SYNTHESIS,
CROSSLINKING AND CHARACTERIZATION OF GLYCIDYL AZIDE LIKE POLYMERS

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ABSTRACT

SYNTHESIS, CROSSLINLING AND CHARACTERIZATION OF GLYCIDYL AZIDE LIKE POLYMERS

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Glycidyl azide polymer (GAP) is an environmentally friendly, important rocket fuel. It is synthesized by substitution of azide groups of sodium azide (NaN_3) with chlorine atoms of polyepichlorohydrine (PECH). This polymer is more energetic than classical polybutadiene based counterparts because it contains one azide group in its repeat unit.

The object of our study is to synthesize modified glycidyl azide polymer (MGAP) which has more than one azide group in its repeat unit, hence more energetic than classical GAP. The object includes also the cross-linking of MGAP and characterizing of the cross-linked MGAP's by means of thermal analysis, calorimetric measurements, tensile strength and swelling tests.

In this study it was found that Modified Glycidyl Azide Polymer (MGAP) with 4.42 azide groups per repeat unit can be synthesized and crosslinked by using Desmodur N-100 as a curing agent.

In order to evaluate the characteristics of MGAP as a solid rocket propellant binder, enthalphy of formation of MGAP and crosslinked MGAP(MGAPXR's) per repeat unit were determined. The results of calorimetry showed that both MGAP and MGAPXR's are at least 4 times more enegetic than that of the classical GAP.

Swelling test were applied to the samples in water and after drying, it was seen that MGAP samples lost about 4 % of their weights which shows that the cross-linking reaction of MGAP with Desmodur N-100 was not complete.

The tensile strength measurement results show that MGAP's have nearly 13 times greater tensile strength values than the classical GAP samples.

Another important result of this study was that MGAP has a higher density (1.44 g/cm^3) than classical GAP (1.30 g/cm^3) and hydroxyl terminated polybutadiene (0.93 g/cm^3), which is a useful property for rocket design because a denser propellant occupies less volume, hence makes it possible to produce lighter rockets.

Key Words: Glycidyl Azide Polymer (GAP), Modified Glycidyl Azide Polymer (MGAP), Polyepichlorohydrine (PECH), Chlorinated polyepichlorohydrine (CPECH), hydroxyl terminated polybutadiene(HTPB).

ÖZ

GLİSİDİL AZİD BENZERİ POLİMERLERİN SENTEZLENMESİ, ÇAPRAZ BAĞLANMASI VE KARAKTERİZASYONU

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Glisidil azid polimeri (GAP) çevre dostu, önemli bir roket yakıtıdır. Sodyum azidin (NaN_3) içerdiği azid gruplarının poliepiklorohidrindeki klor atomları ile yerdeğiştirmesiyle elde edilir. GAP'ın her yinelenen grubunda bir azid grubu olduğundan bu polimer, klasik polibutadien bazlı bağlayıcılardan daha enerjiktir.

Bu çalışmanın amacı, her yinelenen grubunda birden fazla azid grubu içeren ve dolayısıyla glisidil azid polimerinden daha enerjik olan modifiye glisidil azid polimerini sentezlemektir. Bu çalışmanın amacı ayrıca sentezlenen MGAP'ın çapraz bağlanmasını ve çapraz bağlanan MGAP' ların ısıl, kalorimetre, gerilme dayanımı ve şişme ölçümleri yardımıyla karakterizasyonunu içermektedir.

Bu çalışmada azidleme oranı tekrarlanan birim başına 4.42 azid gurubu içeren modifiye glisidil azid polymerinin sentezlenebileceği ve Desmodur N-100 ile çapraz bağlanabileceği bulunmuştur.

MGAP' ın katı roket yakıtı bağlayıcısı olarak özelliklerini belirlemek amacı ile MGAP' ın ve çapraz bağlanmış MGAPXR' ların yanma ısısı ve oluşma entalpisi ölçülmüştür. Kalorimetre sonuçları, MGAP ve MGAPXR' ların klasik GAP'a göre 4 kat daha enerjik olduğunu göstermiştir.

Şişirme testleri örneklere su içinde uygulanmıştır, kurutmadan sonra örneklerin ağırlıklarının yaklaşık %4' ünü kaybettikleri gözlenmiştir. Bu MGAP' ın Desmodur ile çapraz bağlanma reaksiyonunun tam olmadığını göstermektedir.

Gerilme dayanımı ölçüm sonuçları MGAP örneklerinin GAP örneklerinkine göre ortalama 13 kat daha fazla gerilme dayanımına sahip olduğunu göstermektedir.

Bu çalışmanın diğer önemli bir sonucuda MGAP (1.44 gr/cm^3) ların GAP'a (1.30gr/cm^3) ve HTPB' e (0.93gr/cm^3) göre çok daha yüksek bir yoğunluğa sahip olduğunu göstermiştir. Bu roket tasarımı için yararlı bir sonuçtur çünkü yoğun bir yakıt daha az hacim kaplar ve dolayısı ile daha hafif roketlerin üretimini olası kılar.

Anahtar sözcükler: Glisidil azid polimeri (GAP), modifiye edilmiş glisidil azid polimeri (MGAP), Poliepiklorohidrin (PECH), klorlanmış poliepiklorohidrin (CPECH), hidroksil sonlandırılmş polibutadien (HTPB).

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

CHAPTER 1

INTRODUCTION

1.1 Solid Propellant Rocket Motors

A solid propellant is a complex and stable mixture of oxidizing and reducing ingredients which, when ignited, burns in a controlled manner to form very hot, low molecular–weight gases. The inormous increase in volume resulting from formation of low molecular weight gases and the great increase in temperature provide the kinetic energy, which is released through the exhaust nozzle of the solid rocket motor. The specific impulse (Isp) is the most important characteristics of a propellant and defined as the ratio of total thrust (the velocity of combusted products) within a period of burning time to total amount of propellant [1].

Composite solid propellant rocket motor is constructed from a case, a propellant grain, a liner, an igniter and an exhaust nozzle as in the Fig 1.1 Motor case is predominantly made from a metal resisting to high internal pressures generated during the combustion. Most commonly preferred metal is steel that has a good elasticity and strenght.

In propellant terminology, grain is defined as the propellant stored in the chamber of a motor with various shaped blocks according to the purpose. Grains are mainly divided into two groups, namely free-standing and case-bonded.

Free-standing grains are filled into a cylindrical plastic cartridge (PVC etc.) and they stay in the case by various support elements such as wedges, springs, and grids

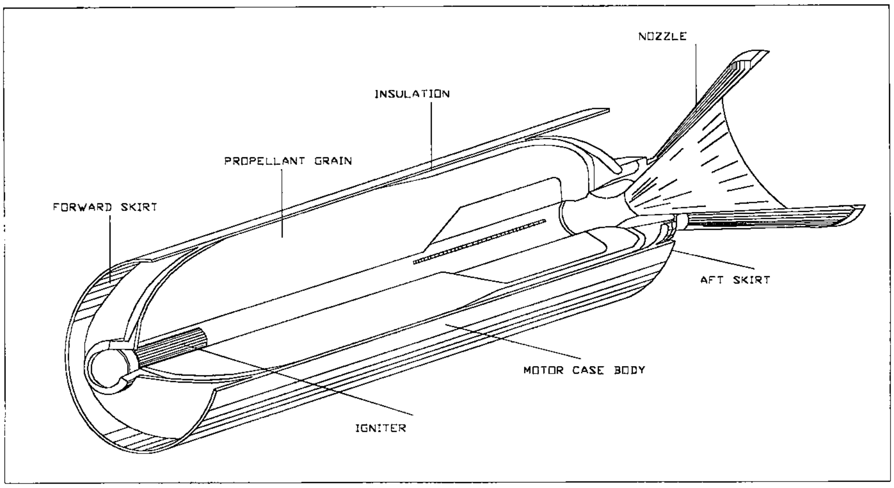


Figure 1.1 Solid Propellant Rocket Motor

Case-bonded grains are produced by directly casting the uncured propellant into the motor case around a centered mandrel with desired shape. After casting, the propellant is cured at a specific temperature belonging to the matrix material and then the mandrel is removed.

As the rocket goes in the sky, temperature of the propellant reaches up to 3500 K° depending on the type of propellant used. At this temperature avoiding from the damage of motor case becomes a must [2]. For doing so a thin layer of some elastomeric materials, which is powered by fibers, are lined to the inner surface of the motor case. This process also lets the propellant be bonded strongly to the motor case.

The igniters used in the rocket motors are commonly pyrotechnics compounds. They include combustible materials such as magnesium and zirconium. The igniters can be in the form of powder, pellets, and grains. They are placed at the head-end closure or at the exhaust nozzle end of the motor.

1.2 Composite Solid Propellants

Generally composite solid propellants are divided into three classes, namely double base, composite modified double base and composite propellants. When the oxidizing and reducing property is contained in the same compound such as nitroglycerin, then the propellant is called as double-base.

If the double base propellant is modified by adding solid oxidizers, then the propellant is named as composite modified double base propellant .

Composite solid propellant is widely used in today's rocket technology and composed of a polymeric binder, a solid oxidizer and a metallic fuel. The reasons why people concentrate on this type are;

* Controllable burning rate
* Stable combustion characteristics
* Good physical and mechanical properties

Although the composite solid propellants have the excellent properties, they are moisture sensitive, and have high flame temperature and depending on the type of ingredients they have smoky exhaust.

1.3 Binder Evolution

The binder is an elastomeric matrix which holds the oxidizer and metallic fuel particles [3]. In addition to being a continuous phase of the propellant, it is also a fuel. An ideal binder must have some propeties as bellow;

* Low molecular weight gases during combustion
* It must be energetic
* Glass transition temperature less than –53 C °
* Hydroxyl terminated (in order to be cross-linked)

Preliminary propellants were produced with binders such as asphalt and PVC(polyvinylchloride), but they were failed because of poor physical properties. Better mechanical and balistic properties were achieved by using liquid polymers which make crosslinking.

The first binder of this type was (Polysulfide) PS although an undesirable quality of the polysulfides was the presence of sulphur atoms in the system. They produced high-molecular-weight exhaust products (sulphur dioxide with a molecular weight of 64), thereby lowering specific impulse since specific impulse is proportional to $(\Delta H^0_{\mathrm{formation}}/M)^{0.5}$ where M is the average molecular weight of exhaust gases. Therefore a large amount of oxidiser had to be mixed with the binder to obtain the high energy desired, hence the binder lost much of its rubber-like quality.

Polyurethanes (PU) arrived after PS's as elastomer fuel binder. The group of polymers known as polyurethanes were made by combining polyols with isocyanates. Compared with the polysulfides, the average molecular weight of the exhaust gases was lower. This was because the polyurethanes contained only carbon, hydrogen, oxygen, and nitrogen atoms (not sulphur). An additional benefit was polymer contained substantial amounts of oxygen. It was not necessary therefore to use as great a percentage of oxidizer in the formulation of the propellant. The increased proportion of binder to oxidizer provides good mechanical properties to the propellant [4].

GAP has been spotlighted because of its high density compared to HTPB, positive heat of formation (94.1 kj/mole-Repeat unit), and capability of start-stop thrust control, due to the unique thermal decomposition behaviour that GAP itself can burn only at elevated pressures more than nearly 3 atm without using an oxidizer [5-14].

1.4 Oxidisers

Today's rocket technology is trying to use environmentally friendly oxidisers. Among the most widely used oxidisers are [15-16];

Ammonium perchlorate; is the most widely used one today. It is characterised by high heat and is a good gas producer (not a smoke producer).

Potassium perchlorate; is used for fast burning rates. It is characterised by high heat and is a low gas producer.

Ammonium nitrate; is used for slower burning rates. It is characterised by low heat. It is a high gas producer and is good for gas generator propellants. It requires a greater amount of binder to make castable propellant, but too much binder produces excessive smoke. It may be the oxidiser for the future. It contains no toxic elements and no solid elements, produces no solids by decomposition, and therefore, together with a high energy non-polluting fuel, could provide a more 'environmentally friendly' solid propellant.

Lithium perchlorate; is a proposed oxidiser, very hygroscopic and may be used in some high-temperature propellants.

1.5 Fuels

Metallic fuel in propellants is used because of its highly exothermic reaction with the oxidisers. Materials used for this purpose are the following;

Lithium aluminium hydride or LAH ($LiAlH_4$)

* Dust is very irritating .

* Very dangerous to handle since it may ignite and burn violently.

* Dust may explode and ignites spontaneously with water, alcohols, ammonium hydroxide, etc.

Magnesium hydride (MgH_2) and Lithium borhydride ($LiBH_4$)

* MgH_2 is relatively non-toxic. $LiBH_4$ is toxic and may release diborane (B_2H_6) on treatment with acids. B_2H_6 is extremely toxic, with a maximum allowable concentration less than 1 ppm

* MgH_2 and $LiBH_4$ are much less hazardous than $LiAlH_4$. They are similar to Mg powder, and release hydrogen.

Powdered metals such as Zirconium (Zr), Beryllium (Be), Aluminum (Al)

* Dust should not be inhaled. Beryllium dusts are very toxic.

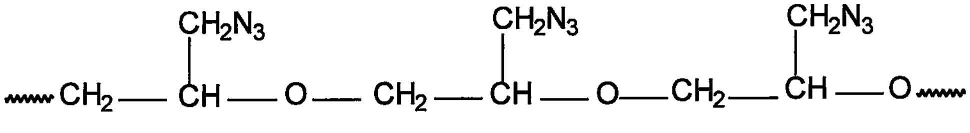
* Finely powdered Zr is ignited by static electricity. Mixtures with oxidising agents are hazardous and easily exploded by static electricity.

* Zr is used in igniters and various pyrotechnic devices while beryllium is an additive in high-energy propellants.

* Aluminum is the most commonly used one because of its highly exothermic reaction with the oxidisers. The presence of aluminum in rocket propellants also reduces or eliminates combustion instability caused by the formation of pressure waves in the motor chamber[17].

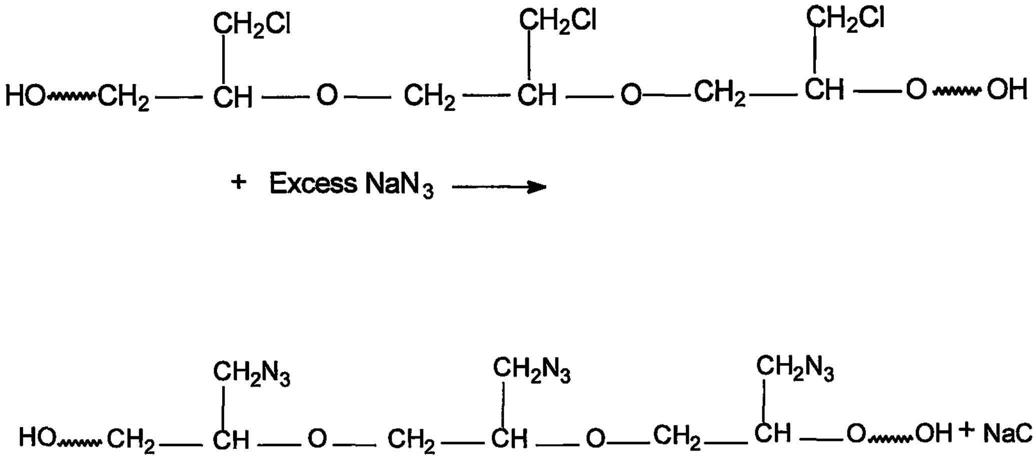
1.6 GAP Case

GAP (1.2) is made from hydroxyl terminated polyepichlorohydrine (PECH) which is reacted with excess sodium azide (NaN_3) in dimethyl sulfoxide (DMSO) . Azide groups substitute the Cl atoms (1.3) in the PECH to give GAP.



$$\sim CH_2-\underset{}{\overset{CH_2N_3}{\overset{|}{CH}}}-O-CH_2-\overset{CH_2N_3}{\overset{|}{CH}}-O-CH_2-\overset{CH_2N_3}{\overset{|}{CH}}-O\sim$$

(1.2)



$$HO\sim\sim CH_2-\underset{}{\overset{CH_2Cl}{\overset{|}{CH}}}-O-CH_2-\overset{CH_2Cl}{\overset{|}{CH}}-O-CH_2-\overset{CH_2Cl}{\overset{|}{CH}}-O\sim\sim OH$$

$$+\ \text{Excess}\ NaN_3 \longrightarrow$$

$$HO\sim\sim CH_2-\overset{CH_2N_3}{\overset{|}{CH}}-O-CH_2-\overset{CH_2N_3}{\overset{|}{CH}}-O-CH_2-\overset{CH_2N_3}{\overset{|}{CH}}-O\sim\sim OH + NaC$$

(1.3)

Optimization studies were first conducted on the production of PECH. These processes led to the successful development of a one step process which (depending on the type of catalyst, initiator and ECH/initiator mole ratio used) yielded polymer exhibiting molecular weights ranging from 1500 to 2600 and hydroxyl functionalities of 1.6 to 3.1. Emphasis was shifted to the ethylene glycol initiated PECH so that GAP with functionalities closer to 2 could be prepared. It was believed that a truly difunctional prepolymer would impart improved propellant mechanical properties [7-12].

Ahad E.[8] developed a new process at Drev in Canada. GAP was prepared in a single step process directly from the monomer ECH and without using any catalyst. The reaction was carried out at 95^{0}C and lasted less than 8 hours. However, this method yielded, GAP of low molecular weight (app.500) that could be mainly utilized as an energetic plasticizer.

Tokui H.[14] in 1990 studied the synthesis, characterization and motor application example of GAP. For this, diol-group-terminated Glycidyl Azide oligomer was synthesized by the reaction of PECH (MW=2500) and NaN_3 in DMSO solution at 100 ^{0}C for 10-12 hours. The test firing results of GAP/AN based propellant grains loaded to an internal burning type motors were illustrated.

There are a lot of studies about the characterization of GAP in the literature. For example Tazikuza M.[23] studied the combustion performances of GAP as a binder for solid rocket propellants with the oxidizers such as ammonium nitrate (AN), octogen, triaminoguanidinennitrate(TAGN). He found that temperature sensitivity of GAP decrases as the ratio of AN increases in the formulation of the binder. He also found that burning rate of GAP with AP(amonum perchlorate), HMX or TAGN oxidizers depends on the partical size, however the burning rate of GAP doesn't change with AN.

In another article Eroğlu M. et.al. [24] studied the spectroscopic and thermal characterization of GAP synthesized from PECH by the presence of phase transfer catalysis.They found that conversion of $-Cl$ to $-N_3$ could be completely achieved in 6 hr. It was also found that completion of $-Cl$ to $-N_3$ could be easily followed by measuring the glass transition temperature and exothermic decomposition of the polymers. The analysis also showed that conversion of PECH to GAP was a first order reaction with a rate constant of 0.74. They also studied the thermal decomposition of GAP. It was shown that the first stage of weight lose of GAP was due to the exothermic decomposition of pendant azide groups. Another result of the study was that Tg of GAP increases as the ratio of undecomposed azide groups decrease.

Eroğlu M. et.al. [25] also studied the GAP-b-PS and GAP-b-PVAc block copolymers by thermal analysis methods. In the study, synthesis of macro-azo-initiator, MI-GAP by the condensation reaction of polydiol (GAP) with azobiscyanopentanoyl chloride was achieved. They found that it can be possible to get polyether and polyvinyl block copolymers having different weight ratio of polyether units by changing the feed ratio of macro-azo-initiators. They concluded that GAP-b-PVAc block copolymers could be used as solid rocket propellant material or energetic plasticizer with different heat capacity.

Ahad E. [26] compared some physical properties of GAP and GAP/Ethylen oxide copolymer binder systems by using tensile strength measurements. The results of the study showed that the GAP/Ethylene oxide copolymer system had higher elongation at break and lower glass transition temperature than GAP system. The curing agent used in this study was isophrene diisocyanate.

Van Tam Bui. et.al.[28] studied the tensile properties of GAP purified by solvent extraction method which is leaving less than 1 % DMSO in the polymer. This study showed that elongation at break values of samples cured with different NCO/OH ratios decrease at high value of that ratio and large amount of remaining DMSO in the samples greater than 2 % has a weakening effect on physical properties.

After these studies about GAP, a new concept appeared in METU Chemistry Department, namely modified glycidyl azide polymer (MGAP). This is an energetic polymer containing the same backbone with the glycidyl azide polymer but much more energetic than GAP.

In Kara Ş.'s master thesis[29], it was found that modified glycidyl azide polymers with different extent of azide groups ranging from 1.1 to 3.4 per repeat unit can be synthesized from the chlorinated PPO and PECH. He also characterized them by means of spectroscopic and thermal analysis techniques and found that as the number of azide groups increases, the Tg's of samples decreased and heat of combustion becomes more negative. Another result found in this study was that although GAP decomposes at 250C°, decomposition of MGAP's occour in two steps, one is between 180-200C° and the other occurs around 450C°.

Kara Ş. obtained MGAP's with a maximum about 3.4 azide groups per repeat unit. This result rises a suspicion about the existence of an upper limit of chlorination extend of PECH and PPO. Öztürk E.[29] using more rigorous reaction conditions showed that there was no such an upper limit. By using mass spectrometry and NMR spectrometry, it was showed that at the initial stages of chlorination, Cl atoms are not randomly distributed over the C atoms, but they are prefentially substituted on methyl C. But methylene and methine carbons can also be chlorinated.

Mass spectrometry showed presence of fully chlorinated repeat units. Öztürk E. also showed that all the Cl atoms on highly chlorinated PPO or PECH can be quantitatively substituted by azide groups. She observed, as the extend of azide substitution increase, solubility of MGAP's in organic solvent decrease but solubility in water increase. MGAP's with higher content of azide groups can only dissolve in water and dimethyl sulfoxide.

1.7. The Aim of this work

In the preceeding works of the department, both PECH and PPO of low molecular weight were azidized to obtain highly energetic MGAP's. However IR spectra of MGAP's showed that carbonyl groups were formed during synthesis of MGAP's. This would indicate degradation of chains. If the degradation is extensive MGAP's would be useless as rocket fuels.

In order to use MGAP as a binder for rocket fuels, it must be cross-linked into grain with proper mechanical properties. Therefore present research is undertaken with the following purposes ;

1. To prevent carbonyl group formation by synthesizing MGAP's in the absence of oxygen.
2. To characterize PECH and MGAP to find the degree of degradation of chains in synthesis.

3. To show that MGAP's can be cross-linked .
4. To characterize cross-linked MGAP's with mechanical and chemical test.
5. To measure the heat of combustion of cross-linked MGAP's.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

Benzene; was supplied by Merck A.G and purified with fractional distillation before use (Bp: 78 ^{0}C at 685 mmHg) and then it was dried over CaH_2 and filtered.

Carbontetrachloride; was supplied by Merck A.G and purified with fractional distillation before use (Bp: 30 ^{0}C at 682 mmHg) and then it was dried over CaH_2 and filtered.

Dimethylsulfoxide; was the product of Merck A.G, dried over CaH_2, filtered and distilled by using rotavapor (Bp: 55 ^{0}C at 3 mmHg).

Polyepichlorohydrine (PECH); was produced by 3M Company and used without further purification.

Sodium azide (NaN_3); was supplied from Merck AG and used without further purification.

Sodium chloride (NaCl); was the product of Atabay Lt. Şti.

Silver Nitrate ($AgNO_3$); was supplied by Merck AG. It was standardized by NaCl solution.

2.2 Molecular Weight Determination with Cryoscopy

Molecular weights of PECH, CPECH and MGAP were determined by freezing point depression of dimethyl sulfoxide (DMSO). In order to determine the cryoscopic constant of DMSO, diazobenzene was used as a standart reagent. The relationship between freezing point depression and cryoscopic constant is shown in the equation 2.1 below.

$$\Delta T = K_S \times m \tag{2.1}$$

ΔT: Freezing point depression
K_S : Cryoscopic constant of solvent
m: Molal concentration of the solute

If ΔT-m graph is drawn, a linear relationship is obtained. The slope of this plot gives the cryoscopic constant of DMSO.

Molecular weights of polymers were determined by plotting $\Delta T/c$ against c (c is the solute concentration in gr/cm^3, ΔT stands for the freezing point depression). This graph gives a linear relationship. In order to determine the molecular weights of polymers, the intercept of this plot is determined. Molecular weights of polymers are calculated by the equation 2.2.

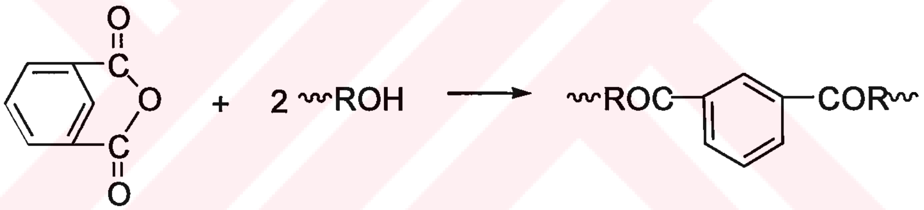
$$1/ Mn = (\lim_{c \to 0} [(\Delta T/c)/c] \times \rho)/ 1000 \times K_S \tag{2.2}$$

ρ : Solvent density in gr/cm^3
K_S : Cryoscopic constant of solvent
c : Solute concentration in gr/cm^3
Mn : Number average molecular weight

2.3 Determination of OH Functionality of Polymers

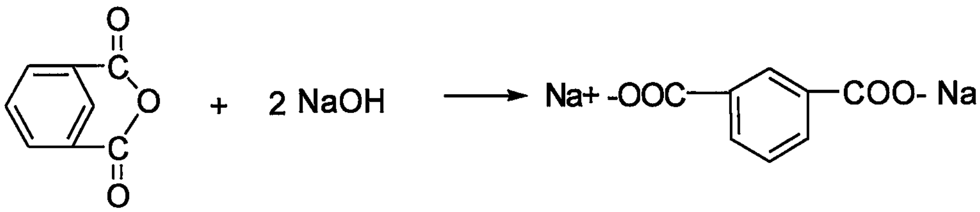
Some linear macromolecules contain functional groups such as –OH, COOH at their chain ends which can be calculated by chemical methods. For example COOH groups can be determined by titration with NaOH or KOH. In this study OH functionality of polymers were determined by phthalic anhydride esterification method. The sample was weighed into a small balloon and refluxed for 2 hours with 0.2 g phthalic anhydride in 10ml pyridine. After reflux 10ml of distilled water was added and then the solution was titrated to a phenolphthalein end point using 0.0575 M NaOH solution.

Esterification reaction (2.1) can be shown as follows;



(2.1)

At the end of the esterification reaction some phthalic anhydride remains unreacted which is calculated by using the reaction (2.2).

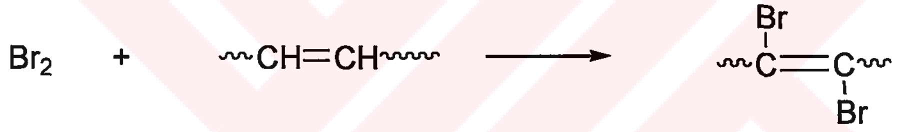


(2.2)

2.4 Double bond determination

The fundamental principle of double bond determination is the addition of bromine to the double bond in the molecule. For this purpose sample was dissolved in 10 ml $CHCl_3$ and 10ml of glacial acetic acid. After cooling in ice-bath, 10 ml of 0.077 M of bromine in glacial acetic acid was poured in. After waiting for 2 minute 25 ml 10 % aqueous potassium iodide (KI) was added and the solution was immediately titrated with 0.044 M NaS_2O_3-$5H_2O$ using starch indicator. The sample and blank difference gave us the amount of double bond.

The essential reactions used in the calculations are shown as follows (2.3. 2.4, 2.5)



$$Br_2 \quad + \quad \sim CH{=}CH \sim \longrightarrow \sim \overset{Br}{\overset{|}{C}} {=} \underset{Br}{\underset{|}{C}} \sim$$

(2.3)

$$Br_2 \quad + \quad 2I^- \longrightarrow I_2 \quad + \quad 2Br^-$$

(2.4)

$$I_2 \quad + \quad 2S_2O_3^{-2} \longrightarrow 2I^- \quad + \quad S_4O_6^{-2}$$

(2.5)

2.5 Procedure

2.5.1 Chlorination of PECH

In order to produce Cl_2 gas, the reaction(2.6) below was utilized;

$$16\,H^{+} + 2\,MnO_4^{-} + 10\,Cl^{-} \rightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,Cl_2\,(g) \qquad (2.6)$$

Chlorine gas was produced by dropwise addition of concentrated H_2SO_4 with a separatory funnel into an aqueous solution of $KMnO_4$ and NaCl. Chlorine gas was passed through water to remove HCl (g). The obtained Cl_2 (g) was allowed to enter into the reaction flask at room temperature. The reactor flask contained PECH in CCl_4 solution. In order to prevent any lose of solvent with the escaping gas stream, the reaction flask was equipped with a reflux condenser. The gas stream finally sent to concentrated aqueous NaOH solution in order to avoid the contamination laboratory atmosphere with Cl_2 gas (Figure 2.1).

After chlorination, the reaction product was separated from CCl_4 mixture by vacuum evaporation. The chlorinated polymer was extracted with benzene and neutralized by adding NaOH and washed with distilled water until the solutions did not show any acidity. Finally, the chlorinated polymer was recovered by freeze-drying the solution on a vacuum-line.

2.5.2 The Extend of Chlorination of PECH

The extend of chlorination was calculated by using the following equation (2.3);

$$R_{Cl} = 92{,}5 \times \Delta m / (m \times 34.5) \qquad (2.3)$$

R_{Cl} is the number of Cl atoms substituted per repeat unit of PECH (92,5 g/mol), Δm is the increase of mass of the sample, m is the mass of PECH used, 34.5 is the theoretical increase of the mass for each mole of chlorine substitution. This equation was validated by the study of Öztürk E.[29].

2.5.3 Azidation of Chlorinated PECH (Synthesis of MGAP)

The reactor shown in Figure (Figure 2.2) was constructed for the azidation of chlorinated PECH. An oil bath was used in order to obtain desired temperature.

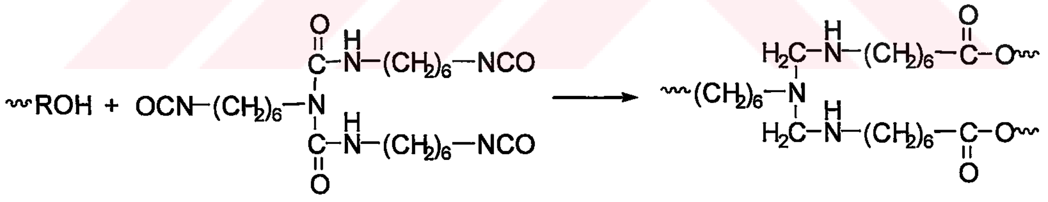
Chlorinated polymers were dissolved in DMSO, excess NaN_3 was added and the mixture was agitated at 95 ^{0}C by using a oil bath for 48 hours. At the end of the reaction, the salts were removed by filtration. DMSO rich phase was evaporated by using a rota-evaporator but the residue contained salts. In order to remove salts (Na^+, Cl^- and excess N_3^-) the product dissolved in water. Undissolved part of the polymer were extracted by filtration and dissolved in DMSO. Then, ion exchanger method was applied to remove inorganic salts from the product in water. In this technique, cation and anion exchanger were added in the solution one after another until no acid colour was seen and no precipitation was occurred by adding $AgNO_3$ to the solution. Water in the polymer solution was evaporated using a vacuum connected rota-evaporator and the obtained salt free polymer was added to the polymer in DMSO, finally all DMSO was removed by vacuum connected rota-evaporator.

2.5.4 Cross-Linking of MGAP

MGAP was cured with the trifunctional isocyanate Desmodur N-100. The binder formulations are usually named as gumstocks [18]. Four different types of gumstocks with different cross-linking ratios, respectively MGAPXR0.9, MGAPXR1.0, MGAPXR1.1, MGAPXR1.2 were prepared. XR is the cross-linking ratio of the polymer which is defined as follows (eq.2.4)

$$XR=NCO/OH = \frac{\text{(NCO functionality of Desmodur N-100)}}{\text{(OH Functionality of sample)}} \qquad (2.4)$$

The reaction of Desmodur with OH groups of the MGAP can be shown as follows



(2.7)

2.5.5 Preparation of Gumstocks

MGAP and curing agent were mixed at different cross-linking ratios. MGAP sample was poured into a beaker and curing agent was added. Mixture was stirred about 5 minutes and kept under vacuum to remove gas bubbles from the gumstocks. Finally mixtures were transferred into the mould and held at 40°C for 6 days.

Calculations of the cross-linking ratios were made by simultaneous solution of equations 2.5 and 2.6

$$m_s+m_d = Mg \tag{2.5}$$

$$XR= \frac{5,2 \times 10^{-3} \times m_d}{3,37 \times 10^{-4} \times m_s} \tag{2.6}$$

m_d :The weight of Desmodur

m_s : The weight of MGAP

M_g : Desired weight of gumstocks

XR : Desired Cross-linking ratio

5.2×10^{-3} : NCO content of Desmodur in mol/g

3.37×10^{-4}: OH content of MGAP in mol/g

2.5.6 Tensile Strength Measurement

Tensile strength measurement was made by Llyod LS 500 tensile testing machine at room temperature. The tensile load cell has a capacity of 100 kN. The gauge dimensions were 30 × 8 ×1 mm. The mechanical properties of interest [27] are defined as follows:

$$\text{Elongation at break} = (\text{gauge length at break/initial gauge length}) \tag{2.7}$$

$$\text{Tensile Strength} = \frac{(\text{ultimate tensile force} \times \text{elongation at break})}{(\text{original cross sectional area})} \tag{2.8}$$

2.5.7 Calorimetric Tests

The calorimeter (Figure 2.3) is composed of a body, a bucket, in the bucket the calorimeter bomb. At the top of the calorimeter there is an O_2 inlet and an electrical terminal pole. The top of the calorimeter can be screwed off the open and the bomb there is a platinum capsule supported to the electric terminal poles, which contains the sample during the experiment. MGAP's were placed into the cotton envelope together with iron fuse wire and two ends of the fuse wire were connected to the electrical terminal poles of the calorimeter bomb.

For the combustion, the following steps were done. The bucket of calorimeter was filled with 2500 grams of distilled water and placed it in the body. The polymer sample was placed in a platinum capsule and was fastened with a 7-cm fuse wire that was connected to the terminals. The bomb was filled with 25 atm of O_2 (g). Then, the bomb in the bucket was placed. After connecting the terminals with ignition unit and closing the cover of the calorimeter, the stirrer of the system was set on. Temperature readings were taken in three separate stages:

The First Stage: After the start of the stirrer, readings were taken in one-minute intervals for 7 minutes.

The Ignition Stage: After ignition, the temperature increased and showed a maximum in about three minutes. The readings were taken in one minute's intervals until the decrease appeared, and then the maximum temperature was noted.

The Last Stage: In the cooling state, 7 more readings were taken with a reading at a minute.

The same procedure was repeated with benzoic acid in order to determine the calorimetric constant. The calorimetric constant was calculated using the following formula;

$$C = (Q_1 \times W_1 + Q_2 \times W_2) / t \qquad (2.9)$$

where;

C = The calorimetric constant

W_1 = Weight of benzoic acid

Q_1 = Heat of combustion of benzoic acid (= 6328 cal / g)

W_2 = Weight of fuse wire

Q_2 = Heat of combustion of fuse wire (= 1400 cal / g)

$t = T - dT$

T = Maximum temperature reading in the ignition step – The last reading in the first stage

$dT = n \times Xlast - (Xfirst - Xlast) / 2$

n = Number of readings taken in the ignition stage

Xlast = (max. temperature reading in stage 1 – the last reading in stage 3) /7

Xfirst = (first temperature reading in stage1– last temperature reading in stage1) /7

2.5.8 Measurement of ΔH_f of MGAP

The extend of formation of one repeat unit of polymer were calculated as follows:

$$\Delta Hc = \Delta Uc + \Delta n \times R \times T \qquad (2.10)$$

$$(\Delta Uc = Q)$$

On the other hand, ΔHc is related with ΔH_f of MGAP' s;

$$(C_3OH_x(N_3)_{6-x}) + (2.5 + x/4)\ O_2\,(g) \rightarrow 3\ CO_2 + (x/2)\ H_2O\ (l) + (3.(6-x)/2)\ N_2(g)$$

(Where x is known from the analysis of the MGAP)

$$\Delta Hc = 3 \times \Delta H_{f, CO2} + x / 2 \times \Delta H_{f, H2O} - \Delta H_{f, sample}$$

(It is assumed that O_2, CO_2 and N_2 are all ideal gaseous under the experimental conditions).

2.5.9 Thermal Characterisation

The most significant assessment of energetic polymers is of course thermal characterisation. For this reason all samples were characterised by the DSC and TGA runs. In this study, a device namely General V4.1C DuPont 2000 was used in order to obtain DSC spectrums. For TGA runs, a device produced by Polymer Laboratories namely PL TGA 1500 was used. The scanning rate of the devices was adjusted to 10 °C per minute and scanning of the samples were made at nitrogen atmosphere.

2.5.10 Water Soluble Fraction of Cross-linked Polymers

Cross-linked polymers with known mass was kept in water (about 0,25g in 30 cm^3) at room temperature for two days, then they were dried until constant weight. The mass difference was due to the soluble fractions of cross-linked polymers.

2.5.11 Swelling Measurements

After extraction of soluble fractions, samples were kept in water at room temperature for two days and swollen samples were weighed. Percentage swelling values was calculated from the following equation:

$$\% \text{ swelling} = [(m_s - m_i) \times d/(m_i)] \times 100 \tag{2.11}$$

Where m_i is the initial mass of sample, m_s is the final mass of the sample and d is density of cross-linked polymer.

2.5.12 Density Measurement

Density was measured by a pycnometer. Calculations were made by using the formula below;

$$\text{Density of polymer} = [(M_2 - M_1) / ((M_3 - M_1) - (M_4 - M_2)) \times (1 / \rho)] \qquad (2.12)$$

P : Density of benzene
M_1 : Empty pycnometer
M_2 : Pycnometer and sample
M_3 : Pycnometer and benzene
M_4 : Pycnometer, sample and benzene

2.5.13 IR Spectroscopy

A Nicholet 510 model FT-IR spectro-photometer was used to get IR spectra of the polymers. Polymers were dissolved in DMSO and dried with calcium hydroxide, then polymers were spread on KBr pellets.

2.5.14 NMR Spectroscopy

^{13}C NMR spectra of the polymeric samples were taken by Bruker-Spectrospin Avance DPX40. Samples were dissolved in CCl_4.

CHAPTER 3

EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Chlorination of PECH

Chlorinated PECH samples showed some carbonyl absorption peaks in IR spectrum. The intensity of these peaks could be partially decreased by sweeping the air in the chlorination reactor by N_2 (g) stream. The presence of these peaks indicated some degradation process accompanying chlorination. With the purpose of measuring the extend of degradation, PECH was characterised both by molecular weight and end group analysis. Results are given in Table 3.1, molecular weight and end group analysis results of PECH and MGAP's were also included for the sake of comparison.

Table 3.1 Characterization Results of Polymers

Sample	Rt	F_{OH} (10^4)	F_{DB} (10^5)	M_{n1}	M_{n2}	F_{OHS} (10^4)	F_{DBS} (10^5)	M_{ns1}	M_{ns2}
PECH	(-)	6,77	8,95	2872	2610	(-)	(-)	(-)	(-)
CPECH-2,50	24	5,14	0,48	(-)	3853	4,33	5,74	(-)	(-)
CPECH-3,31	36	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)
CPECH-4,42	96	3,84	0,32	6279	5165	2,97	3,93	6525	5937
CPECH-4,91	120	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)
MGAP-4,42	48	3,37	0,32	7700	5879	2.62	3.46	7415	6745

M_{n1} : Number average molecular weight determined by cryoscopic method
M_{n2} : Number average molecular weight determined by end group analysis
Rt : Clorination time (hour)
F_{OH} : OH functionality
F_{DB} : Double bond functionality

In table 3.1 F_{OH} and F_{DB} as well as M_{n1} values are experimentally measured quantities. M_{n2} values are calculated assuming that there are only two types of end groups of chains (OH and double bond).

F_{OHS} and F_{DBS} values were stoichiometrically calculated hydroxyl and double bond functionalities. These quantities were calculated by assuming the hydroxyl and double bond content of samples were not changed during chlorination and subsequent azidation of samples. This assumption more or less holds in hydroxyl functionality but F_{DB} functionalities are about 8% of F_{DBS} values. This shows that in chlorination the majority of double bonds are chlorinated.

M_{ns1} and M_{ns2} values in these tables were also stoichiometrically calculated molecular weights. M_{ns1} values were calculated that the change in the M_{n1} value of PECH in CPECH and MGAP is only due to the increase of molecular mass of the repeat units in chlorination and azidation. Similarly M_{ns2} values were calculated from M_{n2} values of PECH.

It appears from Table 3.1 M_n and M_{ns} values are in accordance, showing PECH chains are not extensively degraded during synthesis of MGAP.

In the Table 3.1 the extend of chlorination increases with the reaction time. However it should be pointed out that the rate of chlorination is also controlled by concentration of reagents, temperature and sunlight.

In this reaction as the temperature increases, rate of reaction increases up to 60C°. Beyond this temperature, reaction rate decreases because solubility of Cl_2 in the solvent(CCl_4) decreases.

Sunlight has an acceleration effect on the reaction due to free radicalic nature of the reaction which can be illusrated with the following reactions;

Cl_2 (l,solution) + hv $\rightarrow$ 2 $Cl^{\cdot}$ (l,solution)

$R_3C\text{-}H + Cl^{\cdot} \rightarrow HCl + R_3C^{\cdot}$

$R_3C^{\cdot}$ + Cl_2 (l,solution) $\rightarrow$ $R_3CCl + Cl^{\cdot}$

Therefore in order to obtain a fast chlorination reaction, temperature was held at 60C° and trained in summer season when the sunlight is intense.

The results shown in Table 3.1 indicated that chlorination extent of PECH could be increased up to 4.91 Cl atoms per mole of repeat unit. However in the previous studies made by Kara Ş.[28] and Öztürk E.[29] maximum chlorination content was only about 4.3 Cl/repeat unit.

Because of some experimental difficulties only CPECH4.42 in Table 3.1 could be converted to MGAP succesfully.

The failure in other synthesis was due to isolation of product from the reaction mixture. MGAP dissolved both in water and DMSO but not in organic solvents. Therefore extraction of MGAP from the reaction mixture by liquid-liquid phase separation was impossible. MGAP2.5 and MGAP4.42 were isolated only after the development of the procedure described in experimental section.

Another difficulty was neutralizing the CCl_4 +PECH solution, after CPECH synthesis. In one case before the proper neutralization, MGAP synthesis was attempted. But HN_3 (g) was suddenly formed under acidic conditions, and all the sample burned with an explosion (HN_3 is an explosive gas).

Although MGAP2.5 was synthesized succesfully but couldn't crosslinked properly. In the attempt of crosslinking MGAP2.5, too much catalyst (dibutylin dilaurate) and high temperature conditions were employed. The resulting rubber was heterogeneous texture with gas bubbles traped in. However after developing the experimental procedure given in the experimental part, crosslinked MGAP4.42 was succesfully obtained in the form of a homogeneous brown rubber.

3.2 IR Spectra of PECH, CPECH and MGAP

C-H (Streching) : This peak was seen between 2870- 3020 cm^{-1} but as expected the intensity of peak clearly decreased in chlorinated PECH(CPECH) (Fig 3.1) relative to the C-O-C peak because, when the PECH is chlorinated C-H bonds are converted to C-Cl bonds in PECH.

C-Cl (streching) : This peak was seen between 650-800 cm^{-1} in the spectra (Fig 3.1 and Fig 3.2) but intensity of the peak increased in chlorinated PECH due to the increase in the number of C-Cl bonds.

C-O-C (Streching): This peak was seen between 1100-1230 cm^{-1} in all spectra (Fig 3.1, 3.2, 3.3).

$C-N_3$ (Streching): This peak was observed at 2104 cm and C-Cl peaks disappeared (Fig.3.3) due to the complete conversion of C-Cl to $C-N_3$ in the CPECH.

There are some peaks observed in the spectra apart from the main peaks above. They give clues about the hydroxyl functionality, double bond functionality of the polymers. On the other hand, there was a peak which gives an idea whether the oxidation happened or not during the chlorination step at which radicalic reaction occurs. Hydroxyl groups of the polymer was seen from the peaks observed between 3100-3600 cm^{-1}. Double bond terminals was also seen from the peaks between 1500-1630 cm^{-1}. During the chlorination step oxidation happened although nitrogen atmosphere was used in the chlorination step. The oxidation peak (C=O) was seen at about 1750 cm^{-1} in the spectrum of CPECH (Fig 3.2) and was inherently seen in MGAP's spectrum(Fig 3.3).

The major peaks observed from the IR spectra of the polymers (Fig 3.1, 3.2,3.3) can be seen from the Table 3.2.

Table 3.2 IR Results

Sampe	C-H	CH(Ben)	C-O-C	C=O	C=C	C-Cl	OH	N3	Fig
PECH	2872	1425	1129	NO	1620	744	3469	NO	3.1
CPEH	3032	1434	1096	1759	1640	780	3356	NO	3.2
MGAP	2874	1450	1079	1750	NO	NO	3343	2105	3.3

NO : Not observed

3.3 NMR Characterization of PECH, CPECH and MGAP

Emprical chemical shift values of chlorinated polymers[30] were estimated from the following formula(2.13):

$$\text{Chemical shift of } \alpha \text{ C} = A + 31\times n^{\alpha} + 10\times n^{\beta} - 5\times n^{\gamma} \qquad (2.13)$$

Where A is the original chemical shift of α C atom in PPO (if methyl C is chosen as α C ; A=17ppm)

β is the next C atom to α C

γ is the other C atom next to β C

n^{α}, n^{β}, n^{γ} are number of Cl atoms on α C, β C, γ C atoms.

PECH : Chemical shift value of methyl, methine and methylene were observed at 43, 70 and 73 ppm respectively.

CPECH : In Elif Öztürk's Study, ^{13}C NMR spectra of chlorinated PECH shows some peaks described as follows;

CH_2Cl = with β CCl and γ CH_2 neighbours at 53 ppm

CH_2Cl = with β CH and γ CCl_2 neighbours at 30 ppm

$CHCl_2$ = with β CH and γ CHCl neighbours at 63 ppm

$CHCl_2$ = with β CCl and γ CHCl neighbours at 74 ppm

$CHCl_2$ = with β CCl and γ CCl_2 neighbours at 68 ppm

CCl_3 = with β CCl and γ CH_2 neighbours at 111 ppm

CCl_3 = with β CH and γ CHCl neighbours at 98 ppm

CCl_3 = with β CCl and γ CHCl neighbours at 105 ppm

CCl_3 = with β CH and γ CCl_2 neighbours at 95 ppm

In our study four peaks were observed as illustrated below

CH_2Cl = with β CH and γ CCl_2 neighbours at 26 ppm

CH_2Cl = with β CCl and γ CH2 neighbours at 53 ppm

CCl3 = with β CH and γ CHCl neighbours at 96 ppm

CCl_3 = with β CCl and γ CH_2 neighbours at 128 ppm

These four peaks reveal that CPECH4.42 had been chlorinated from methyl methine and methylene carbons.

MGAP : Spectrum of MGAP(Fig.3.6) reveals that all chlorinated carbon peaks disappeared. Since no information about the chemical shift of the azide groups are available in the literature, detailed analysis of MGAP with ^{13}C NMR spectra could not be done.

3.4 Thermal Characterization of MGAP

MGAP's might be used in the future rocket technology because of its energetic property due to the azide groups in the structure. Azide groups make a positive contribution to the heat of combustion. In the development of propellant formulations, it is important to know the decomposition properties of each energetic ingredient so as to understood the combustion behaviour of the developed propellant. Therefore decomposition properties of the samples, which was prepared with different NCO/OH ratios, were followed by DSC and TGA runs. Also the decomposition trend of uncross-linked MGAP was analysed in the same manner.

From the DSC thermograms in Fig. 3.7 and 3.8, it was seen that Tg's of samples showed an increase which is seen in going from MGAP (Tg = -47.75 °C) to MGAPXR0,9 (Tg = -22.92 °C) but the increase was not clearly observed for MGAPXR1,0 (Fig 3.9) and MGAPXR1,1 (Fig 3.10). Although TGA runs of the samples (Figs 3.11, 3.12, 3.13, 3.14) show a continuous decomposition behaviour, it could be observed that the fastest decomposition occours between 150 and 200°C at which the samples lose approximately 50 % of their weights. The second decomposition that is slower than the first one occours between 200 and 370 °C at which samples lose about 30 % of their masses. Although all the samples were dried, TGA runs of the samples show a weight lose due to possible moisture evaporation between 0 and 100°C. Finally from the TGA runs, it was observed that MGAP4.42 remained about 11.84 % of its mass and MGAPXR samples remained apprximately 23 % of their masses as residue after the decomposition process was completed.

3.5 Calorimetric Characterization

In order to estimate the combustion enthalpy of MGAP's , they were combusted in a calorimetry bomb. Calorimetric constant were found by combustion of benzoic acid. The results are shown in the Table 3.3.

Table 3.3 Calorimetric Test Results

Sample	ΔH_C (kj/molRu)	ΔH_C (kj/kg)	ΔH_f (kj/mol)
GAP	-2221	-21092	105
MGAP1.1	-2957	-23923	354
MGAP1.6	-2957	-23923	1154
MGAP3.1	-3360	-18152	2075
MGAP3.4	-3907	-19792	2346
MGAP3.83	-6195	-28813	4704
MGAP4.32	-7704	-32766	6283
MGAP4.42	-8335	-34844	6924
MGAPXR0.9	-8452	-35333	7046
MGAPXR1.0	-8281	-34618	6875
MGAPXR1.1	-8294	-34673	6888
MGAPXR1.2	-8725	-36474	7319

ΔH_C : Heat of Combustion

ΔH_f : Heat of Formation

Not : MGAP's between 1.1 and 3.4 made by Kara Ş.[28].

MGAP3.83 and MGAP4.32 made by Öztürk E.[29].

In the present study, azidation ratio of MGAP was 4,42 and its heat of combustion was found about 8300. It can be concluded that there was no regular effect of increasing NCO/OH ratio on the heat of combustion of MGAP's. Since the performance of rocket propellants such as specific impulse or thrust power is proportional to the heat of combustion, the presently developed MGAP in this study may be a successful candidate of the future rocket propellants.

3.6 Tensile Testing

One of assessments made for the energetic binders is the tensile test to provide the elongation at break and tensile strength of those binders. Tensile properties of MGAP's prepared with different NCO/OH ratios are presented in Table3.4.

Table 3.4 Tensile Test Results

Sample	PEb	PEy	YS(MPa)	US(MPa)	TS(MPa)	Figures
MGAPXR0.9	159	6.6	0.47	1.40	2.23	3.15
MGAPXR1.0	125	5.2	1.43	3.41	4.26	3.16
MGAPXR1.1	124	5.3	1.84	4.23	5.24	3.17
MGAPXR1.2	124	4.5	2.01	4.84	6.00	3.18
GAPXR0.9*	180	(-)	(-)	(-)	0.32	(-)
GAPXR1.0*	230	(-)	(-)	(-)	0.24	(-)
GAPXR1.1*	160	(-)	(-)	(-)	0.38	(-)
GAPXR1.2*	170	(-)	(-)	(-)	0.42	(-)

* : Data were taken from the literature [27]

PEb: Percentage elongation at break
PEy: Percentage elongation at yield
YS : Yield strength
US : Ultimate strength
TS : Tensile Strength

In general percentage elongation at break decreases with increasing NCO/OH ratio while the tensile strenght insreases. This may be attributed to the following causes; the isocyanate molecules constitute the hard segments of MGAP chains that the increasing NCO/OH ratio corresponds to the dominant effect of the hard segments over the soft ones. A larger NCO/OH ratio may increase the crosslinking density between the MGAP chains which makes them stronger. Finally the excess of isocyanate compound may produce some polyisocyanate, named biuret which is a rigid polymer. In Table 3.4 MGAP samples are stronger than the clssical GAP samples with respect to their tensile strength values, the reason of this may be low cross-linking density of GAP samples because the GAP samples had been crosslinked with TDI (2,4and2,6-tolylene diisocyanate) which is diisocyanate having low cross-linking capacity when compared to the Desmodur N-100.

3.7 Swelling Test

In this study, swelling tests were conducted on the crosslinked MGAP samples in water for 48 hour at room temprature. After swelling of samples they were immediately weighed and dried at oven whether the samples lose weight or not which gives a clue about the crosslinking quality. This procedure repeated two times as described in the experimental part. The results are shown in the Table 3.5.

Table 3.5 Swelling Test Results

Sample	Swelling %	Weight lose %
MGAPXR0.9	14.0	4.5
MGAPXR1.0	12.4	3.5
MGAPXR1.1	12.1	3.0
MGAPXR1.2	10.2	2.7

From the results of the table 3.5, it can be said that with increasing the NCO/OH ratio of crosslinked samples, percentage swelling values decreases, the reason of the swelling decrease can be the increasing crosslinking density of the polymer chains. From the results it is seen that all samples lost some of their weights which is decreasing as the NCO/OH ratio increases, the reason of this behaviour can be attributed to the uncrosslinked segments of MGAP's that is soluble in water.

3.8 Density Measurement

Density measurement was made with pycnometer by using toluene at room temperature. It was seen that density of MGAP's were 1.44 g/cm^3. Results are shown in Table 3.6 ;

Table 3.6 Density of Polymers

Sample	d(g/cm^3)	V(m^3)
MGAPXR	1.44	0.069
GAP	1.30	0.077
HTPB	0.93	0.107

V : Volume of 100 kg binder

From the Table 3.6, it can be concluded that MGAP have higher density and occupies lesser volume than classical GAP and HTPB, which means that a rocket made with this binder will have a lesser weight and may travel longer distances.

CHAPTER 4

CONCLUSIONS

- In this study it was shown that MGAP with 4.42 azide groups in its repeat units can be synthesised. However, although nitrogen atmosphere was used in the chlorination step, the oxidation of the resulting CPECH and MGAP could not be entirely avoided, which caused chain breakage in the polymers.

- Experimentally found and stoichiometrically calculated hydroxyl and double bond functionalities of PECH and MGAP showed that an extensive degradation of chains does not occur in the synthesis.
- This study showed that MGAP 4.42 can be cross-linked with Desmodur N-100 as a curing agent.

- Heat of combustion and heat of formation values of MGAP's are about four times greater than those of classical GAP's. This shows that MGAP's are about four times more energetic than GAP's, which makes MGAP's to be a successful candidate for the future rocket propellant binders.

- Tensile strenght measurements showed that MGAPXR's are much more stronger than classical GAP samples with respect to their tensile strength values.

- Finally it was found that MGAP has a higher density than GAP and HTPB binders which means that a rocket made with MGAP binder will have a lesser volume and hence will be lighter than those made with GAP and HTPB.

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APPENDICES

FIGURES

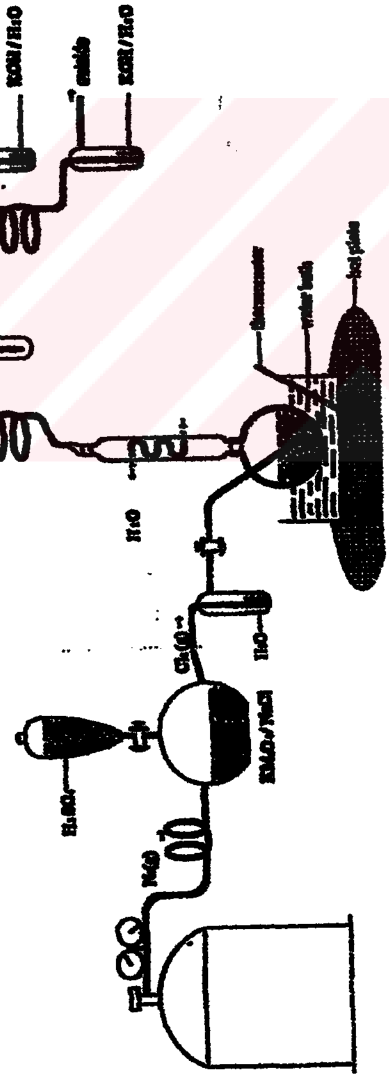

Figure 2.1 Chlorination of Polymers

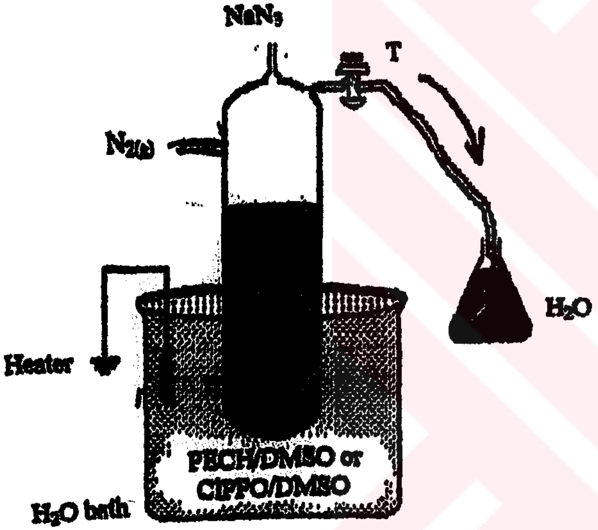

Figure 2.2 The Reactor for Azidation

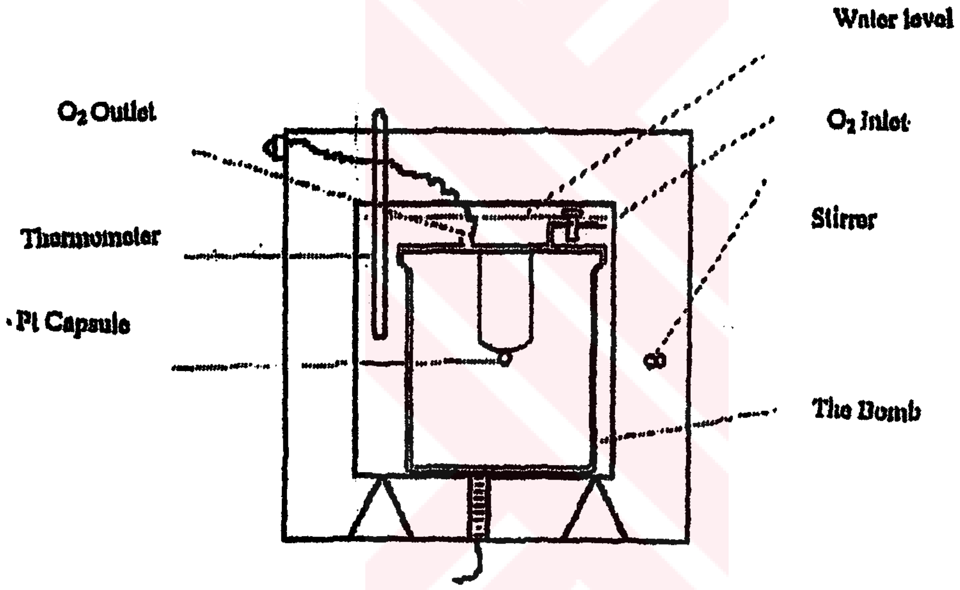

Figure 2.3 The Calorimeter

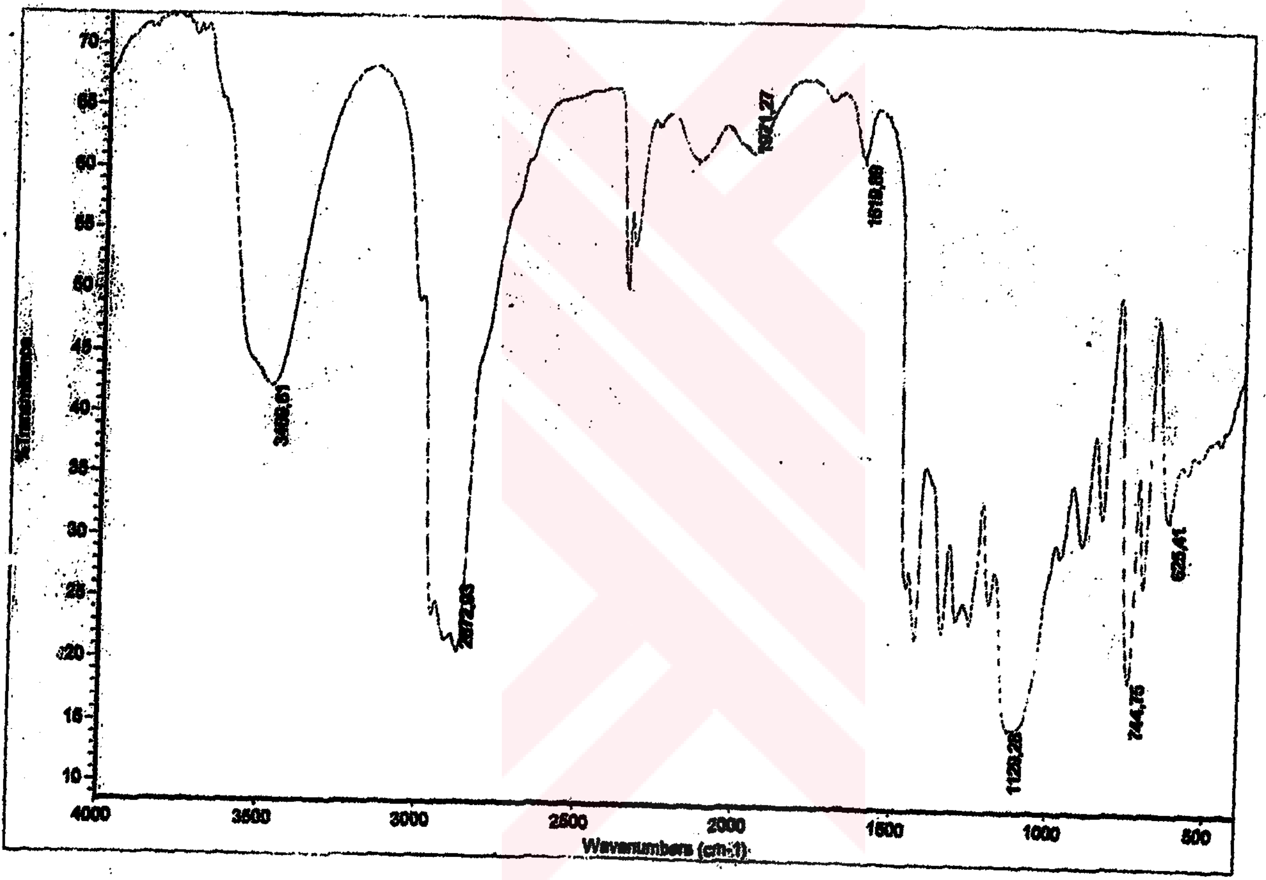

Figure 3.1 IR Spectrum of PECH

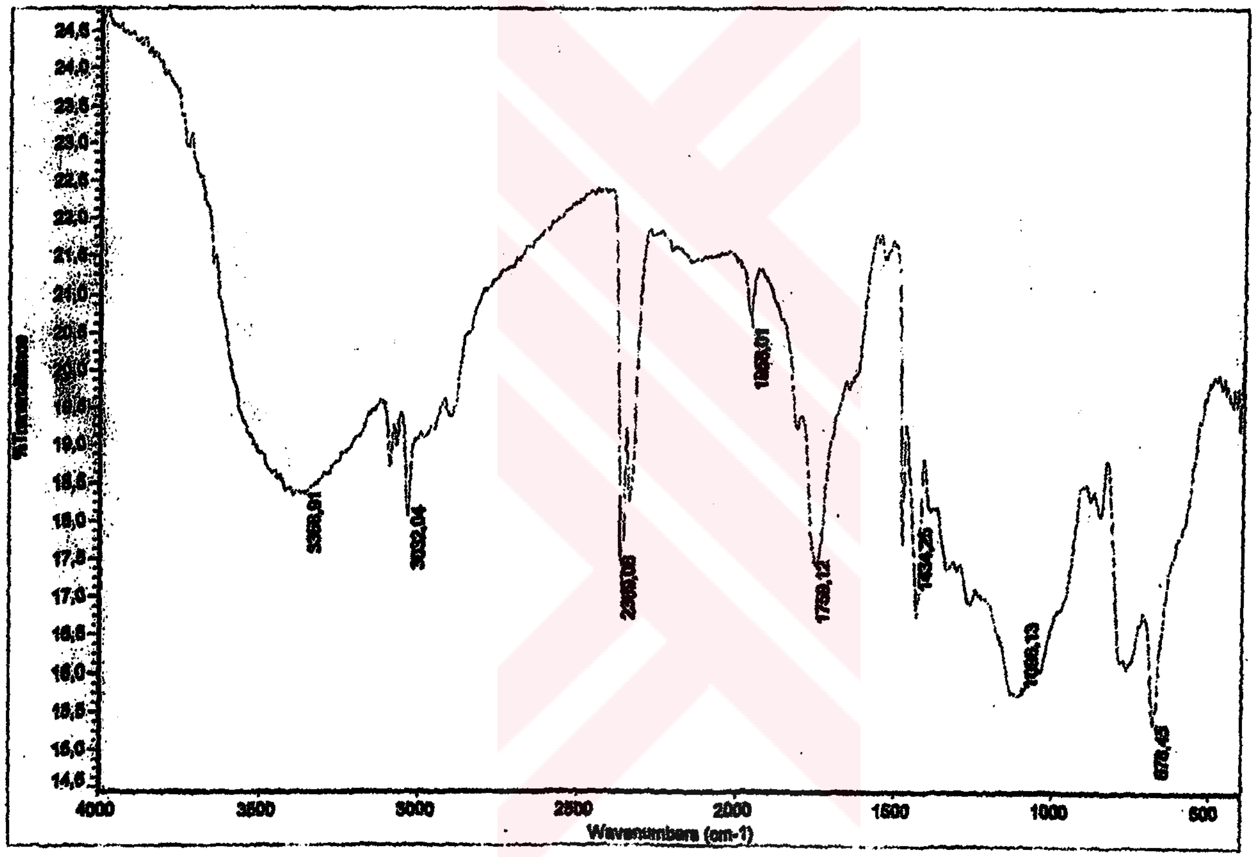

Figure 3.2 IR Spectrum of CPECH

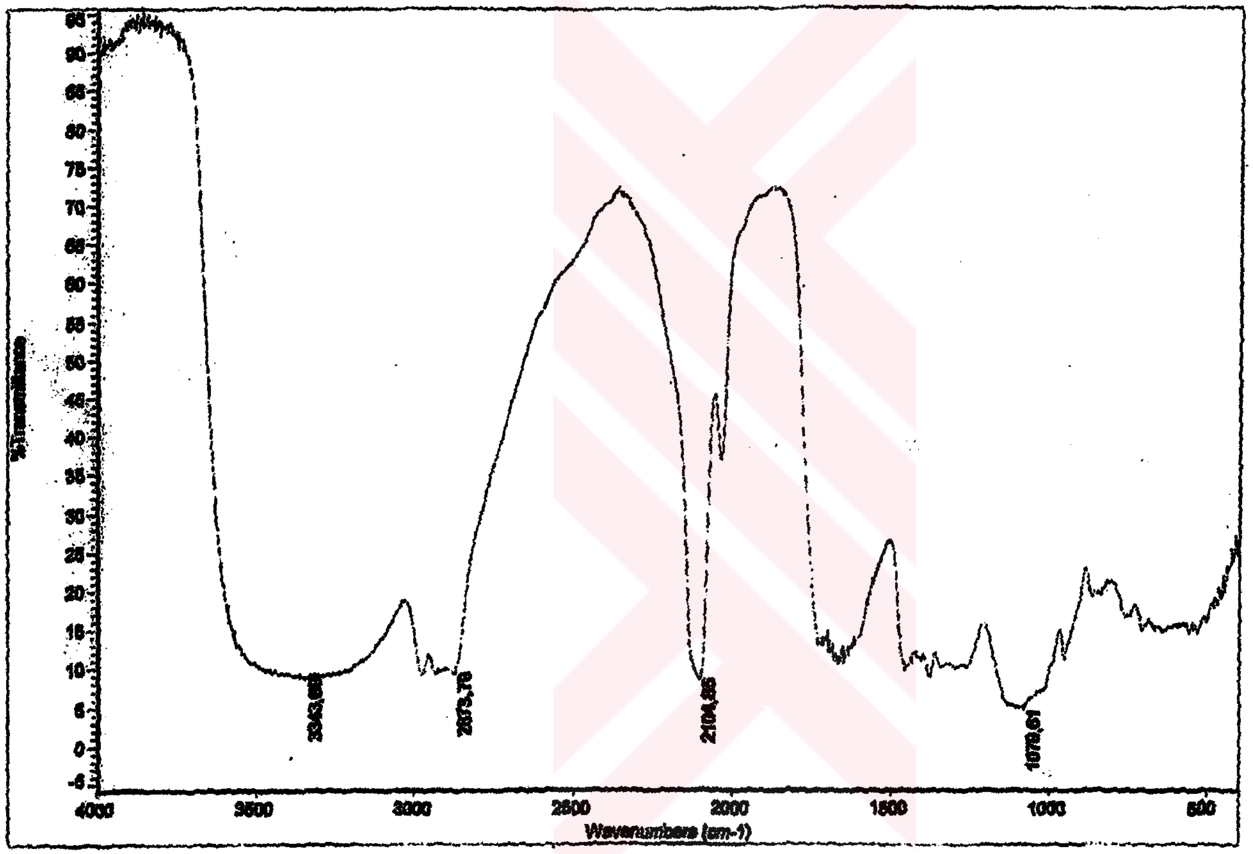

Figure 3.3 IR Spectrum of MGAP

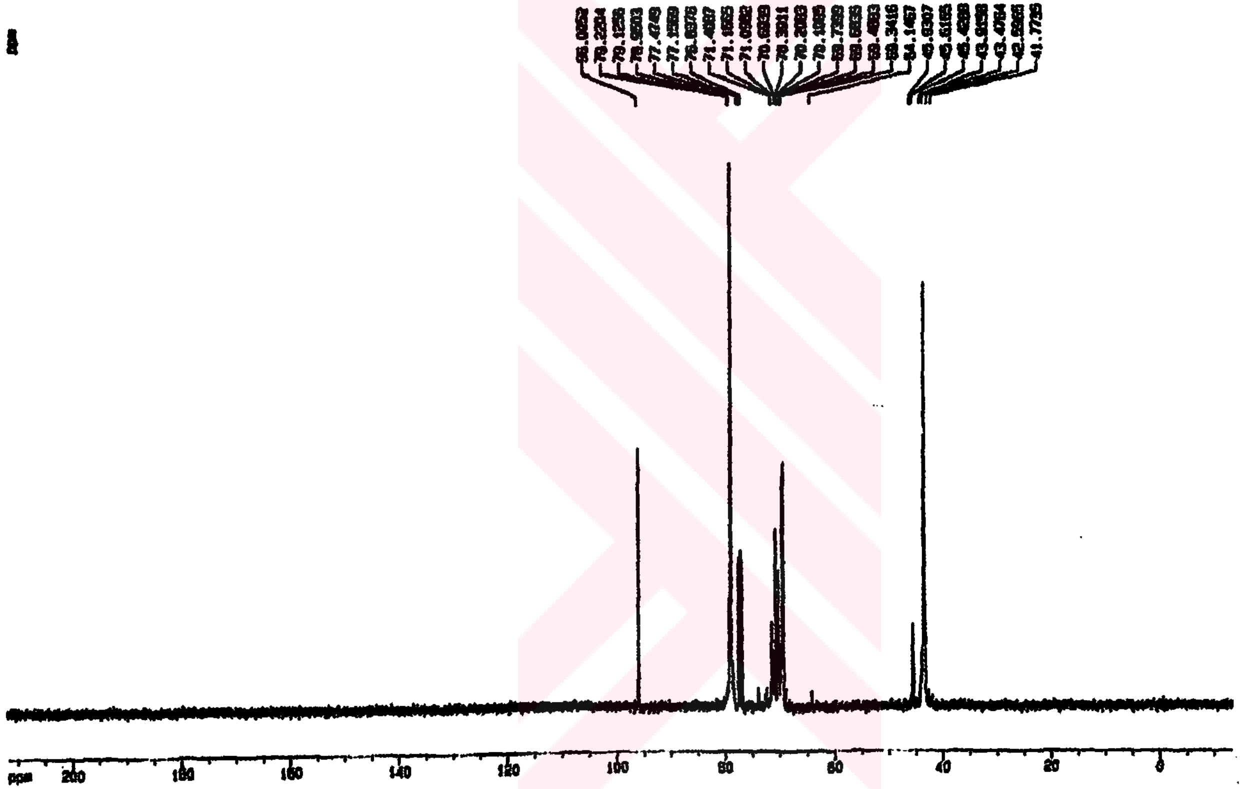

Figure 3.4 NMR Spectrum of PECH

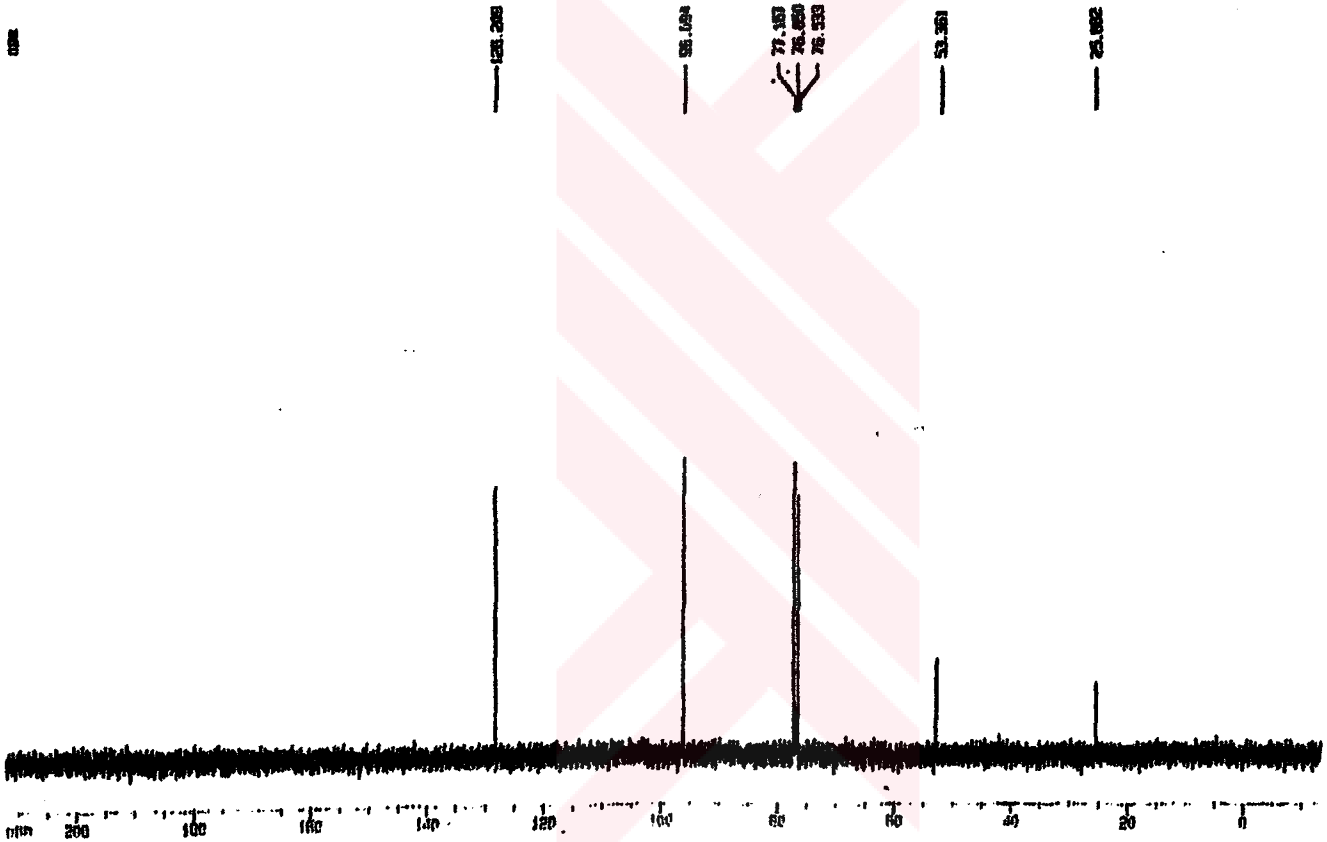

Figure 3.5 NMR Spectrum of CPECH

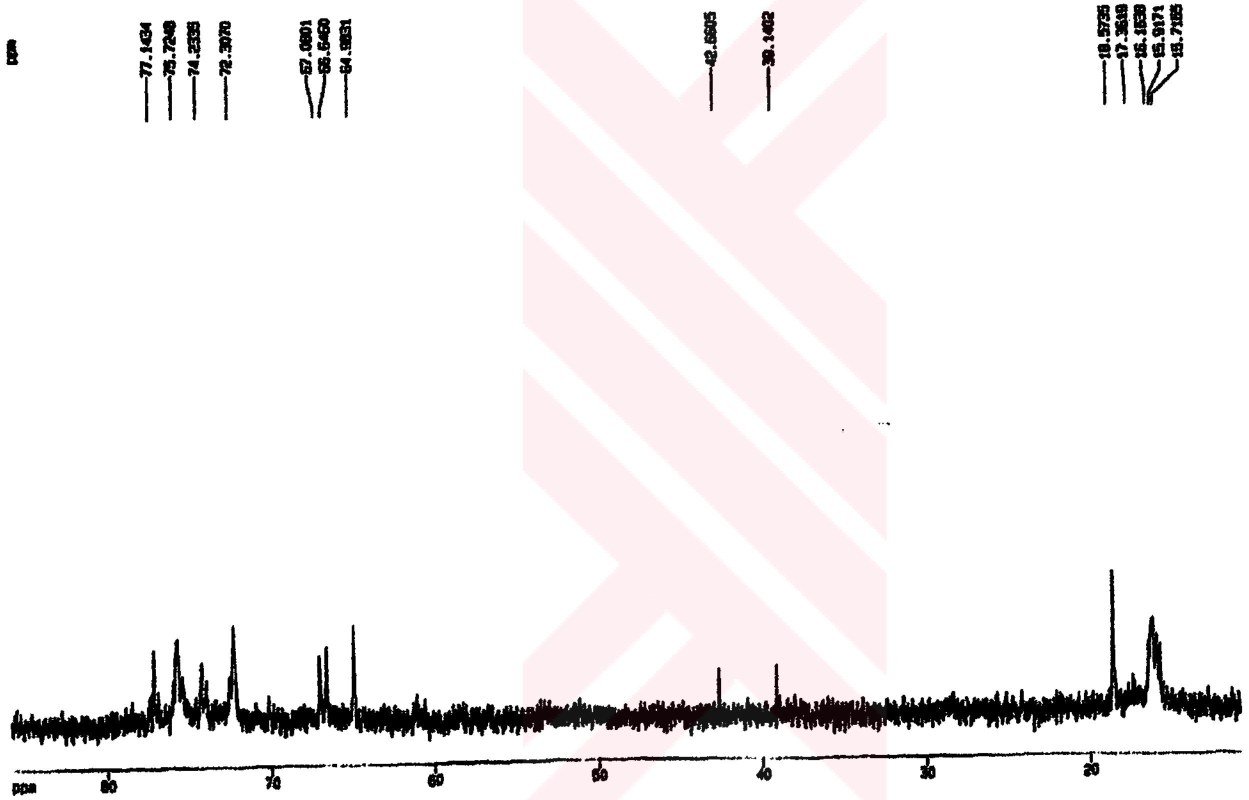

Figure 3.6 NMR Spectrum of MGAP

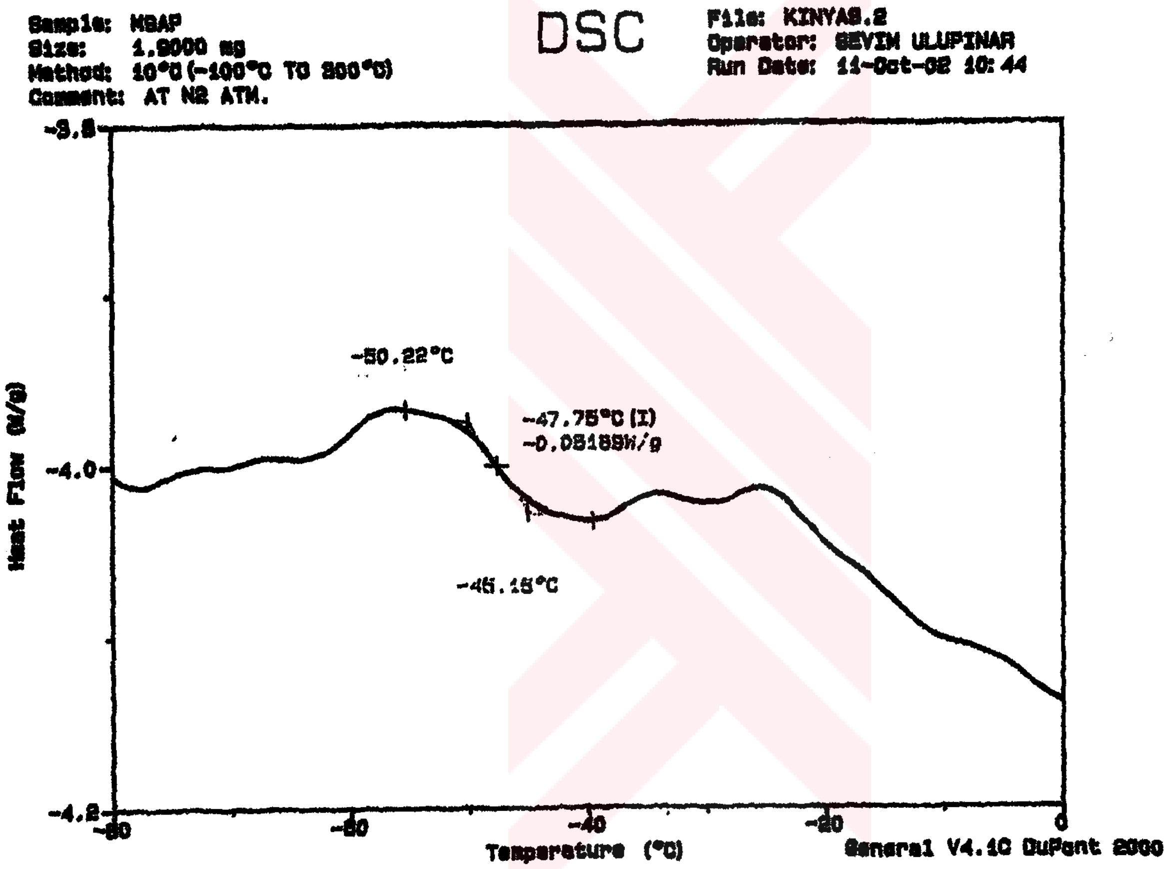

Figure 3.7 DSC Thermogram of MGAP

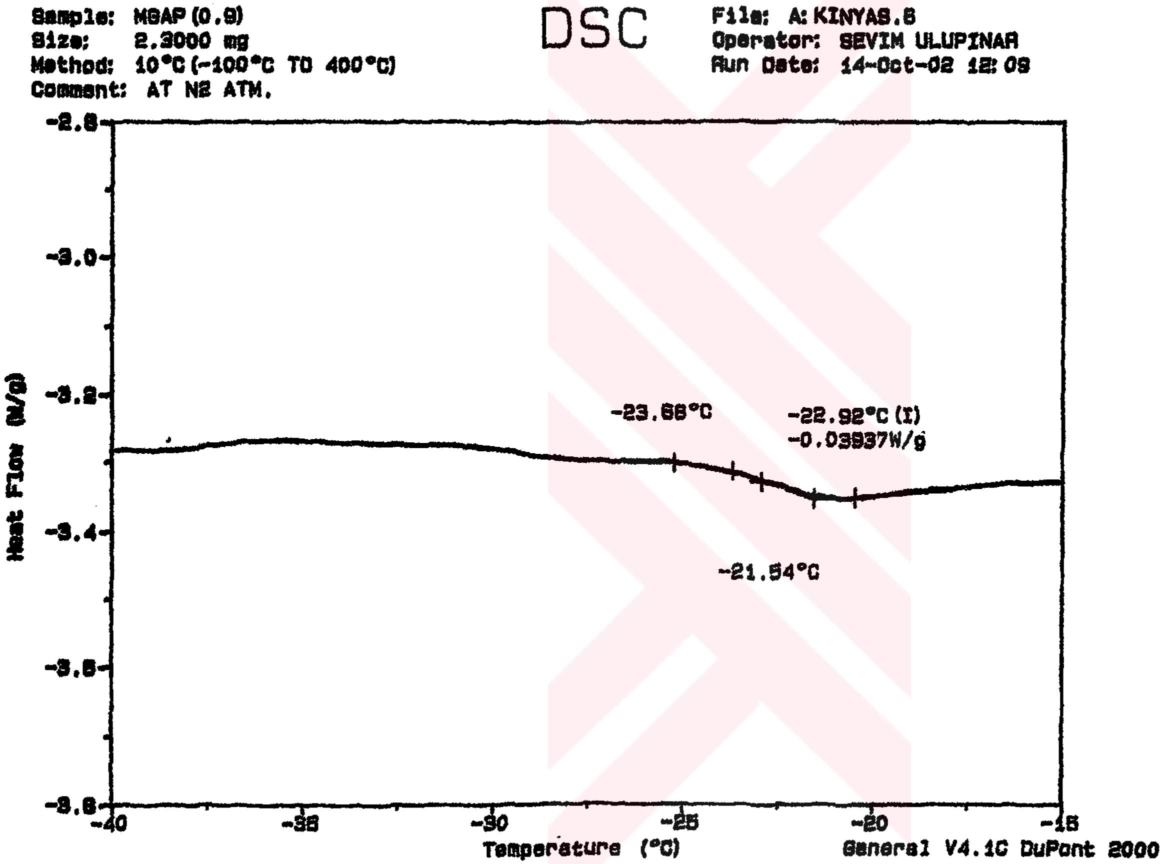

Figure 3.8 DSC Thermogram of MGAPXR0.9

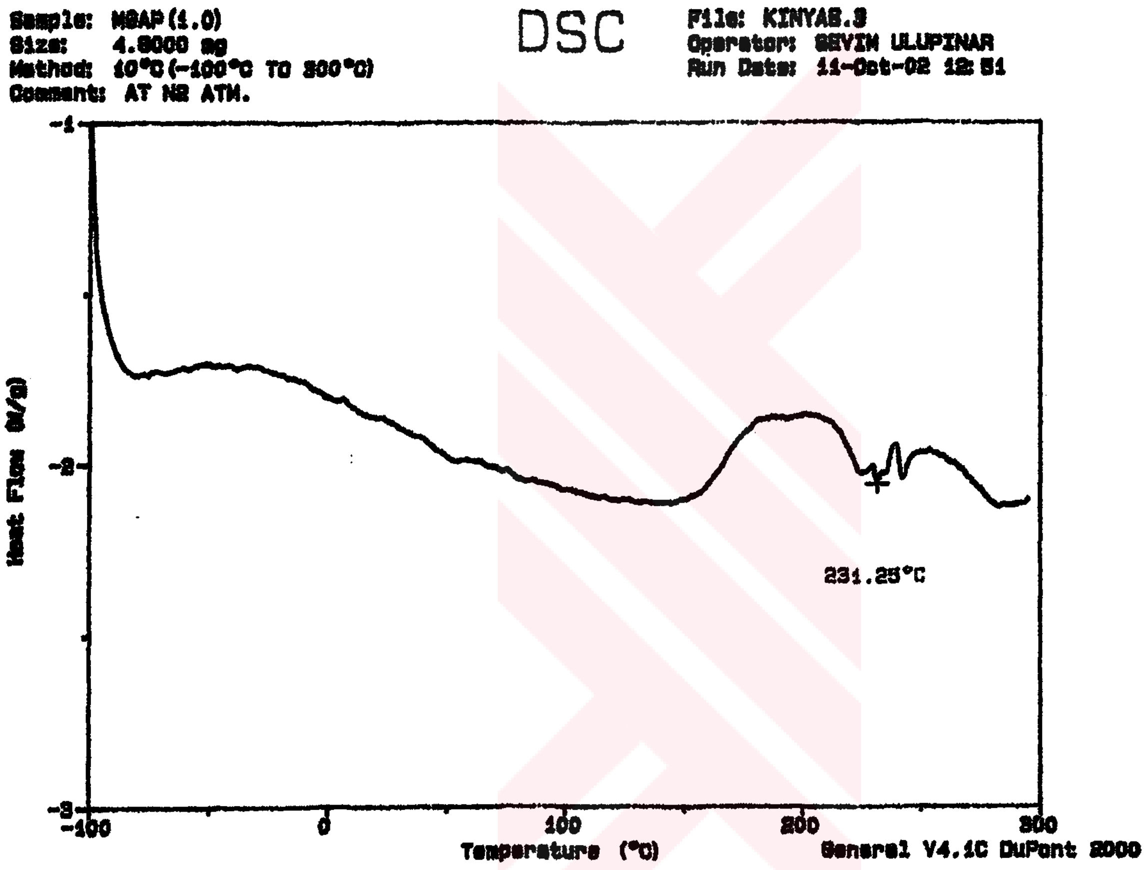

Figure 3.9 DSC Thermogram of MGAPXR1.0

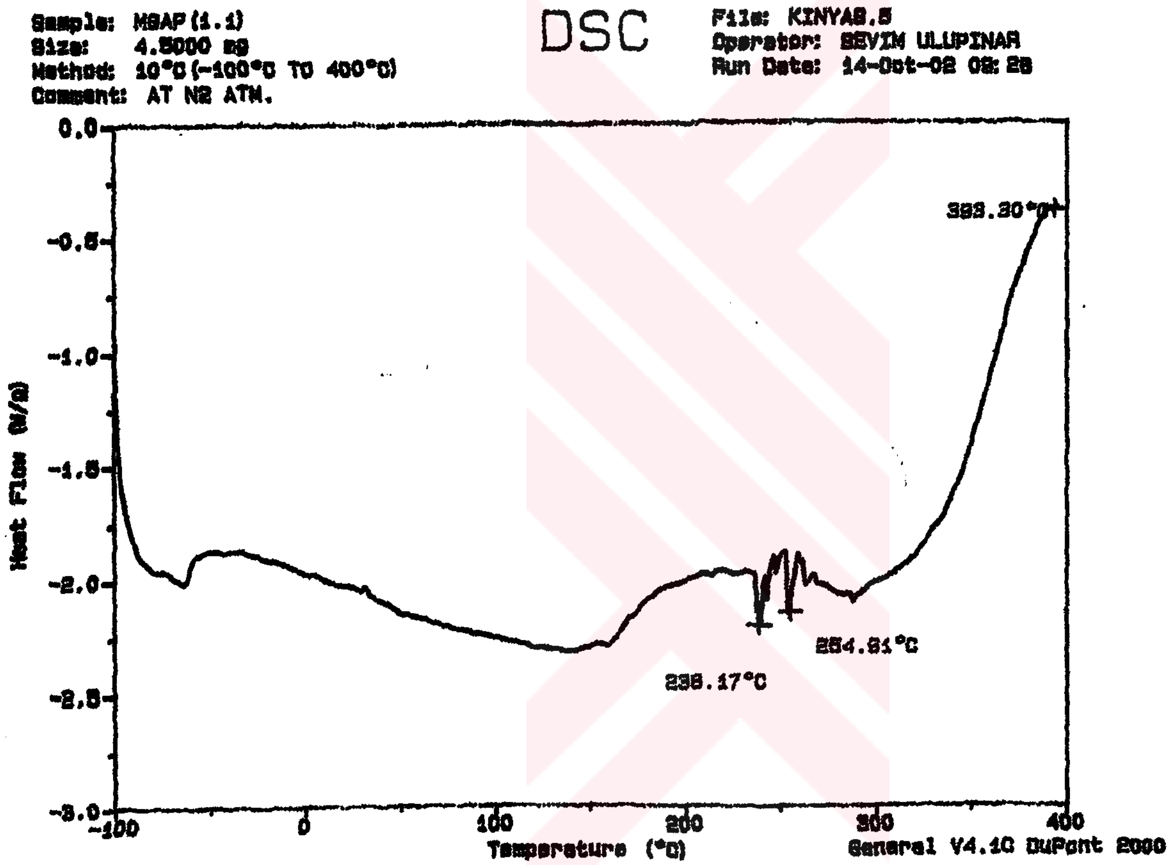

Figure 3.10 DSC Thermogram of MGAPXR1.1

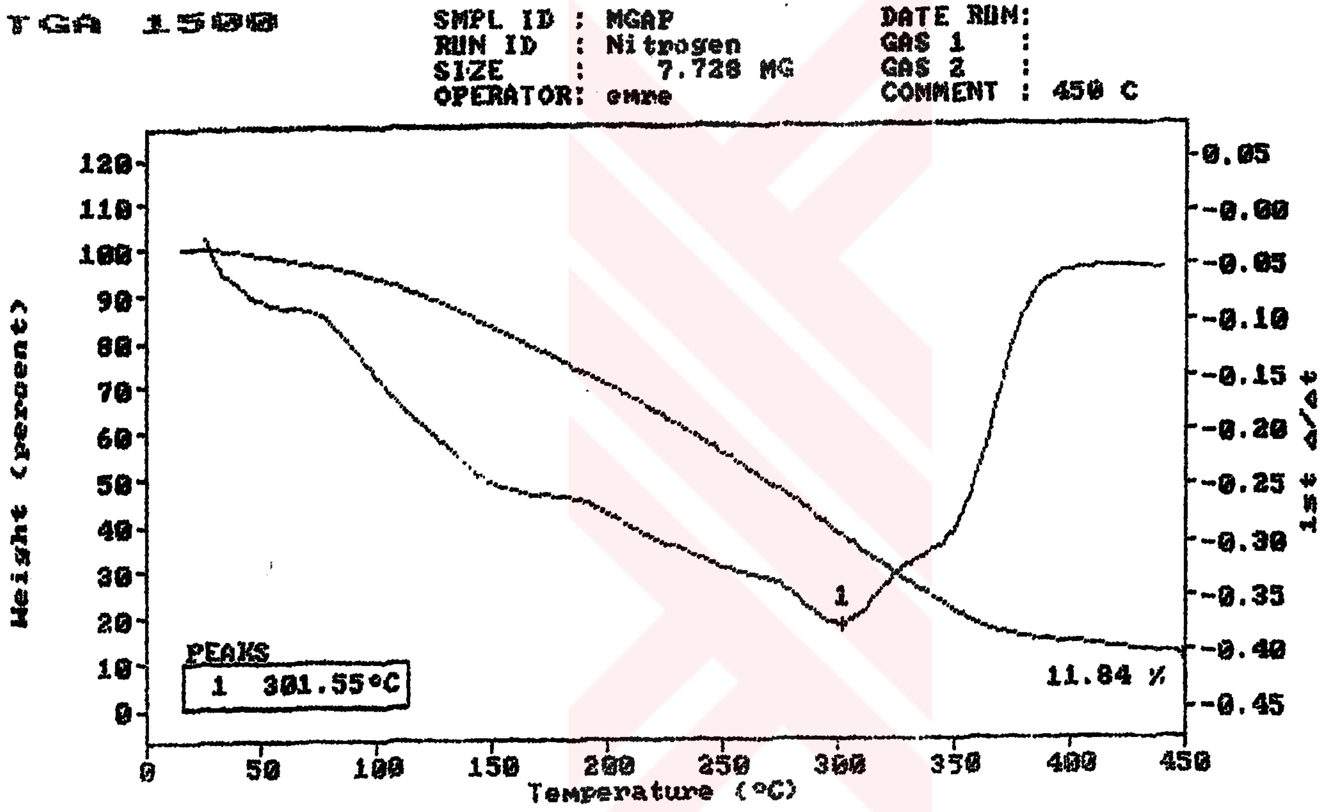

Figure 3.11 TGA Thermogram of MGAP

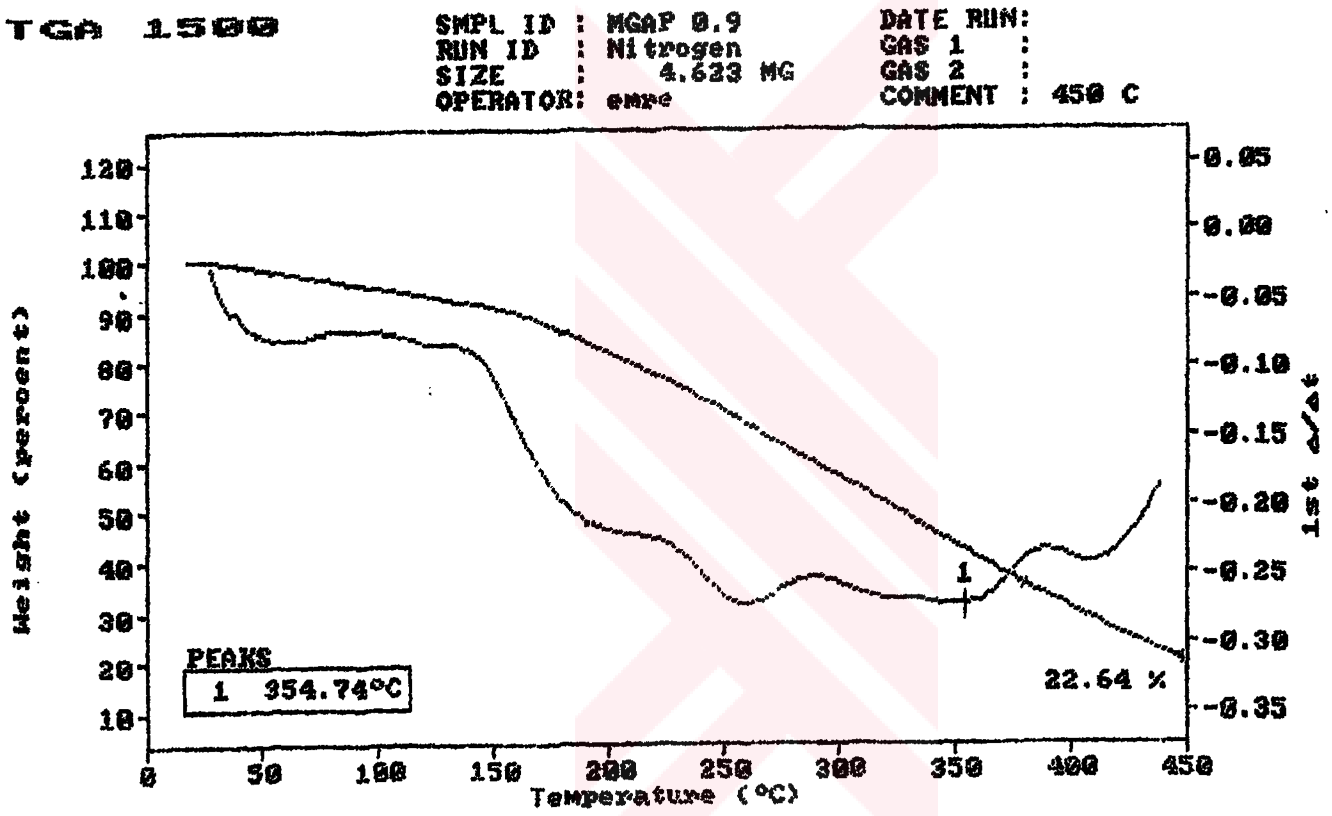

Figure 3.12 TGA Thermogram of MGAPXR0.9

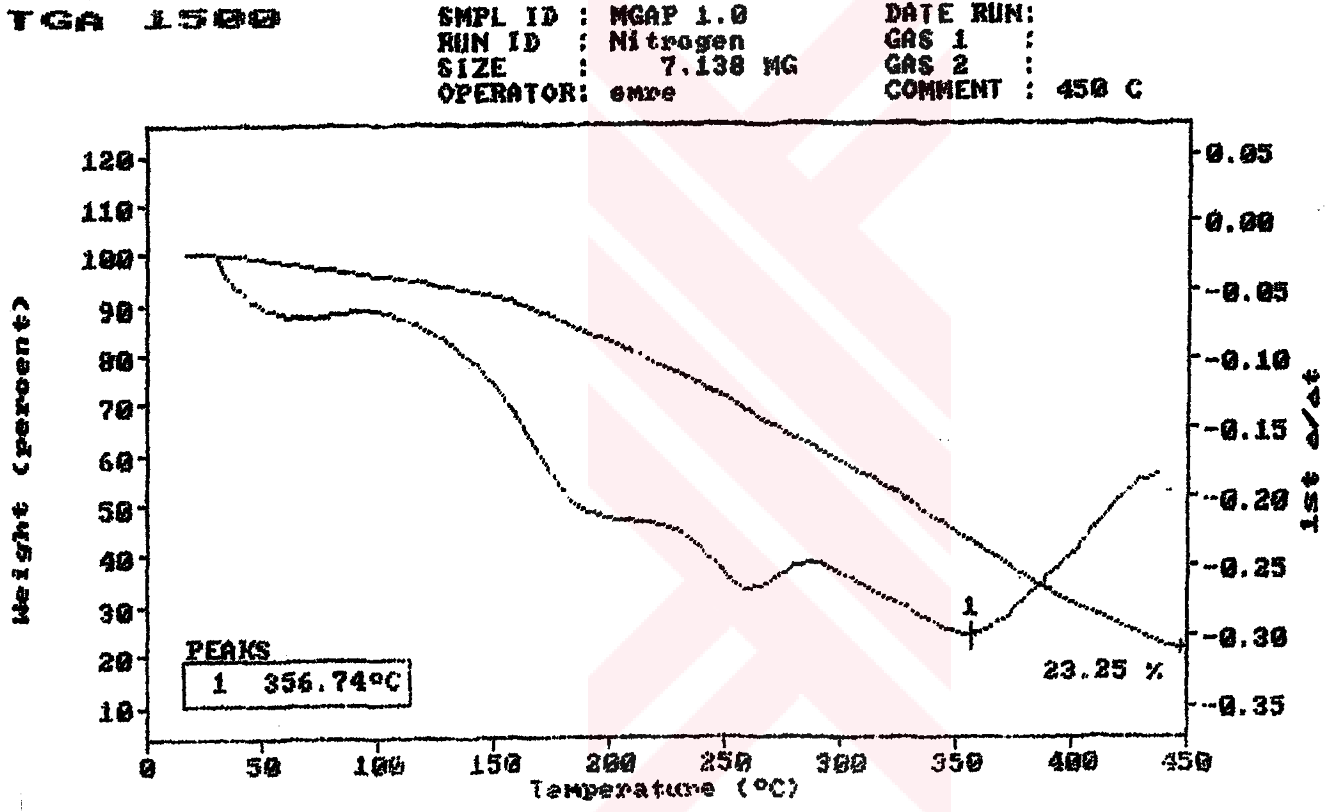

Figure 3.13 TGA Thermogram of MGAPXR1.0

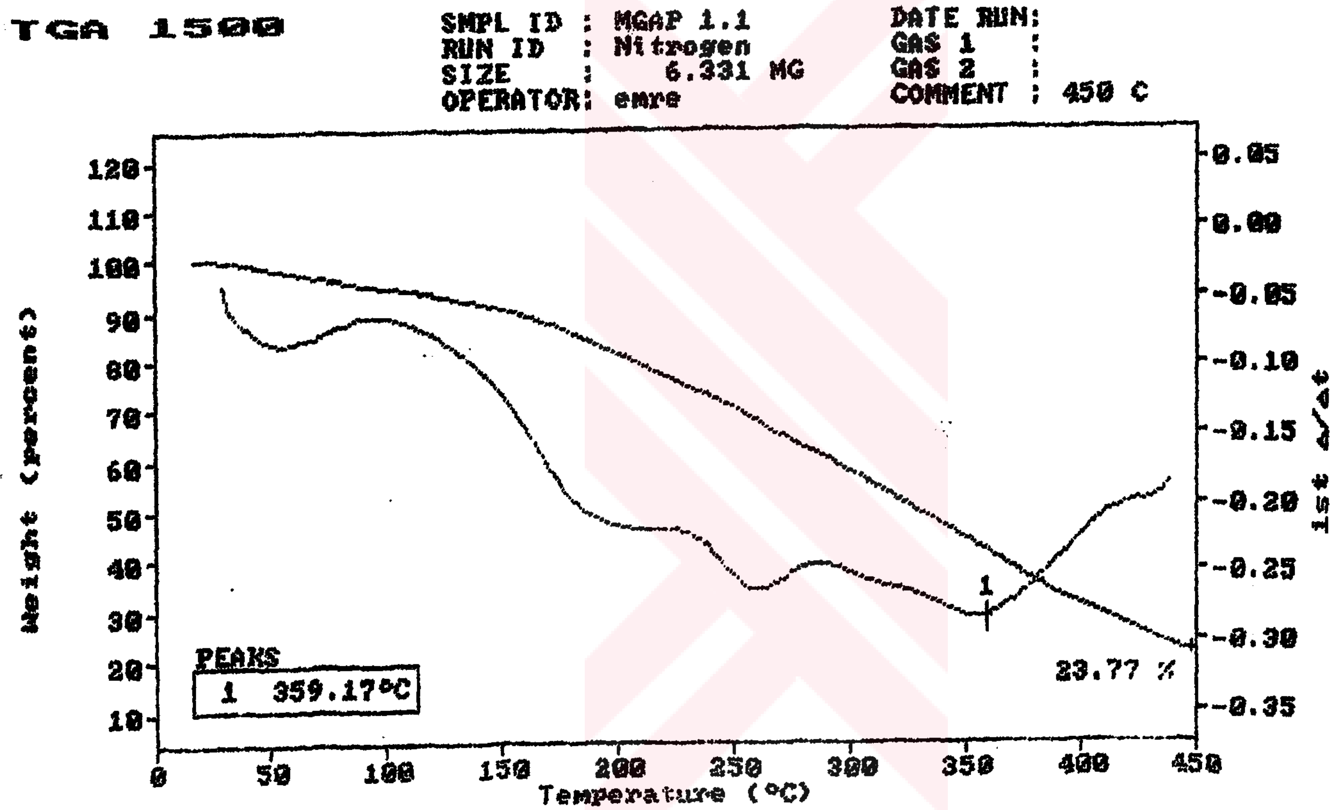

Figure 3.14 TGA Thermogram of MGAPXR1.1

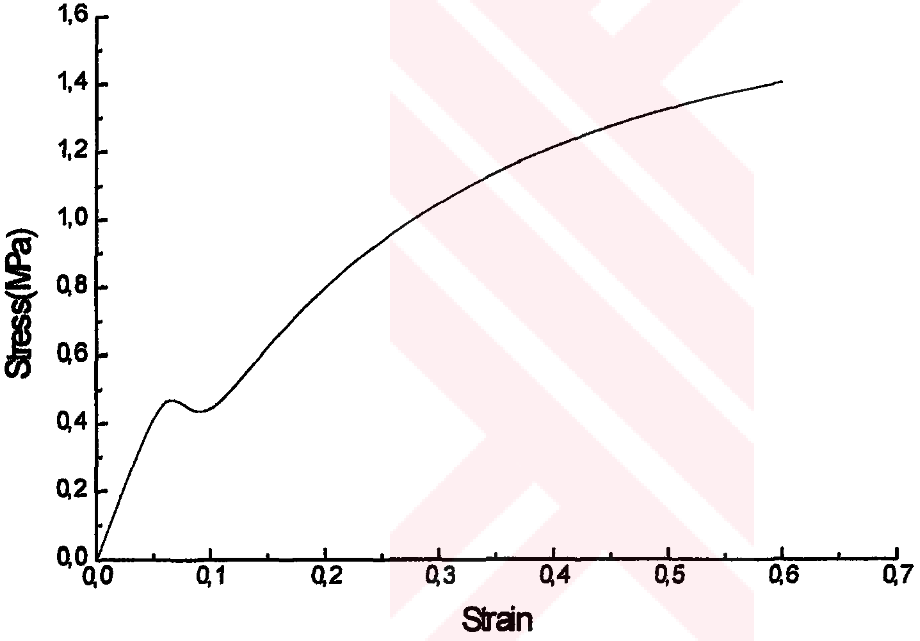

Figure 3.15 Stress-Strain Curve of MGAPXR0.9

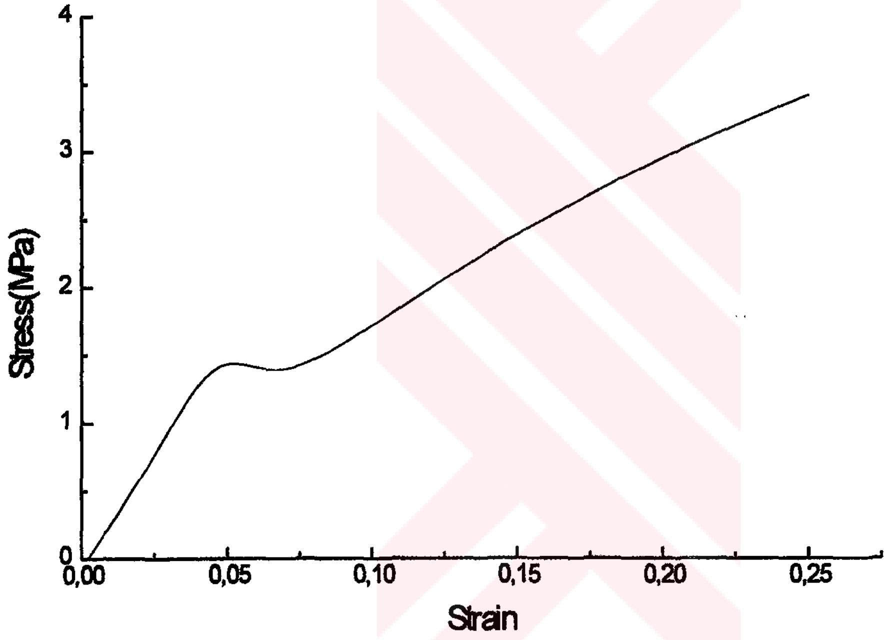

Figure 3.16 Stress-Strain Curve of MGAPXR1.0

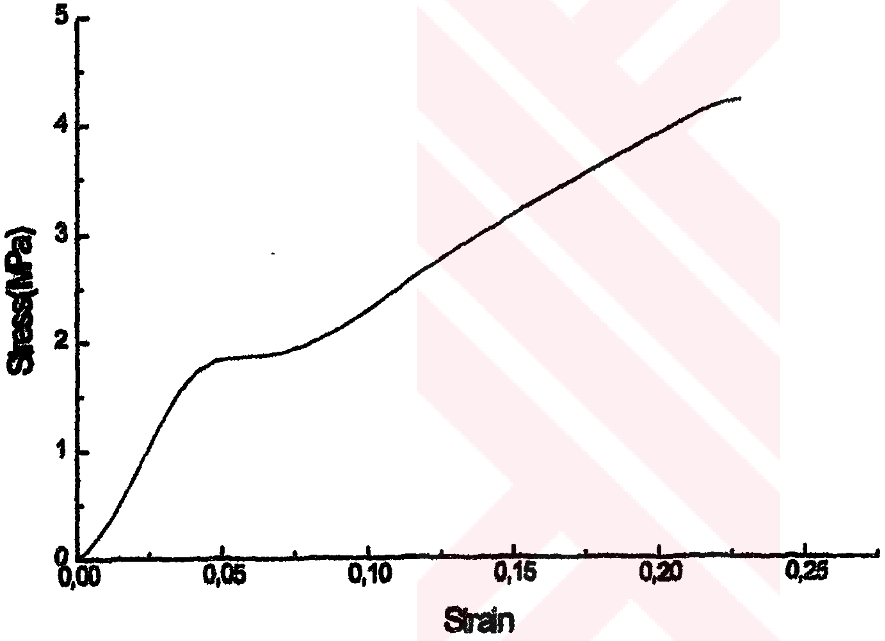

Figure 3.17 Stress-Strain Curve of MGAPXR1.1

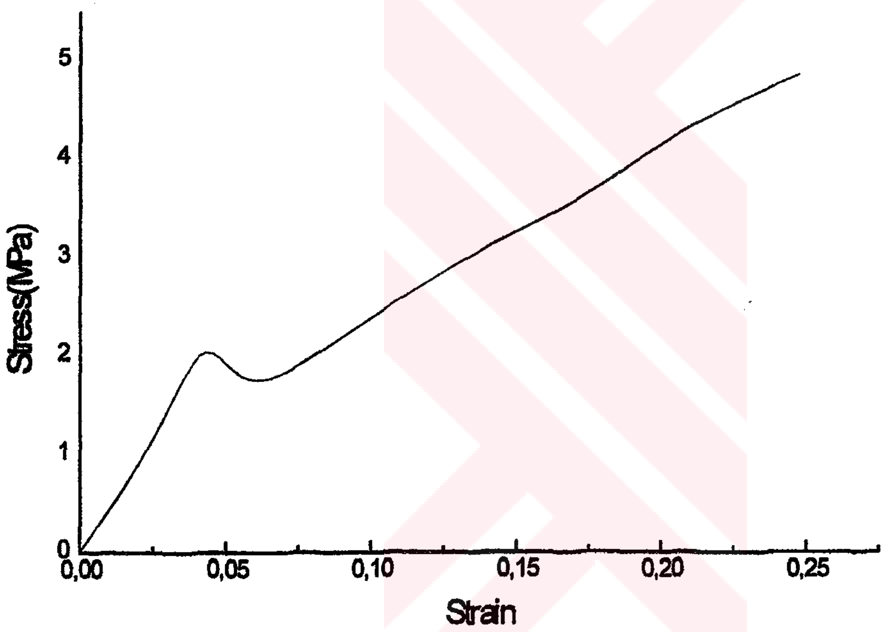

Figure 3.18 Stress-Strain Curve of MGAPXR1.2