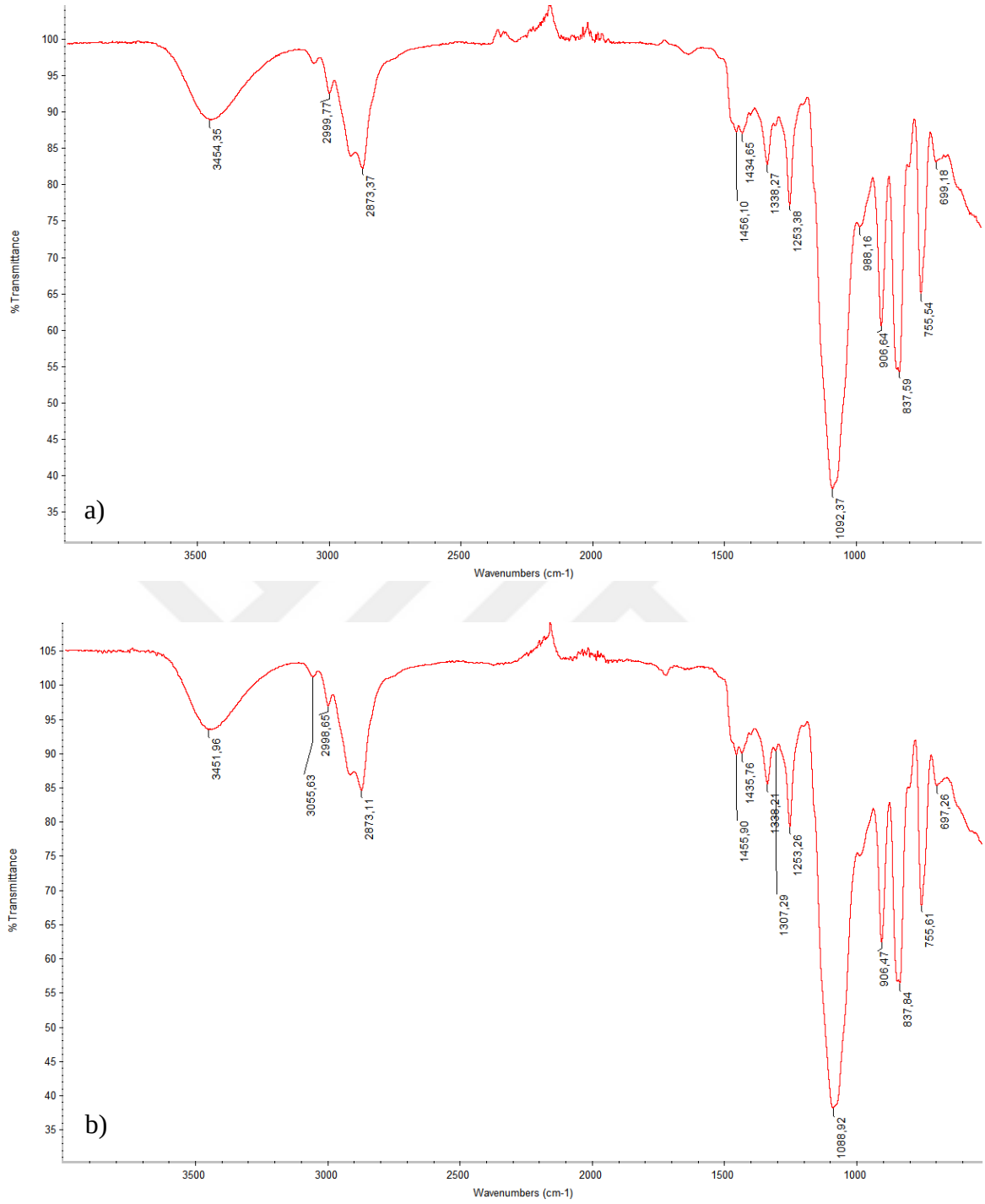


Figure 4. 1. FTIR Spectra of a) Ex-313 and b) blank sample of Ex-313.

4.1.2. EPP under the Curing Conditions

4.0 g of EPP was heated under the same conditions (170 ℃ in 4 hours) envisioned for the curing of EPP to investigate whether or not there was a self-crosslinking of between

EPP. Although the blank sample became slightly more viscous than EPP, no significant change was detected in the IR spectrum of EPP (Figure 4.2).

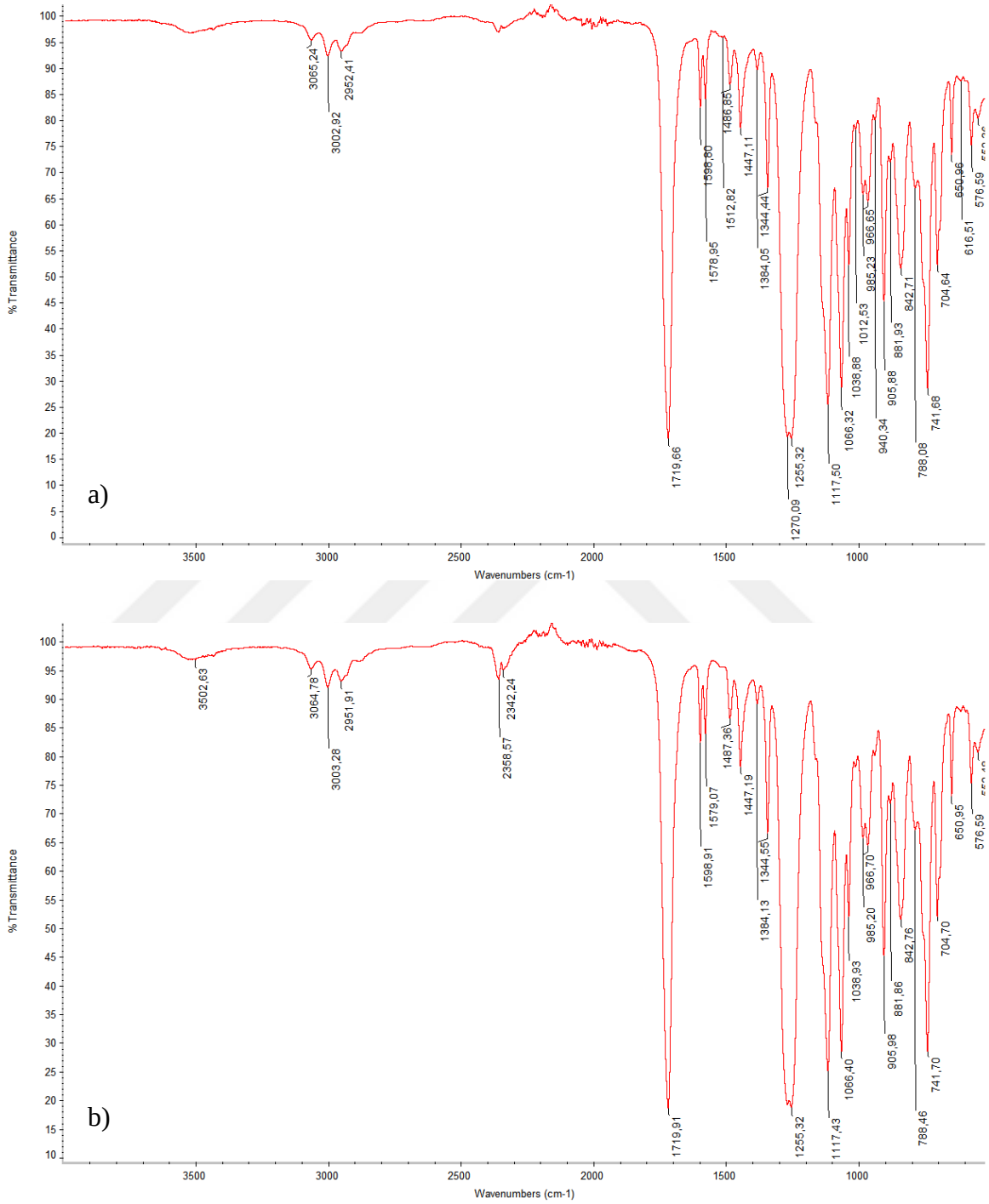


Figure 4. 2. FTIR spectra of a) EPP and b) blank sample of EPP.

As a result, we concluded that no significant reaction was taking place with Ex-313 or EPP at the curing conditions chosen, alone. Therefore, it is safe to state that any change on the epoxy resins in the presence of the amide groups will be due to the amides.

4.2. Studies on the Reaction of EX-313 with Various Amides

4.2.1. Reaction with Polyacrylamide

Ex-313 was first reacted with polyacrylamide to form a crosslinked structure. The reason for the choice of the polyacrylamide was to mimic a reaction that was successfully used in the synthesis of new rubber to NYLON 6.6 adhesives [28]. In the reference patents polyacrylic acid is used to crosslink Ex-313 through an addition reaction. It was thought that replacing the carboxylic functionality with the primary amide would lead to better adhesive properties since both NYLON 6.6 and the reaction product of the primary amide with the epoxy should in principle contain secondary amide functionalities that should form additional hydrogen bonding.

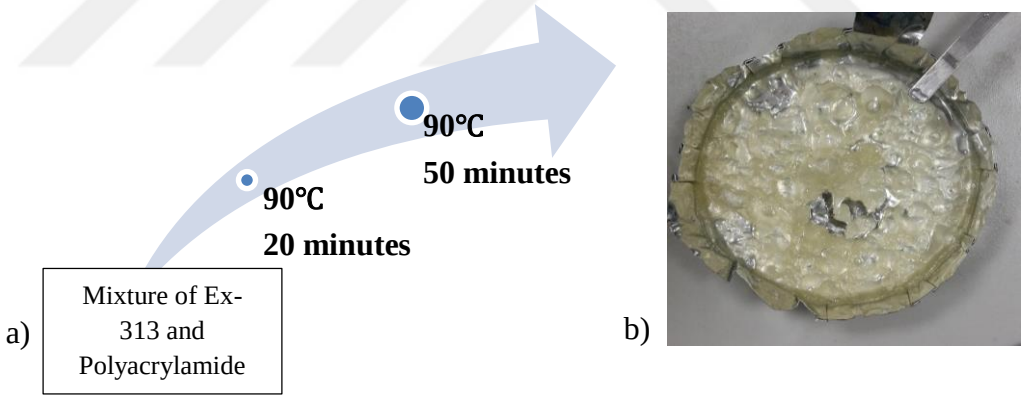


Figure 4. 3. a) Heating process of oven sample, b) Sample after heating process.

Initially, Ex-313 was mixed with polyacrylamide in 1:1 mole ratio (based on epoxy and amide functionalities) in open aluminum pan. Samples were heated at 90 ℃ for 20 minutes and first sample was taken then the remaining sample was heated for another 50 minutes (Figure 4.3.).

We observed that polyacrylamide and Ex-313 during the heating process phase separated from each other where the latter formed an oily layer (Figure 4.3.) on the top of the solidified polyacrylamide. Thus, the reaction between polyacrylamide and EX-313 became very unlikely, yet the analyses very carried on the samples. The so-called product

had very rough and heterogeneous surface which rendered to take a representative FTIR sample almost impossible. However, some analyses were carried out to detect some hint of reaction between the two components.

In the 20 minute sample, unreacted amide dominated the IR spectrum as understood from the amide peaks at 3339 cm^{-1}, 3193 cm^{-1} (primary N-H stretching), 1654 cm^{-1} (amide C=O) and 1610 cm^{-1} (N-H vibration) (Figure 4.5.).

However, in the 50-minute sample, despite the noisy baseline, some new intense peaks could be detected. Peak at 1735cm^{-1} seemed to indicate the formation of new aliphatic esters. However, other alternative and possible functional group with similar absorption peaks was the imides. In literature it is said that polyacrylamides can form imide. It is stated that, although at room temperature hydrolysis of polyacrylamide is not possible without hydrolyzing agents, elevated temperatures (93°C) can give rise to hydrolysis at appreciable rates [28]. Polyacrylamide then accordingly may be able to give self-crosslinking *via* either intra- or intermolecular imidization by reacting with the residual carboxylic acids formed upon hydrolysis as shown in Figure 4. 4. [30]. However, the latter reaction is not expected at the experimental temperatures used in our case. Therefore, we believe that these peaks seem to indicate some residual ester formation. The possible mechanism of this transformation will be discussed in Section 4.2.2.

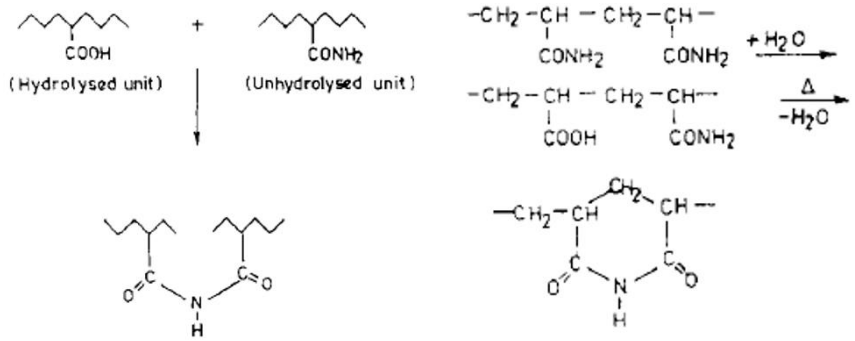


Figure 4. 4. Self-Crosslinking of Polyacrylamide [31].

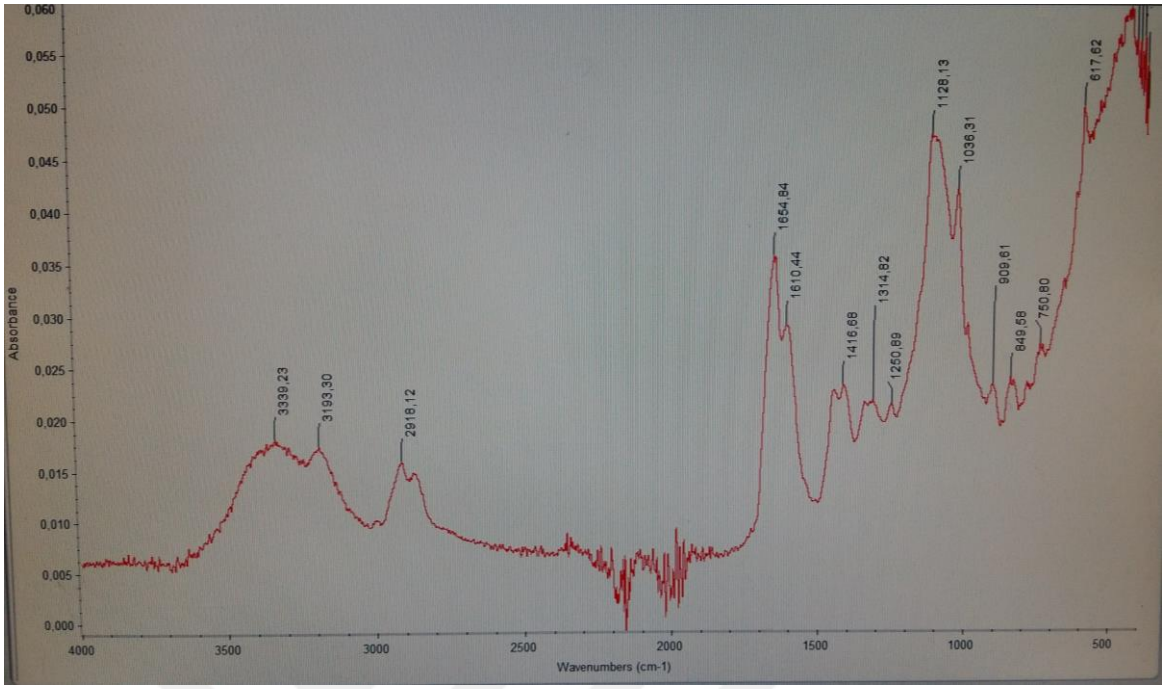


Figure 4. 5. Polyacrylamide Ex-313 90℃ for 20 minutes.

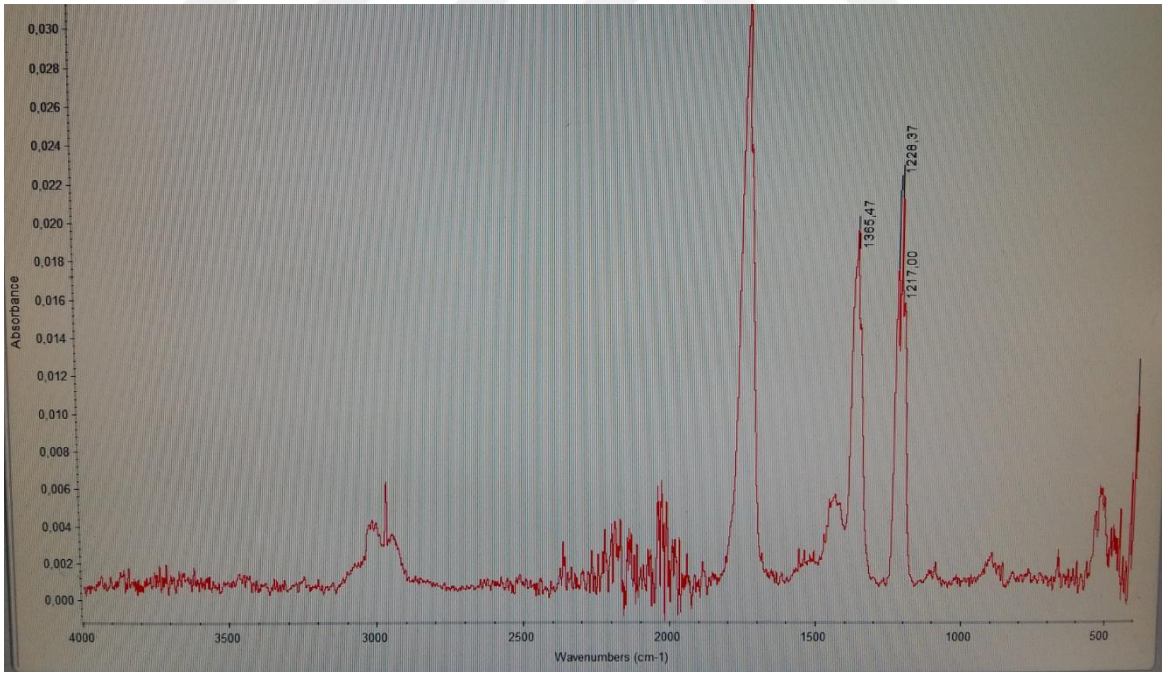


Figure 4. 6. FTIR Spectrum of Sample of Ex-313 and polyacrylamide after heating process.

Thus, due to early phase separation of the components, no significant homogenous reaction could be achieved. This was most probably due to the very polar nature and coagulative properties of the polyacrylamide [31]. Further investigation with

polyacrylamide was abandoned since the system was found to be incompatible with any potential industrial application. However, the possibility of some ester formation from the reaction of epoxides with the amide was found interesting. Therefore, further investigation on this reaction was envisaged. This time monofunctional amides rather than multifunctional polyacrylamide, were chosen as model compounds, for potentially better solubility and ease of analyses.

4.2.2. Reaction with Acetamide

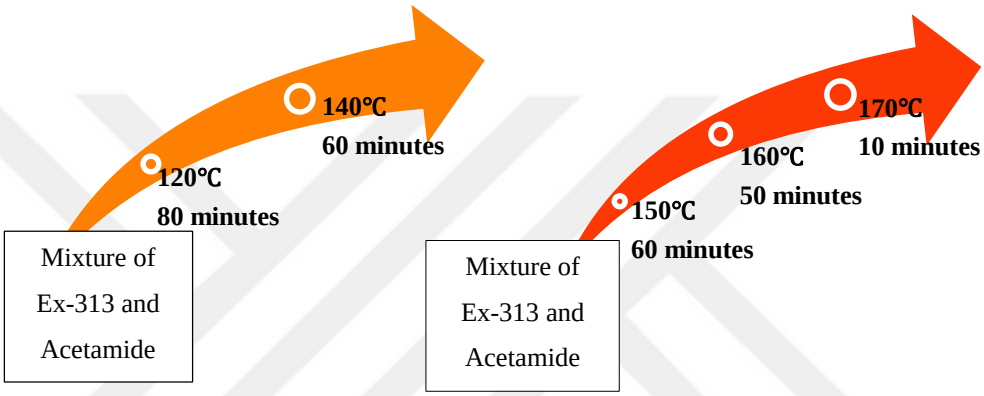


Figure 4. 7. Heating process of Ex-313 and acetamide mixtures at oven.

Ex-313 and acetamide were mixed in 1:1 mole ratio and heated at different temperatures in the oven. Two main heating processes were used. In the first process, the mixture was first heated to 120℃, left for 80 minutes, then the temperature was raised to 140℃ for 60 minutes. In the second process, samples were prepared in the same manner but this time the initial temperature was set to 150 ℃ (60 min), then it was first raised to 160℃ (50 min), and finally to 170℃ (10 minutes) (Figure 4.7). Samples were taken for FTIR analysis at the end of each temperature plateau (Figure 4.9 and Figure 4.10).

In the early stages of the experiment, despite its high boiling point (220℃), acetamide was found to sublime partially during the process. Since in the experiments carried out, a special attention was paid to stoichiometric balance of the components, this was a problem. As a solution, new set of experiment was carried out in sealed reactions vessels, stirring was introduced (for faster reaction prior to potential phase change) and samples were gradually heated to 170℃ in 4 hours (Figure 4.8).

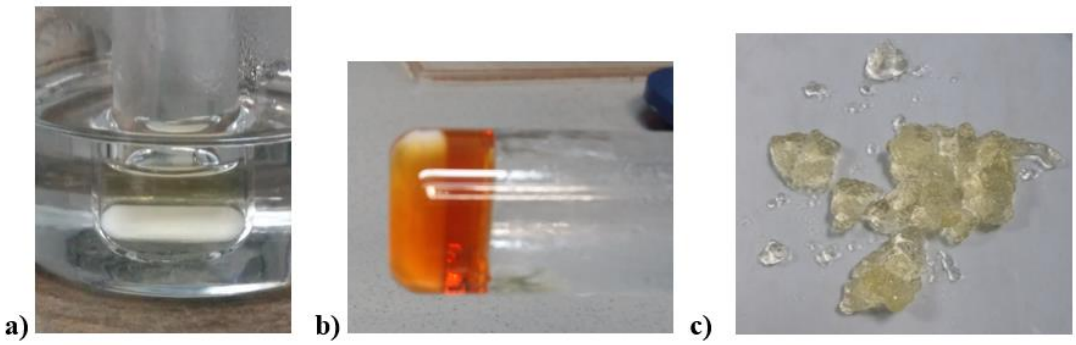


Figure 4. 8. Photos of Ex-313 and acetamide mixture in sealed condition; a) During heating, b) After heating (impure sample), c) After purification.

According to FTIR results (see Figure 4.9, 4.10, 4.11), a new absorption peak at 1735 cm^{-1} corresponding potentially to aliphatic ester C=O band was observed in all open and sealed samples. Also, there is a remarkable decrease in amide band I at 1668cm^{-1} corresponding to amide C=O, and amide band II at 1616cm^{-1} corresponding to N-H bending. In addition, primary amide N-H stretching peaks at 3350 cm^{-1} and 3411 cm^{-1} were almost vanished. The residual amide bands in spectra show the existence of little amount of unreacted acetamide. Although, the decrease in amide peaks in open system can be attributed to the sublimation of acetamide, the decreases observed in sealed reactions show that the concentration of the amide is reduced by some reaction.

When samples taken from the open and sealed reaction mixtures are compared significant differences were observed. In the open samples, there is almost no decrease in the oxirane ring stretching peaks at 859cm^{-1} and 907cm^{-1}. However, in the FTIR spectra of the sealed sample, only a small peak at 853cm^{-1} is observed. While in sealed sample spectra there is an increase in the intensity of OH peak at 3372 cm^{-1} which is caused by oxirane ring opening, this peak stayed almost same throughout the proses of in open samples.

Thus the results from the sealed systems indicate a reaction between the epoxide and amide functionalities. As shown in Figure 4.11. the reaction seem to undergo an insertion/ rearrangement type of reaction which may be responsible for the formation of ester group as evidenced by the peak at 1732 cm^{-1}. A potential mechanism for the formation of ester together with amine is proposed in Figure 4.12 which may happen through intermolecular or intramolecular nucleophilic attack of the amide to the epoxide. The expected addition reaction of amide to oxirane group according to the proposed mechanism is still happening

but it is only an intermediate reaction that carries on to the formation of esters. The FTIR results where no shift to lower frequency in the amide band I and amide band II is observed strengthen this idea (Figure 4.11).

T_g value of the closed sample was measured as 47.9 ℃ and it is more viscous than both EX-313 and corresponding open samples. Considering the FTIR results, it can be said that closed reaction medium results in better yield. However, no suitable solvent to dissolve samples was found and therefore detailed analysis could not be done by NMR. But this reaction process resulted in new type of molecule whose solubility behaviour was different than the starting materials.

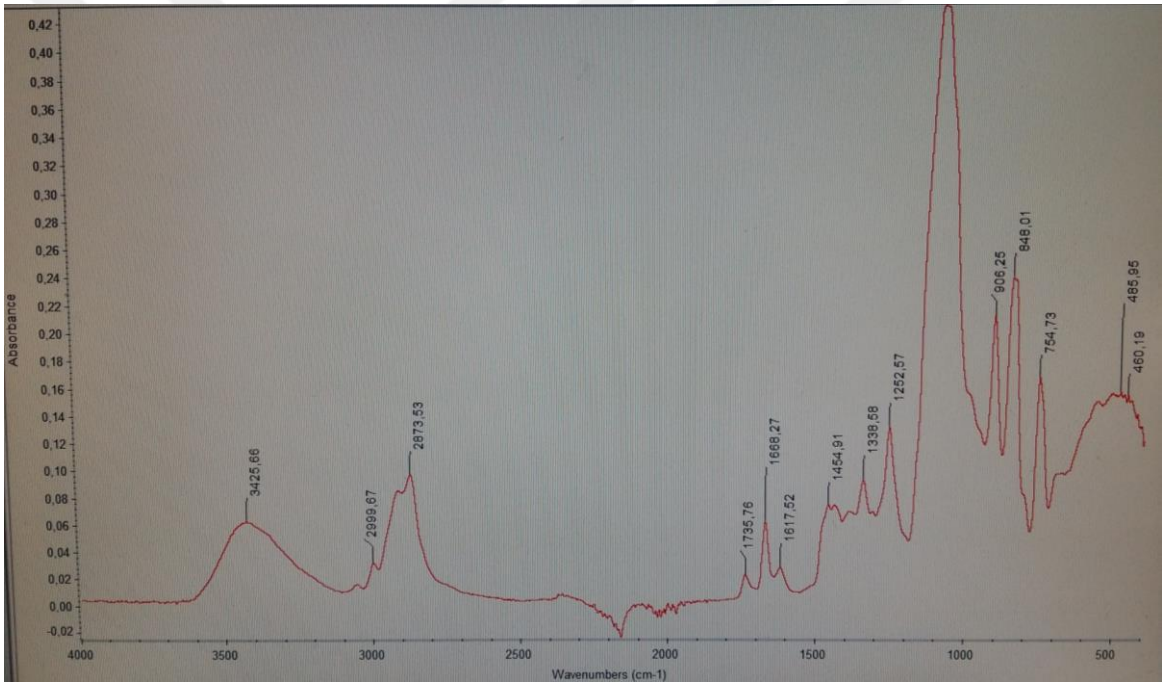


Figure 4. 9. FTIR Spectrum of mixture of Ex-313 and acetamide heated at 120℃ for 80 minutes.

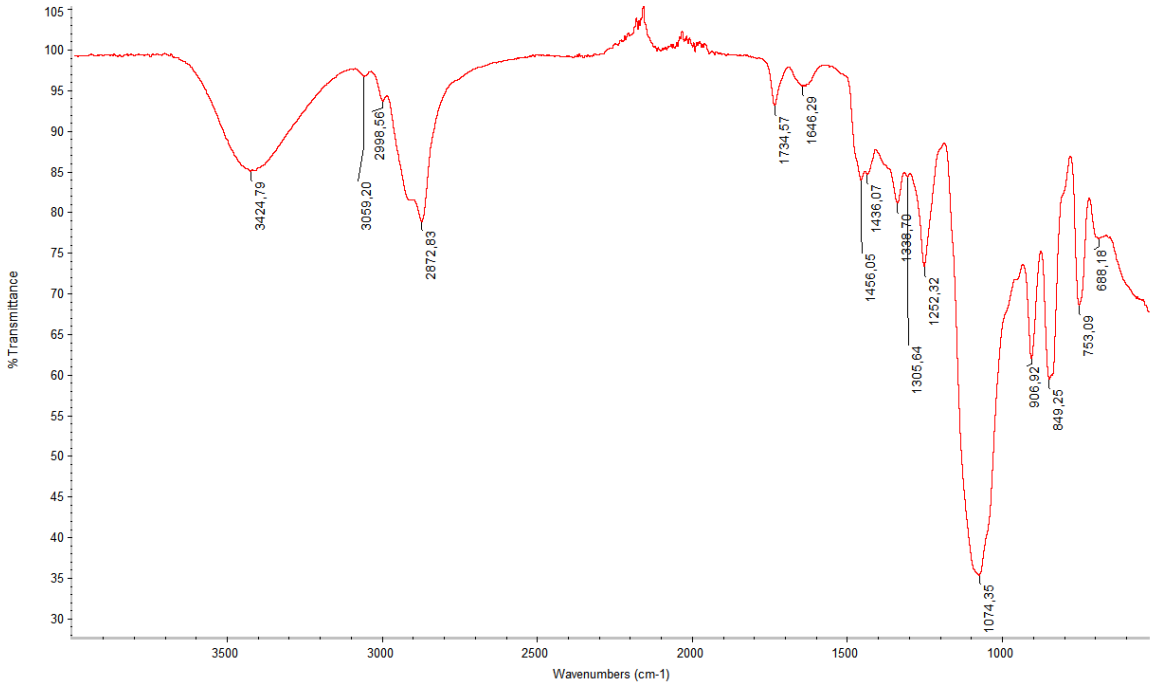


Figure 4. 10. FTIR Spectrum of final control sample of Ex-313 and acetamide mixture heated at 170℃ for 10 minutes.

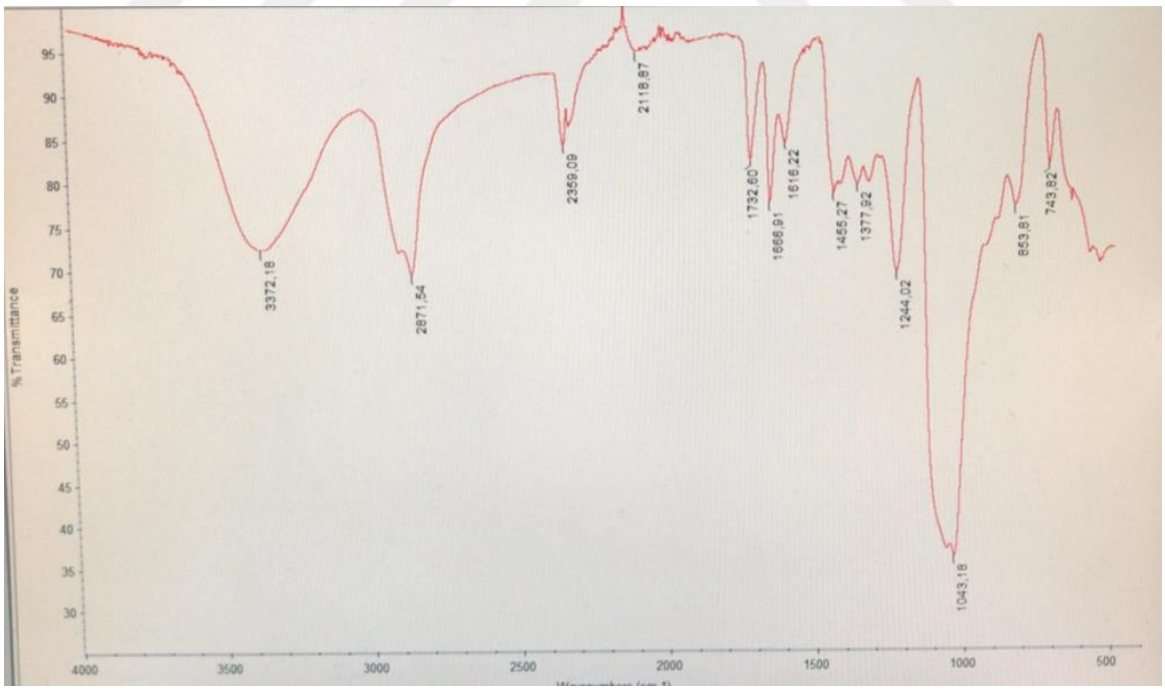


Figure 4. 11. FTIR Spectrum of final control sample of Ex-313 and acetamide mixture which heated at sealed condition.

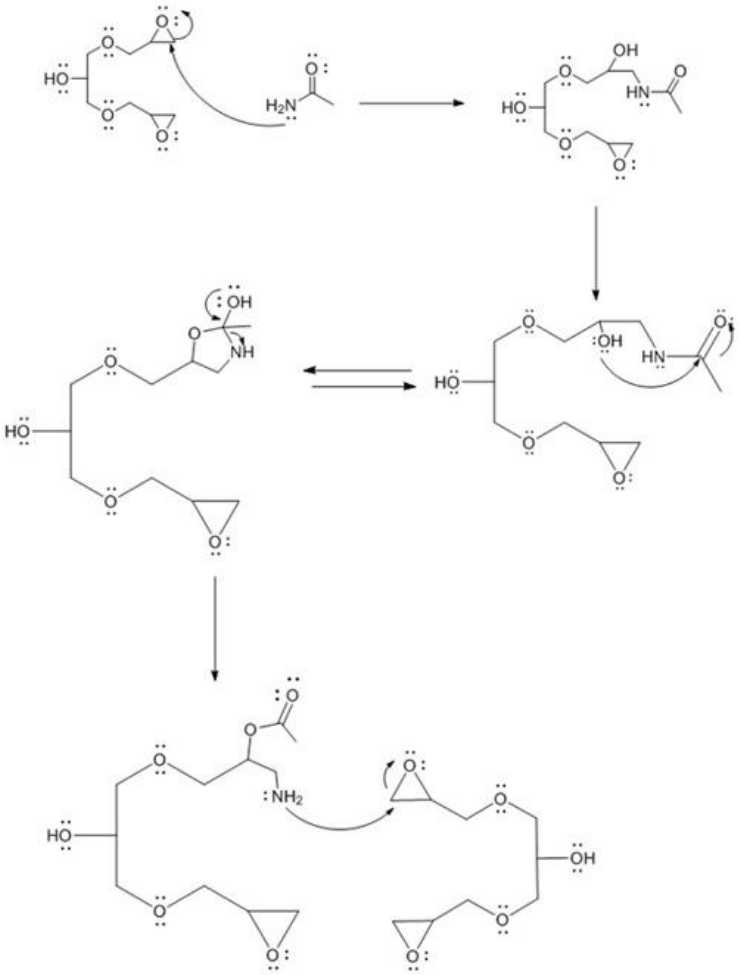


Figure 4. 12. Probable reaction pathway based on rearrangement reaction mechanism.

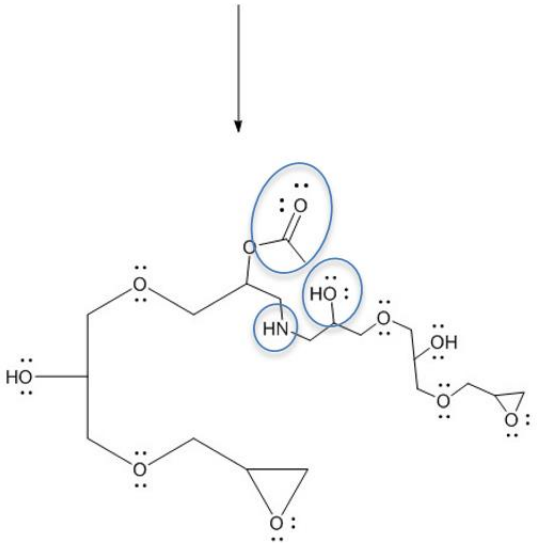


Figure 4. 13. Probable reaction pathway based on rearrangement reaction mechanism (Continued).

4.2.3. Reaction with Benzamide

Ex-313 and benzamide were mixed in 1:1 mole ratio, continuously stirred and heated from 25℃ up to 175℃ in 4 hours. The resulting material was dissolved in DCM and the solution was extracted. During the extraction there was an intermediate phase between the organic and water phases. This layer was removed and studied for dissolution in chloroform, THF and N-methyl pyrrolidone but none of these solvents dissolved the samples. However, its IR spectrum was taken (Figure 4.14).

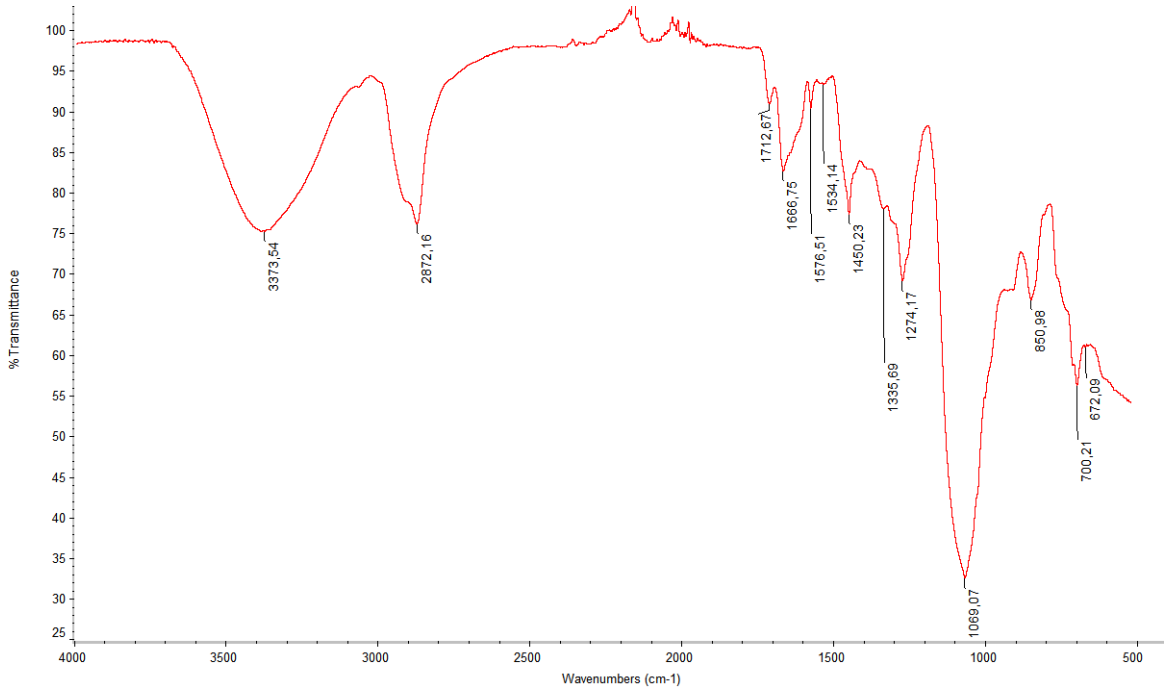


Figure 4. 14. Intermediate phase obtained during extraction of sample of Ex-313 and benzamide.

Figure 4. 15. shows the comparative FTIR spectra of benzamide, the extracted and purified sample and EX-313 respectively. In both the spectra of pure sample and intermediate phase sample, the appearance of new peak at 1712 cm^{-1} indicated the formation of aromatic ester carbonyl group.

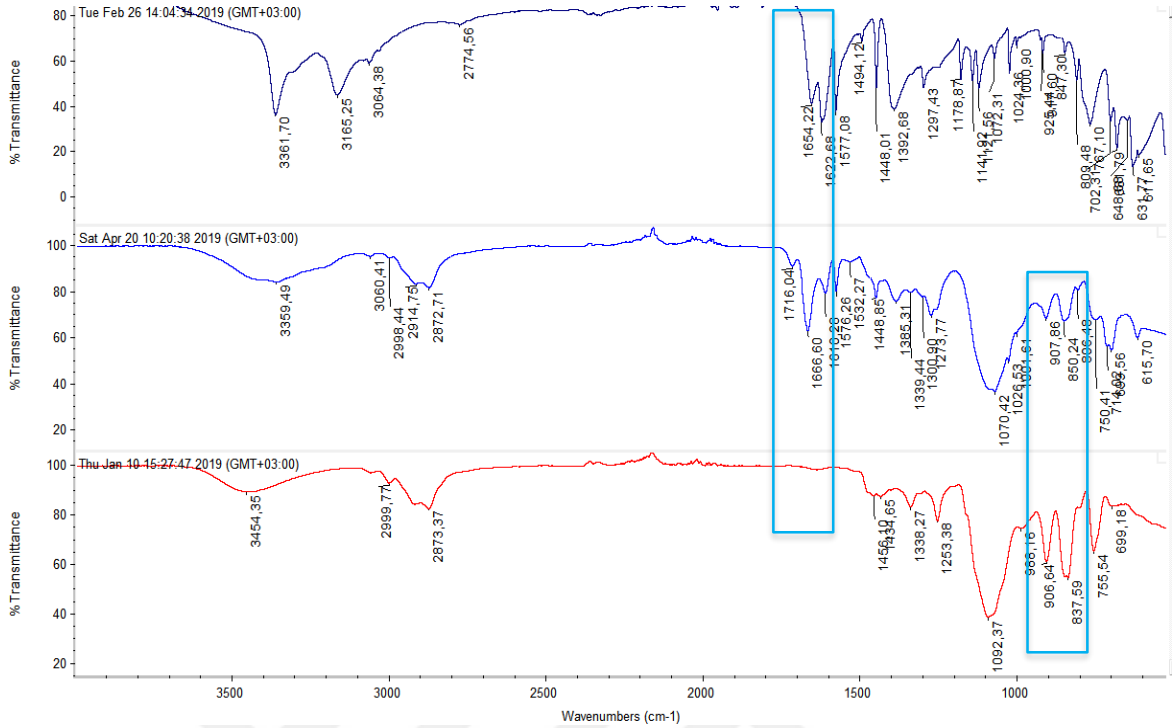
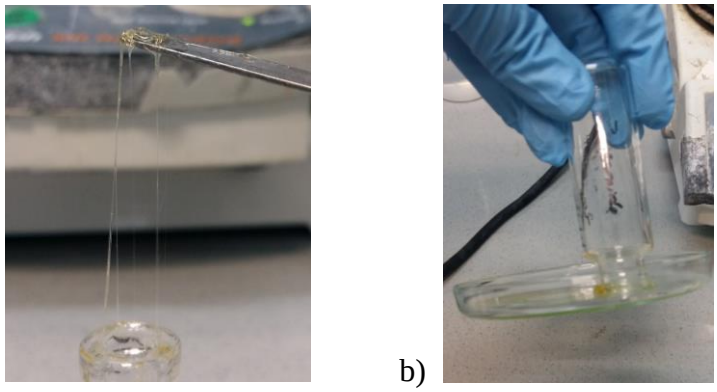


Figure 4. 15. FTIR Spectrum Comparison. a) Benzamide, b) Pure sample of Ex-313 and benzamide, c) Ex313.



a) b)

Figure 4. 16. Purifies reaction product of Ex-313 and benzamide.

Tg value for pure sample was found 37.1 ℃. Unlike Ex-313, which is liquid at room temperature, this sample was a sticky viscous gel like material that showed good adhesion to glass as shown Figure 4.16.

In the LC-MS analysis of the closed samples, various peaks in the range of 300-1100 dalton are observed these may indicate that the reaction does not proceed with single step but next nucleophilic addition can be possible by the formed amine to the epoxide.

In ^{1}H-NMR spectra of pure sample (DMSO-d_6, 400MHz), the doublet observed at δ=8.05 and 8.07 ppm confirms *ortho* hydrogen, the peaks at δ= 7.59-7.62 ppm and δ= 7.5 ppm verified *para* and *meta* hydrogens of aromatic ester. While the peaks in the range of δ= 7.52-7.56 ppm and δ=7.43-7.47 ppm corresponds to aromatic protons of residual benzamide (Figure 4. 19).

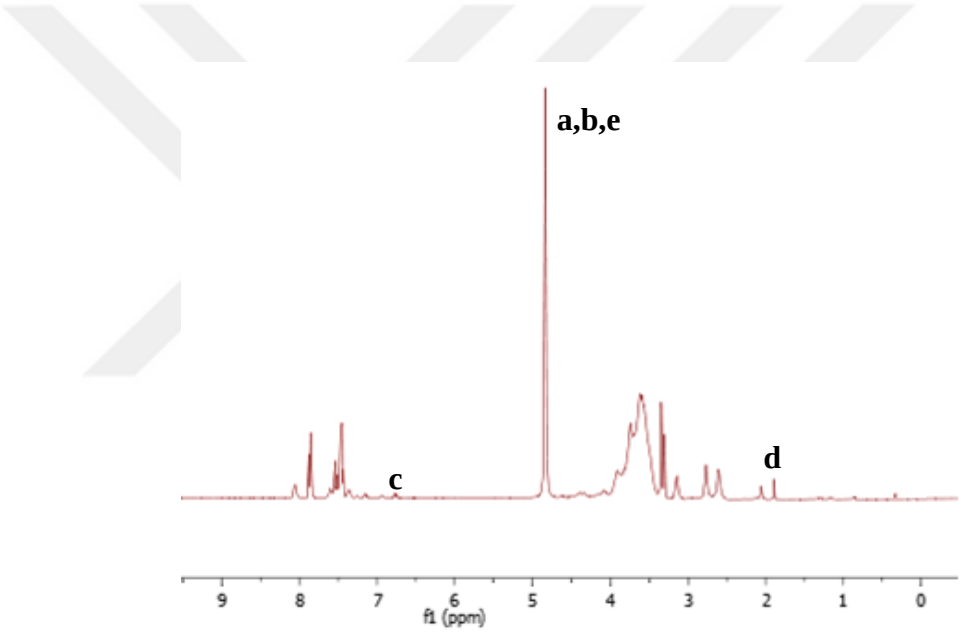


Figure 4. 17. ^{1}H-NMR Spectrum of pure sample of Ex-313 and benzamide.

The peaks in the range between δ=6.67-6.81 ppm may point out some C=C-H proton with a potential formation of vinyl ethers. Also, there was an intense sharp peak at δ=4.48 ppm that is attributed to alcohol proton (C-O**H**), aromatic ester proton (O=C-O-C-**H**) and vinyl ether proton C=C-O-**H** which locate same region. The peaks at δ=2.61, 2.77 and 3.4 ppm correspond to unreacted oxirane rings. Secondary amine proton (N-**H**) was seen at δ=1.81 (Figure 4.17).

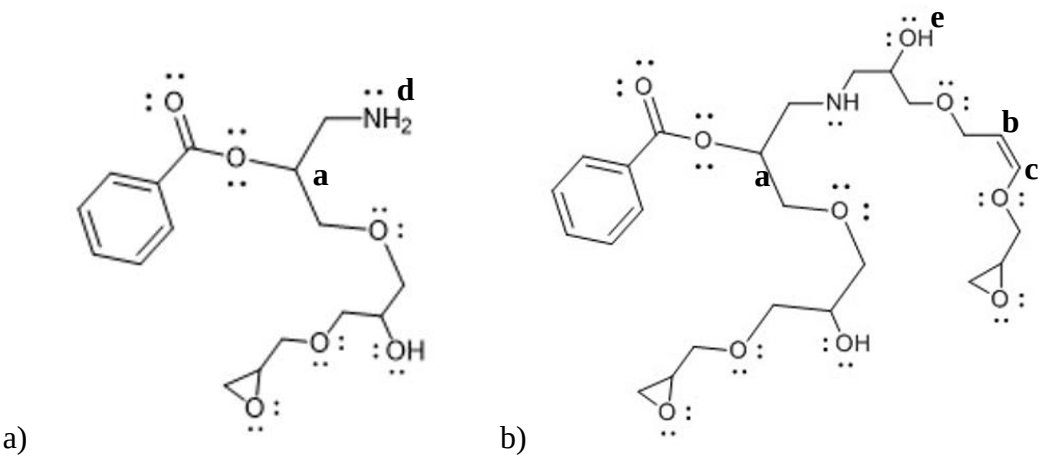


Figure 4. 18. Probable products a) ester formation, b) next sample formed by nucleophilic attack by amine to oxirane and vinyl formation.

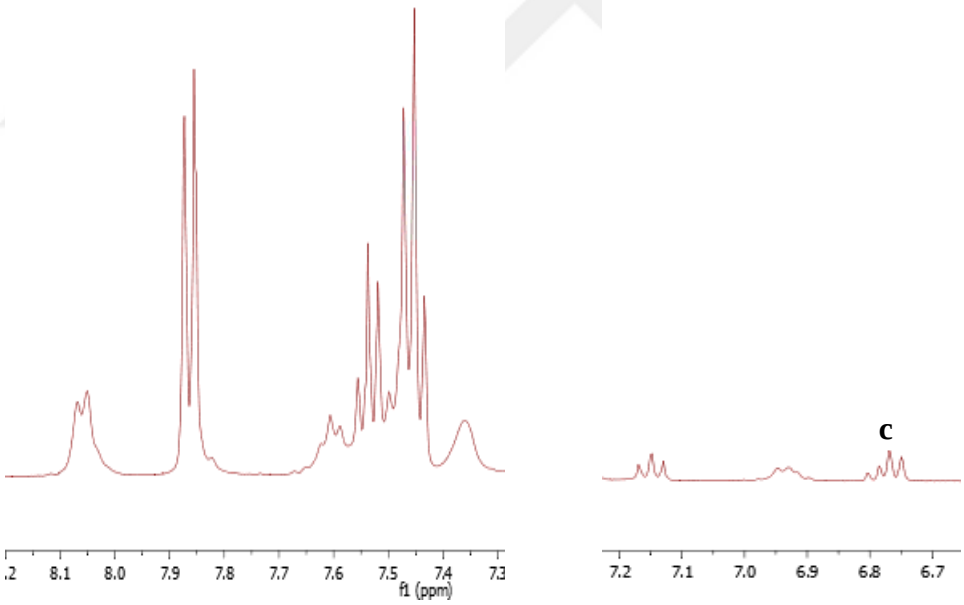


Figure 4. 19. Specific parts of ^{1}H-NMR Spectrum of sample of benzamide and Ex-313 in d_6-DMSO.

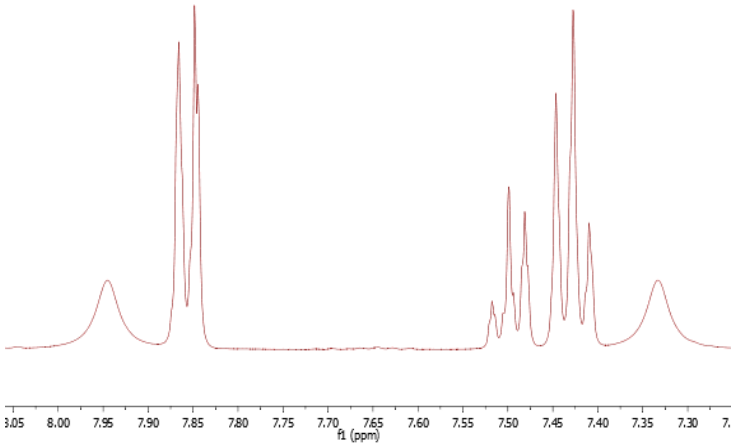


Figure 4. 20. Specific parts of ^{1}H-NMR Spectrum of Benzamide in d_6-DMSO.

In the light of the FTIR and $^{1-}$H-NMR spectras, possible reaction pathways are shown in Figure 4.21. and Figure 4. 22.

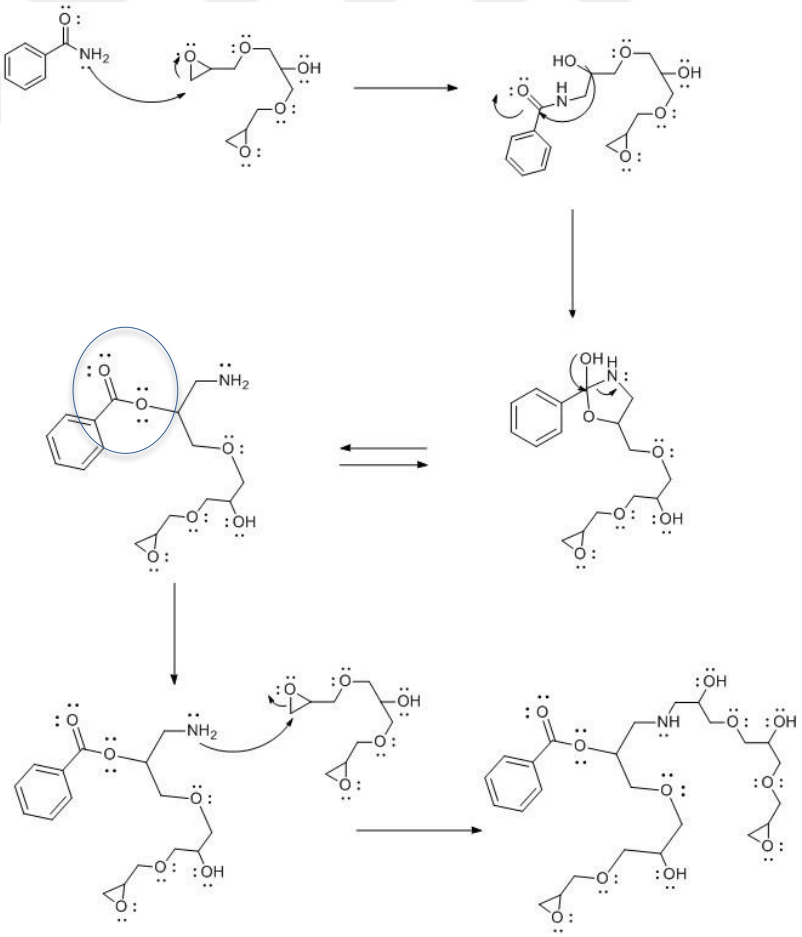


Figure 4. 21. Probable reaction pathway for pure sample based on insertion/rearrangement reaction mechanism.

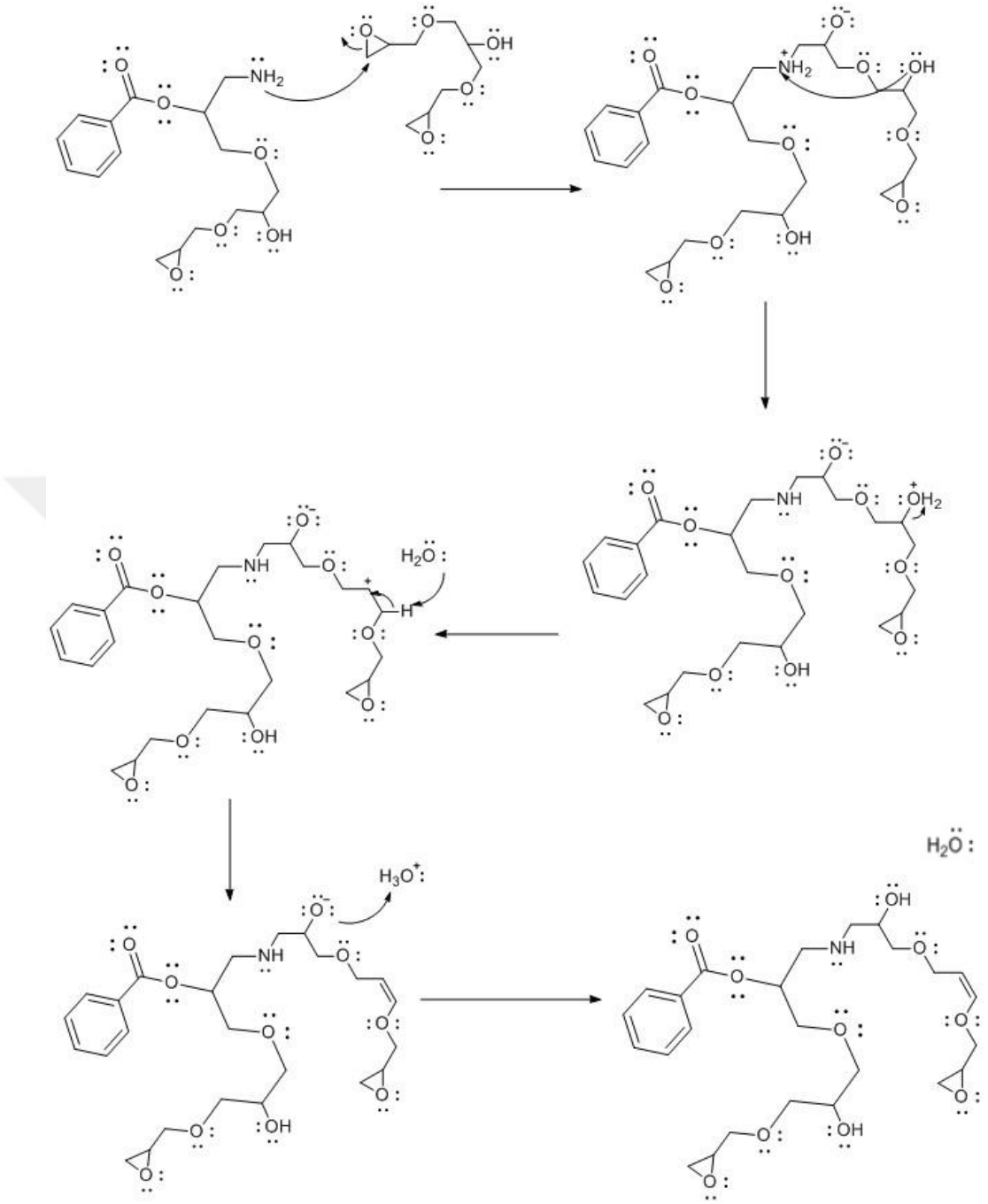


Figure 4. 22. Probable pathway for vinyl ether formation and final structure.

4.3. Curing Reaction between EPP and Various Amides

4.3.1. Reaction with Acetamide

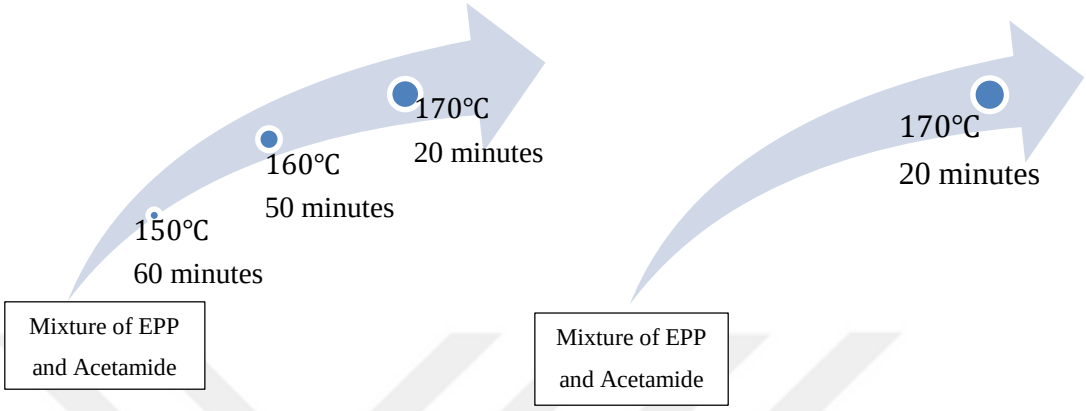


Figure 4. 23. Heating process of samples of EPP and acetamide in oven.

Two mixtures containing EPP and acetamide in 1:1 mole ratio were prepared. First sample was heated using different temperature ramps. In the first process, sample were heated at 150 ℃ for 60 minutes, then at 160℃ for 50 minutes, finally at 170℃ 20 minutes, then the process was terminated. At each temperature change point, samples were taken for FTIR analysis. The other sample was heated directly at 170℃ for 20 minutes (Figure 4.23).

The results of gradually heated open sample indicated diminishing of both amide stretching peaks in the 3347-3350cm^{-1} range and C=O stretching peak at 1671cm^{-1} and no new peak formation (Figure 4.24). The results again pointed out an early and fast sublimation of acetamide, as mentioned earlier in Section 4.2.2.

However, the another open sample heated directly put to 170℃ (for 20 minutes) shows new peak formation at 3400cm^{-1} corresponds to OH stretching and oxirane peaks (870cm^{-1} and 906cm^{-1}) were almost vanished. It is most likely that due to the high process temperature (170℃), the amide and epoxide had a chance to react before the sublimation of the acetamide took place (Figure 4.25.).

New experiment was carried out in closed system, stirring and purification steps were introduced. In this process, the sample was heated from 25℃ to 170℃ in 4 hours (unlike the previous experiments). The closed sample showed increase in the absorption peaks of O-H stretching at 3400 cm^{-1} and decrease in oxirane peaks at 852 cm^{-1} and 924 cm^{-1} indicating

a possible ring opening process. Interestingly this time almost no peaks were observed around 1735cm^{-1} which were previously (in the case of EX313-acetamide) attributed to the aliphatic polyester stretching bands (Figure 4.26.).

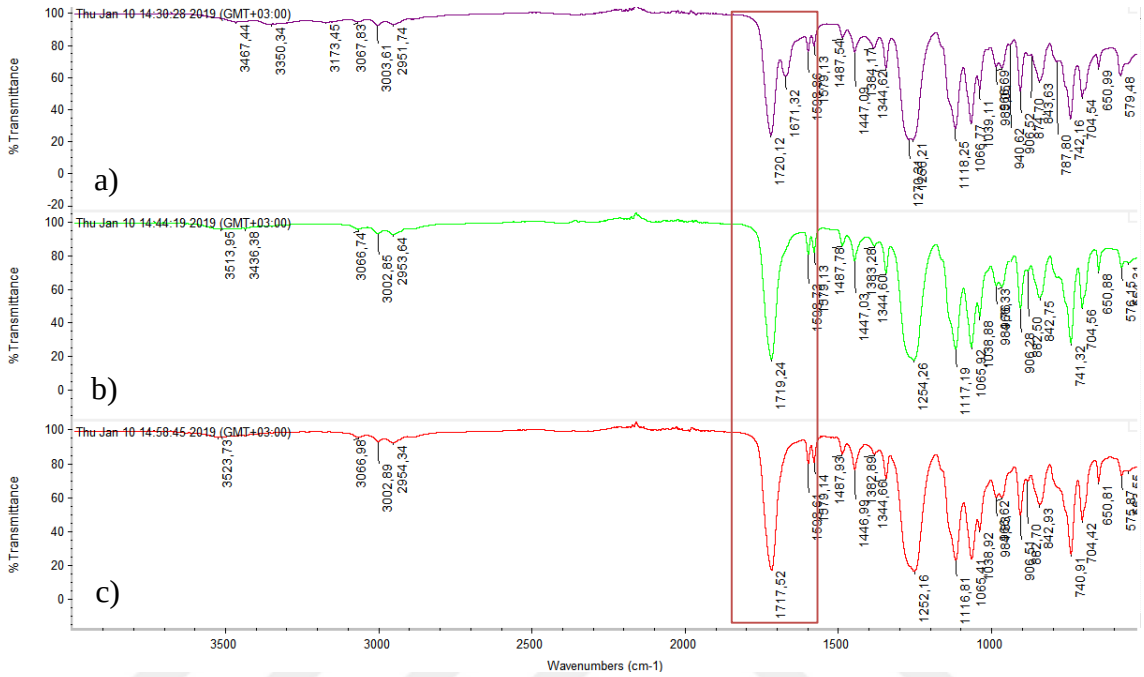


Figure 4. 24. FTIR Spectrum comparison of samples of EPP and acetamide taken at (a)150℃, (b)160℃, (c) and 170℃ in sealed reactor.

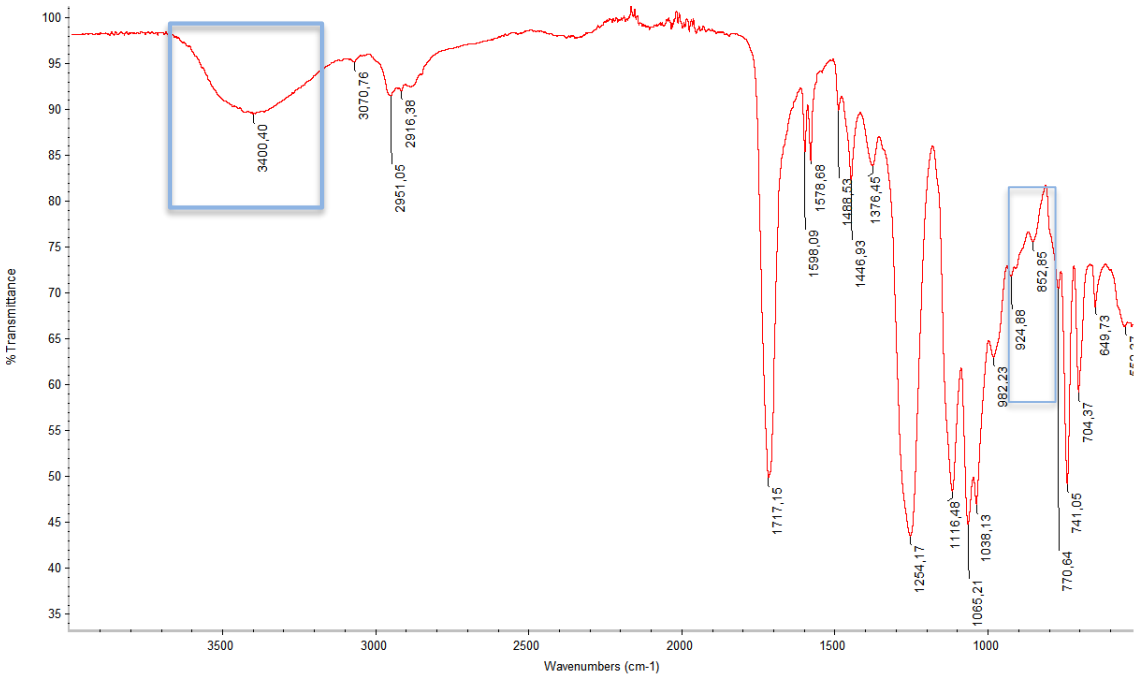


Figure 4. 25. FTIR Spectrum of second open reactor.

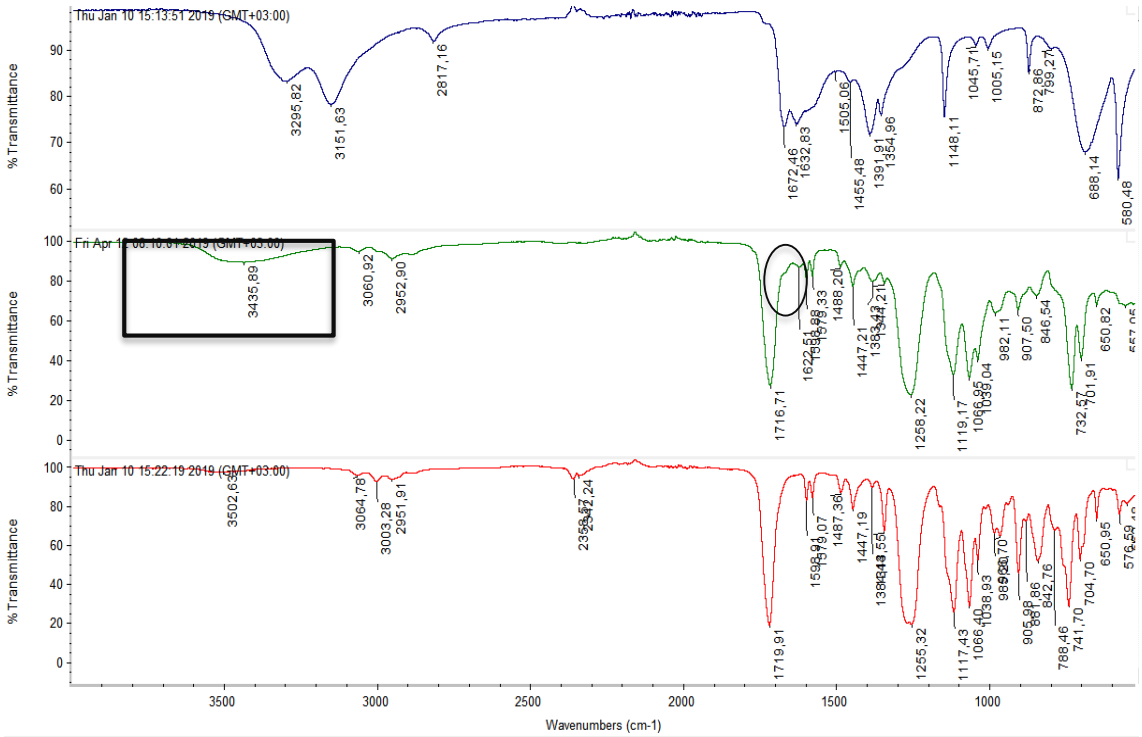


Figure 4. 26. FTIR Spectra comparison a) Acetamide, b) Sealed sample after purification, c) EPP.

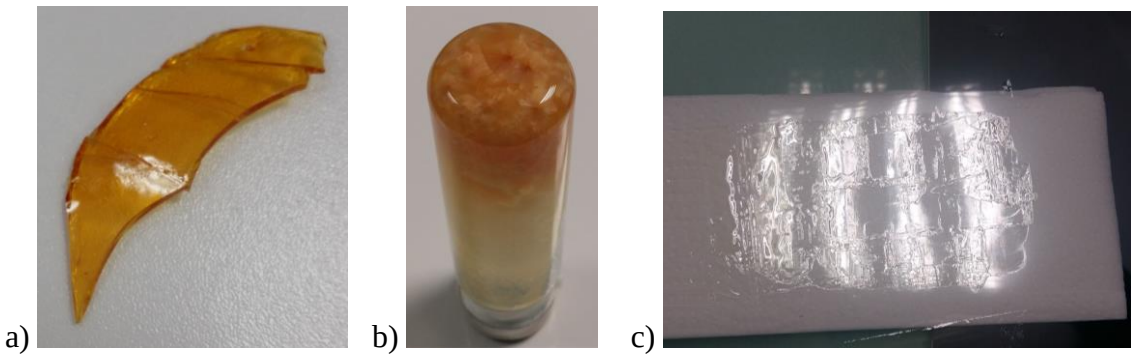


Figure 4. 27. Sample of EPP and acetamide a) heated at 170℃ at oven b) After heating in sealed condition c) Pure sealed sample.

As shown Figure 4.27., open sample heated directly at 170℃ became hard and brittle which is considerably different from the sealed sample in terms of structure which is sticky.

As shown in Figure 4. 29, ^{1}H-NMR (DMSO-d_6, 400MHz) analysis was carried out and observed peaks in the range in δ=5.08-5.6 ppm verified formation of alcohol (C-O**H**) and peaks in the range in δ=4.85-4.91 ppm verified methoxy proton (-C**H**-OH). The peak in δ=4.69 ppm is attributed to aromatic ester proton (O=C-O-C-**H**). Residual DCM peaks seen

in δ=5.73. In Figure 4.31., the peaks in δ=2.03-1.90 show acetamide protons joining the structure (-C**H**$_3$). The peaks at δ=2.62, 2.81 ppm correspond to unreacted oxirane rings. Results point out an addition mechanism, since there is no indication that the previously observed ester formation pathway is taking place. Figure 4. 31. Shows a probable reaction pathway and product based on the FTIR results. The fact that the viscosity increases significantly shows that the reaction product is most probably a multi addition oligomeric product.

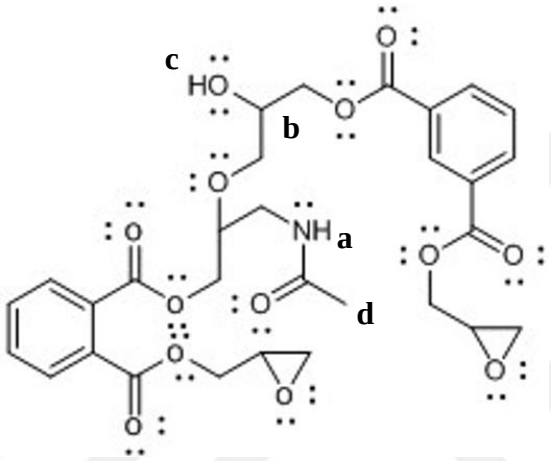


Figure 4. 28. Probable structure of sealed sample.

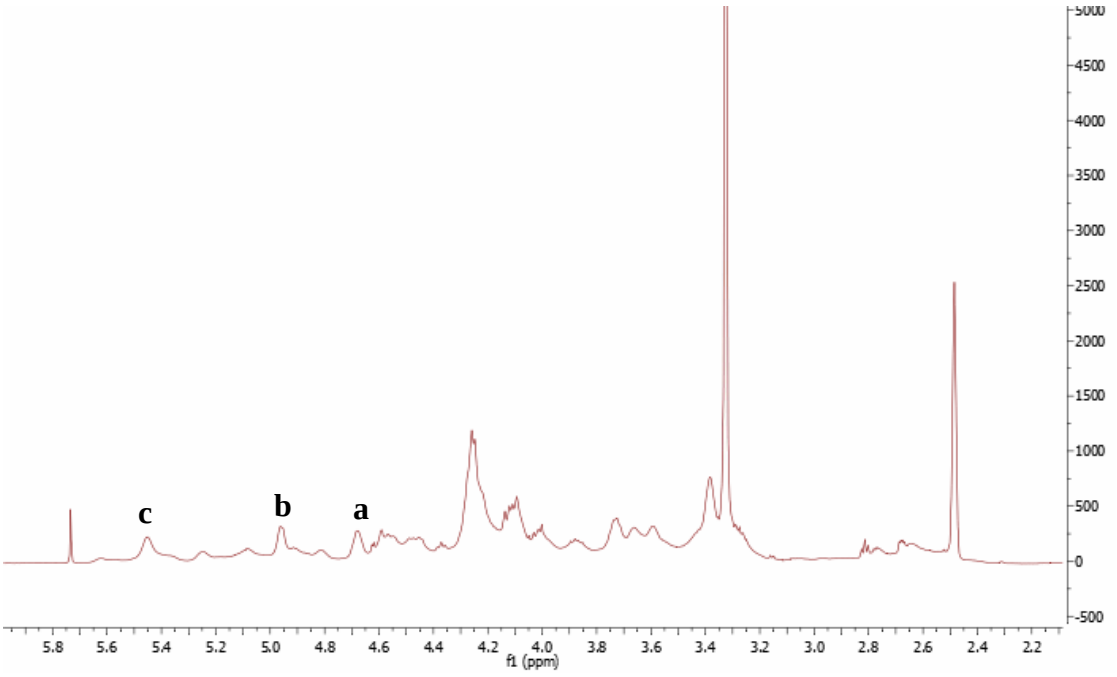


Figure 4. 29. Specific parts of ^{1}H-NMR Spectrum of sealed sample in d_6-DMSO.

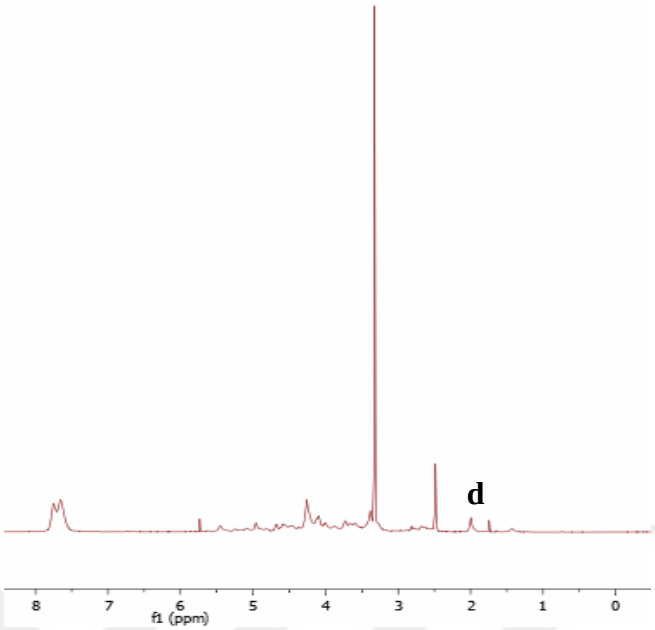


Figure 4. 30. ^{1}H-NMR spectra of sealed sample.

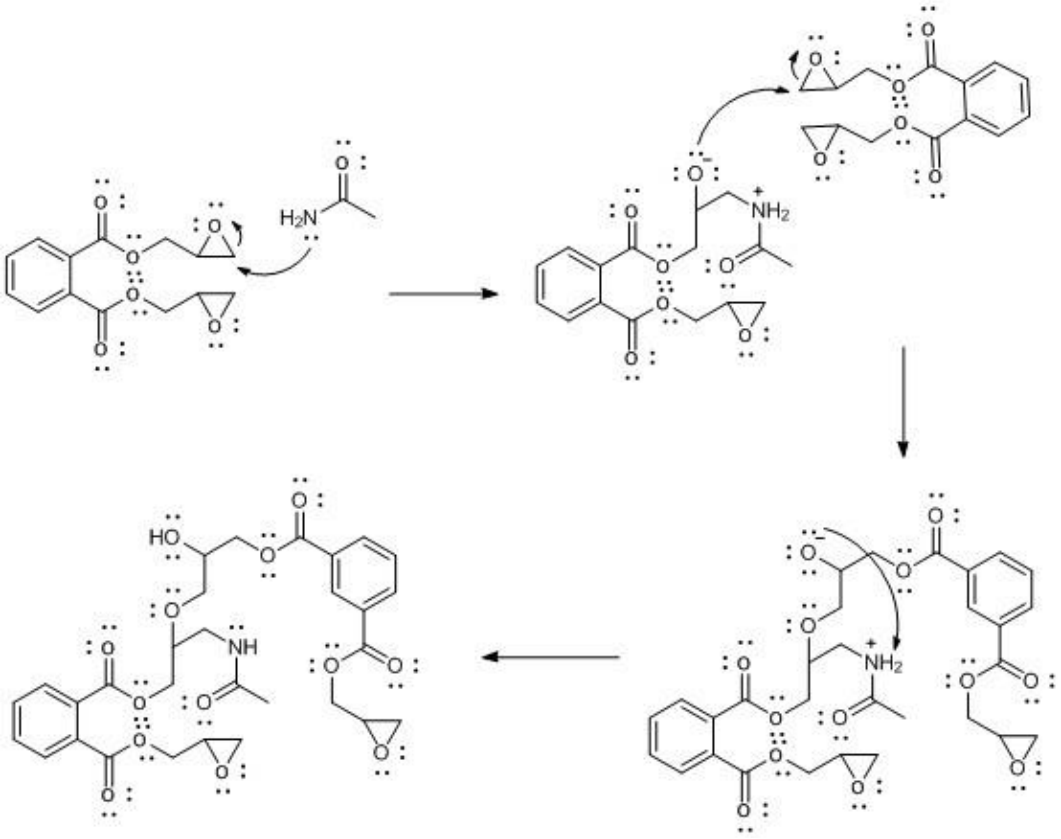


Figure 4. 31. Probable reaction pathway and product structure.

4.3.2. Reaction with Benzamide

Sample consisting of EPP and benzamide in 1:1 mole ratio in sealed reaction vessel was continuously stirred and heated from 25℃up to 170℃in 4 hours. While cooling sample at room temperature, white precipitations that were thought to be benzamide flakes was observed in the liquid sample. As shown in Figure 4. 32. there is no new peak formation or chemical shifts for benzamide and EPP absorption peaks, so it is concluded that neither addition nor insertion/rearrangement reaction could be realized.

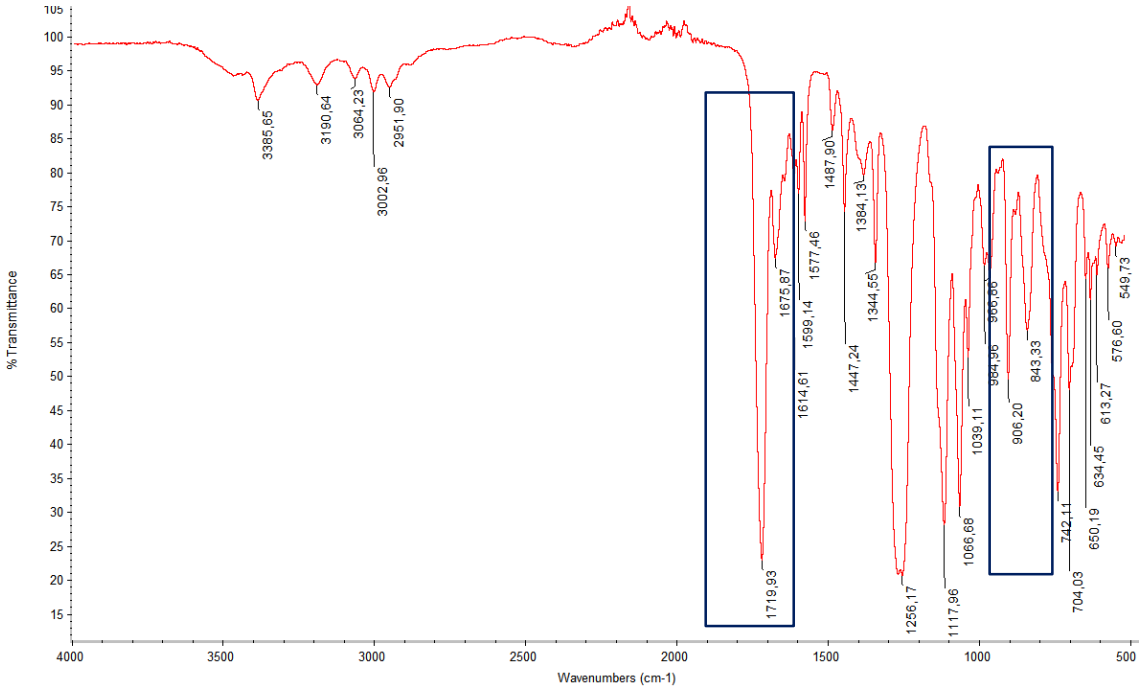


Figure 4. 32. FTIR analysis of closed sample of EPP and benzamide.

5. CONCLUSIONS

- According to results, monomeric amides can attack the epoxide ring in the temperature range 120℃-170℃.
- Epoxy monomers containing ester groups neighboring to oxirane ring are more reactive towards addition reactions. Thus, nucleophilic addition to oxirane ring of EPP became faster, instead of rearrangement to form ester, reaction continued in accordance with nucleophilic addition pathway.
- On the other hand, compared to EPP, Ex-313 has relatively low reactivity, and reaction became slower for next substitution. Following nucleophilic attack of amide to oxirane ring, molecule had chance for rearrangement and formed ester group. So, insertion/rearrangement led to the reaction containing Ex-313.

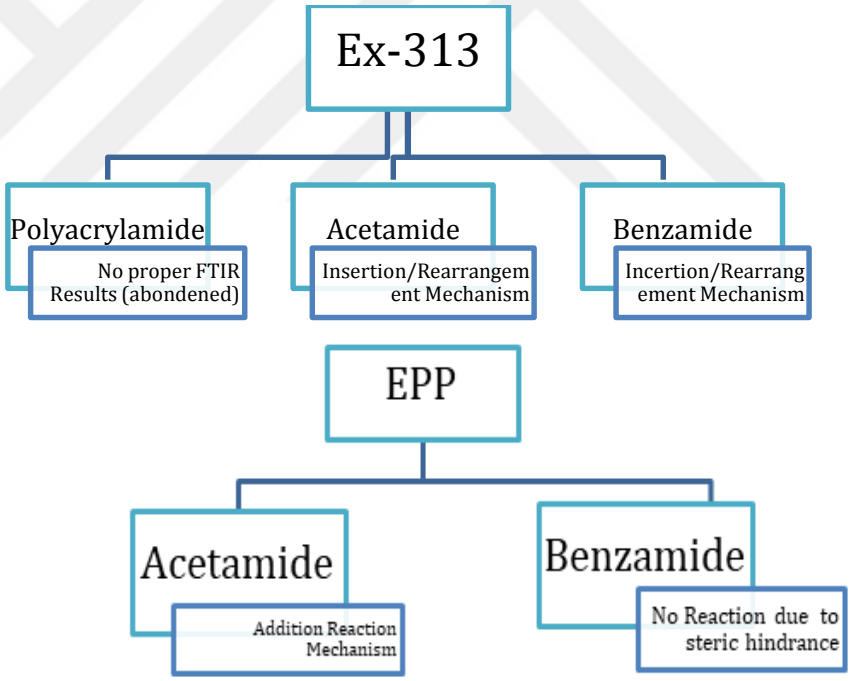


Figure 5. 1. Schematic summary of results.

6. FUTURE WORK

- Samples with various molar ratio of amide and epoxy monomers should be studied.
- Mono epoxides will be studied with monomeric amides to prevent oligomeric structure.
- For alternative mechanism, computational analysis should be investigated, and more logical pathway must be determined depending on transition state energies. Since the transition from the amide to ester is less favorable thermodynamically.
- High molecular weight di-or multifunctional amide polymers will be used to reach complete crosslinked structure and these products' chemical and physical properties should be analyzed.
- Additionally, experiments may be carried out using various catalysts to enhance the reactivity.

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APPENDIX A: SPECTROSCOPY DATA

This section includes ^{1}H-NMR Spectroscopy and DSC Analysis of synthesized polymers. Necessary expansions were made on the data for easy interpretation.

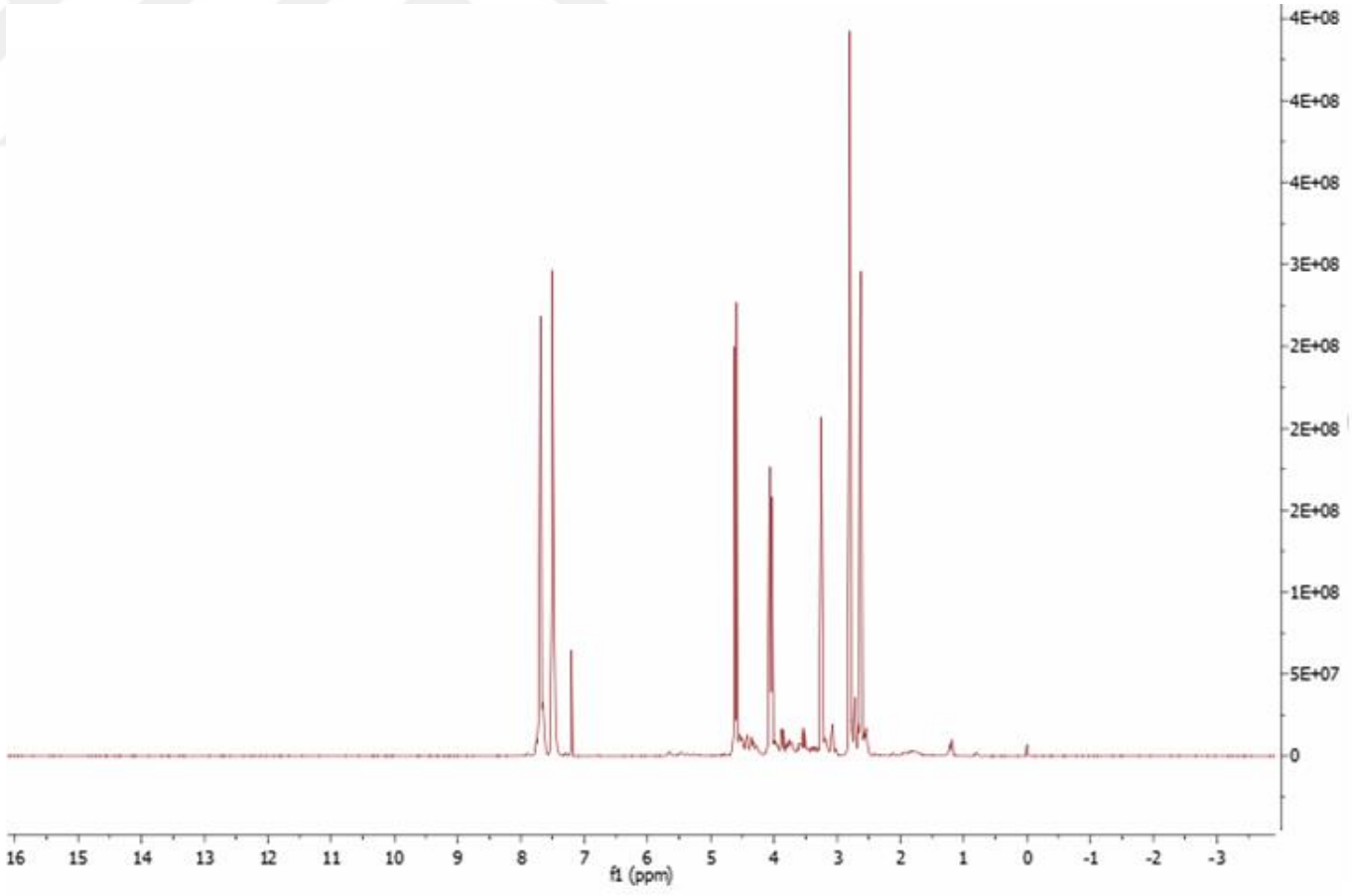


Figure A. 1. EPP in $CDCl_3$.

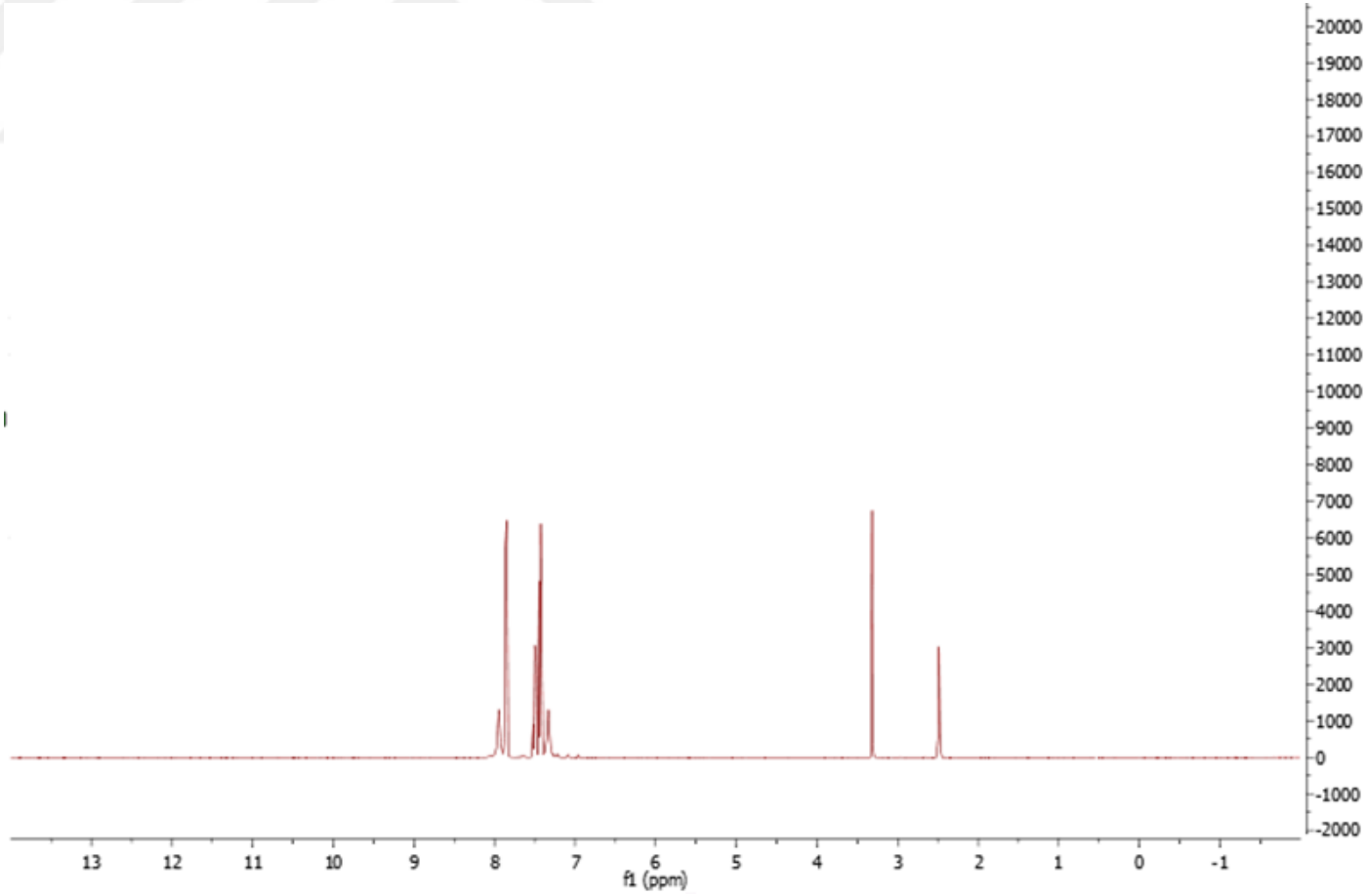


Figure A. 2. Benzamide in d_6-DMSO.

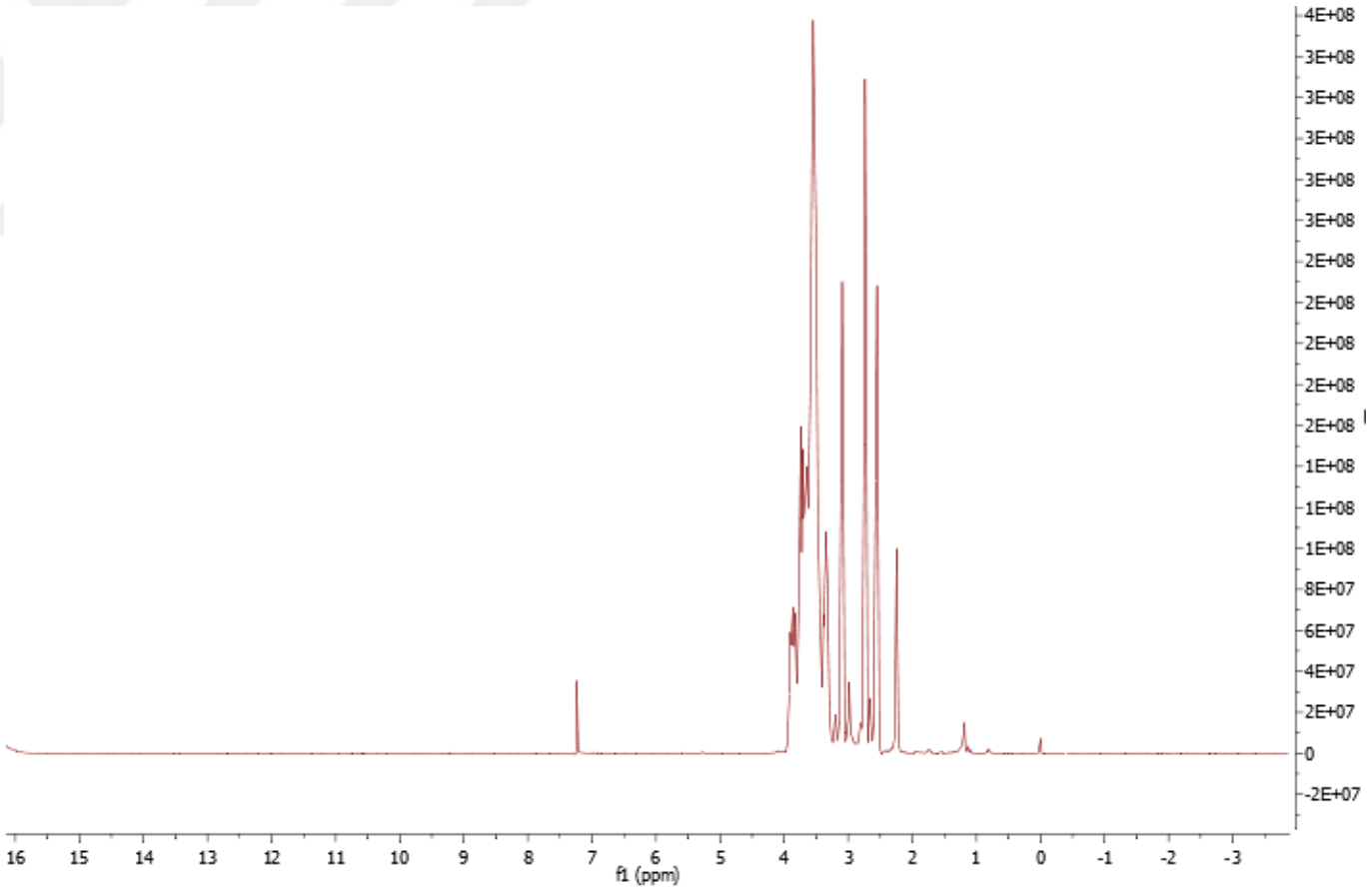


Figure A. 3. Ex-313 in $CDCl_3$.

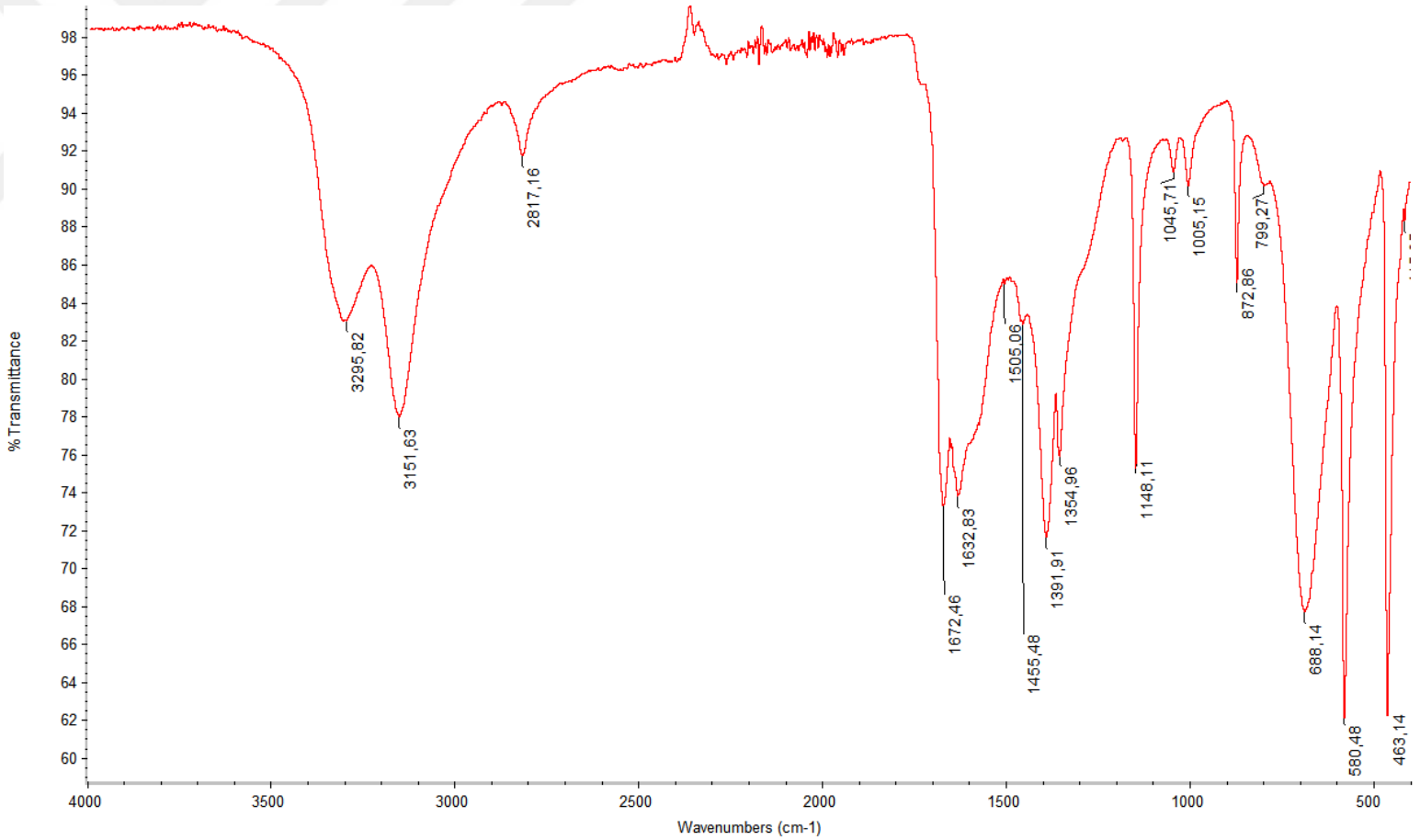


Figure A. 4. FTIR spectra of acetamide.

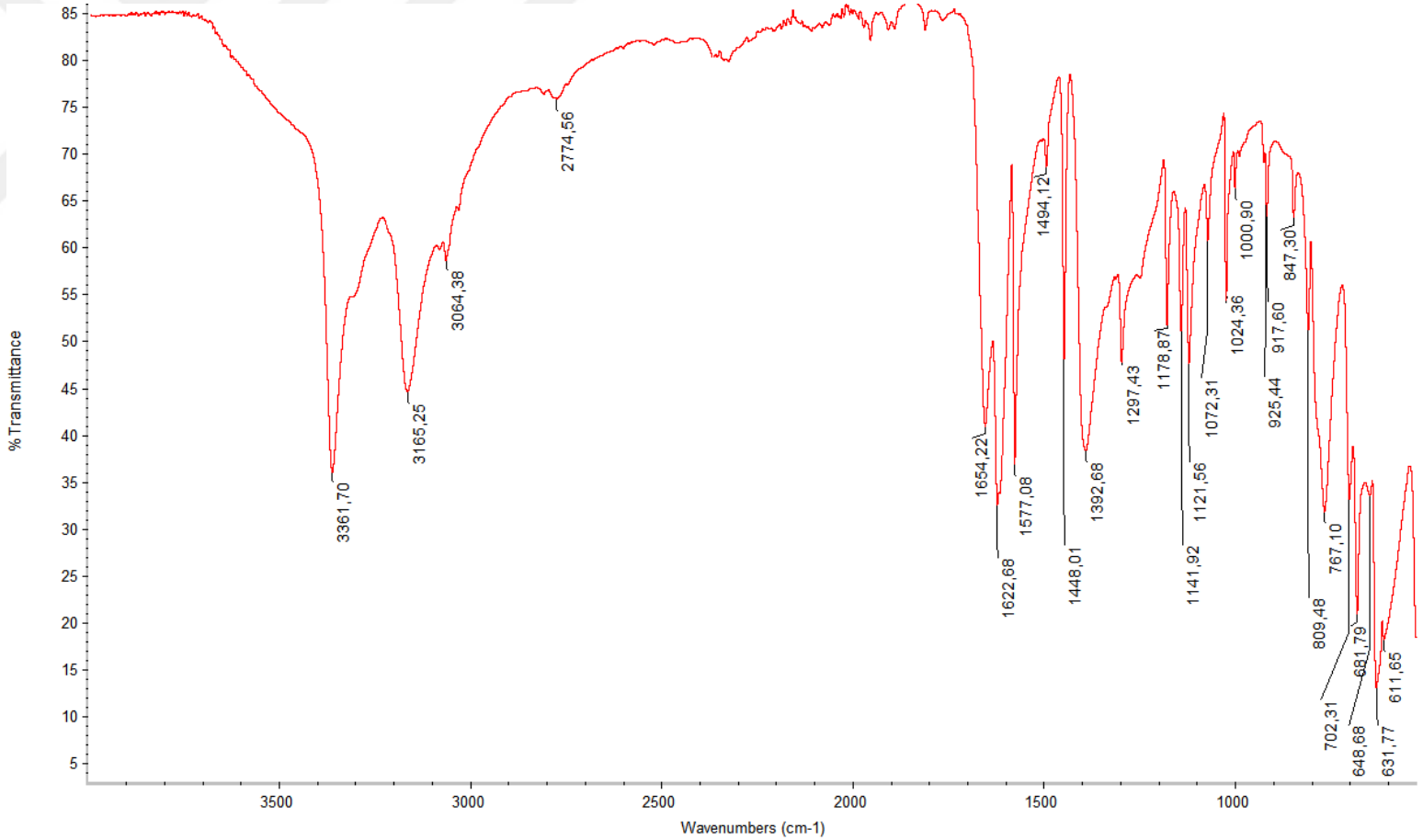


Figure A. 5. FTIR spectra of benzamide.

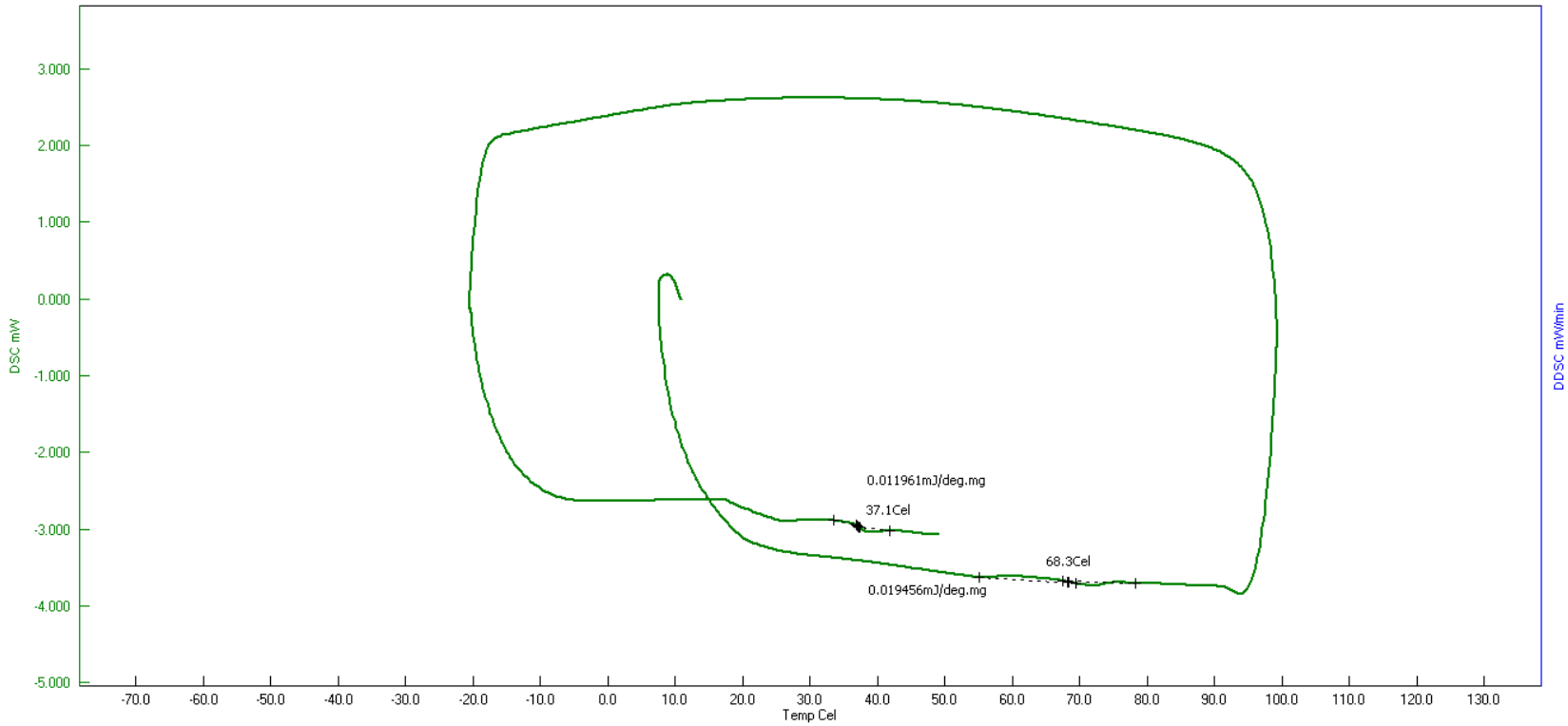


Figure A. 6. Closed sample of benzamide and Ex-313.

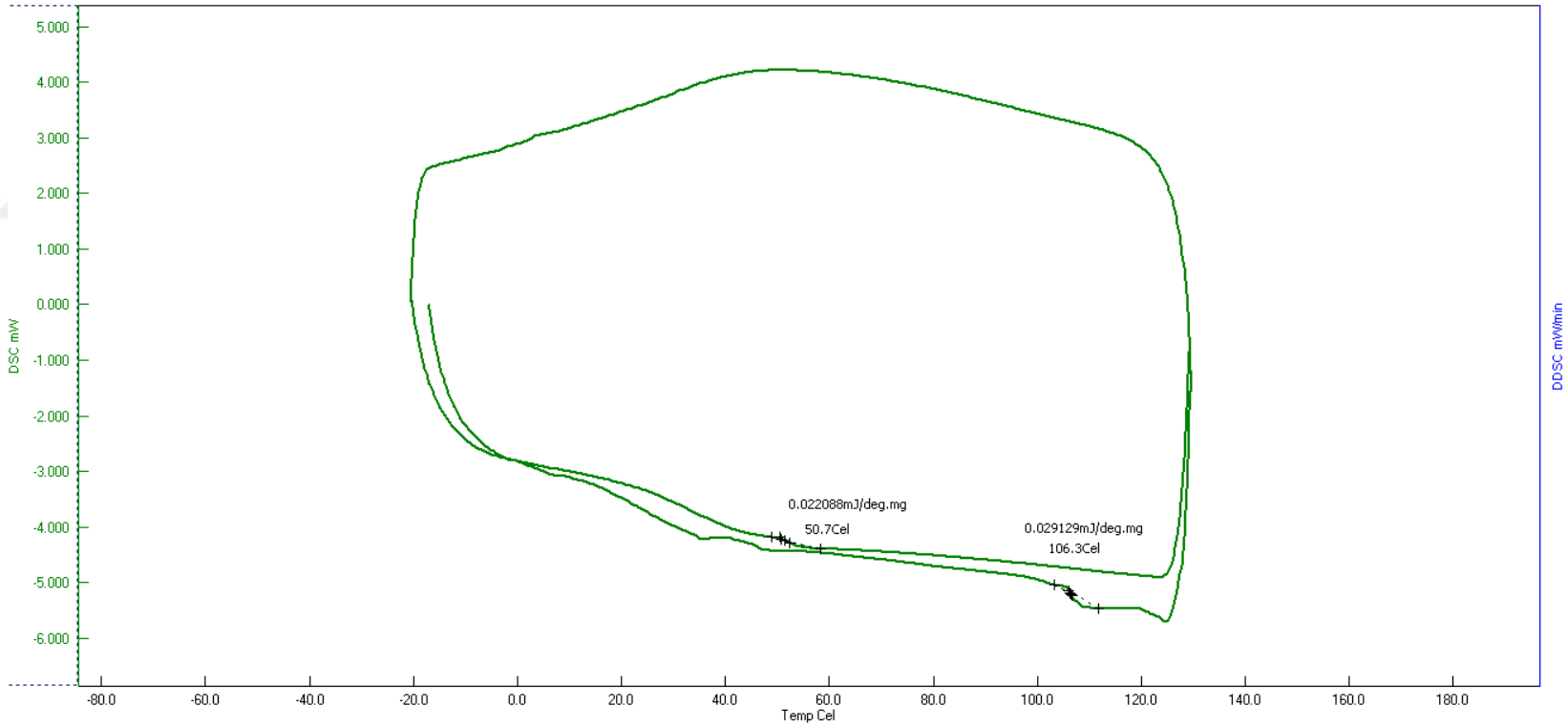


Figure A. 7. Sample of EPP and acetamide sample heated at directly 170℃ in oven.

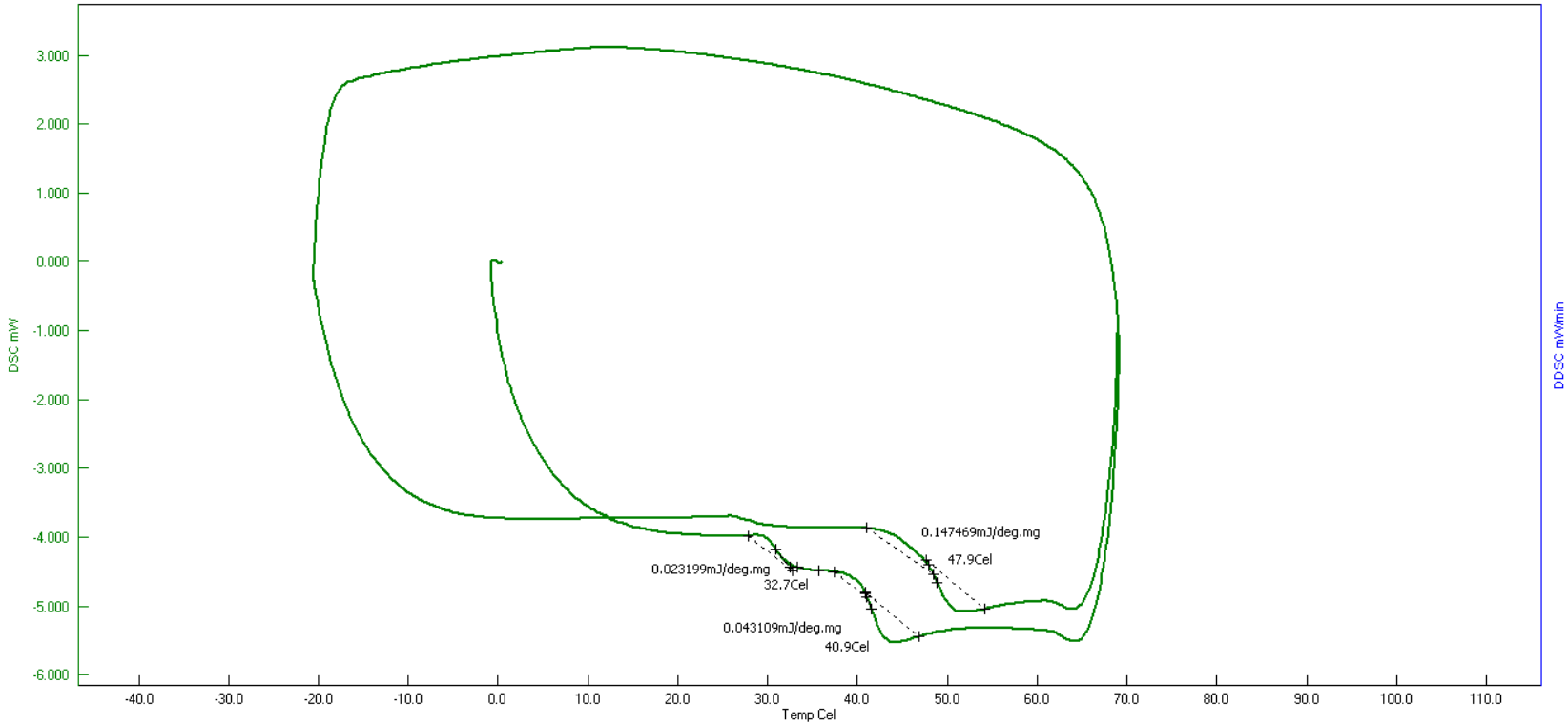


Figure A. 8. Sealed sample of acetamide and Ex-313.

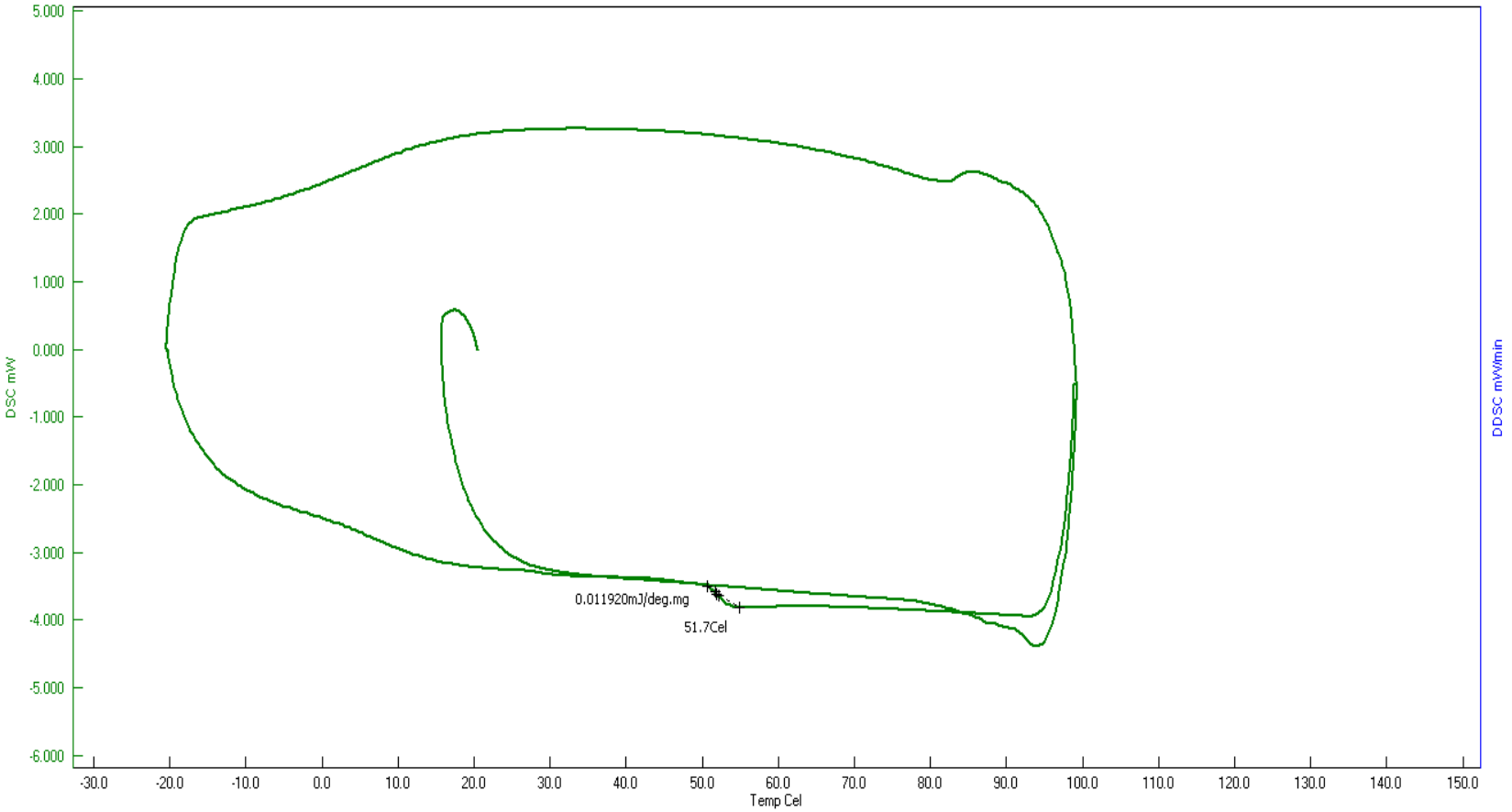


Figure A. 9. Sealed sample of acetamide and EPP.

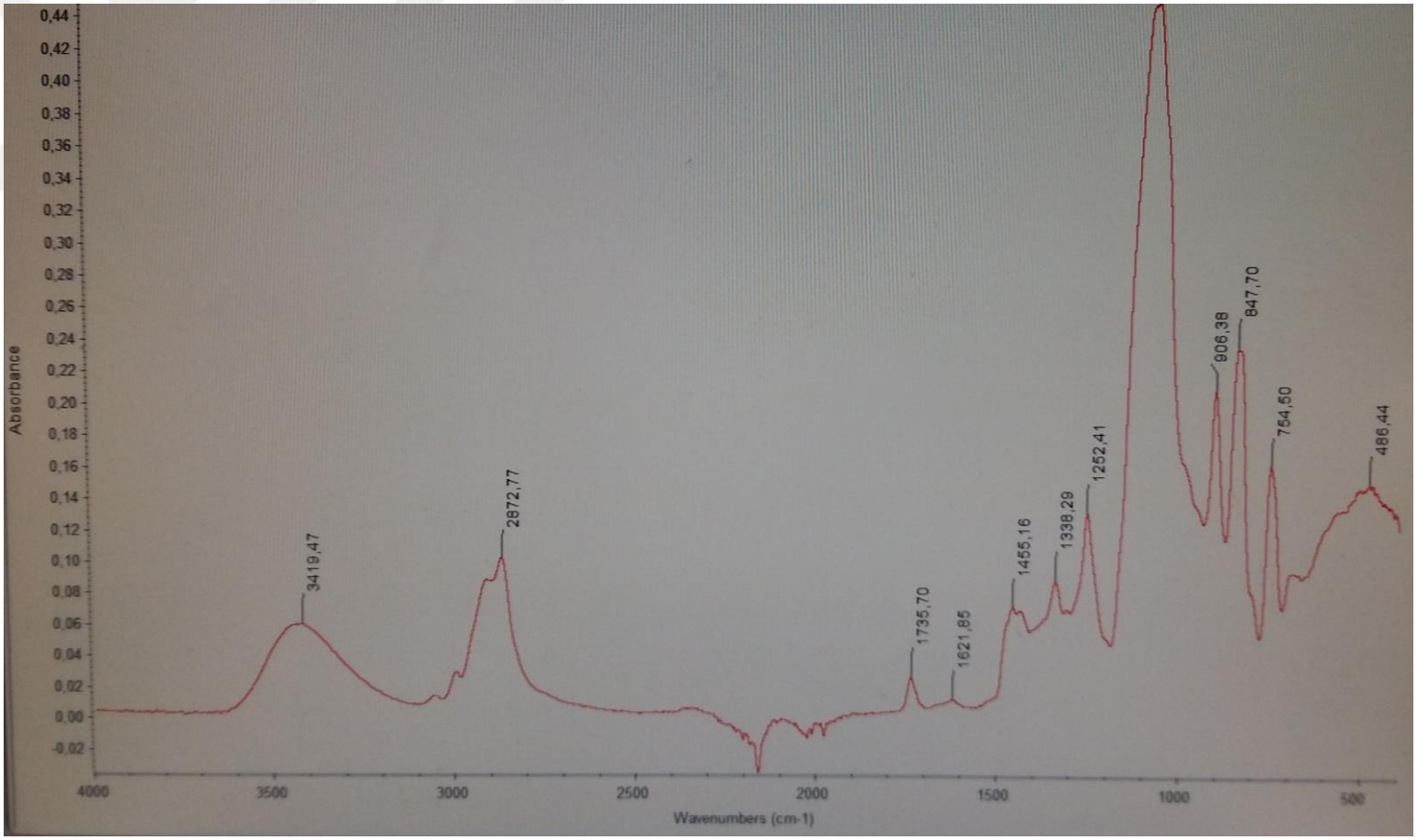


Figure A. 10. Open sample of Ex-313 and acetamide at 140℃ 60 minutes.

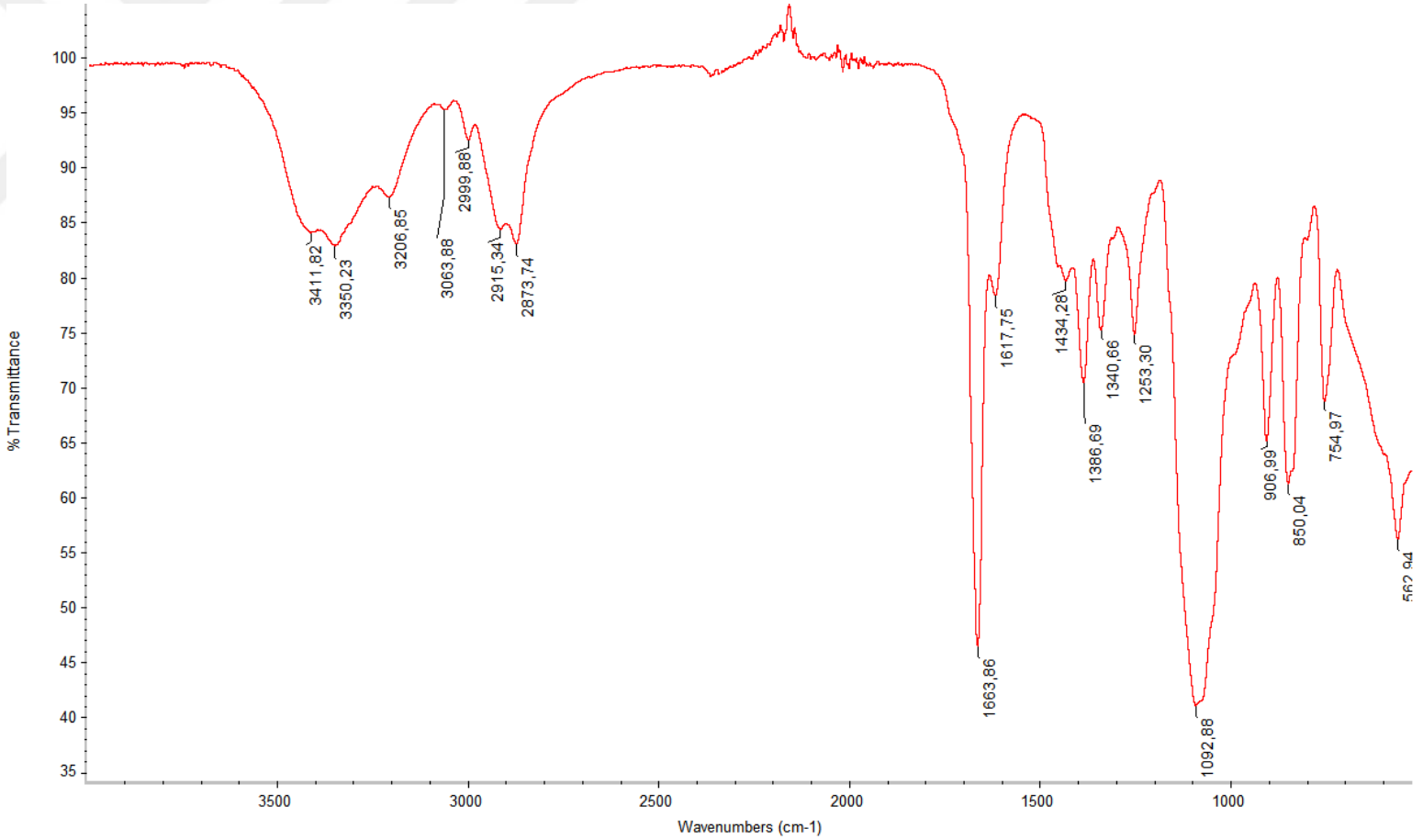


Figure A. 11. Open sample of Ex-313 and acetamide at 150℃ 60 minutes.

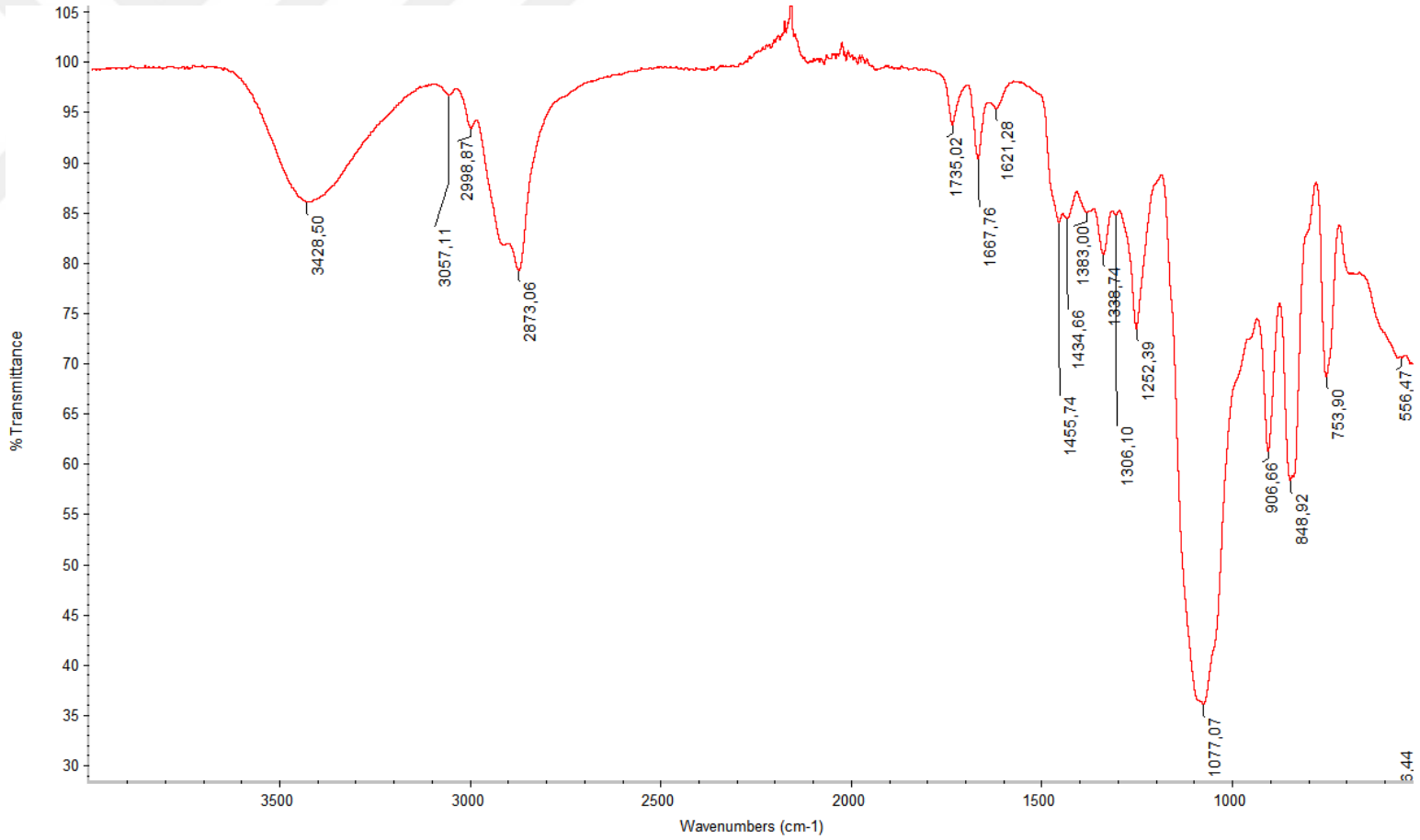


Figure A. 12. Open sample of Ex-313 and acetamide at 160℃ 50 minutes.

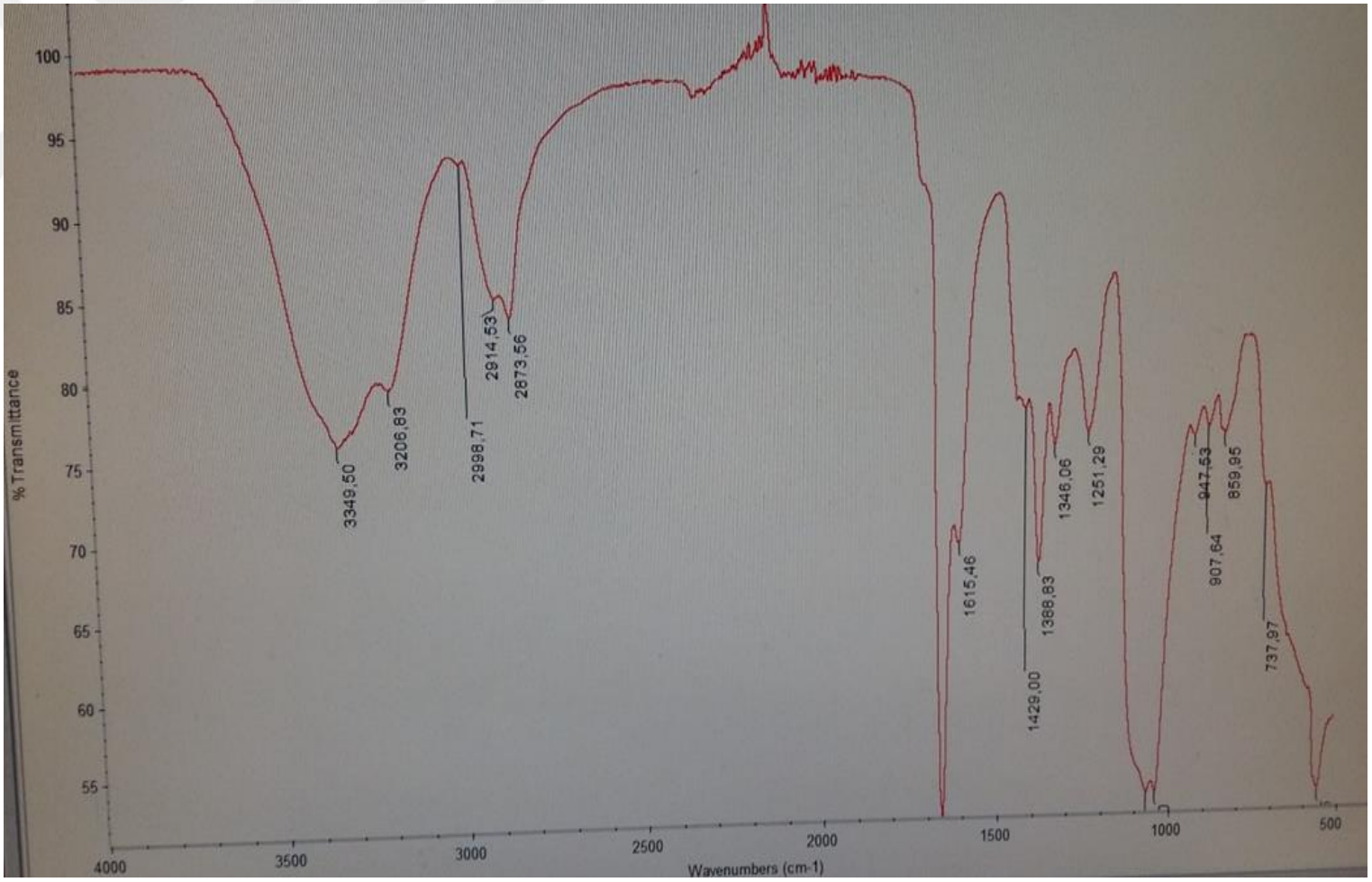


Figure A. 13. Impure sample of Ex-313 and acetamide after heating.

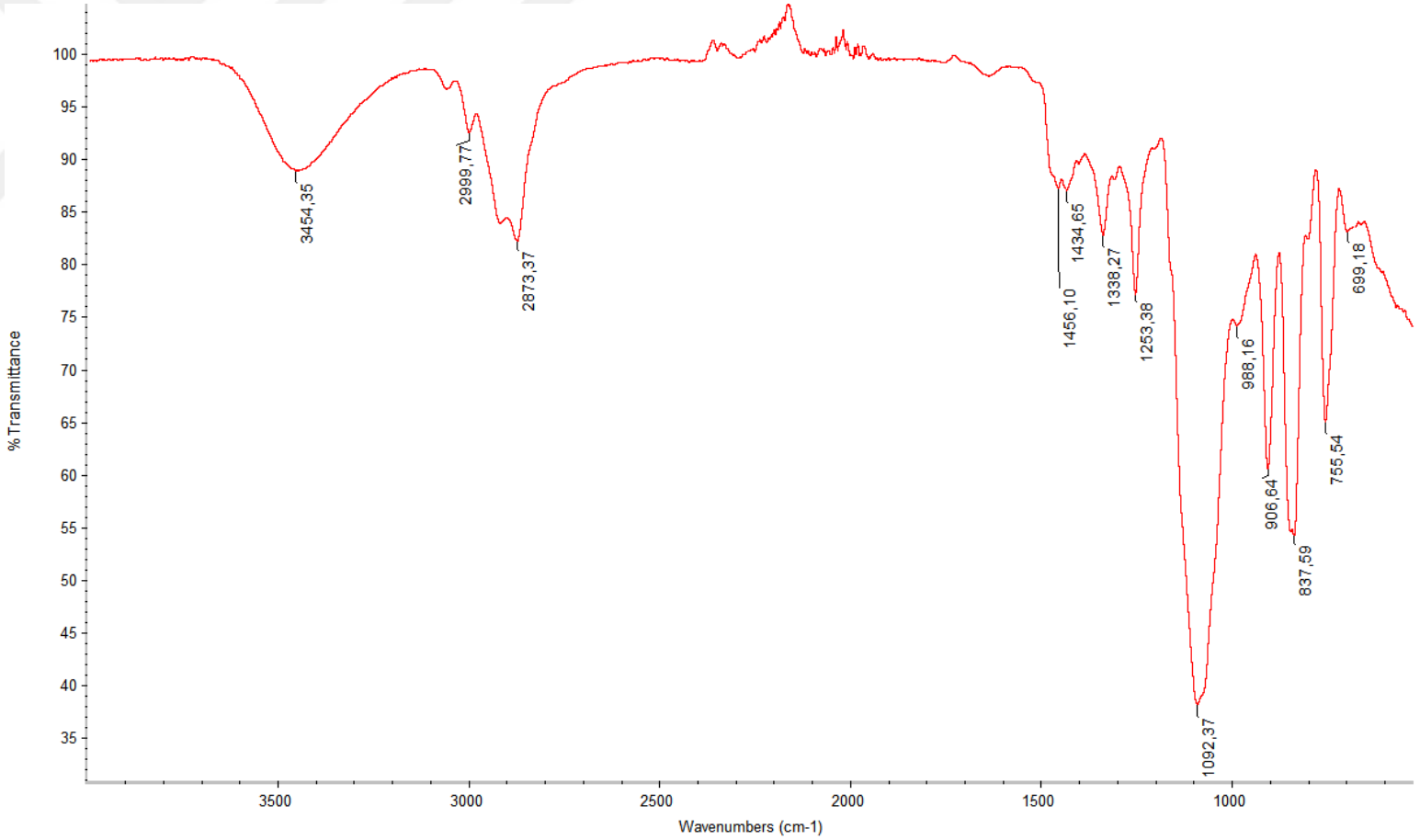


Figure A. 14. FTIR Spectra of Ex-313.

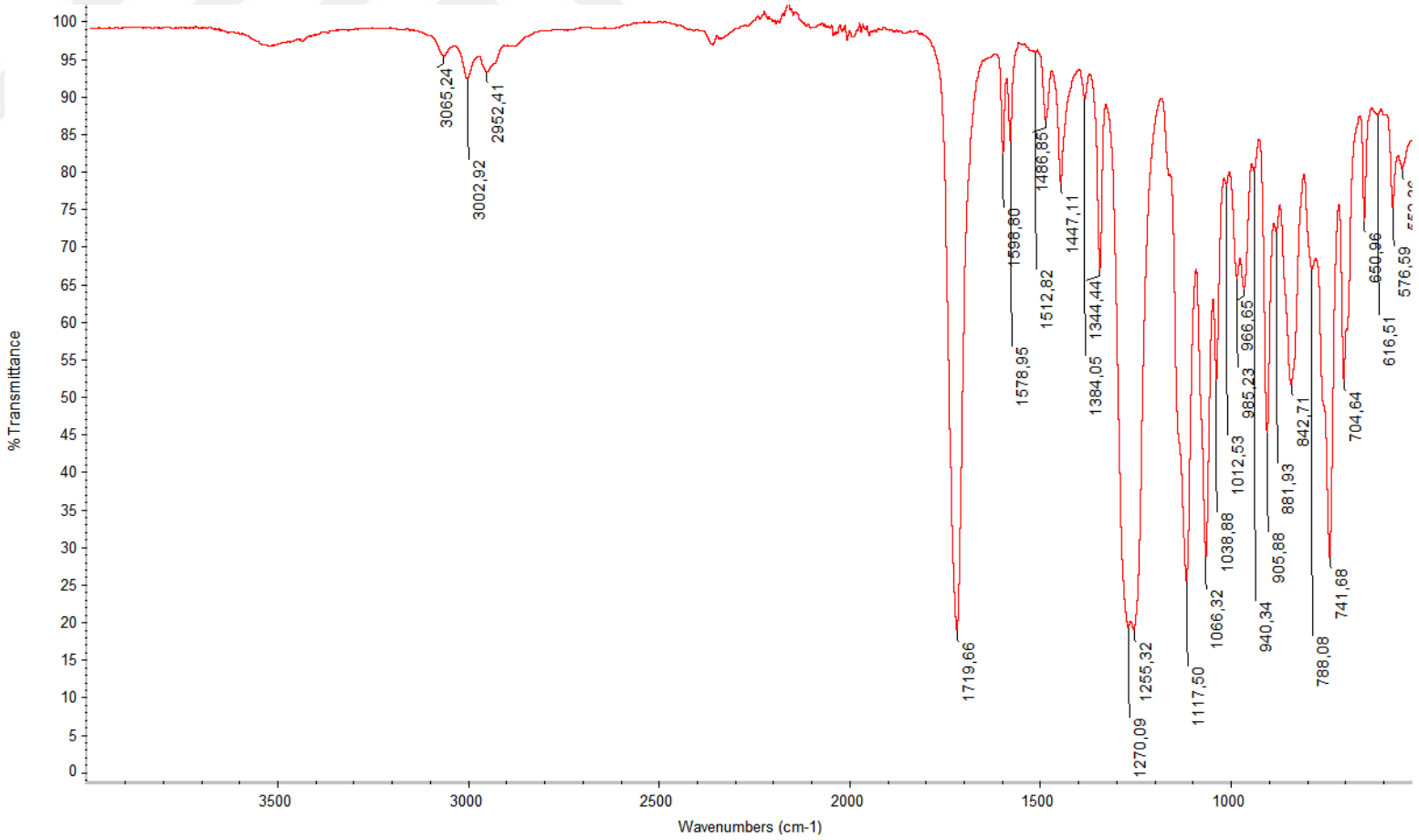


Figure A. 15. FTIR spectra of EPP.

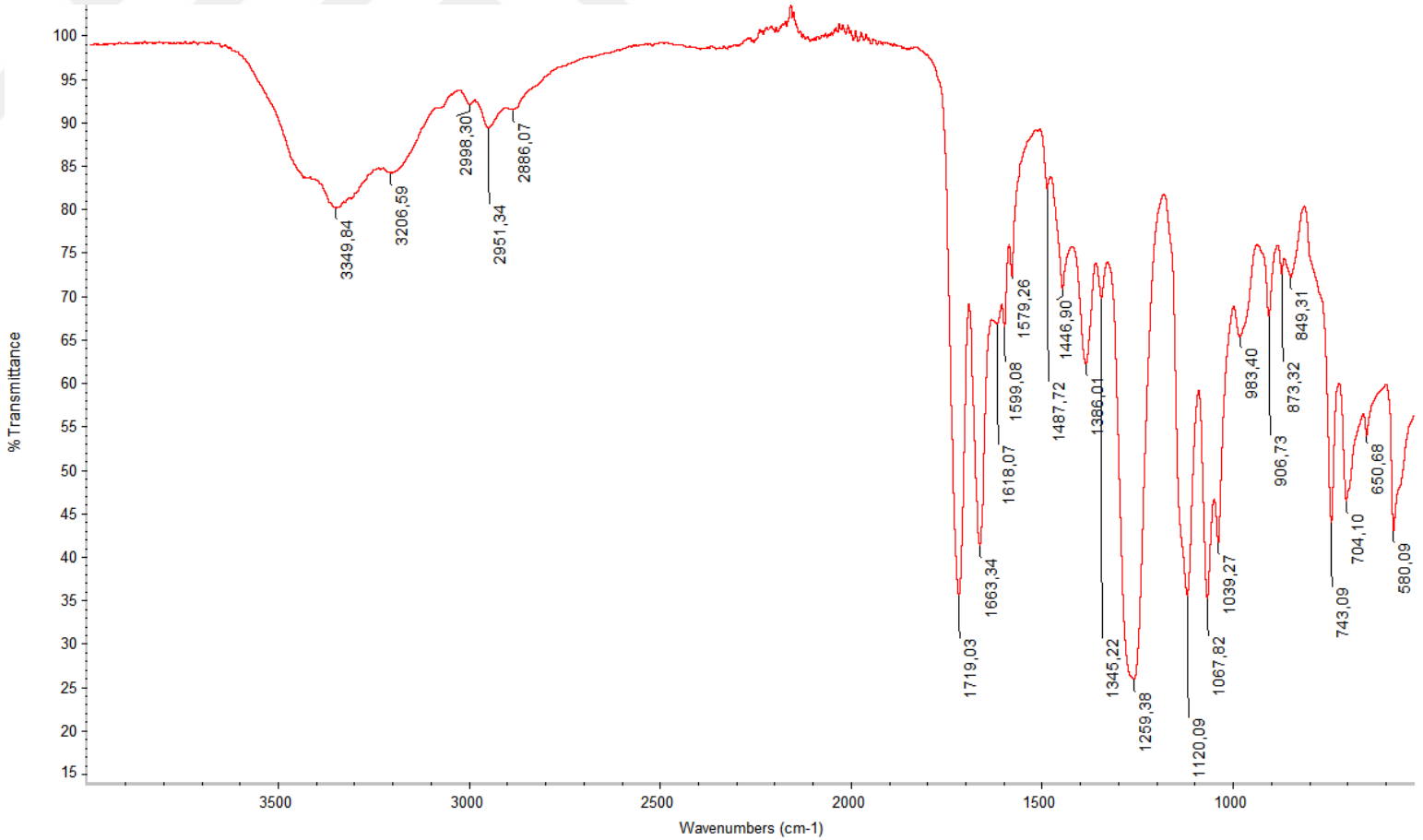


Figure A. 16. FTIR Spectra of sealed sample of acetamide and EPP after heating.