CHAIN EXTENSION REACTIONS OF UNSATURATED POLYESTERS USING DIFUNCTIONAL MOLECULES

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Hep ışıldamaları dileği ile

Alican ve Cem'e

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ABSTRACT

CHAIN EXTENSION REACTIONS OF UNSATURATED POLYESTERS USING DIFUNCTIONAL MOLECULES

In this study the effectiveness of various chain extenders in increasing the molecular weight of unsaturated polyesters was investigated. For this purpose eight different chain extenders (with di or multi-functionalities) such as epoxides, isocyanates and bisoxazolines were added to short chain oligomeric polyesters with molecular weights of 500-700 and the desired molecular weight of 1500-2000 was reached within very short times.

Diglycidyl ether of bisphenol A, 1,2;7,8-diepoxyoctane and epoxidized soybean oil reacted with carboxylic end groups of unsaturated polyesters within 30-60 minutes; two blocked isocyanates, namely diphenylmethane-bis-4,4’-N,N’-ethyleneurea and diphenylmethane-bis-4,4’-carbamoyl-Є-caprolactam reacted with both carboxylic and hydroxylic end groups of the unsaturated polyesters to reach the desired molecular weight within less than one hour. Isocyanated soybean oil reacted with hydroxyl end groups of the polyester chains. 1,3-phenylene-bis-oxazoline and 2,2’-bis-2-oxazoline gave a fast reaction with the carboxylic end groups of the oligomeric polyesters within a reaction time as short as 5 minutes. With the help of these extenders the conventional polyesterification reaction time can be reduced from 20 hours to 6-7 hours, diol loss can be eliminated and product yields can be increased by about 5 per cent.

After dilution with styrene to give a styrene concentration of 35 per cent, the resins were cured in the usual manner and the mechanical and thermal properties of the cured resins were found to be comparable to that of the commercial reference product. Thus, the industrial use of the chain extended polyesters was verified. Gel times remained close to that of the commercial reference product (10-15 minutes). T_g values were found about 80-90 ^{o}C and the TGA data showed that the 5 per cent weight loss temperature in many cases was about 230-275 ^{o}C, very comparable to that of the commercial reference product.

ÖZET

DOYMAMIŞ POLİESTERLERİN ÇİFT FONKSİYONLU MOLEKÜLLER İLE ZİNCİR UZATMA REAKSİYONLARI

Bu çalışmada farklı zincir uzatıcı moleküllerin poliesterlerin moleküler ağırlıklarını artırmadaki etkinlikleri ölçülmüştür. Bu amaç çerçevesinde iki ya da daha çok fonksiyonalitesi olan sekiz zincir uzatıcı (epoksitler, izosiyanatlar ve bisoksazolinler) 500-700 moleküler ağırlıklı oligomerik poliesterler ile reaksiyona sokulmuş ve istenen moleküler ağırlığa (1500-2000) kısa sürede ulaşılmıştır.

Bisphenol A diglisidil eteri, 1,2;7,8-diepoksioktan ve epokside soya yağı, doymamış poliesterlerin karboksilik asit uçları ile 30-60 dakikada reaksiyona girmiştir; benzer şekilde iki bloklanmış izosiyanat (difenilmetan-bis-4,4’-N,N’-etilenüre ve difenilmetan-bis-4,4’-karbamoil-Є-kaprolaktam) poliesterlerin karboksilik ve hidroksilik uçları ile bir saatten daha kısa sürelerde reaksiyona girmiştir. İzosiyanatlı soya yağı ise poliesterlerin hidroksil uç grupları ile reaksiyona girmiştir. 1,3-fenilin-bis-oksazolin ve 2,2’-bis-2-oksazolin oligomerik poliesterlerin karboksilik uçları ile 5 dakika gibi kısa bir sürede reaksiyona girmişlerdir. Bu zincir uzatıcı moleküller sayesinde konvansiyonel poliesterifikasyon reaksiyon süresi 20 saatten 6-7 saate indirilebilmekte, diol kaybı ortadan kaldırılabilmekte ve reaksiyon verimi yüzde 5 civarında artırılabilmektedir.

Poliesterlerin yüzde 35 oranında stirende çözülmesi ile elde edilen rezinler serbest radikal polimerizasyonu yolu ile çapraz bağlanmış ve son ürünlerin mekanik ve termal özellikleri referans alınan ticari poliestere benzer bulunmuştur. Böylelikle, zincir uzatma yolu ile üretilen poliesterlerin ticari kullanımı da onaylanmış olmaktadır. Jelleşme süreleri referans ticari ürüne yakın bulunmuştur (10-15 dakika). T_g değerleri 80-90 ^oC civarındadır ve TGA sonuçları yüzde 5 lik ağırlık kaybı sıcaklığının 230-275 ^oC civarında olduğunu göstermiştir. Tüm bu sonuçlar referans alınan ticari poliesterin değerlerine çok yakındır.

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LIST OF ABBREVIATIONS

AMC-2	Commercial catalyst (Aerojet Fine Chemicals)
ASTM	American Society for Testing and Materials
ATR-IR	Attenuated Total Reflectance Infrared
BO	Bisoxazoline
CP	Cross Polarization
DABCO	1,4-diazabicyclo[2.2.2]octane
DEO	Diepoxyoctane
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential Scanning Calorimetry
ESO	Epoxidized Soybean Oil
GPC	Gel Permeation Chromatography
IR	Infrared
ISO	International Standards Organization
IV	Intrinsic Viscosity
MAS	Magic Angle Spinning
MDI	Methylene diphenyl diisocyanate
MDI-C	Diphenylmethane-bis-4,4’-carbamoyl- Є –caprolactam
MDI-E	Diphenylmethane-bis-4,4’-ethyleneurea
MEKP	Methyl ethyl ketone peroxide
$\overline{M}_n$	Number average Molecular Weight
NMR	Nuclear Magnetic Resonance
PBO	Phenylene-bis-oxazoline
PDI	Polydispersity Index
PET	Polyethyleneterephthalate
PMDA	Pyromellitic dianhydride
RTM	Resin transfer molding
SONCO	Isocyanated Soybean Oil
TDI	Toluene diisocyanate
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
UPE	Unsaturated Polyester

1. INTRODUCTION

1.1. Unsaturated Polyesters

1.1.1. Structure and Basic Properties

Unsaturated polyesters (UPE) are thermoset polymers most commonly employed as the matrix for glass fiber reinforced composite materials. They are products of polycondensation reactions of saturated and unsaturated diacids (or anhydrides) with glycols and contain the unsaturation in their backbone. Once the polycondensation has provided the linear polyester of a molecular weight about 1500-3000, the polymer is dissolved in a reactive diluent like styrene and finally is processed into a rigid thermoset with the help of free radical copolymerization through the styrene and maleate unsaturation. Figure 1.1 illustrates the production of unsaturated polyesters and crosslinking in styrene.

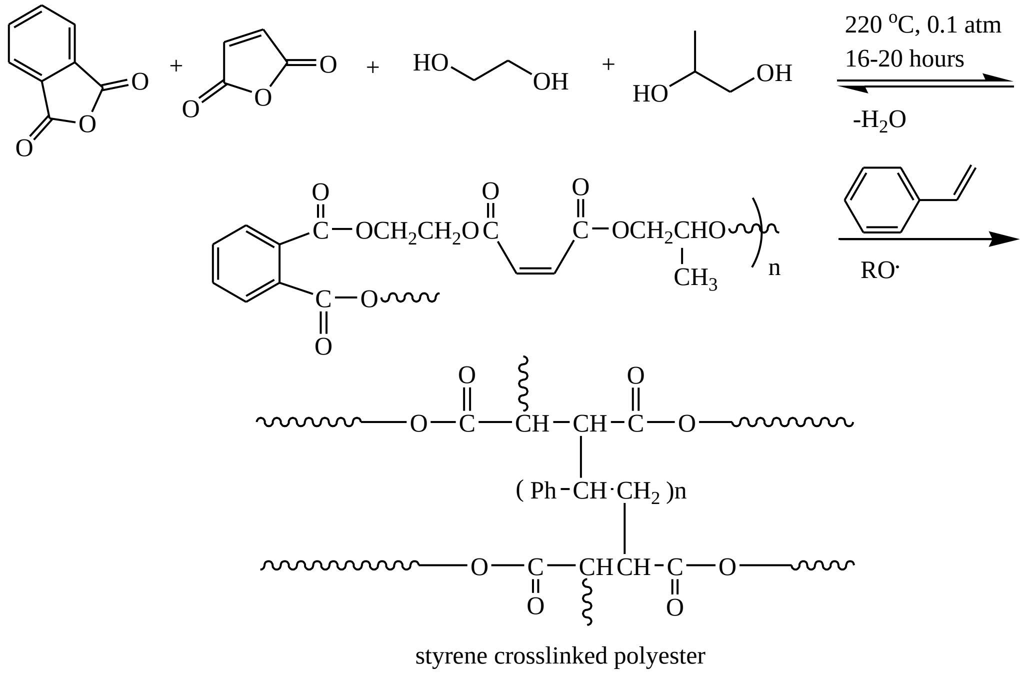


Figure 1.1. Synthesis and crosslinking of unsaturated polyesters

The degree of crosslinking can be controlled through the concentration of unsaturated acids or unsaturated glycols, whereas the length of crosslink segment depends on the concentration of the crosslinking agent. The crosslinking agent, most commonly styrene, at the same time serves as the diluent for the unsaturated polyester resin and enables its processibility. With the help of this solvent a relatively low viscosity polymer is obtained which can be compounded with fibers, fillers or with other polymers. In conventional unsaturated polyesters the styrene content varies between 30-50 per cent concentrations.

Final properties of unsaturated polyesters primarily depend on the starting materials used. The adjustment of the molar ratio of the saturated and the unsaturated carboxylic acids is an important method to tailor the properties of the resin. This ratio controls the reactivity of the unsaturated polyester and also the crosslink density of the final network. If the saturated acid is used in a molar excess the reactive unsaturated bonds will be distributed in the polyester chain sparsely, and the reactivity of the unsaturated polyester will be lower. If the unsaturated acid is used in molar excess, the double bond distribution will be denser; the reactivity will be higher leading to a much intense network in the cured resin. In such a case the final product will be more brittle exhibiting poor mechanical properties.

Flexibility and rigidity are also determined by the choice of the employed acids and glycols. Flexibility can be attained by using flexibilizing acids like adipic acid or long chain polyethylene glycols. Rigidity, on the other hand, can be introduced through the use of aromatic acids or glycols. Finally, the crosslinking diluent affects the mechanical properties of the polyester. Styrene for instance, generally increases rigidity, whereas alfa-methyl styrene imparts flexibility. The amount of the crosslinking diluent is also responsible for the properties of the final product. Hietalahti et.al. studied the correlations between the styrene amount and the length of the styrene segments in the polyester with the help of solid-state ^{13}C nuclear magnetic resonance. They were able to show that the mechanical properties were improved with increasing styrene content [1].

Additional properties can be attributed to unsaturated polyesters by introducing functional groups onto starting materials. Isophthalic acid improves corrosion resistance and dibromophthalic anhydride for instance, gives flame retardant property.

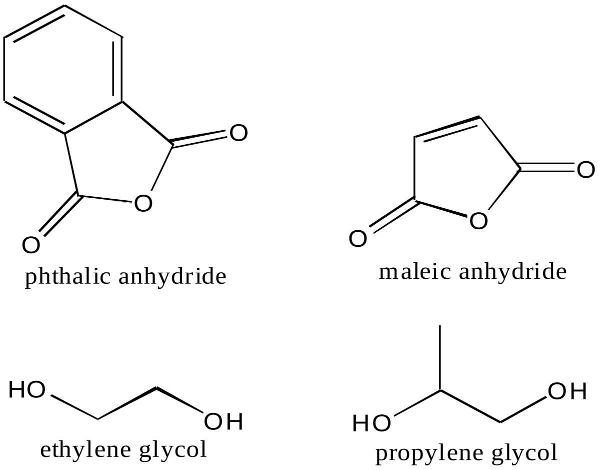
Different diols also provide varying properties; like diethylene glycol giving more flexible material with higher toughness and propylene glycol attributing better stiffness. Ethylene glycol is generally used because of its low price and reactivity at relatively lower temperatures. Table 1.1 shows the properties of unsaturated polyesters in relation to starting materials.

Table 1.1. Properties of UPEs in relation to starting materials [2]

STARTING MATERIALS	**PROPERTIES**
Maleic anhydride	Branched polyesters compared to those from fumaric acid Lower reactivity compared to those from fumaric acid
Fumaric acid	Increased reactivity of polyesters
Phthalic anhydride	Polyesters with low molecular masses Improved hardness and stiffness in cured resins Good compatibility with styrene
Terephthalic acid	Improved hardness and stiffness in cured resins Increased heat deflection temperature
Isophthalic acid	Higher molecular masses Excellent physical and chemical properties Improved hardness and stiffness in cured resins
Adipic acid	More flexible chains Soft products Increased toughness Reduced water and weathering resistance

Ethylene glycol	Reduced solubility of unsaturated polyester in the vinyl monomer
Propylene glycol	Increased rigidity Good compatibility with styrene
Diethylene glycol	More flexible chains Soft products Increased toughness Reduced water resistance
Neopentyl glycol	Good corrosion, UV, water, and chemical resistance
Hydrogenated bisphenol A	Good corrosion, water, and chemical resistance

The polyesters employed in this study are products of polycondensation of phthalic anhydride and maleic anhydride with ethylene glycol and propylene glycol.



phthalic anhydride

maleic anhydride

ethylene glycol

propylene glycol

Figure 1.2. Raw materials of the unsaturated polyesters used in this study

The wide range of composition and compounding possibilities of unsaturated polyesters made them important industrial products. Although the basic chemistry of unsaturated polyesters has not changed much since its accelerated development in 1950’s, application oriented development for unsaturated polyesters continues to provide tailored solutions in various fields. At the beginning of 1990’s the environmental problems caused by styrene emission from the processing of unsaturated polyesters were debated and new reactive diluents were searched. Today, additives lowering styrene emission or leading to flame retardation are being investigated in order to provide wider application areas in industry.

Unsaturated polyesters are one of the most widely used polymers in composite applications. They are extensively employed in construction, transportation, marine and automotive industries as composites with glass fiber. Typical applications are boat hulls, construction panels, pipes, automotive parts, sports equipment, and wind generator blades [3]. A special use is in gel coats, which are employed as colored and protecting surface coatings in composites. Unsaturated polyester resins are versatile materials in processing into a composite product. They can be processed by hand lay-up and spray lay-up lamination, casting, compression molding, resin transfer molding (RTM) as well as by vacuum infusion and filament winding [4].

1.1.2. Unsaturated Polyesters among Plastics

In general, plastics are divided into two main groups: Thermoplastics and Thermosets. A thermoplastic material can be dissolved and melted. Hence, thermoplastics can be molded through heating to molten and repeated solidification. On the other hand, being a crosslinked material a thermoset is insoluble and infusible. Table 1.2 shows the categories of plastics.

Table 1.2. Categories of plastics

PLASTICS	
Thermoplastic	**Thermoset**
Engineering plastics Examples: PET, PBT,Nylon, PC, PEEK, PEK	UPE (Unsaturated polyester) EP (Epoxy resin) PF (Phenolic resin) MF (Melamine resin)
Universal plastics Examples : PE, PP, PS, PMMA, PVA	UF (Urea resin) SI (Silicone resin) PI (Polyimide) PU (Polyurethane)
Alloys Examples : PPO+PS, PC+ABS, PBT+PET	PABM (Polyamide bis maleimide) BT (Bismaleimide triazine) DAP (Polyarylphthalate)

PET: Polyethyleneterephthalate; PBT: Polybutylene terephthalate; PC: Polycarbonate; PEEK:Polyether ether ketone; PEK: Polyetherketone; PE: Polyethylene; PP:Polypropylene; PS: Polystyrene; PMMA: Polymethylmethacrylate; PVA: Polyvinylacetate; PPO: Poly (p-phenyleneoxide); ABS: Acrylonitrile butadiene styrene

Commonly the curing is done in the mold. During this molding process, in case of unsaturated polyesters, reinforcing fibers are added to the resin in order to increase mechanical properties of the final product. The molding process of unsaturated polyesters is illustrated in Figures 1.3 and 1.4.

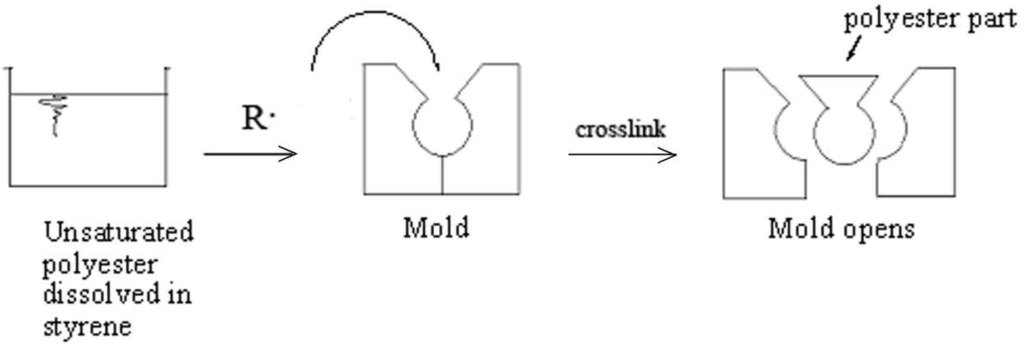


Figure1.3. Molding of unsaturated polyesters

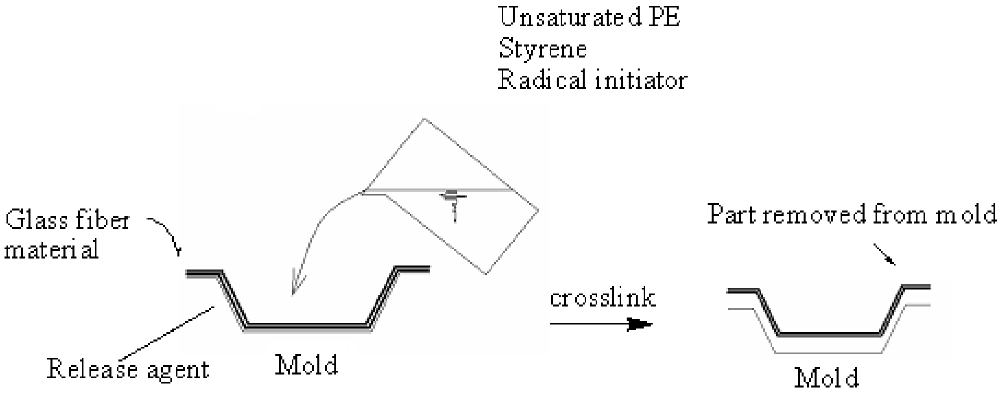


Figure 1.4. Molding of unsaturated polyesters with glass fiber

1.1.3. Progress of polyesterification

The polyesterification reaction is a reversible step-growth polymerization. Carboxyl and hydroxyl terminated polyester chains of various lengths are present in the reaction medium at all times. The molecular weight of the polymer continues to increase until the desired molecular weight is reached and the reaction is stopped. During this process, the carboxylic acid end groups are being used up upon the reaction with hydroxylic end groups. The acid number of the polyester decreases parallel to molecular weight increase.

Commercial polyesterification is carried out until a low acid number such as 20-30 is reached, indicating that carboxylic acid ends are depleted in the medium. At this point the linear unsaturated polyester is a viscous material of a low degree of polymerization and has a molecular weight between 1500-3000.

In the industrial manufacture of polyesters, the acid number decreases from 225 to 20-30 in about 16-20 hours. This decrease in acid number is shown in Figure 1.5. In unsaturated polyester synthesis, acid number has been traditionally used as a measure of molecular weight. The reaction is considered complete when the acid number of the polymer (determined by titration with potassium hydroxide, using phenolphthalein as indicator) is about 20-30.

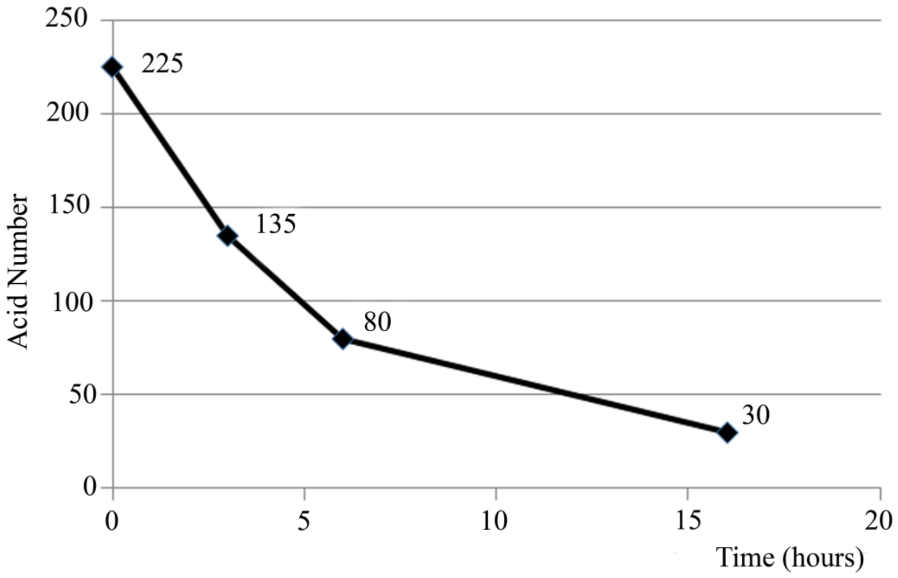


Figure 1.5. Decreasing acid number during a standard commercial polyesterification

Measuring the decrease in acid number is a practical and reliable method to monitor the esterification reaction. Alternatively, for polyesters molecular weight increase can be followed by increase in viscosity.

As part of this study, Gel Permeation Chromatography (GPC) can serve as another method to observe the molecular weight increase in unsaturated polyesters. In the present work GPC is used to follow molecular weight increase. This method was the most reliable, because chain extenders were used in the reaction medium. A chain extender that reacts only with one acidic end of an oligomeric chain would result in a decrease in acid number without a molecular weight increase. Therefore acid/base titration method would give misleading information about molecular weight. A typical GPC curve for the polyesters used in this study is shown in Figure 3.7, under the “Experimental” section and Figure 1.6 illustrates the molecular weight increase during an industrial polyesterification without an added chain extender.

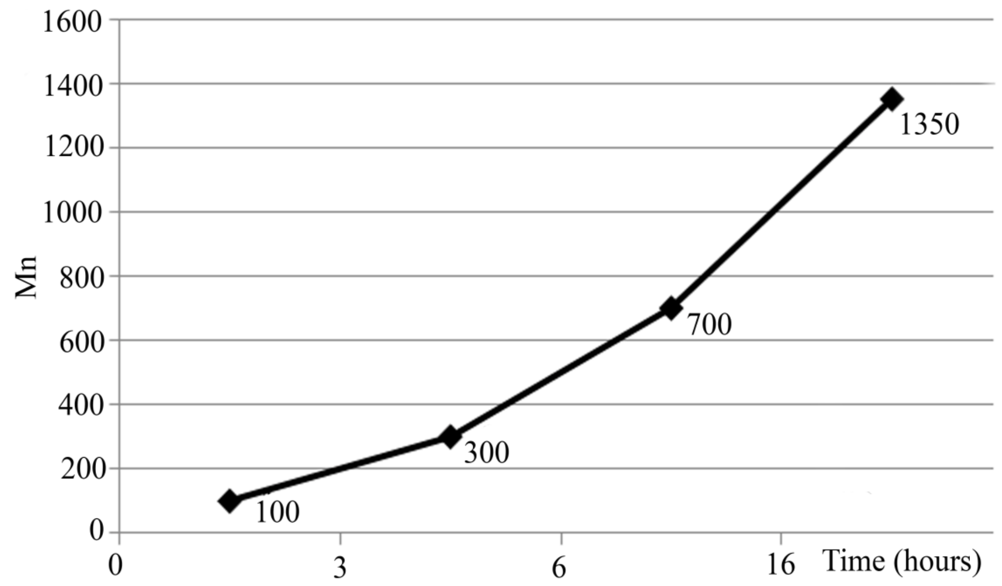


Figure 1.6. Increasing molecular weight during a standard commercial polyesterification

1.1.4. Solubility, Crosslinking and Gel Time

The polyester backbone which is prepared from a mixture of the desired saturated and unsaturated acids and the glycols which are condensed into a viscous polymer of a molecular weight about 1500-3000 becomes ready to be dissolved in a vinyl monomer. Styrene is frequently used as comonomer for UPE resins. Variations in the styrene content affect the resulting properties of the final material. Commonly about 35 per cent styrene is used to dissolve the polyester.

Crosslinking, which occurs through free-radical polymerization, begins upon introduction of an initiator, usually an organic peroxide. An accelerator like cobalt naphthenate is added to promote easy start of curing at room temperature. The reactivity of the unsaturated polyester towards the crosslinking reaction is derived from the maleic anhydride component. By increasing the degree of unsaturation the crosslinking reaction can be accelerated. During polyesterification at elevated temperatures, a rather high degree of maleate/fumarate isomerization also takes place. This becomes of major importance in the crosslinking process, because fumarate unsaturation is about 20 times more reactive than the maleate towards free radical polymerization. Too short gel times would limit the processability of the resin. To prevent premature gelation and to inhibit styrene polymerization, usually hydroquinone or other free radical inhibitors are added.

The cure of unsaturated polyester resins is accompanied by some shrinkage. This shrinkage usually causes severe manufacturing problems like surface waviness, shrink mark formation or dimensional control problems. The shrinkage control mechanism of UPE resins cured at high and low temperatures has been studied extensively and many researchers concentrated to overcome the shrinkage problem proposing different solutions. An efficient and a common way to reduce the shrinkage is to introduce thermoplastics as “low profile” additives in the resin system [5].

In some cases when the impact resistance of the polyester is to be improved, polyfunctional isocyanates have been added to the resin concurrently or in a separate step during the crosslinking. These compounds were successful in improving the impact resistance of hydroxyl terminated unsaturated polyester resins, however, the increase in shrinkage limited their commercial application. In a more recent study, another composition including polyisocyanates was employed during the cure process, which is characterized by low shrinkage on curing [6].

The crosslinking kinetics and the gel time are vital parameters in industrial production of unsaturated polyesters. In relation to the present study, the added chain extender should not alter curing parameters. According to the standard ISO 2535 (2001) the gel time is defined as the time of first gel formation at ambient temperature [7]. At this point approximately 3 per cent of the double bonds have reacted; the material is lightly crosslinked and goes from liquid to gel.

The expansion of unsaturated polyesters into varied fields of application has increased the demand for special resins requiring tailored cure conditions. Although in many cases fast cures at elevated temperatures can be tolerated, and may even be desirable, there is an increasing number of applications that require low exotherm temperatures. At the same time the fabrication of parts requiring such low curing temperatures must be economical, i.e. the cure must be attained within a minimum time.

1.1.5. Mechanical Properties and Reinforcement

Unsaturated polyesters, like other thermoset polymers, exhibit many useful characteristics due to the high degree of crosslinking between polymer chains. Typical qualities are high glass transition temperature, high modulus and specific strength, creep resistance and good solvent resistance. The drawback of dense crosslinking is the production of inherently brittle material with low fracture toughness in comparison to other engineering plastics. Superior properties coupled with ease of processing have led to numerous applications of these polymers, perhaps most importantly as matrix materials for fiber reinforced composites. In fact, among the thermosetting resins, unsaturated polyesters, are one of the most commonly used matrix resins for commodity fiber-reinforced plastics [8].

A composite is defined as a combination of at least two chemically distinct phases, the matrix and the reinforcement, which are separated by a distinguishable interface. In the composite the unsaturated polyester holds the reinforcement in place; it transfers the external loads to the reinforcement and protects the reinforcement from the environment. If individual fibers are fractured, the matrix will redistribute the load to the surrounding fibers thus preventing the complete failure of the material. Without the reinforcement unsaturated polyesters have very low fracture toughness. The composite product will exhibit a broad range of mechanical, chemical, thermal and physical properties depending on the composition of the unsaturated polyester [9].

Considerable research to improve fracture toughness has provided various solutions. The conventional approach is to introduce micrometer sized particles as reinforcement (elastomeric, thermoplastic or ceramic) into the polymer matrix in order to improve the fracture toughness to a certain extent. More recently, it has been demonstrated that the addition of nanometer sized fillers significantly enhance the mechanical properties of unsaturated polyesters [10]. Naturally occurring plant fibers such as coir fiber were also used as reinforcement in composites [11]. Table 1.3 summarizes changing mechanical properties of unsaturated polyesters upon glass fiber reinforcement.

Table 1.3. Mechanical properties of unsaturated polyesters upon glass fiber reinforcement

Mechanical Properties	Phthalic acid Unreinforced	Phthalic acid Reinforced 30 per cent glass fiber	Isophtalic acid Unreinforced	Isophthalic acid Reinforced 30 per cent glass fiber
Ultimate Flexural Strength (MPa)	82	175	90	193
Flexural Modulus (MPa)	4000	5500	4500	6300
Ultimate Tensile Strength (MPa)	41	89	62	105
Tensile Modulus	4000	5000	4400	8200
Elongation at Break (per cent)	2	1.4	2.1	1.6
Heat Deflection Temperature (^{o}C)	70	150	100	220

1.1.6. Tailored Industrial Applications for Further Improvement of Mechanical Properties of Polyesters

The use of fibers in improving the mechanical properties of unsaturated polyesters may remain insufficient when stronger properties are needed. In fact, fiber reinforced unsaturated polyesters provide molded material with excellent impact resistance, however when it comes to more demanding applications like automobile outer structures, helmets or bumper beams, tailored solutions are needed. Usually the physical strength of an unsaturated polyester increases with increasing molecular weight, but the use of comparatively high molecular weight is limited by the increasing viscosity hence the processibility of the resin.

Most of the tailored industrial applications deal with improving mechanical properties of unsaturated polyesters in different ways and try to overcome the problems arising from the basic characteristics of unsaturated polyesters like:

- High T_g
- Too brittle for engineering applications
- Craze and fractures
- Possible damage during use or demoulding

Block copolymerization of unsaturated polyester resins with liquid rubbers in order to increase toughness and impact resistance has been studied by Cherian and Thachil [12]. An elastomeric phase was incorporated into the polymer matrix and improved properties were observed. The scanning electron micrographs of fracture surfaces of unmodified and modified UPE resins are shown in Figure 1.7. In the micrograph in Figure 1.7.(a), the fracture path for unmodified resin is narrow and continuous, indicating rapid crack propagation. The micrograph of HTPB modified resin in Figure 1.7.(b) shows plenty of cracks far broader and discontinuous than for Figure 1.7.(a). Cracks propagate from the surface across the cross-sectional area and the abrupt fracture propagation along a wide front suggests better load-bearing characteristics for the resin. Referring to HTNR modified resin (Fig. 1.7.(c)), the fracture paths are broader and less continuous. This leads to high energy absorption and toughness. CTBN-modified resin shows the best results, as can be seen from the micrograph in Figure 1.7.(d). The fracture paths have a feathery texture with large width. They are also discontinuous and convoluted. The fracture spreads from the bottom upward.

When compared to the unmodified UPE sample, following the addition of 10 per cent of the elastomer, elongation at break, toughness and impact strength showed an improvement above 100 per cent in most cases. Water absorption was increased about 40-60 per cent, 60 per cent being in case of the hydroxyl terminated polybutadiene modified UPE. These results point to high toughness and load-bearing characteristics for the new polymer [12].

Hydroxyl terminated unsaturated polyester resins have been treated with polyisocyanate compounds with the aim of producing low density foamed resins. Polyisocyanates and water were added to the resin during the cure process and the evolving carbon dioxide gas expanded the liquid resin.

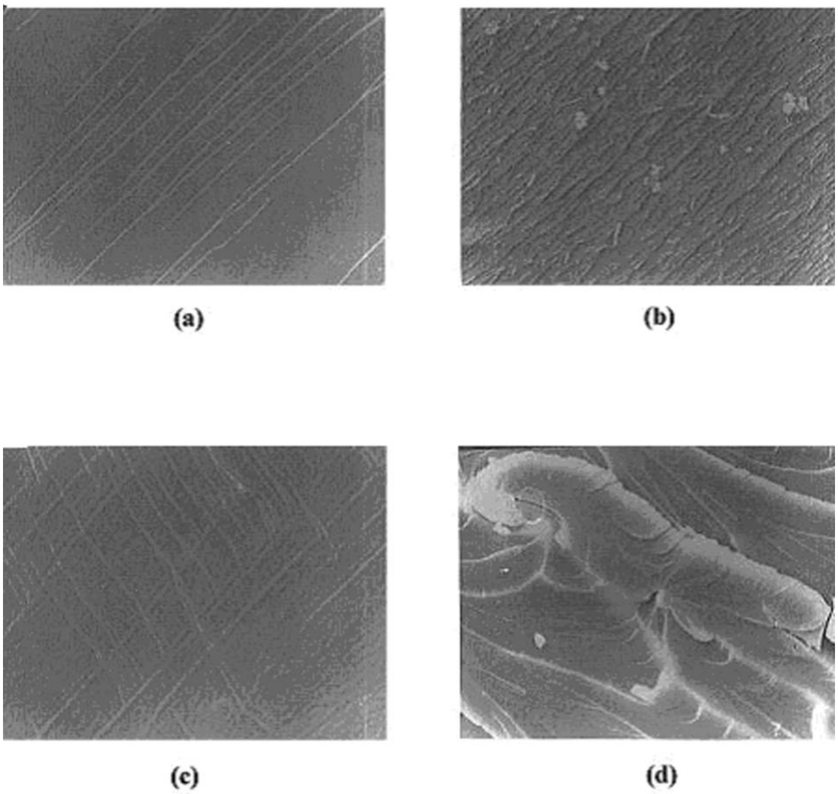


Figure 1.7. Scanning electron micrographs of fracture surfaces: (a) UPE (b) UPE-co-HTPB, (c) UPE-co-HTNR, (d) UPE-co-CTBN

[HTPB: hydroxyl terminated polybutadiene; HTNR: hydroxyl terminated natural rubber; CTBN: carboxyl terminated nitrile rubber]

For this purpose mixtures of 2,4- and 2,6- toluene diisocyanates have been used primarily, but polymeric MDI compounds have also been employed [13,14].

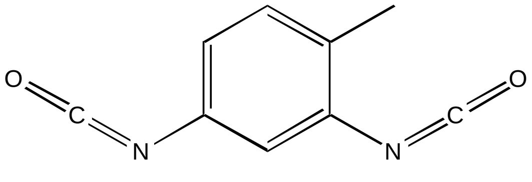


Figure 1.8. The structure of 2,4-toluene diisocyanate

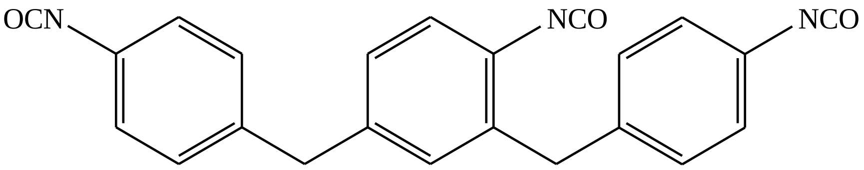


Figure 1.9. The structure of polymethylene polyphenyl polyisocyanate (polymeric MDI)

Polyester resins have been used in the production of many molded parts, containers or sheet. It is known that polyesters, when subjected to heat in a wet atmosphere exhibit some hydrolytic instability. In such a case the polyester looses from its physical properties due to degradation of polymer chains. The tendency is primarily explained by the hydrolysis of the ester linkages under the catalysis of the acidic end groups of the polymer chains.

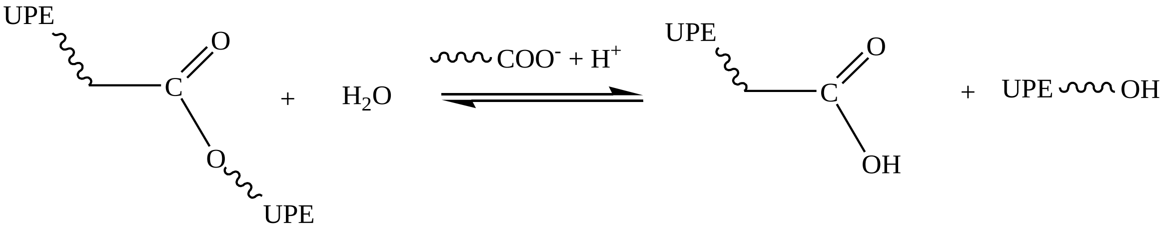


Figure 1.10. Hydrolysis of UPE chains through ester linkages

The end-capping method has been proposed to enhance the hydrolytic stability of polyesters [15]. This method removes the acidic end groups and produces hydrolytically stable polyester. The difficulty here was to find the appropriate end-capping agent that does not decompose or evaporate during the end-capping reaction. In order to overcome this difficulty, polymeric end-capping agents which are thermally stable have been proposed. One invention makes use of an epoxy or amino functional group as a polymeric end-capping agent. To search the efficacy of the end-capping agent the polymers were immersed in hot water. The polyesters modified by the polymeric end-capping agents exhibited much smaller decrease in intrinsic viscosity when compared to the unmodified polyester. The end-capping agents and intrinsic viscosity differences are shown in detail in Table 1.4.

Table 1.4. The effect of end-capping on intrinsic viscosity of PET [15]

End-capping agent	Ethylene glycidyl methacrylate copolymer	Epoxy-ethylene ethylacrylate copolymer	Epoxy-styrene Butadiene styrene Block copolymer	Amino-polyethylene copolymer	Blank
Intrinsic viscosity before immersion	0.60	0.60	0.60	0.60	0.60
Intrinsic viscosity after immersion	0.58	0.57	0.58	0.57	0.35

1.2. Methods to Increase the Yield of Polyesterification

Polyesterification is a reversible polycondensation reaction. Industrial production of unsaturated polyesters requires elevated temperatures (150-290 ^{o}C) and vacuum is generally applied during the last steps of the reaction to distill off the by-product water and to continuously shift the reaction towards the high molecular weight polyester. The total reaction time is 16- 20 or even 25 hours, requiring multiple operator shifts in manufacture. Other important drawbacks like discoloration of the product and loss of diol due to evaporation (with environmental problems) are also common. The cost of the process increases in both economical and environmental terms.

During polymerization, at elevated temperatures, in addition to the difficulties of the equilibrium reaction, a variety of side reactions occur. Particularly in maleic anhydride based polyesters cis/trans isomerization takes place. Unsaturated polyesters from maleic anhydride and various diols were examined by means of ^{1}H and ^{13}C NMR spectroscopy by J. Grobelny [16]. As the carbons of the diol units were sensitive to maleate/fumarate transformation the process could be followed in detail. Maleate/fumarate isomerization largely affects the final properties of the crosslinked material. It is known that the fumarate based polyesters show much higher reactivity in the crosslinking process and can produce materials that are too brittle.

The worldwide consumption of thermoset resins, including unsaturated polyesters as the major member, is more than 22 million tons/year [3]. Today, it is still a growing market continuously challenged to produce light weight, high performance and high quality materials. Therefore, to facilitate the polyesterification reaction and to increase the yield in big scale industrial applications turns out to be a considerable challenge to the producer.

Methods to increase the yield of polyesterification are being extensively investigated to reach higher yields. Two methods already being employed are:

(i) Catalysis
(ii) Removal of water by azeotropic distillation

1.2.1. Catalysis

Polyesterification is an equilibrium reaction with many reversible steps all of which are catalyzed by acids. Industrial production is usually carried out in the presence of an added acid catalyst, which unfortunately brings in some important drawbacks. Catalysts cannot be removed from the bulk at the end of the reaction. Therefore the polyester can easily be hydrolyzed back to the starting materials.

In addition, some unwanted side reactions are also catalyzed by acids. Cis-trans isomerization of maleate double bonds and double bond saturations are typical examples. Dehydration of diols to ethers is another major side reaction.

Zinc acetate, *p*-toluenesulfonic acid, dibutyltin oxide, titanium benzenesulfonate and alkoxytitanium complexes are often used as catalysts in polyesterification reactions.

Synthesis of unsaturated polyesters using adipic acid, ethylene glycol and fumaric acid in the absence and presence of phosphoric acid have been analyzed with respect to reaction kinetics and chain length [17].

Different metal compounds have been claimed to catalyze the esterification reaction efficiently. The activity of metal ions in these reactions has been reported in decreasing order as [18]:

$$Sn^{2+} > Ti^{4+} >> Zn^{2+} > Pb^{2+} = Co^{2+} = Cd^{2+}$$

Some metal oxides and metal-organic salts are also common catalysts for the polyesterification reaction. Extensive screening of potential catalysts for esterification has shown that Sn^{2+} is a good catalyst for polyesterification [19]. L. Nondek and J. Malek have focused on compounds that catalyze the reaction of ethylene glycol with isophthalic acid [20].

Tin compounds that are reported in literature to have good activity in direct esterification include tin (II) oxide and tin(IV) oxides, and other oxalate, carboxylate and alkyl tin compounds. A tin quelate of 3-hydroxy-2-methyl-4-pyrone has been reported to catalyze the polyesterification of terephthalic acid, neopentyl glycol and trimethylolpropane [19]. The catalyst was prepared according to the reaction shown in Figure 1.11.

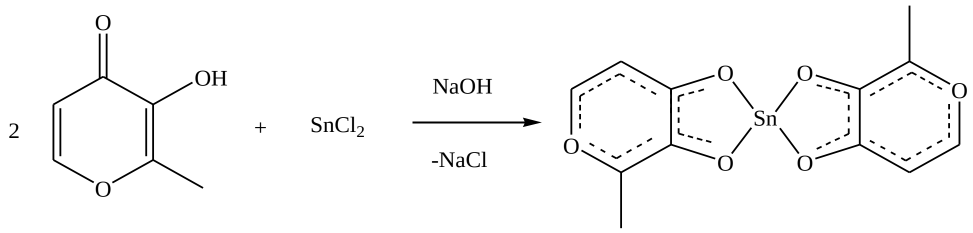


Figure 1.11. Tin catalyst

The catalytic behavior of tetrabutoxy titanium in polyesterification between diacids and diols has been studied with model reactions [21]. The behavior of this catalyst was found to be complex and medium dependent. A decrease of the vacuum and increase of the acid concentration led to poor catalytic activity which is also observed when the reaction was carried out in a hydrophilic medium such as polyoxy-ethylene. When the alcohol is in excess, the catalyst was found to be much more efficient.

Another titanium catalyst, a complex of a phosphorus compound such as phosphorous acid, diphenylphosphite or dibutylphosphite and titanium compound was reported to catalyze polyesterification reactions of aromatic dicarboxylic acids with aliphatic diols [22].

Scandium trifluoromethane sulfonate ($Sc(OTf)_3$) and scandium trifluoromethane sulfonamide ($Sc(NTf)_3$) have been reported to catalyze room temperature polycondensation of dicarboxylic acids and diols [23].

1.2.2. Removal of Water by Azeotropic Distillation

Azeotropic polycondensation in the presence of organic solvents such as
toluene or xylene are used in order to shift the polyesterification towards the product. In this case the reaction takes place at lower temperatures and it is possible to avoid losses of volatile reactants. When these solvents are used, the boiling point of the water-azeotrope is 84 ^{o}C in case of toluene and 94 ^{o}C in case of xylene. The remaining organic solvent is then removed by vacuum distillation. The drawbacks of this process are incomplete solvent removal and the requirement of a more complicated distillation system.

Wenfang and Ranby [24] employed azeotropic distillation using toluene for the synthesis of unsaturated polyesters. The unsaturated polyesters have been prepared by a two-step condensation polymerization. According to this method, in the first step, an excess of glycol components are esterified with phthalic anhydride in toluene as solvent, which, towards the end of the reaction, removes the water by azeotropic distillation.

P. A. Cusack analyzed the flame retardant properties of tin(IV) oxide in unsaturated polyester thermosets. In this procedure xylene is added towards the end of the reaction to remove water [25].

Similarly, G. A. Skinner et. al. have improved the yield of the polyesterification reaction by removal of water with the help of xylene-water azeotrope [26].

1.3. Chain Extension Method for Unsaturated Polyesters

In the present work chain extension is used to overcome manufacturing problems of unsaturated polyesters. During the step-growth polymerization an extender molecule capable of reacting with the end groups of the short polyester chains is added to the reactor. A rapid molecular weight increase of the unsaturated polyester follows, shortening the polyesterification time substantially by coupling medium length chains. Chain extension eliminates the major problems associated with long reaction times and high temperatures. In terms of industrial production, the benefits brought on by the extenders such as shortened reaction time, reduced energy use and increased yield present a major advantage.

Chain extenders are (preferably low molecular weight) monomers that possess at least two functional groups capable of reacting with polymer end groups. A typical chain extension reaction is illustrated in Figure 1.12.

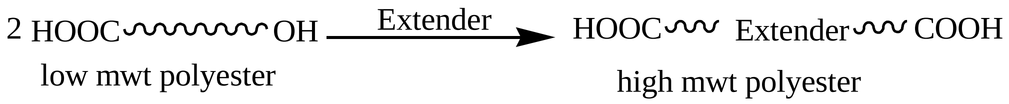


Figure 1.12. The chain extension reaction

In terms of production cost and efficiency, methods that shorten the production time and provide milder reaction conditions are valuable. Chain extension reactions are an effective way of shortening production times. In the strategy of chain extension the standard polyesterification is carried out to a much lesser extent, and the oligomers obtained are chain extended with a suitable chain extender molecule that reacts without producing by-products. As less water is removed by condensation, the yield of the final polyester is also increased.

In case of unsaturated polyesters, in principle, any difunctional (or higher functionality) chemical that reacts fast with the hydroxyl or carboxyl end groups of polycondensates may be used as chain extender. The concentration and the correct time of addition of the extender are important issues in industrial applications. In principle, the minimum amount of the extender to provide rapid and sufficient increase in molecular weight is considered as the optimum amount. The basic requirements needed for an effective chain extender are listed below:

- High reactivity
- Reaction only with end groups
- Not toxic
- No by-products
- No side reactions
- Linear chains, no branching
- Accurately dosable
- Does not interfere with free radical crosslinking reaction
- Does not alter the thermal and physical properties of the final crosslinked product

1.4. Chain Extenders in Other Industrial Polyesters

Polyesters like polyethylene terephthalate or polybutylene terephthalate and nylons are produced by melt condensation processes, where the molecular weight of the resin increases steadily, as does the viscosity of the melt. Actually the conversion of the polycondensation reaction and hence the molecular weight of the final polyester is limited by the viscosity of the melt. However, higher molecular weight resins are much more preferred as they provide much stronger mechanical properties of the final polyester. A common method to increase the molecular weight of the polyester is solid-state postcondensation. This process is performed in tumble driers under high vacuum and high temperatures for extended periods of time (12-20h). Solid-stating is characterized by very high capital costs and high production costs.

However, a chain extender can be simply added to the polymer during extrusion, which enables a rapid viscosity increase. Polymers that exhibit the same strong properties as those obtained by solid-state postcondensation are obtained within minutes. No branching takes place and the same molecular weight distribution is obtained. The viscosity of the polymer increases with the amount of added chain extender.

Chain extension reactions are employed in increasing the molecular weight of degraded recycled polyethyleneterephthalate (PET). The reaction of diepoxide compounds with PET renders rapid viscosity increase and this method is widely used in regaining mechanical and physical properties of PET.

Another chain extender pyromellitic dianhydride (PMDA) is generally used with PET at concentrations between 0.05-2 per cent to increase the molecular weight. Incarnato et. al. [27] used PMDA to increase the molecular weight of PET industrial scraps from a PET processing plant. They found that concentrations of PMDA between 0.5-0.75 per cent promote chain extension reactions that lead to molecular weight increase and a broadening of molecular weight distribution. The reaction of PMDA with polyester chains is illustrated in Figure 1.13. Figure 1.14 shows the intrinsic viscosity increase in PET bottle flakes treated with different amounts of pyromellitic dianhydride at 280 ^{o}C.

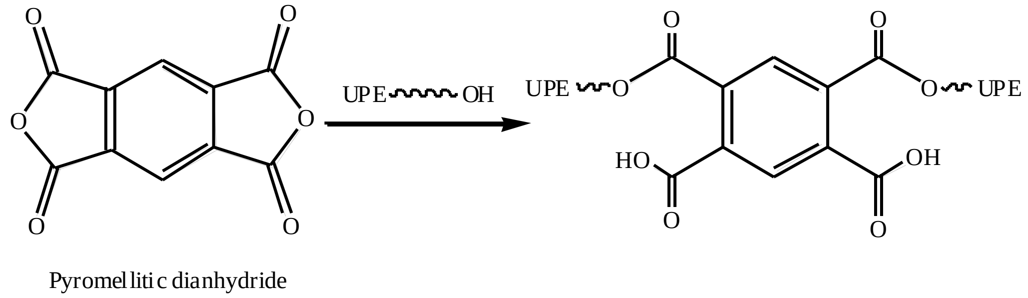


Figure 1.13. Reaction of unsaturated polyesters with PMDA

In case of polyethyleneterephthalate, chain extenders used in small amounts (less than 1 per cent) are effective in increasing the molecular weight because, PET being a high molecular weight polymer has long enough chains that upon coupling easily go to high molecular weight polymer.

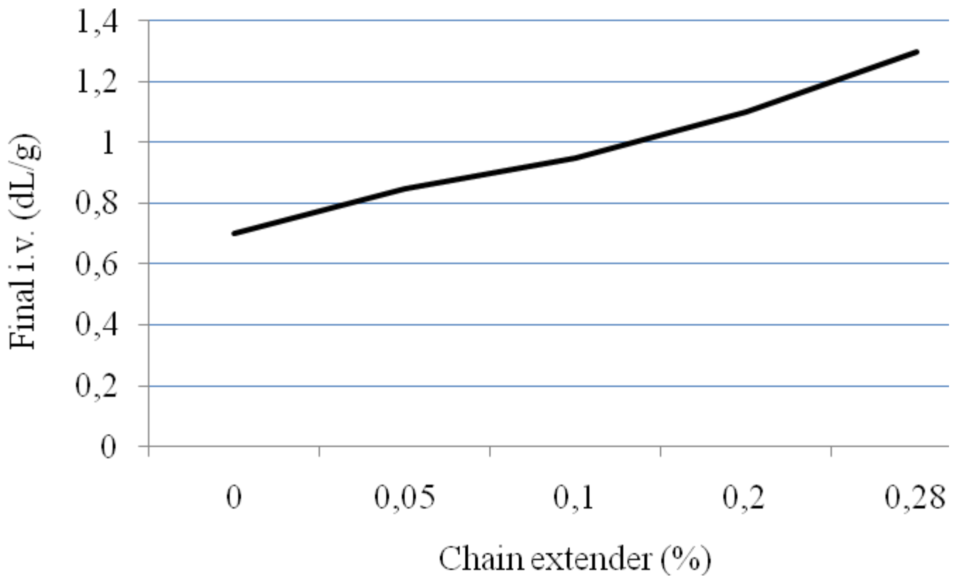


Figure 1.14. Intrinsic viscosity increase in PET bottle flakes treated with different amounts of PMDA at 280 ^{o}C

In case of unsaturated polyesters, relatively higher amounts of extenders are needed, because the oligomeric chains during polycondensation are much shorter and a much higher number of polymer ends are present in the medium requiring a larger amount of extender molecules.

Traditional chain extenders for PET are compounds such as dianhydrides, bisoxazolines, diepoxides that react with either or both the –OH and the –COOH end groups of the polyester or both. Difunctional chain extenders promote linear chain extension, while three or tetrafunctional chain extenders promote chain branching. Such reactive compounds are also known as “repair additives” since they can reverse the molecular weight loss of hydrolytically damaged PET. Many of the chain extenders used for PET are commercially available.

1.5. Chain Extender Molecules Used in this Study

1.5.1. Epoxide Chain Extenders

The carboxylate anion is a strong nucleophile which readily reacts with the strained oxirane ring. The reaction of epoxide groups with carboxylic acids forms the basis of epoxy resins, which are an important segment of industrial polymers used in various applications such as coatings, adhesives, laminates, castings, encapsulations and moldings.

With the help of the same reaction, diepoxide compounds can be used as chain extenders for UPE. They readily react with carboxylic end groups of polymer chains to provide rapid molecular weight increase.

In this study three diepoxide chain extenders were examined: (1) Diglycidyl ether of bisphenol A (DGEBA) (2) Epoxidized soybean oil (ESO) and (3) 1,2;7,8-diepoxyoctane (DEO).

1.5.1.1. Diglycidylether of Bisphenol A (DGEBA). Diglycidylether of bisphenol is a chemical compound used as constituent of epoxy resins. It is derived from bisphenol A and employed for its crosslinking properties. The structure as can be seen in Figure 1.15 contains two epoxy functionalities, making this compound a candidate for chain extension reactions.

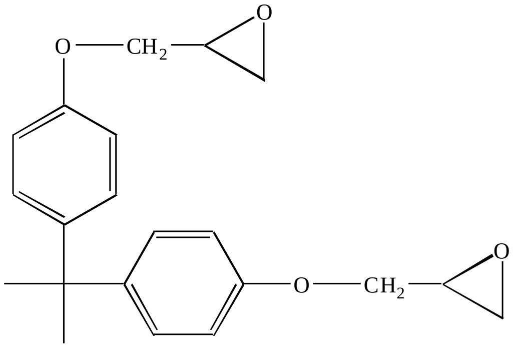


Figure 1.15. Diglycidylether of bisphenol A (DGEBA)

The reaction of DGEBA (Molecular weight 340 g/mole)with carboxylic acid end groups of the polyester provides hydroxyl and methyl groups and phenyl rings to the polyester. The introduced phenyl rings are expected to increase rigidity.

1.5.1.2. Epoxidized Soybean Oil (ESO). The basic chemical structure of vegetable oil is the unsaturated triglyceride. The double bonds in the triglyceride structure can be epoxidized and the epoxide groups can further be used as functional groups. ESO

(Molecular weight about 900 g/mole) is obtained from soybean oil by peracid oxidation and there are no reports of its use in chain extension reactions of PET. It is a renewable raw material offering environmental benefits. The ESO sample used in this work contains an average of 4.2 epoxy groups per triglyceride as determined by HI titration. Figure 1.16 shows the triglyceride structure in epoxidized soybean oil.

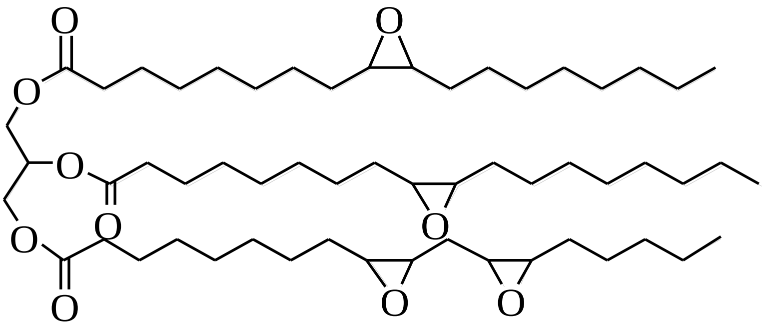


Figure 1.16. Epoxidized soybean oil (ESO)

Compared to difunctional epoxides like DGEBA and 1,2;7,8-diepoxyoctane, ESO can bring an advantage in chain extension reactions because of its higher epoxide number. However this advantage carries the risk of early gelation in the reaction medium due to ring opening polymerization and cross-linking through epoxy groups.

AMC-2 catalyst is used when carrying out chain extension with ESO. This catalyst is a trivalent organic chromium complex [28] and is designed for specific catalysis of the acid-epoxy reaction causing little etherification polymerization through the oxirane moiety as shown in Figure 1.17.

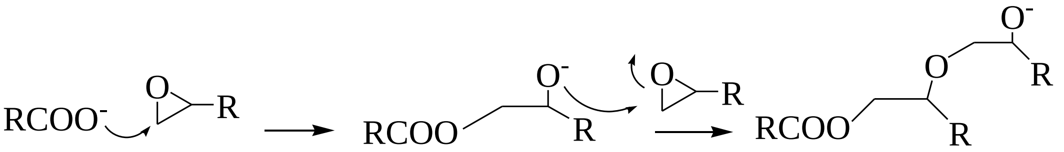


Figure 1.17. Polymerization of epoxide functionalities

1.5.1.3. Diepoxyoctane (DEO). 1,2;7,8-diepoxy octane (Molecular weight 142 g/mole) is a commercially available compound basically used for crosslinking. The epoxide groups easily react with the carboxylic ends of oligomeric unsaturated polyester chains introducing –OH and methylene groups to the unsaturated polyester chain. The advantage of this extender is that the introduced methylene groups are exactly the same as the ones coming from the ethylene glycol used in the polyesterification. Therefore, the physical properties of the resulting polyester are expected to remain unchanged. The structure of 1,2;7,8-diepoxyoctane is shown in Figure 1.18.

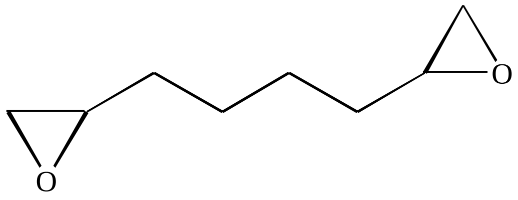
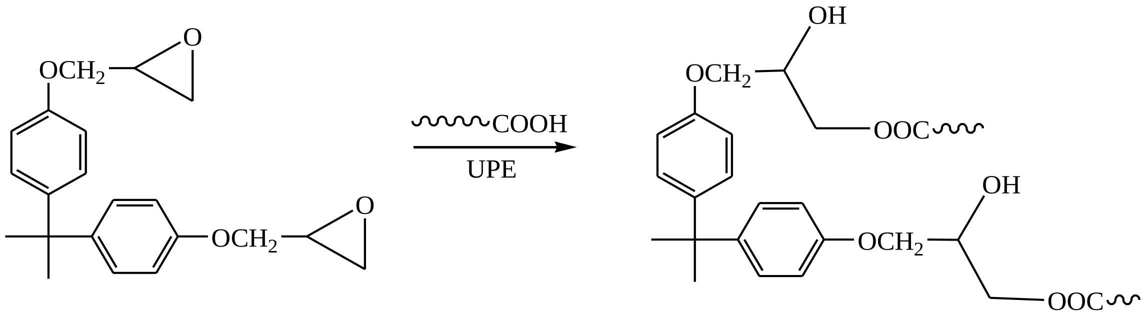
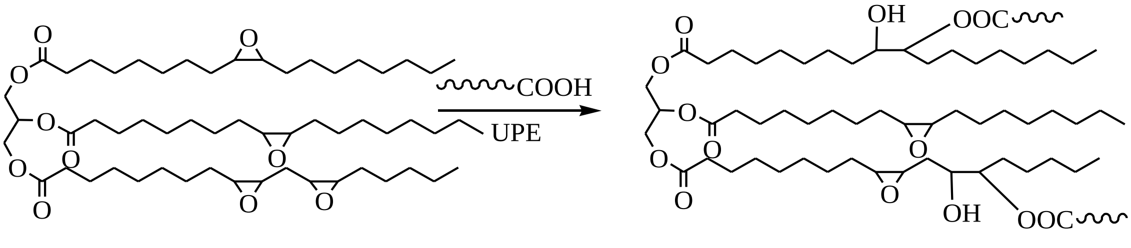


Figure 1.18. 1,2;7,8-Diepoxyoctane (DEO)

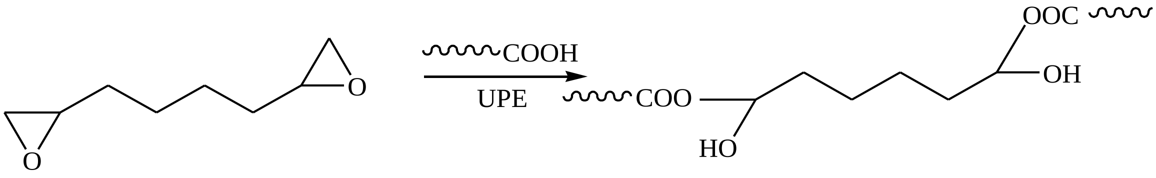
The reactions of the epoxide chain extenders with unsaturated polyesters are illustrated in Figure 1.19.



Diglycidylether of bisphenol A



Epoxidized soybean oil

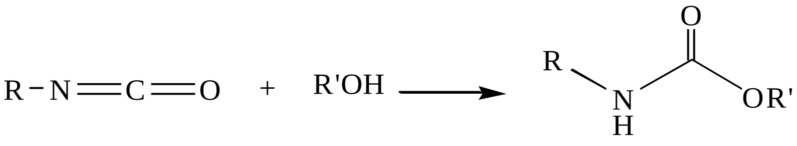


1,2;7,8-Diepoxyoctane

Figure 1.19. Reactions of the epoxide chain extenders with unsaturated polyesters

1.5.2. Isocyanate Chain Extenders

The reactions of isocyanates with various alcohols have been subject to a large number of studies. These investigations have shown that the relative reaction rates of alcohols are primary>secondary>tertiary in the formation of urethanes. By the use of appropriate catalysts it has been possible to speed up the reactions between hydroxyl and isocyanate groups. A range of polyurethane materials such as foams, coatings, adhesives and elastomers can be obtained from these reactions [29].



R’ reactivity = $1^o > 2^o > 3^o$

Figure 1.20. Reaction of alcohols with isocyanates

The reaction of isocyanates with carboxylate groups has been subject to less attention. Nevertheless, examples of isocyanate-carboxylic acid reactions to yield amides and carbon dioxide as shown in Figure 1.21 can be found in the literature [30].

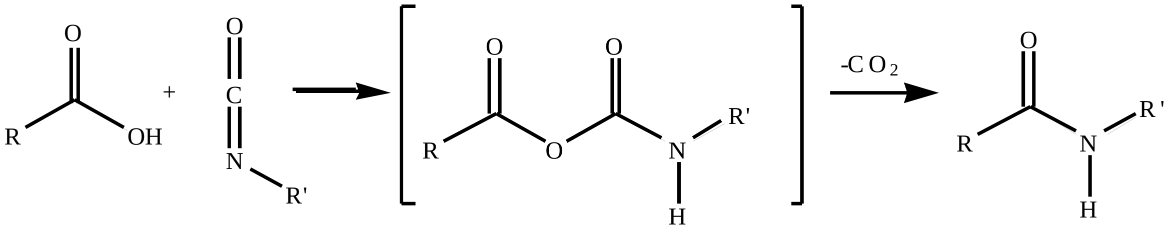
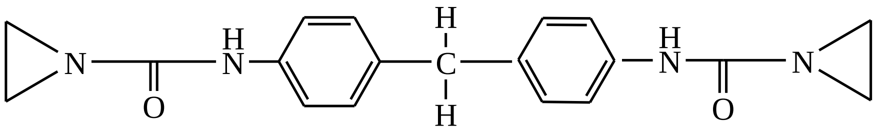


Figure 1.21. Reaction of carboxylic acids with isocyanates

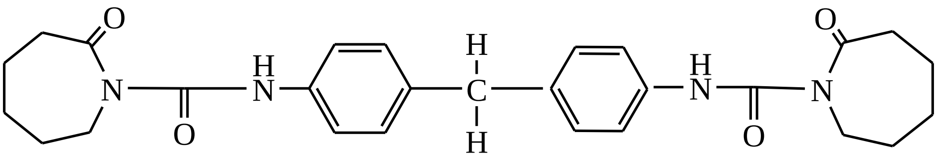
In the present work, three isocyanate extenders are investigated: Two blocked diisocyanates, namely diphenylmethane-bis-4,4’-ethyleneurea (MDI-E) and diphenylmethane-bis-4,4’-carbamoyl- Є –caprolactam (MDI-C) and one plant oil based diisocyanate, isocyanated soybean oil (SONCO). An important advantage of diisocyanate compounds is that they are capable of reacting with *both* (carboxyl and hydroxyl) end groups of the polyester chains.

1.5.2.1. Blocked Isocyanates. In industrial applications blocked isocyanates are often employed as crosslinking agents upon their rearrangement to methylene diphenyl diisocyanate (MDI). They have widespread use in many coatings areas like automotive, maintenance, and industrial finishing. An excellent review on blocked isocyanates is provided by D.A Wicks and Z.W. Wicks [31]. The major advantage of blocked isocyanate extenders is related to safety. These compounds can easily be handled during manufacture and added in small weight ratios to the polyesterification reactor.

The two blocked diisocyanate extenders used in this study, MDI-E and MDI-C are commercially available and are mainly used as crosslinking agents to improve bonding strength of various adhesives [32]. They are sold as emulsions; however, in this study they were precipitated out of the emulsions and were used in solid form. Their structures are shown in Figure 1.22.



MDI-E



MDI-C

Figure 1.22. The structures of MDI-E and MDI-C

These blocked extenders possess functional groups that are capable of reacting with the polyester end groups without deblocking to isocyanates. At temperatures below 160 °C deblocking does not occur and the aziridine blocked compound reacts with carboxylic end groups of UPE to provide the high molecular weight polymer. The reaction of carboxylic end groups with the aziridine rings is illustrated in Figure 1.23.

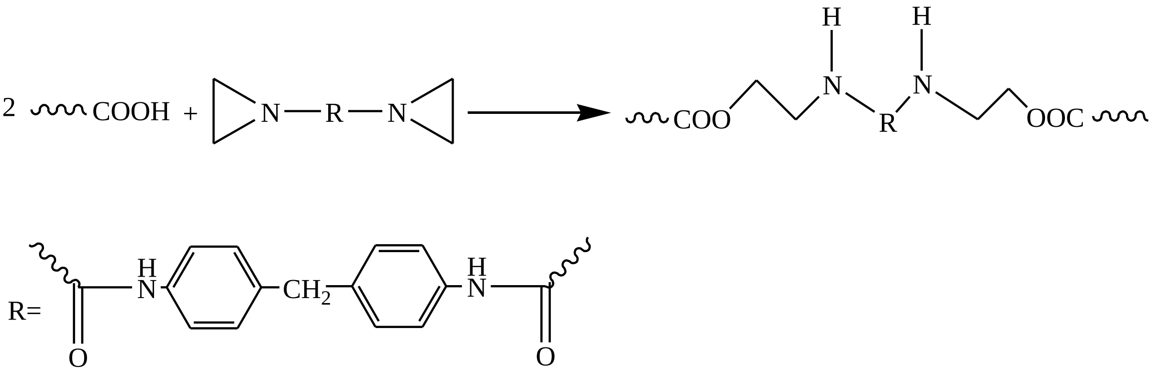


Figure 1.23. Reaction of MDI-E with carboxylic end groups by aziridine ring opening

The second blocked isocyanate, MDI-C is a caproplactam blocked MDI, used as an adhesion promoter for rubber and other elastomers to textile fibers and cords such as polyester [33]. Caprolactam blocked isocyanates do not deblock to MDI and caprolactam at temperatures lower than 150-160 °C [34]. When the chain extension reaction is carried out at a lower temperature such as 120 °C, normal deblocking does not take place. Caprolactam blocked isocyanates react by the addition of a nucleophile (in this case the –OH ends of the polyester chain) to either of the carbonyl groups [35] (a or b) as shown in Figure 1.24.

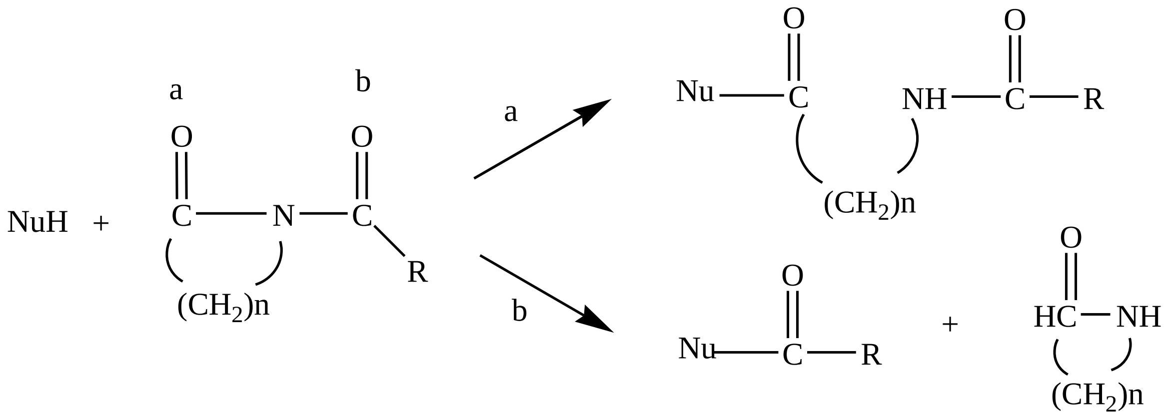


Figure 1.24. Reaction mechanisms of a caprolactam blocked isocyanate with a nucleophile

The first route (a) is a ring opening mechanism, whereas the second route (b) operates through liberation of caprolactam.

1.5.2.2. Isocyanated Soybean Oil. In the present study a natural source isocyanate, SONCO is also investigated for effective chain extension. The importance of SONCO as chain extender lies in the fact that it originates from a plant oil, can easily be synthesized and biodegrades easily. Other triglyceride containing polymers biodegraded easily as shown by soil burial tests [36].

SONCO is synthesized from allylic brominated soybean oil with the help of silver isocyanate according to the reaction scheme in Figure 1.25.

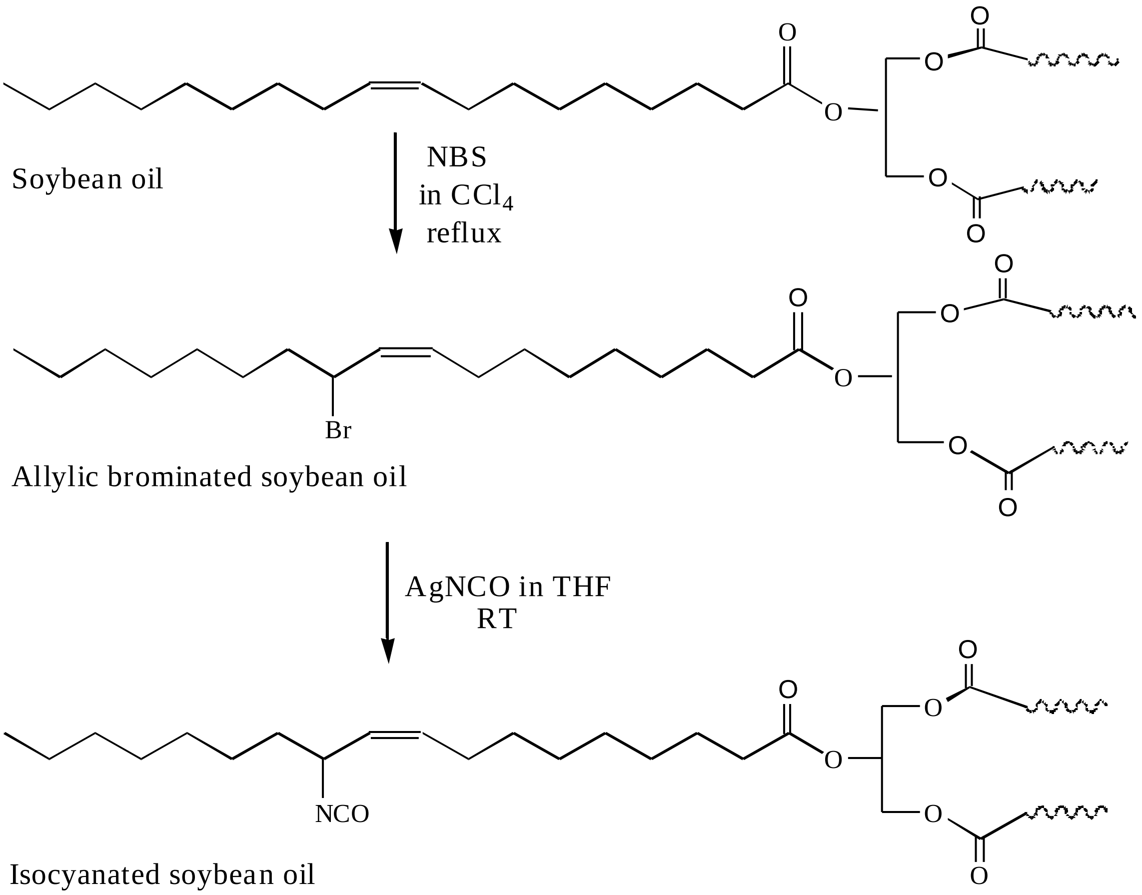


Figure 1.25. Synthesis of SONCO

In an earlier study carried out in our laboratory SONCO was successfully reacted with diols to yield polyurethanes [37]. The easy hydrolysis of the triglyceride renders the final polyester product biodegradable. SONCO has a molecular weight of about 1000 and contains an average number of 2.1 isocyanate groups per triglyceride. The isocyanate number is particularly important in chain extension, because at least two reactive sites are needed. In SONCO the average number of isocyanate groups looks promising; however, these are not terminal isocyanate groups on the long triglyceride chains. This should be expected to retard the chain extension reaction compared to the blocked diisocyanate extenders. Reactions of the two blocked isocyanates and isocyanated soybean oil with unsaturated polyesters are shown in Figure 1.26.

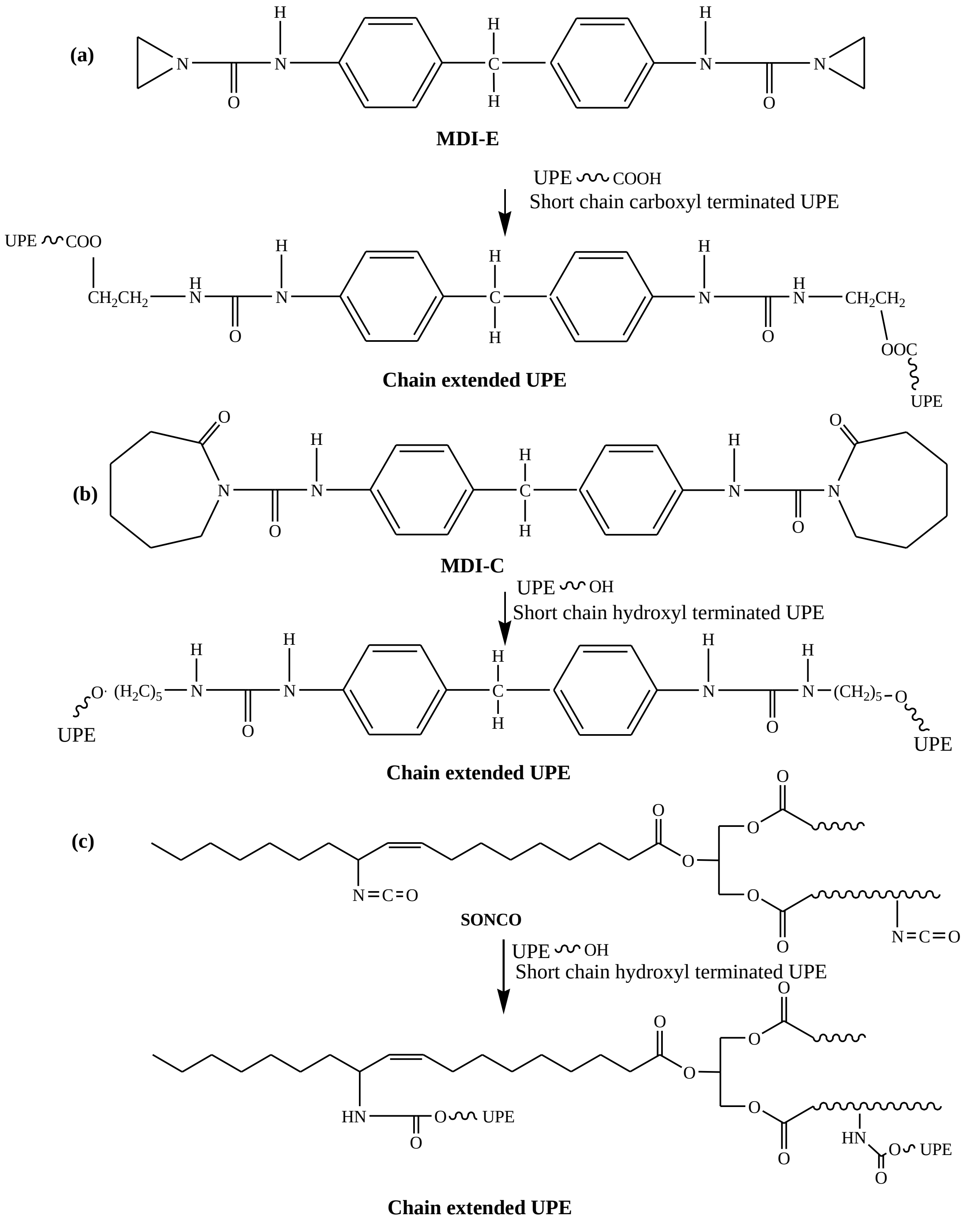
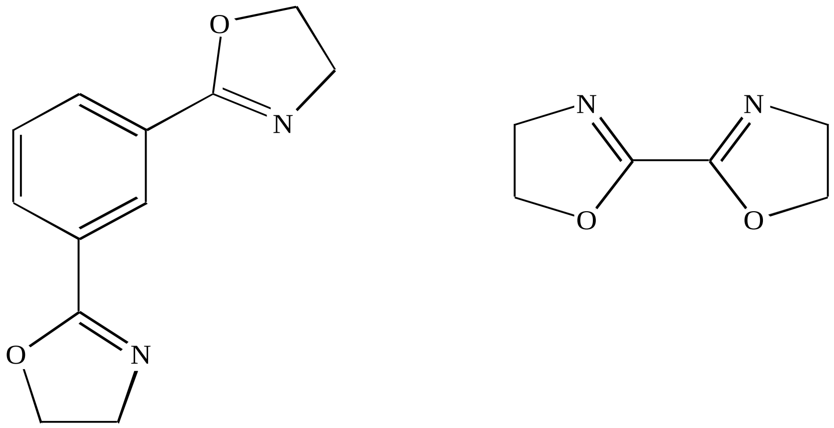


Figure 1.26. Blocked isocyanates and SONCO as chain extenders: (a) Diphenylmethane-bis-4,4’-N,N’-ethyleneurea (MDI-E) (b) Diphenylmethane-bis-4,4’-carbamoyl-Є-caprolactam(MDI-C) and (c) Isocyanated soybean oil (SONCO)

1.5.3. Bisoxazolines

Cyclic bis(iminoether)s, namely bis(2-oxazoline)s are versatile difunctional compounds reactive toward molecules containing several kinds of reactive groups. Step-growth polymerization of bis(2-oxazoline)s with acidic comonomers such as carboxylic diacids, thiocarboxylic acids, dithiols and diphenols leads to polymer compounds containing amide groups. Several authors have shown that [38] reactions of bisoxazolines with carboxylic acids are very fast under processing conditions. The reaction goes to high conversions within minutes without emitting any volatiles.



1,3-phenylene-bis-oxazoline (1,3-PBO)

2,2'-bis-2-oxazoline (BO)

Figure 1.27. Bisoxazoline chain extenders

In the present study two different bis oxazolines were investigated for their effectiveness in chain extension without altering solubility or thermal and mechanical properties of the final product. The reaction between an oxazoline and a carboxylic acid gives a poly(ester)amide, and is in principle reversible at high temperatures.

Loontjens and coworkers [35] have shown that the ester amide bond is stable at 200 ^{o}C for one hour, however at the processing temperatures such as 285 ^{o}C the reaction produces the starting materials. Therefore the chain extension reactions of unsaturated polyesters were carried out at a much lower temperature, which at the same time suits industrial applications.

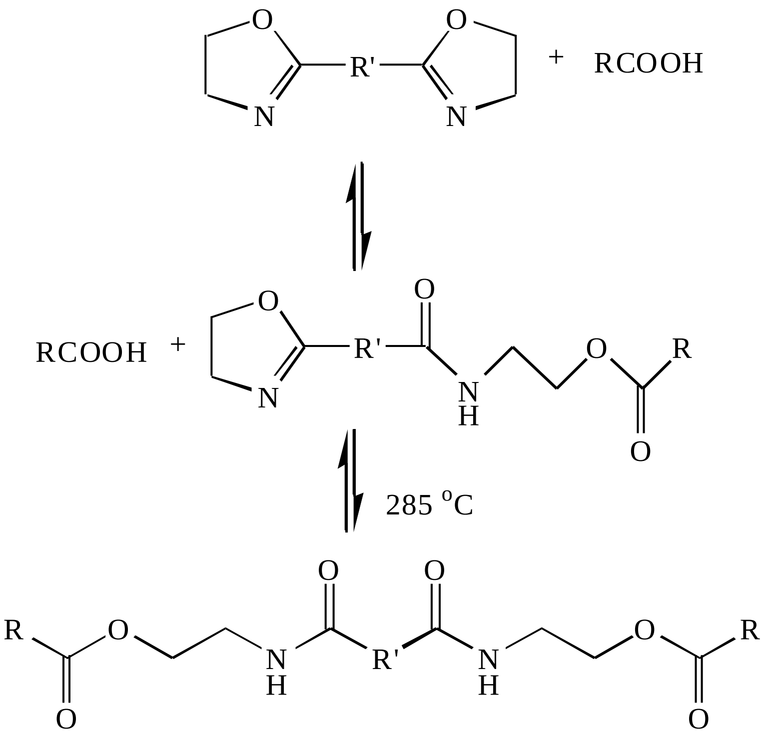


Figure 1.28. Reaction of bisoxazolines with carboxylic acids

The reaction of bisoxazolines with carboxylic acid end groups of polyesters according to Figure 1.29 results in an addition mechanism and gives linear poly(ester-amide)s.

Bisoxazolines have been subject to various studies related to PET to favor viscosity increase especially in fiber manufacture with recycled PET [39].

Karayannidis studied the effect of 1,4-phenylene bis oxazoline on the intrinsic viscosity increase of polyethyleneterephthalate (PET) during extrusion. Interestingly, these authors observed enhanced results when phthalic anhydride was added to the initial sample, before the addition of phenylene bis oxazoline. This technique succeeded in increasing the carboxyl end groups by reacting phthalic anhydride with the hydroxyl end groups of PET. After this initial modification, PBO proved to be an effective chain extender.

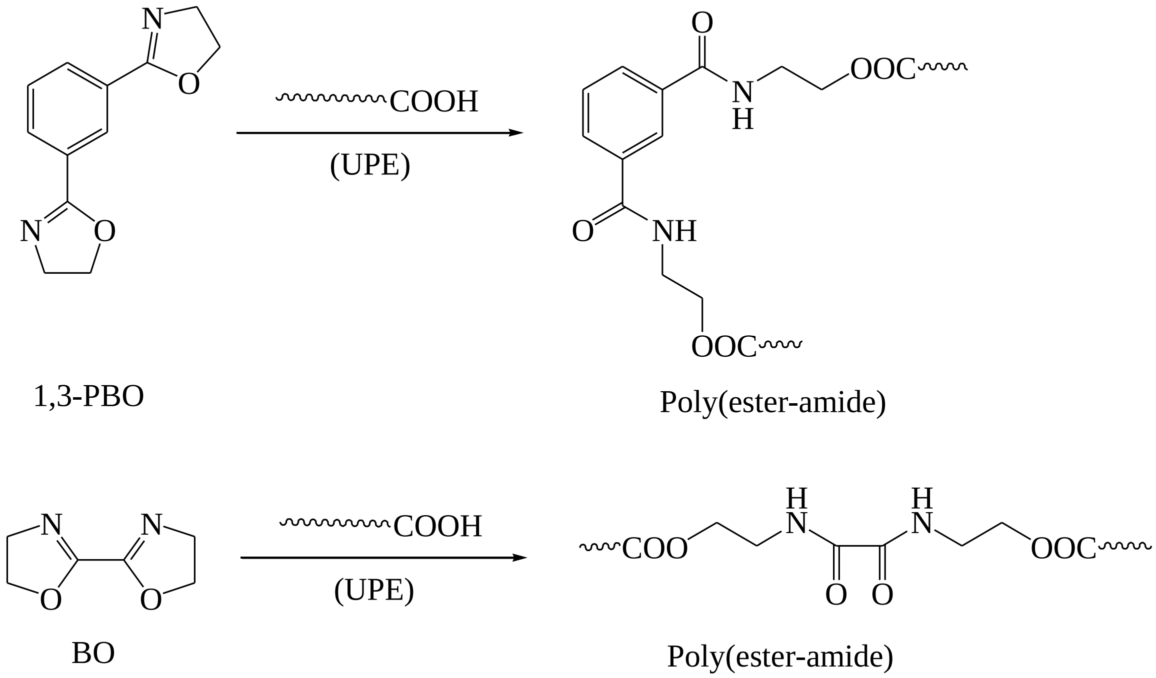


Figure 1.29. Chain extension reactions with bisoxazolines

One important advantage of this reaction is that no by-products are produced and the reaction between carboxylic ends and bisoxazolines takes place readily at temperatures far below 220 ^{o}C, the required temperature for polycondensation. It is also contemplated that the aromatic amide introduced during chain extension may provide hydrogen bonding sites and increase chain rigidity and lead to an increase in the storage modulus and heat deflection temperature of the final cross linked polyester.

1.6. The Importance of Chain Extender Concentration

Even though chain extenders are usually used in small amounts they introduce new linkages to the backbone of unsaturated polyesters. These linkages can change physical and chemical behavior of the polymer. Therefore the amount of the extender added to the reaction medium turns out to be an important issue. This in turn, is determined by the time chosen to add the extender. Because initially, the growing chains are rather short and one would need a high concentration of extender to reach the desired molecular weight rapidly. Whereas as the reaction proceeds, oligomeric chains become longer and therefore a lower amount of extender is needed to do the same job. This fact is illustrated in Figure 1.30.

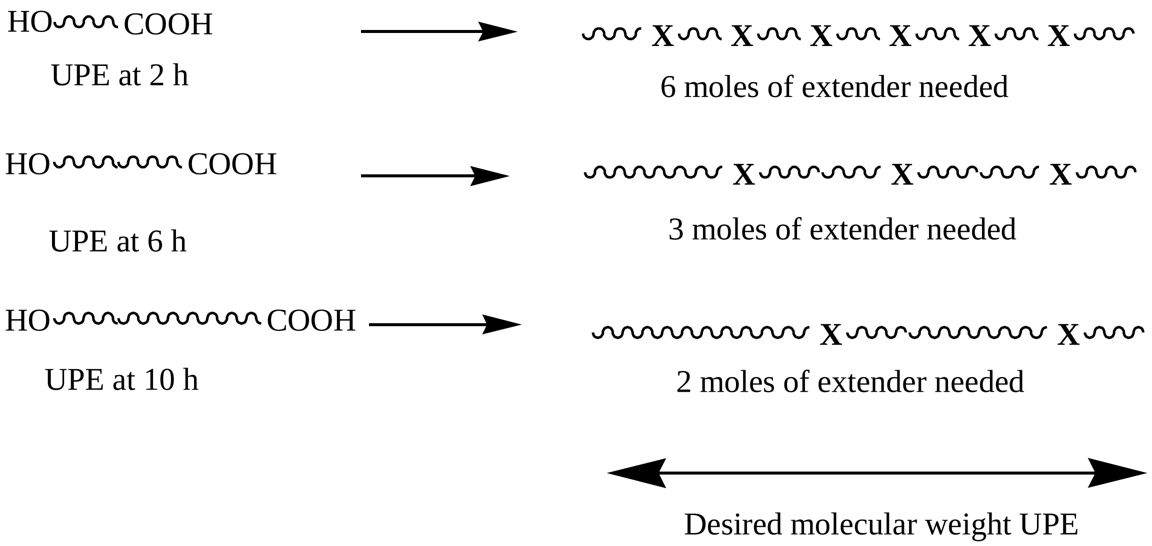


Figure 1.30. The importance of chain extender concentration

In industrial applications, where the manufacture is in tons, to choose the optimum amount of extender is of utmost importance. First of all, due to the possible change in chemical and physical properties of the final product; and also because of the gained economies.

As the polycondensation reaction proceeds the acid number of the polyester decreases continuously. At the beginning of the polycondensation reaction, when the polymer chains are short, the end group concentration is high. Therefore a higher concentration of extender (stoichiometrically) is needed to couple polymeric chains. As the polycondensation proceeds, the acid number decreases and the needed amount of the extender decreases correspondingly. This might be important when determining the time when to add the extender. This fact is plotted in Figure 1.31. for theoretical amounts of a diepoxide extender (DGEBA) with a molecular weight of 340 g/mol. In this study, the lowest amount of chain extender providing the desired molecular weight within a given time is considered optimum.

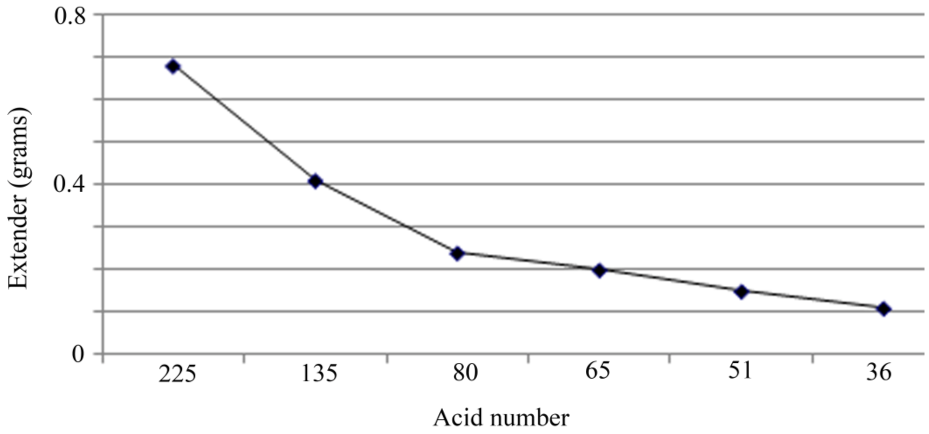


Figure 1.31. The relation of the amount of extender to the acid number

For each extender the investigation was started by using the stoichiometric (theoretical) amount of the extender calculated from the acid number of the short chain UPE. Then this amount was decreased gradually until the extender did not provide the desired molecular weight increase. Further studies on solubility, gel time and on thermal and mechanical properties were always carried out with those samples, where optimum amounts were used.

1.7. Industrial Importance of Chain Extension

The industrial production of unsaturated polyesters requires demanding conditions and long times because of the nature of the polyesterification, which is an equilibrium reaction. Solid-state postcondensation is a costly way of increasing the molecular weight of the polymers and benefits of other techniques remain limited. The advantage of chain extension is that it can be carried out directly in the reactor after a reduction in temperature. The diol loss due to evaporation that is usually encountered in the late stages of commercial UPE manufacture is also eliminated, giving economies in raw material and minimizing pollution.

In this method the weight loss arising from water removal is eliminated and the yield of the process increases by the addition of the extenders. In industrial practice shortened reaction time, reduced energy use or increased yield present a major advantage.

The price gain obtained this way would offset the price of the extender that needs to be used. The reduction in labor and energy costs when the overall reaction time is reduced from 20 hours to 6-7 hours will depend on the actual scale of the reaction and the design of the reactor.

2. RESEARCH OBJECTIVES

The objective of this research project is to use various chain extenders to increase the molecular weight of unsaturated polyesters. Short chain polyesters taken from a polyesterification reaction at the early stages of the reaction will be chain extended to the desired molecular weight in a short time. Three different groups of chain extenders were studied:

(i) Di or multi functional epoxide chain extenders, which react with the carboxylic end groups of the polyester chains

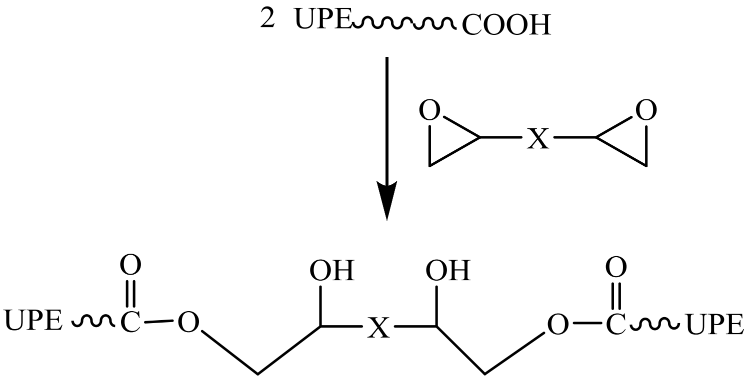


Figure 2.1. Reaction of epoxides with unsaturated polyesters

(ii) Di or multifunctional isocyanate extenders and blocked isocyanates which react with the hydroxylic and carboxylic end groups of the polyester chains

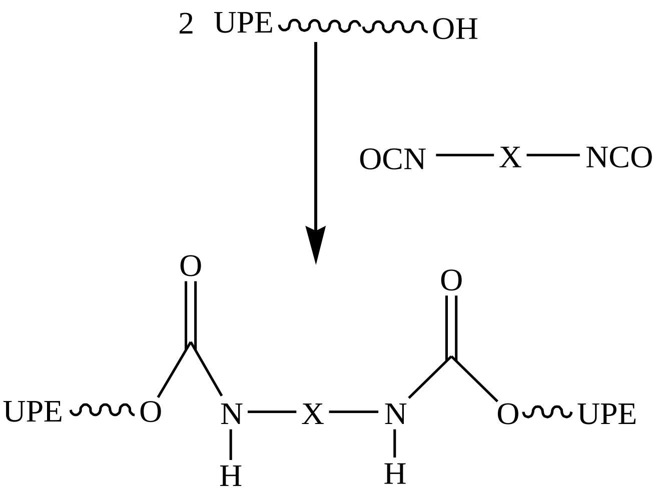


Figure 2.2. Reaction of isocyanates with unsaturated polyesters

(iii) Bisoxazolines, which react with carboxylic end groups of the polyester chains

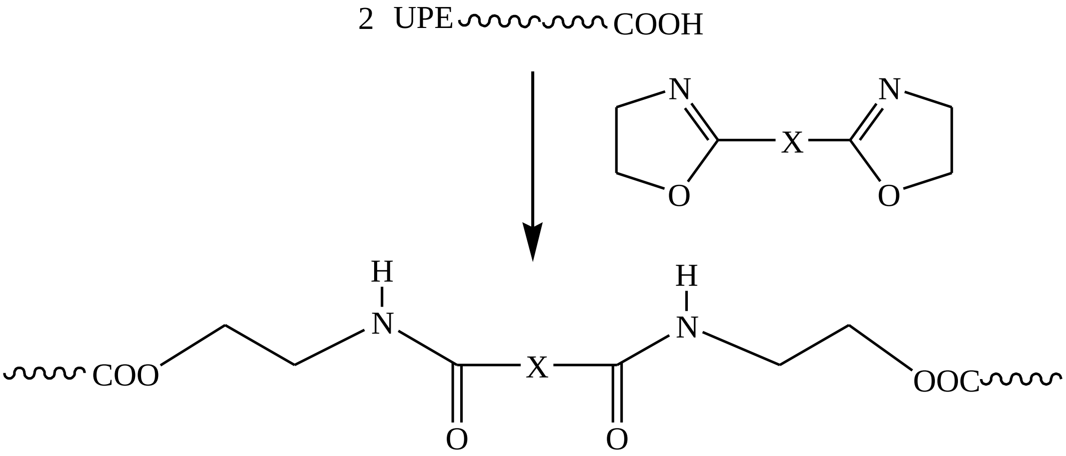


Figure 2.3. Reaction of bisoxazolines with unsaturated polyesters

Another major objective of this project was to characterize and examine chain extended polymers with respect to solubility, gel time, cure time and final thermal and mechanical properties and compare them to a commercial reference polyester.

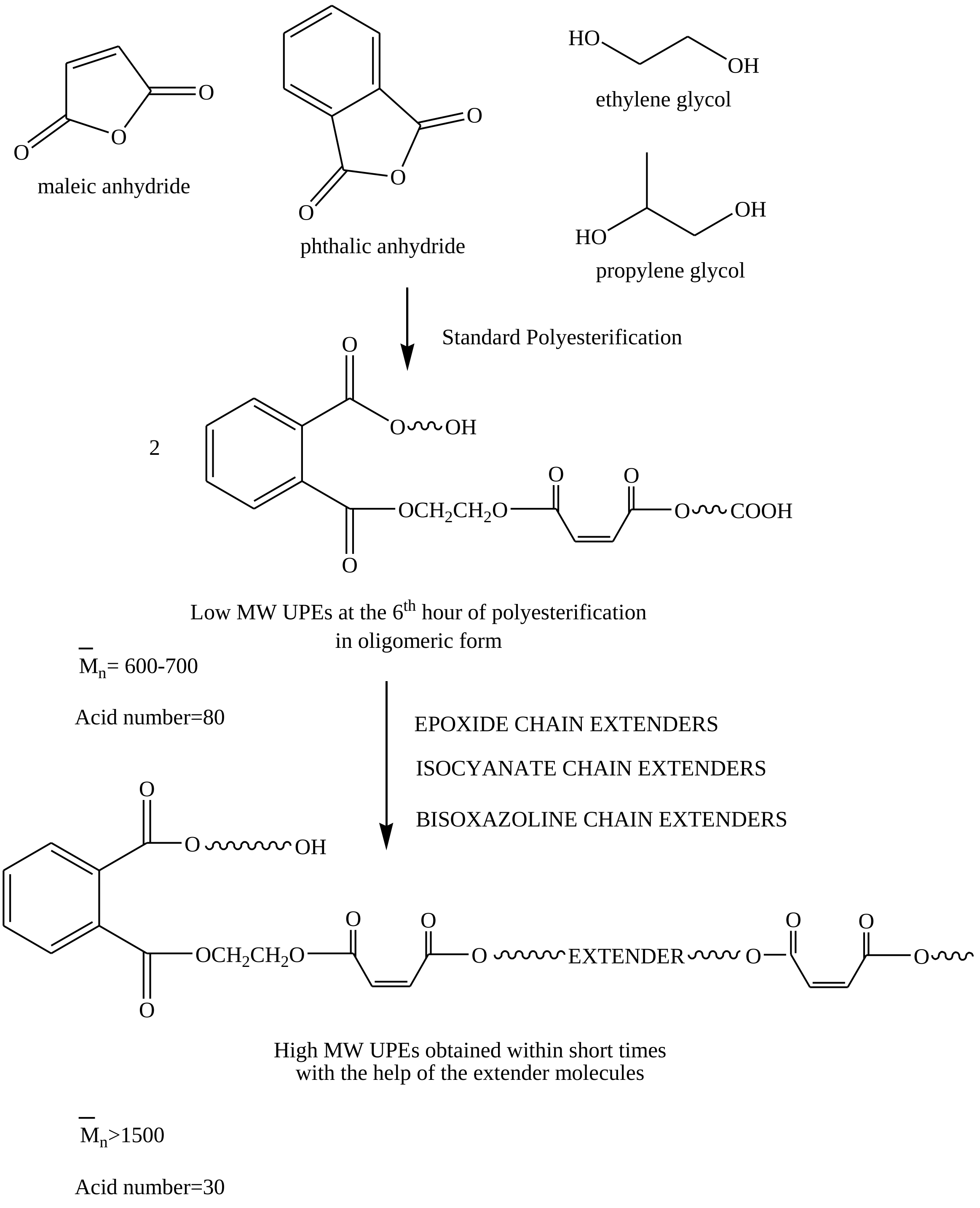


Figure 2.4. Schematic presentation of research objectives

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Starting materials for chain extension reactions were short chain unsaturated polyesters with an acid number of 80. The molecular weight of these oligomers varied between 500-700. These short chain polyesters were taken from the reactor at the 6th hour of a 16 hour industrial UPE synthesis. They were supplied by Cam Elyaf A.Ş., a major producer of polyesters in Turkey.

Diglycidyl ether of bisphenol A is an epoxy resin commercially available as Epon 828 and was supplied by Cam Elyaf A.Ş. The epoxidized soybean oil (ESO) was a product of Akdeniz Kimya A.Ş. (Istanbul, Turkey). 1,2;7,8-Diepoxyoctane (DEO) was bought from Merck (Darmstadt, Germany). AMC-2 catalyst was supplied by Aerojet Fine Chemicals (Rancho Cordova, CA).

Diphenylmethane-bis-4,4’-N,N’-ethyleneurea and Diphenylmethane-bis-4,4’-carbamoyl-Є- caprolactam were supplied by Meisei Chemical Works Ltd. (Kyoto, Japan), with the commercial names SU-125F and DM 3031 respectively, as water emulsions.

2,2’-(1,3-phenylene)-bis (2-oxazoline) was bought from Degussa AG (Dusseldorf, Germany) and 2,2’-bis(2-oxazoline) was bought from TCI Europe (Zwijndrecht, Belgium).

GPC samples were prepared by dissolving the unsaturated polyester samples in tetrahydrofuran (THF), bought from J. T. Baker (Deventer, Holland).

Methyl ethyl ketone peroxide (MEKP) and Cobalt naphthenate (6 per cent solution in dibutyl phthalate) were supplied by Cam Elyaf A.Ş., (Istanbul, Turkey).

3.1.2. Apparatus

The molecular weight increase was monitored utilizing gel permeation chromatography, a Viscotec VE-2001 (GPC max) Analysis system (Viscotek, Houston, Texas) with a PL Gel 5 micrometer MIXED-C Column that was calibrated against polystyrene standards. THF was used as solvent at room temperature with a flow rate of 1 mL/min.

^{1}H-NMR spectroscopy was run using Varian Mercury-Vx 400 MHz NMR Instrument (Varian Associates, Palo Alto, California).

^{13}C solid state NMR spectra of four different samples of unsaturated polyesters were taken at the Max-Planck Institute for Polymer Research, Mainz, Germany.
The first two spectra (those of reference polyester and the one extended with ESO) were taken using a 700 MHz solid state NMR (Bruker) and the last two (DGEBA and DEO) were taken using 500 MHz solid state NMR (Bruker).

IR characterization of compounds was performed by Thermo Nicolet, FTIR 380 spectrometer, using the diamond ATR accessory. The DMA tests were done between 20-180 ^{o}C on 40x12x2 mm samples using DMA Q800, TA Instruments (New Castle, Delaware, USA) in single cantilever mode at a frequency of 1 Hz and at 25 ^{o}C with a heating rate of 3 °C/min. The measurements range was between room temperature and 155 ^{o}C. Thermal gravimetric analyses were carried out using “Thermal Analyses” Q-50 Instrument, TA Instruments (New Castle, Delaware, USA) with a heating rate of 10 degrees/min starting from room temperature to 600 ^{o}C where nitrogen gas was purged at a rate of 60 mL/min.

3.2. Characterization of the Unsaturated Polyester

The unsaturated polyester used in this study was characterized by ^{1}H-NMR and FTIR spectroscopy. The ^{1}H-NMR spectrum of the commercial reference polyester is shown in Figure 3.1. The peaks at 7.5–8 ppm originate from the phthalate group (H_a); the ones at 4.3 ppm are due to ethylene glycol (H_b); and at 6.8 ppm are due to the vinyl protons of the fumarate (H_c). Propylene glycol which is also present as the second diol gives rise to two types of peaks; they appear at 5.3 (H_d) and 1.2 (H_e) ppm.

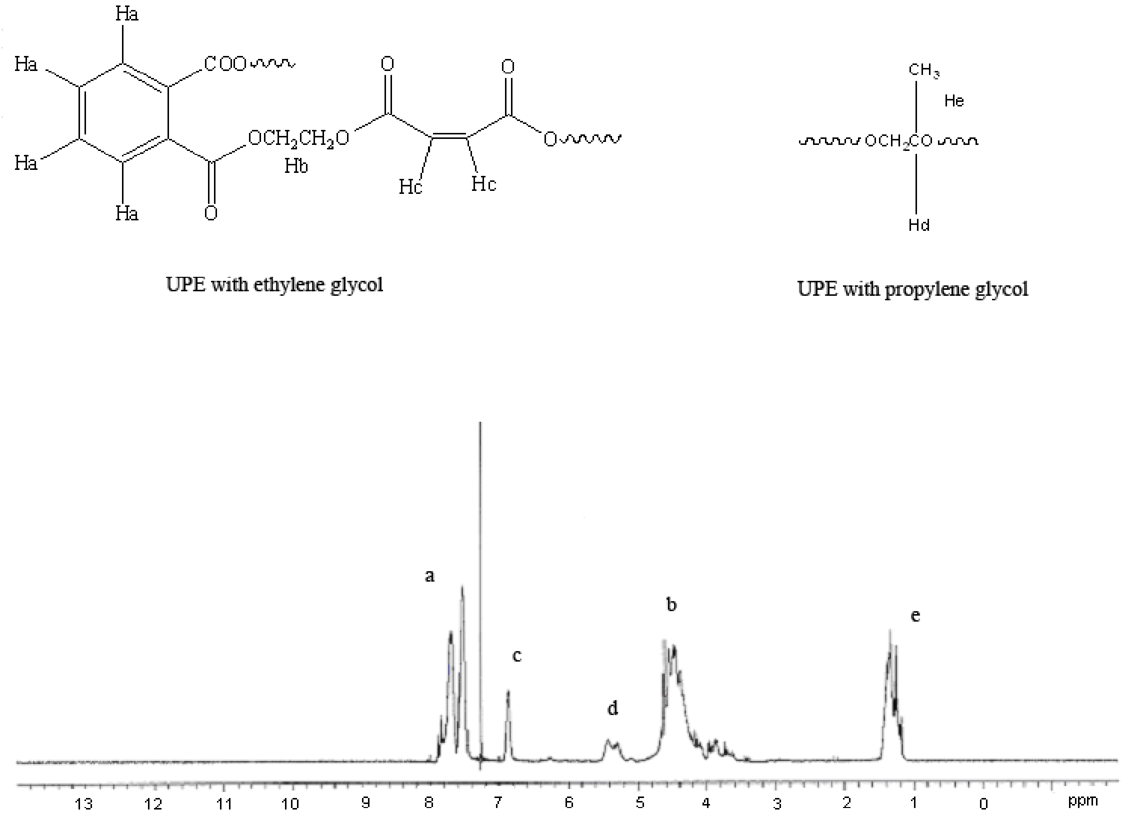


Figure 3.1. ^{1}H-NMR of the reference unsaturated polyester

The FTIR spectrum of the reference polyester is shown in Figure 3.2. The characteristic ester carbonyl was detected at 1716 cm^{-1}.

3.3. Determination of the Acid Number of UPE Samples

3.3.1. Preparation of 0.5 N Potassium Hydroxide Solutions

For the titration of UPE samples 0.5 N KOH was needed. A sample solution was prepared by dissolving 3.1540g of Potassium hydrogen phthalate (KHP) in 80 mL boiled and cooled distilled water.

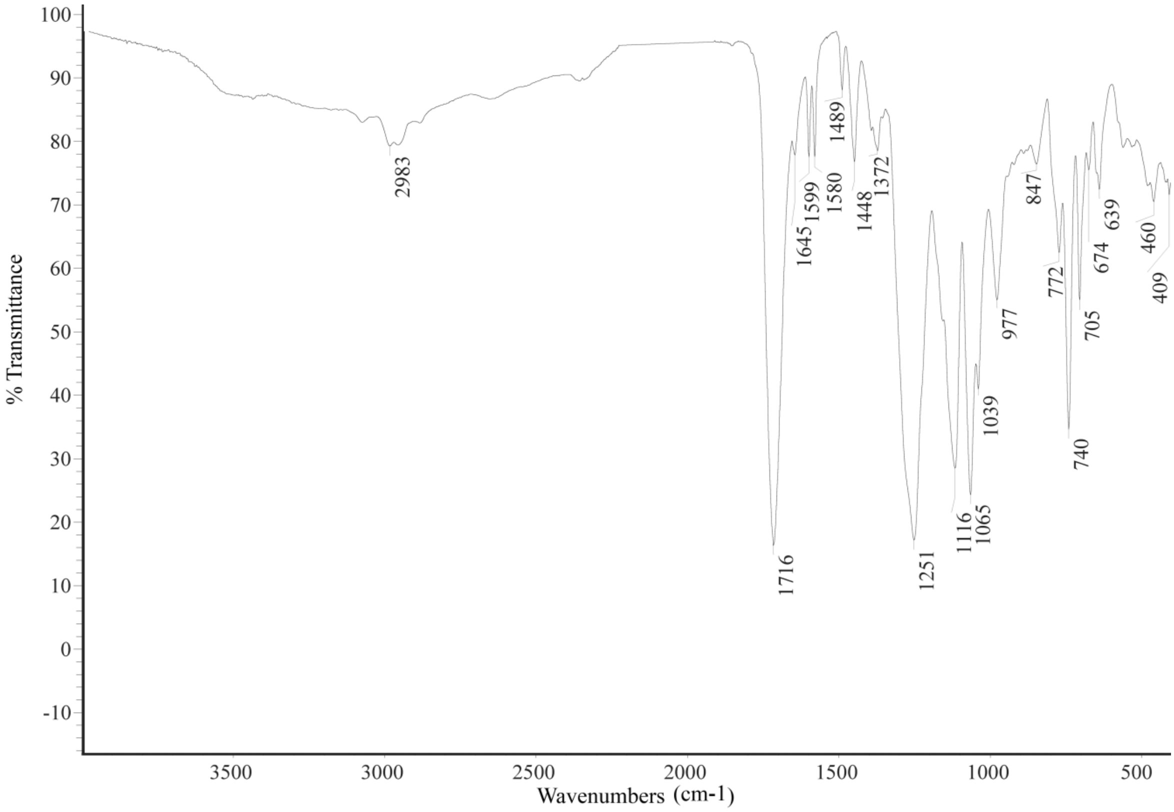


Figure 3.2. FTIR spectrum of the reference unsaturated polyester

This solution was titrated against KOH. From the amount of the used KOH the normality of the KOH solution was calculated as 0.5003.

3.3.2. Acid Number Determination

Acid number determination was done according to ASTM D 974-64 [40]. The unsaturated polyester sample was dissolved in 1:1 acetone:toluene mixture and titrated against 0.5 N KOH, in the presence of 2-3 drops of 1 per cent phenolphthalein indicator. The acid number of UPE was found as 80-82.

3.4. Calculation of Stoichiometric (theoretical) Amounts

Stoichiometric amounts of extenders were calculated from the acid number of the polyester. The acid number is defined as mg KOH/g sample. For an acid number of 80 the required number of moles of KOH to titrate the carboxylic groups in 1 g of sample was calculated as follows:

80 mg KOH/g UPE sample
= 0.080 g KOH/g UPE sample
= 0.080 g/56 g/mol = 1.43×10^{-3} mol of KOH

which equals the number of moles of the carboxylic acid groups in the sample. As one extender molecule reacts with two polyester end groups, this number was divided by two to find the required number of moles of the extender. This amount was taken as the stoichiometric (theoretical) amount required for the chain extension reaction. Lower amounts giving the desired molecular weight increase were searched and the minimum amount leading to the desired molecular weight within a certain time interval is chosen as optimum. The investigations of weight ratios for the three extenders are given separately under the corresponding section of chain extension reactions.

3.5. Chain Extension Reactions

3.5.1. Chain Extension with Diepoxide Extenders

Typical reactions for diepoxide chain extenders were done in bulk and at temperatures between 130 and 160 ^{o}C. Short-chain UPE, diepoxide, and 1 per cent by weight AMC-2 catalyst were heated and stirred for a given time. At the end of the extension reactions the resins obtained were cooled and dissolved in styrene to give a 65 per cent solids solution, and cured at room temperature using 2 per cent Methyl ethyl ketone peroxide (MEKP) and 0.25 per cent Cobalt naphthenate (6 per cent solution in dibutyl phthalate) and then post cured at 80 ^{o}C for 3 hours. Gel times were measured as the time of first gel formation at ambient temperature according to the standard ISO 2535 (2001) [7].

The investigation of weight ratios was started with the theoretical amount and the increase in molecular weight was monitored until the desired $\overline{M}_n$ was reached. Then this amount was gradually decreased in order to find the optimum amount of extender to give the desired molecular weight. Table 3.1 summarizes the molecular weights obtained within two hours using diepoxide extenders.

Table 3.1. Examined weight ratios of epoxide extenders

Run	**Extender**	**Extender (wt per cent)**	**Temperature (^{o}C)**	**$\overline{M}_n$ in 120 minutes**
1	DGEBA	20	100	1200
2	DGEBA	12	130	1300
3*	DGEBA	12	160	1920
4	DGEBA	8	130	625
5	ESO	31	130	Gelled
6	ESO	25	130	900
7	ESO	20	160	Gelled
8*	ESO	16	160	1015
9	DEO	9	160	1980
10*	DEO	9	140	1970

*Best set of conditions

3.5.2. Chain Extension with Blocked Isocyanates and SONCO

Typical reactions were done in bulk and at temperatures between 100-120 ^{o}C. The deblocking temperature of the blocked isocyanates is above 120 ^{o}C. 1,4-diazabicyclo[2.2.2]octane (DABCO) is used as catalyst and the investigated weight ratios are shown in Table 3.2. The obtained resins were cooled and were dissolved in styrene to give a 65 per cent solids solution. Finally the resins were cured at room temperature using 2 per cent MEKP and 0.25 per cent Cobalt naphthenate (6 per cent solution in dibutyl phthalate) and post cured at 80 ^{o}C for 3 hours. Gel times were measured as the time of first gel formation at ambient temperature according to the standard ISO 2535 (2001) [7]. The obtained chain extended unsaturated polyester samples, were used for thermal and mechanical investigations.

Initially 8 per cent of extender was employed and then this amount was gradually decreased to find the optimum amount of extender, which was the minimum amount to give the desired molecular weight under specified conditions. Table 3.1 summarizes the molecular weights obtained within two hours using blocked isocyanates and SONCO as extenders.

Table 3.2. Examined weight ratios of diisocyanate extenders

Run	**Extender**	**Extender (wt per cent)**	**Temperature(^{o}C)**	**$\overline{M}_n$ in 120 minutes**
1	Blank	0	120	800*
2	MDI-E	8	120	1850
3	MDI-E	5	120	1800
4	MDI-C	5	120	1300
5	SONCO	12	120	850
6	SONCO	20	120	1050

*In all runs the starting $\overline{M}_n$ value was 800.

3.5.3. Chain Extension with Bisoxazoline Extenders

Two different bisoxazolines 2,2,’-(1,3-phenylene)-bis-(2-oxazoline) and 2,2’-bis(2-oxazoline) were investigated as chain extenders for short chain unsaturated polyesters. In a typical reaction, oligomeric UPE was mixed with bisoxazoline at 160 ^{o}C under nitrogen and stirred for 30-60 minutes, without catalysis. Various weight ratios of extenders were tried. First, the stoichiometric amount was employed and then this amount was decreased gradually until the extender did not provide the desired molecular weight increase. The ratios of the reagents are given in Table 3.3.

At the end of the extension reactions the resins obtained were cooled and dissolved in styrene to give a 65 per cent solids solution, and cured at room temperature using 2 per cent Methyl ethyl ketone peroxide (MEKP) and 0.25 per cent Cobalt naphthenate (6 per cent solution in dibutyl phthalate) and then post cured at 80 ^{o}C for 3 hours. Gel times were measured as the time of first gel formation at ambient temperature according to the standard ISO 2535 (2001) [7].

Table 3.3. Examined weight ratios of bisoxazoline extenders at 160 ^{o}C

Reaction time (min)	$\overline{M}_n$				
	Control (no extender)	15 per cent 1,3-PBO stoichiometric amount (pdi*)	3 per cent** 1,3-PBO (pdi)	10 per cent BO stoichiometric amount (pdi)	4 per cent ** BO (pdi)
0	1030	1030 (1,5)	1030 (1,5)	1030 (1,5)	1030 (1,5)
5	1030	1700 (1,8)	1400 (1,8)	1420 (1,9)	1410 (1,6)
30	< 1150	1700 (1,8)	1500 (2,0)	1400 (1,7)	1470 (1,7)
60	<1150	-	1600 (2,3)	1600 (1,7)	1520 (1,8)

*Polydispersity Index; **Optimum amount

3.6. Characterization of the Blocked Isocyanates

The two blocked isocyanates (Diphenylmethane-bis-4,4’-N,N’-ethyleneurea and Diphenylmethane-bis-4,4’-carbamoyl-Є-caprolactam) were bought in the form of emulsions. Addition of 10 per cent $CaCl_2$ (aqueous) solution gave a phase separation. Centrifuging, decantation and drying gave the desired blocked isocyanates, which were used without further purification. The ^{1}H-NMR spectra of MDI-E and MDI-C are shown in Figure 3.3 and 3.4, respectively.

The aziridine ring protons appear at 2.2 ppm at the benzylic –C**H**$_2$ protons are detected at at 3.8-4 ppm. The protons on the aromatic ring appear in the aromatic region 7-8 ppm.

The benzylic protons were detectable at 3.8-4 ppm and the caprolactam protons were detected at 2.7 and 3.6 ppm.

3.7. Synthesis of Isocyanated Soybean Oil (SONCO)

Isocyanated soybean oil was synthesized according to the method described by Çaylı and Küsefoğlu [37]. 8 g allylic brominated soybean oil (ABSO) was dissolved in 20 ml of dry THF. 6 g of AgNCO slurry in 60 ml dry THF was added in 3 portions with 1 hour intervals at room temperature.

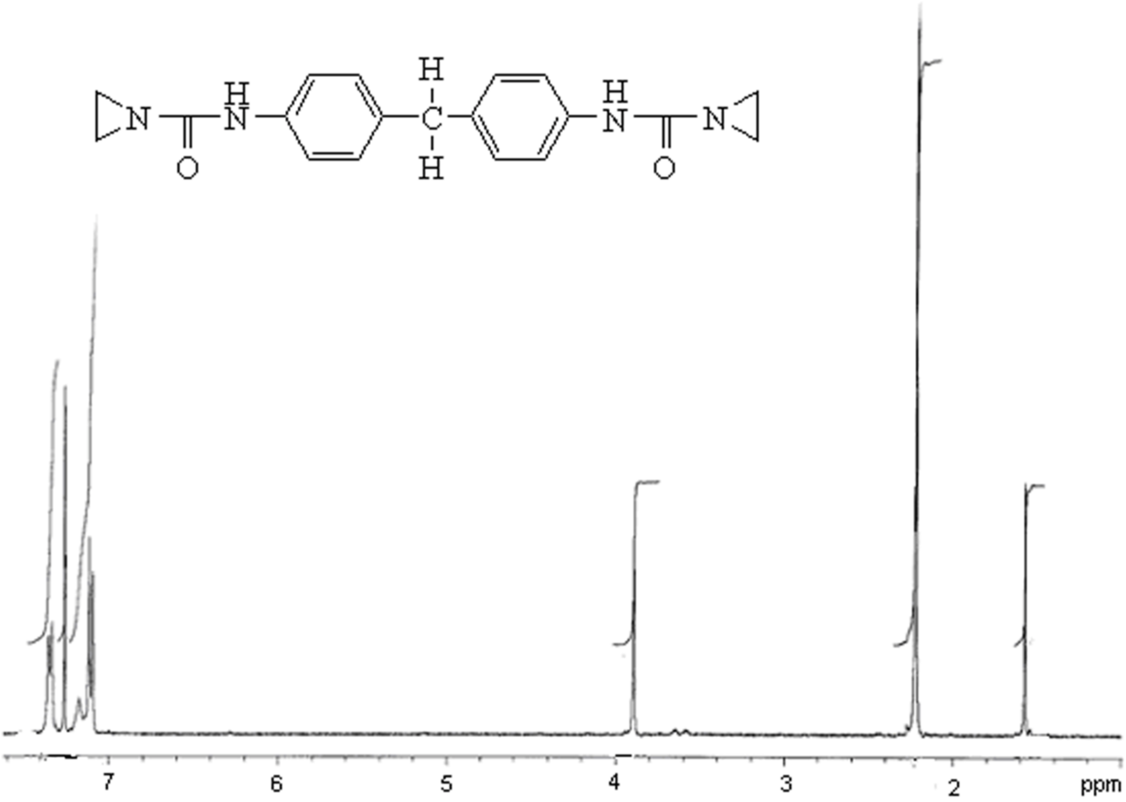


Figure 3.3. ^{1}H-NMR spectrum of diphenylmethane-bis-4,4'-N,N'-ethyleneurea

Stirring was continued for 4 more hours and the flask was kept overnight at room temperature. During the whole operation the flask should be dry and should be covered with aluminum foil.

^{1}H-NMR analysis of the product indicated the presence of 2.1 isocyanate groups, on the average, per triglyceride molecule. This number was determined by summing the integration values of the peaks at 3.9 ppm arising from the proton geminal to the isocyanate group with the integration values of the peaks at 4.8 ppm arising from double allylic alfa proton of the NCO group. The sum of these integration values was compared to the triglyceride CH_3 protons at 0.8 ppm, taken as 9 protons per triglyceride.

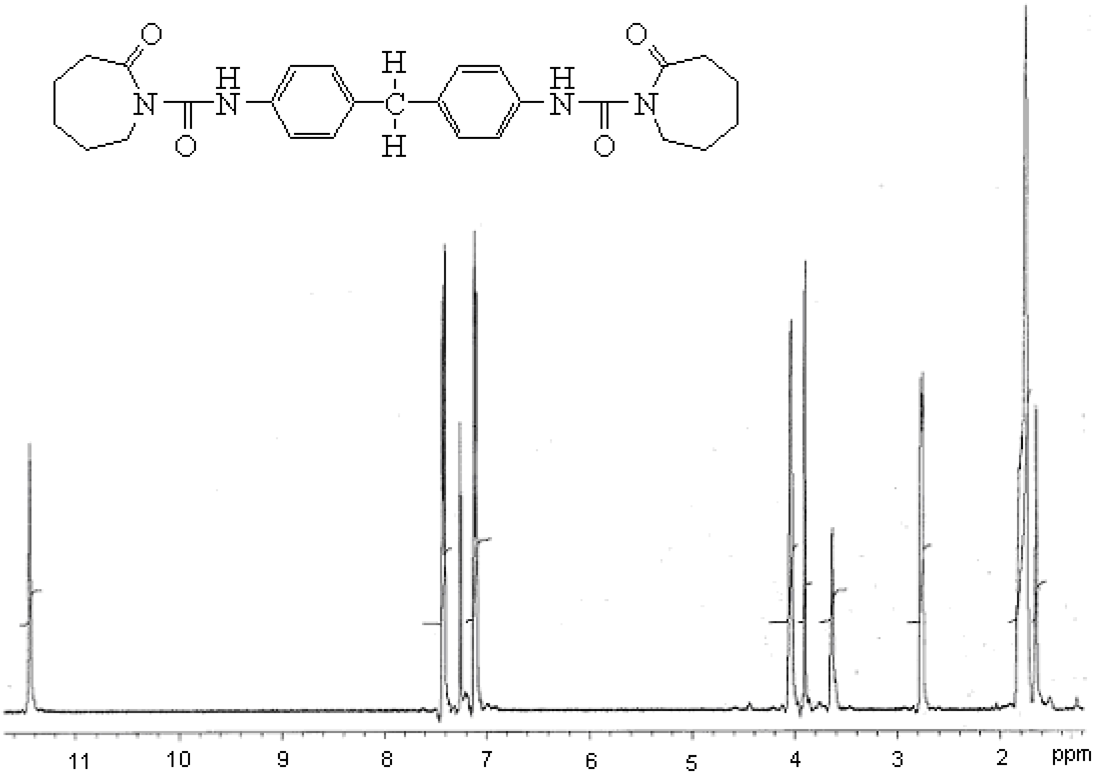


Figure 3.4. ^{1}H-NMR spectrum of diphenylmethane-bis-4,4'-carbamoyl-Є-caprolactam

Peaks belonging to isocyanated soybean oil were as follows: 0.8 (-C$\mathbf{H}_3$), 1 (triplet, -CH=CH-CH$_2$-C$\mathbf{H}_3$), 1.2-1.4 (-C$\mathbf{H}_2$-), 1.6 (β to carbonyl group, -CH$_2$-CH$_2$-C(=O)-OC$\mathbf{H}_2$-), 2.25 (α to carbonyl group, (-C$\mathbf{H}_2$-C(=O)-OCH$_2$-), 2.75 (double allylic position, -CH=CH-C$\mathbf{H}_2$-CH=CH-), 3.9 (CH=CH-C**H**-NCO), 4.1 and 4.3 (multiplet, glycerin protons, -O-C$\mathbf{H}_2$-), 4.5 (broad, -CH=CH-C**H**(Br)), 4.8 (-CH=CH-C**H**(NCO)-CH=CH-), 5.25 (center proton of glycerin, -O-CH$_2$-C**H**O-CH$_2$O-), 5.4 (C**H**=C**H**-CH$_2$-CH=C**H**-CH(NCO)), 5.8 (-CH=C**H**-CH(NCO)-C**H**=CH-).

3.8. Gel Permeation Chromatography (GPC) Sample Preparation

GPC samples for all polyesters were prepared by dissolving 6-10 mg of sample in the measured volume of dry THF to obtain a concentration of 2 mg/mL. The prepared solution was then transferred into a GPC vial with the help of a 5 mL syringe through a PTFE 0.45 µm, of 13 mm diameter syringe filter bought from Teknokroma. A typical GPC curve of the reference commercial polyester is shown in Figure 3.7.

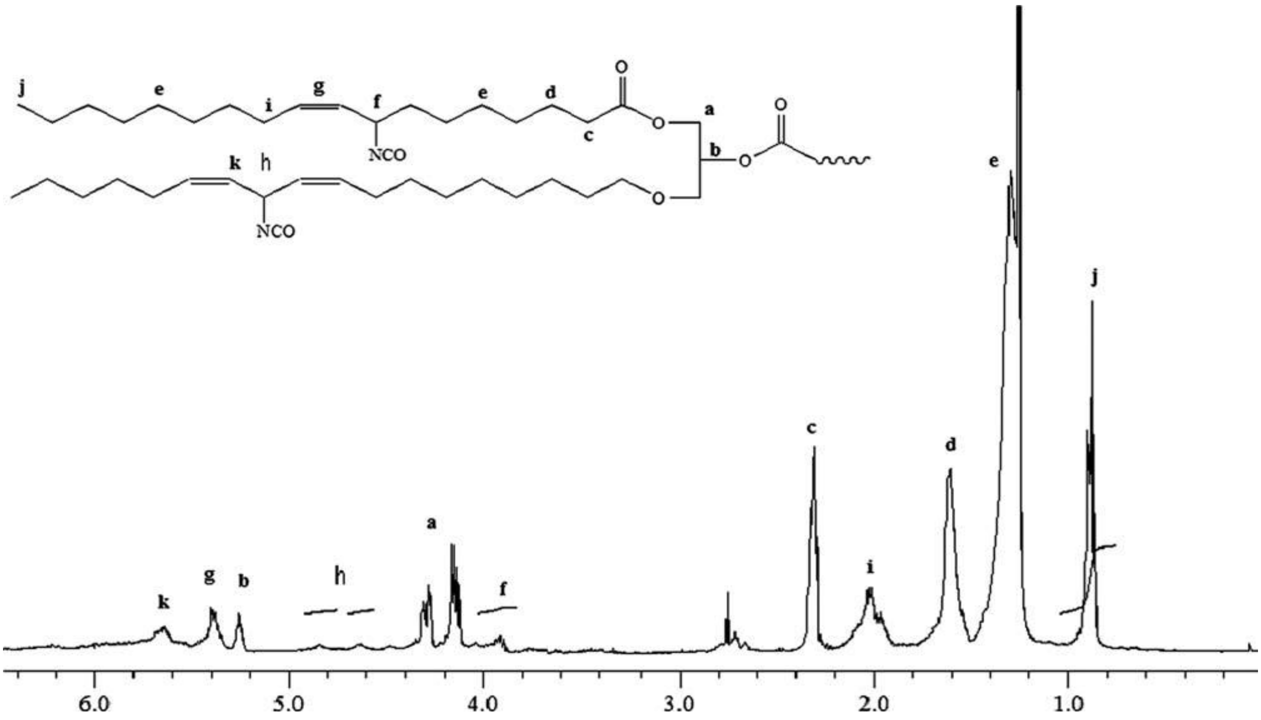


Figure 3.5. ^{1}H-NMR spectrum of SONCO

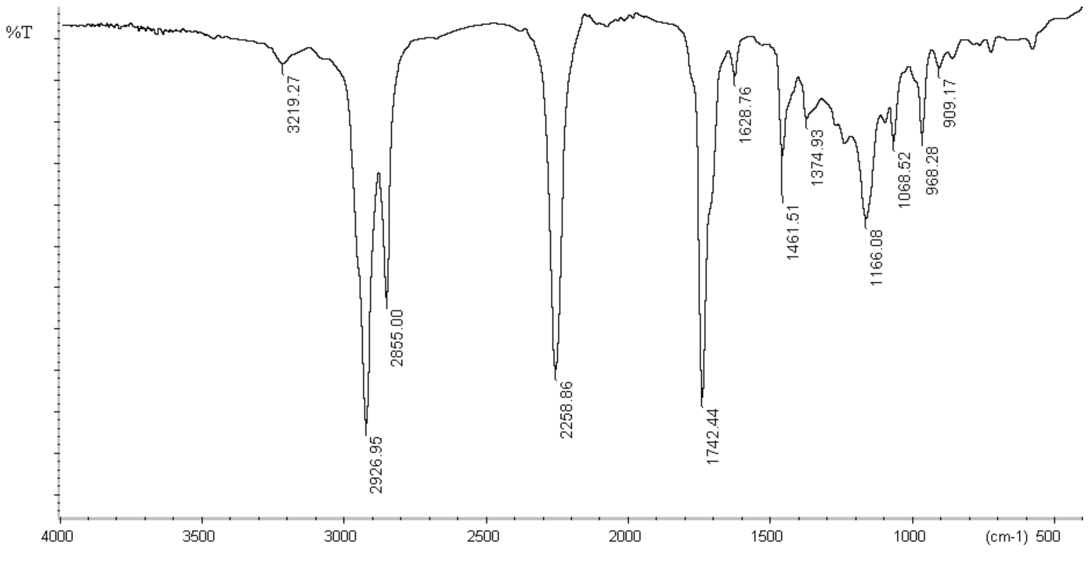


Figure 3.6. ATR-IR spectrum of SONCO

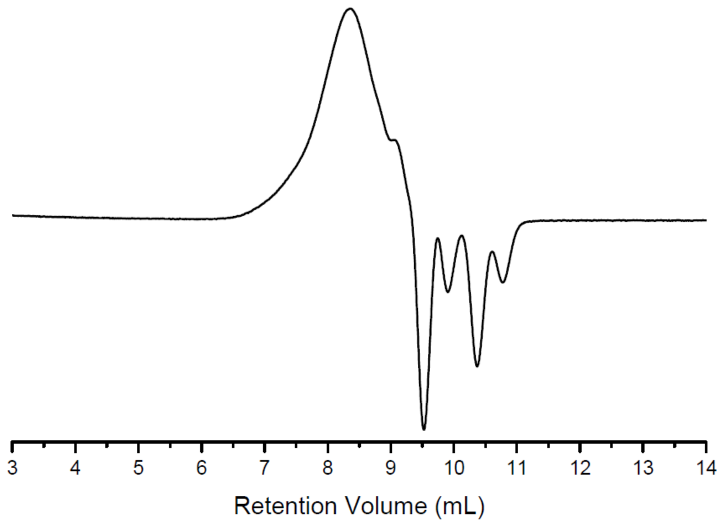


Figure 3.7. Typical GPC curve of the reference commercial polyester

4. RESULTS AND DISCUSSION

4.1. Epoxide Chain Extenders

4.1.1. Chain Extension Reactions with Diepoxides

4.1.1.1. Chain Extension with Diglycidylether of Bisphenol A (DGEBA)

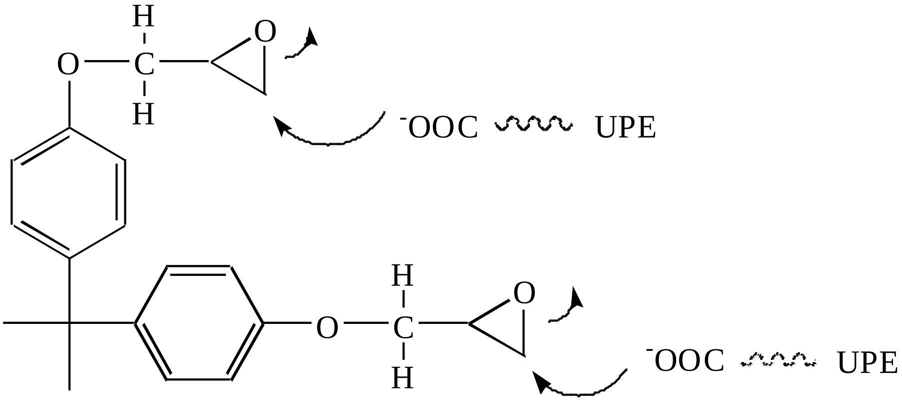


Figure 4.1. Diglycidylether of Bisphenol A (DGEBA)

Diglycidylether of bisphenol A (DGEBA, Molecular Weight: 340 g/mol) has been used in chain extension of PET, where it gave satisfactory results by reactive blending [41]. Products were characterized by carboxylic end group analysis, intrinsic viscosity, and Differential Scanning Calorimetry (DSC). In another study, DGEBA was used to increase the resistance of PET to hydrolysis by chain extension and by blocking the polar carboxylic groups. Correlations between the physical properties of PET and used diepoxide extender amounts have also been investigated. PET chain extension is a useful practice when recycled PET fiber is used as raw material for spinning of new fibers [42].

DGEBA was thought to be a promising chain extender also for unsaturated polyesters because of its capacity of fast reaction with carboxylic end groups of polyesters. In the case of chain extension reactions with unsaturated polyesters, the stoichiometric amount of the extender was calculated from the amount of the carboxylic acid end groups in the sample as determined by the acid number. DGEBA lead to a satisfactory molecular weight increase by using one equivalent of epoxy groups per carboxylic end groups of the UPE. However, in industrial practice, reducing the extender amount to a minimum is more profitable. Therefore, the amount of DGEBA was gradually decreased in order to find the minimum amount that gave the desired molecular weight increase. Various weight ratios were examined and the optimum weight ratio was found as 12 per cent extender by weight. The results of this investigation are summarized in Table 3.1. (Examined weight ratios of epoxide extenders) under the section “Experimental”.

When PET is chain extended with DGEBA, lower amounts (1-5 per cent) of DGEBA gave satisfactory results. PET has a much higher molecular weight (>200,000) than UPE, therefore in the case of PET only a few extension reactions lead to large increases in molecular weight. Partially hydrolyzed PET chains are long enough and even with low amounts of extenders regaining the desired molecular weight is not difficult. UPE oligomers used in this work have very low molecular weights and the end group concentration is much higher. Therefore higher concentrations of chain extenders are required to reach the desired molecular weight in a reasonably short time.

Epoxides are known to give an undesirable ring opening polymerization through epoxide functionalities as shown in Figure 1.17 under the section “Introduction”. AMC-2 catalyst, a trivalent organic chromium complex, is claimed to:

(i) Prevent polymerization of epoxy compounds
(ii) Increase the rate of carboxylic acid-epoxy reactions.

In order to benefit from these properties of this catalyst, AMC-2 was used in 1 per cent weight ratio whenever diepoxy extenders were employed. As another precaution in order to minimize possible polymerization through epoxy functionalities, the epoxide extenders were added to the reaction medium slowly within a period of 30 minutes. The reactions were run in bulk, particularly in order to better simulate industrial applications eliminating solvent removal problems.

As a control reaction, the polyester used in the chain extension reactions was heated and stirred under the same conditions without an extender. In this case where the temperature was below that of polycondensation the molecular weight did not increase.

Figure 4.2 shows the increase of the molecular weight of UPE with 12 per cent DGEBA at 160 °C.

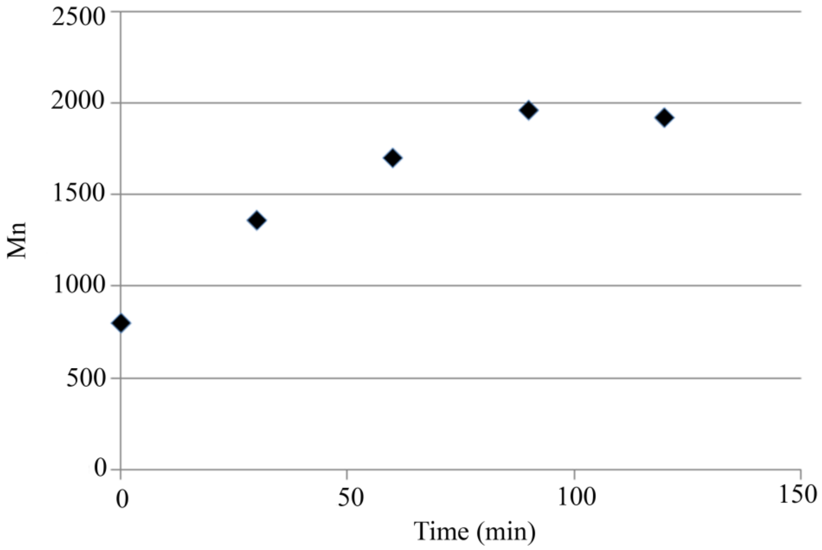


Figure 4.2. Molecular weight increase of UPE chain extended with DGEBA at 160 °C

At 130 °C the number average molecular weight increased from 750 to 1300 within 2 hours. However, when the reaction was repeated at 160 °C, for the same sample the $\overline{M}_n$ value exceeded 1900 within 2 hours; moreover, at the end of 1 hour the $\overline{M}_n$ value was 1700 which coincides with a satisfactory chain length for commercial UPE. At the end of the 16-20 hours industrial production, UPE reaches a molecular weight of about 1500; therefore, a number average molecular weight of 1700 is already above the desired molecular weight. When the extender monomer is added to the reactor at the 6th hour during manufacture, one should expect to go to the desired molecular weight within only one more hour. Thus it was concluded that the desired molecular weight would be obtained in 7 hours instead of 16-20 hours.

<u>4.1.1.2. Chain Extension with Epoxidized Soybean Oil (ESO).</u> ESO (Molecular Weight: 900 g/mol) is obtained from soybean oil by peracid oxidation and there are no reports of its

use in chain extension reactions of PET. It is a renewable raw material and offers environmental benefits due to its fast biodegradability.

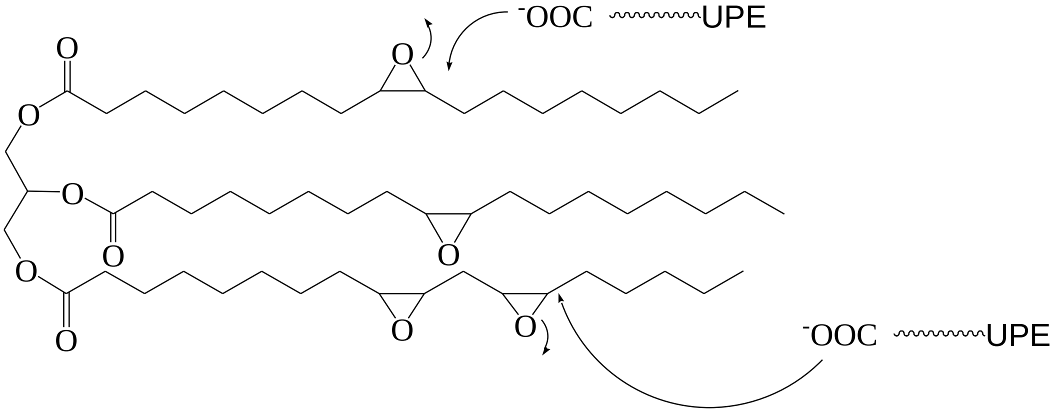


Figure 4.3. Epoxidized soybean oil (ESO)

Depending on the degree of oxidation epoxidized soybean oil may contain different numbers of epoxide functionalities. In industry this natural source product is commonly used for its plasticizing effect related to its long alkyl chains. The epoxidized soybean oil used in this work contains an average of 4.2 epoxy groups per triglyceride as determined by HI titration. Compared to other difunctional epoxides like DGEBA and 1,2;7,8-diepoxyoctane, ESO can bring an advantage in chain extension reactions because of this higher number of reactive sites. However, this advantage carries the risk of early gelation in the reaction medium due to ring opening polymerization and crosslinking through epoxy groups. Actually when ESO was added fast to the reaction medium gelation occurred within 30 min at 160 °C as reported in Table 3.1 under the “Experimental” section.

Another issue is related to reaction temperature. In the case of ESO, the reaction must be run at a higher temperature compared to the other two epoxide extenders, because in ESO the epoxy groups are internal and therefore less reactive.

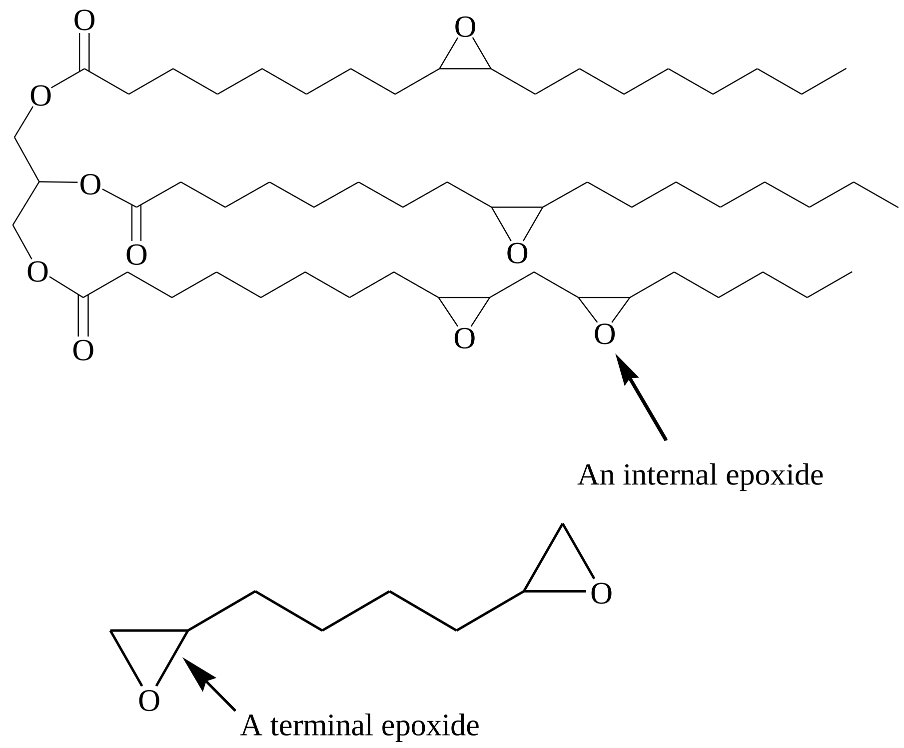


Figure 4.4. An internal and a terminal epoxide

Various weight ratios were tried and the optimum weight ratio was found to be 20 per cent. The reaction was run at 160 ^{o}C. ESO was added slowly to the reaction medium within 30-45 minutes, AMC-2 catalyst was added in 1 per cent weight ratio. The $\overline{M}_n$ value increased from 470 to 1015 within 2 hours as shown in Figure 4.5.

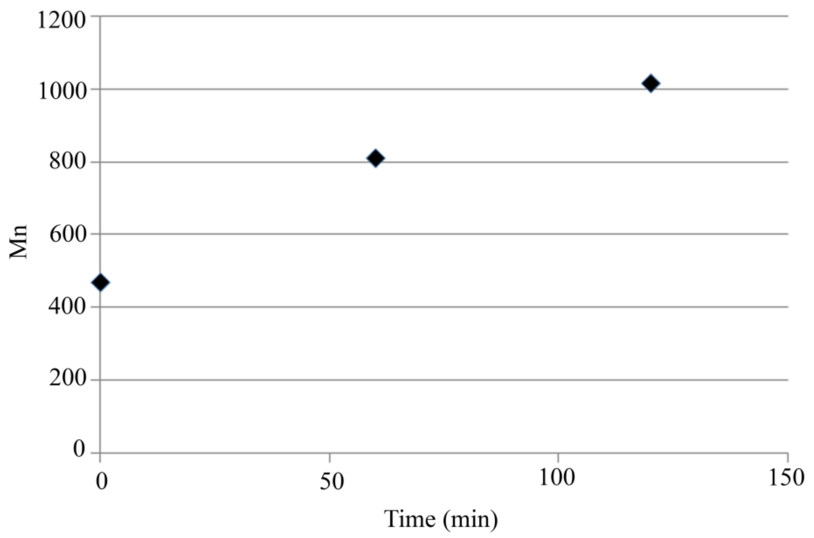


Figure 4.5. Molecular weight increase of UPE chain extended with ESO at 160 ^{o}C

At the end of the chain extension reaction, the product was extracted with n-pentane to remove any unreacted ESO which could lead to a decrease in the mechanical properties of the ESO-chain extended polyester. For this purpose a soxhlet extraction apparatus was employed and the extraction was carried out for 12 hours. No unreacted ESO was detected in the product. In addition, the chain extended polyesters before and after the extraction gave exactly the same infrared spectra, again in accordance with the fact that unreacted ESO was not present in the final product.

4.1.1.3. Chain Extension with 1,2;7,8-Diepoxyoctane (DEO)

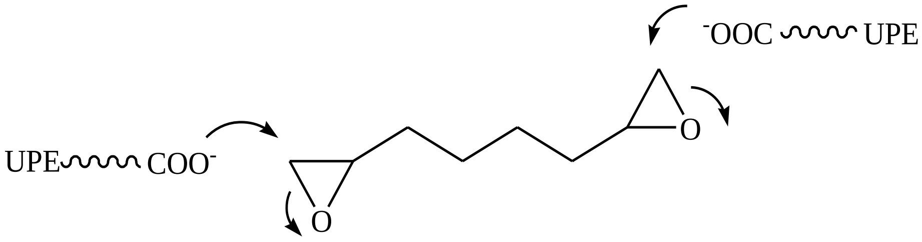


Figure 4.6. 1,2;7,8-Diepoxyoctane (DEO)

The advantage 1,2;7,8-diepoxyoctane is its relatively low molecular weight (Molecular Weight: 142 g/mol) which allows the use of lower weight percentages, a benefit particularly important in industrial applications. Besides this extender does not introduce groups to the polymer chain that are different than the already existing ones as the two epoxy functionalities are separated just by methylene groups. However, in the case of chain extension with DGEBA the phenyl ring is a new moiety to the chain and in the case of ESO, long alkyl chains are introduced to the polyester. Therefore final mechanical and thermal properties of the DEO chain extended polymer should remain unaltered.

AMC-2 catalyst was employed in a 1 per cent weight ratio, to minimize unwanted polymerization through epoxide rings. DEO was used in 10 per cent weight ratio and the reaction was run at 140 ^{o}C. Within 2 hours the $\overline{M}_n$ increased from 700 to 1970 as shown in Figure 4.7. This is the highest increase among multi epoxide extenders examined at the end of 2 hours at 140 ^{o}C as shown in Table 3.1.

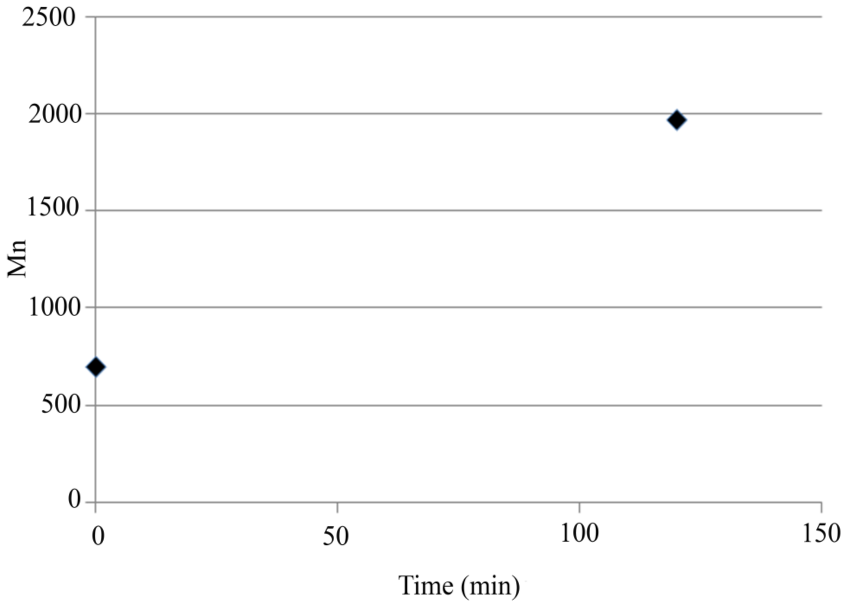


Figure 4.7. Molecular weight increase of UPE chain extended with DEO at 140 ^{o}C

Table 4.1 summarizes the $\overline{M}_n$ values obtained with the three epoxide extenders at various temperatures.

Table 4.1. $\overline{M}_n$ values obtained with the three epoxide extenders at different temperatures

Time (min)	UPE extended with DGEBA at 130 ^{o}C $\overline{M}_n$	UPE extended with DGEBA at 160 ^{o}C $\overline{M}_n$	UPE extended with ESO at 160 ^{o}C $\overline{M}_n$	UPE extended with DEO at 140 ^{o}C $\overline{M}_n$
0	750	800	470	700
30	915	1360	-	-
60	1180	1700	810	-
90	1230	1960	-	-
120	1300	1920	1015	1970

4.1.2. Characterization of Polyesters Extended with Epoxides

One of the most important properties of a chain extender is that it reacts only with the end groups of the polymer chains. This way, polymer chains are to be coupled with each other easily and further reactions do not occur. New linkages are introduced to the polymer chains; however chemical and physical properties of the chain extended material are expected to remain unaltered. Following each chain extension the polyesters were characterized by spectroscopy to verify the existence of the extender molecule and the structure of the material.

4.1.2.1. ^{1}H-NMR Characterization. The ^{1}H-NMR spectrum of the commercial reference polyester is shown in Figure 3.1. The peaks at 7.5–8 ppm originate from the phthalate group (H_a); the ones at 4.3 ppm are due to ethylene glycol (H_b); and at 6.8 ppm are due to the vinyl protons of the fumarate (H_c). Propylene glycol which is also present as the second diol gives rise to two types of peaks; they appear at 5.3 (H_d) and 1.2 (H_e) ppm. These peaks were detectable in all chain extended polyesters.

In case of chain extension with DGEBA, peaks due to phenyl groups of DGEBA (7 ppm) were detectable in the spectrum. The protons originating from isomerization to fumaric acid (2 ppm) and peaks due to methyl groups of DGEBA (1.5 ppm) were observed.

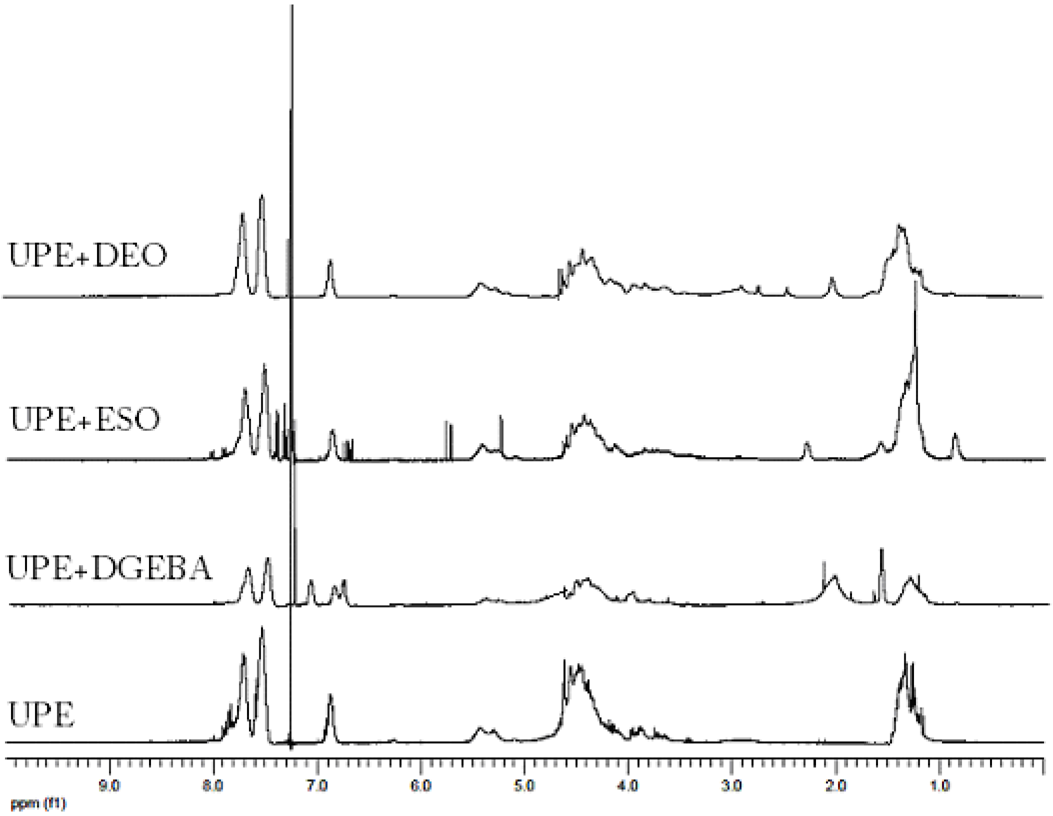


Figure 4.8. Overlay of ^{1}H-NMR spectra for chain epoxide chain extended polyesters

In the ^{1}H-NMR spectrum of the ESO chain extended polymer, the peaks due to the following groups of the ESO were identified: The peak at 0.9 ppm belongs to the terminal methyl groups of ESO. The fatty acid part in the ESO gives rise to the large peak at 1.4 ppm; and the small peak at 1.8 ppm is due to the protons beta to the carbonyl and the peak at 2.4 ppm alfa to carbonyl groups in the ESO. Finally, the peaks at 4.0–4.4 ppm arise from the ESO glycerol.

In the ^{1}H-NMR spectrum of the DEO chain extended polyester in addition to the usual polyester peaks, peaks due to the -C**H**$_2$- groups of diepoxyoctane were detected at 2.5-3 ppm. All of the discussed spectra are shown for comparison in Figure 4.8.

4.1.2.2. CP/MAS ^{13}C Solid State NMR of Epoxide Extended Polyesters. The crosslinked final samples were also analyzed by ^{13}C CP/MAS NMR spectroscopy. The advantage of this method is that the cured final products can be examined by using powdered samples directly. However, overlapping peaks constitute a disadvantage.

In solid state NMR, shorter transverse relaxation times and residual anisotropic broadening that is not fully averaged by rotation lead to broad lines. Typically lines are 10-100 times broader. The signal can be enhanced by a double resonance technique called cross polarization (CP). In cross polarization, first protons are polarized which is much easier compared to ^{13}C nuclei. Then this polarization is transferred to neighboring ^{13}C nuclei. This way the carbon signal can be enhanced by a factor of about 4 times. The CP experiment is often combined with the Magic Angle Spinning (MAS) technique (CP/MAS NMR).

Solid-state ^{13}C NMR spectroscopy has been used to study the structure of cured polyester resins. Hietalahti et. al. investigated the influence of styrene content on the length of styrene sequences in a cured unsaturated polyester resin, and estimated the amount of unreacted double bonds in the cured polyester with the help of solid-state ^{13}C-NMR spectroscopy [43]. The ^{13}C CP/MAS NMR spectrum of the reference unsaturated polyester used in this study is shown in Figure 4.9.

The carbonyl chemical shifts due fumarate units were observed in the region 165-173 ppm. Unfortunately, the carbonyl peaks from the phthalate units also appear in the same region, causing an overlap of peaks. When the chain extended polyesters were characterized, in some cases the peaks became sharper as the chain mobility increased. This was observed in the case of DEO chain extended UPE where chains could gain mobility due to ethylene groups between the epoxide reactive sites.

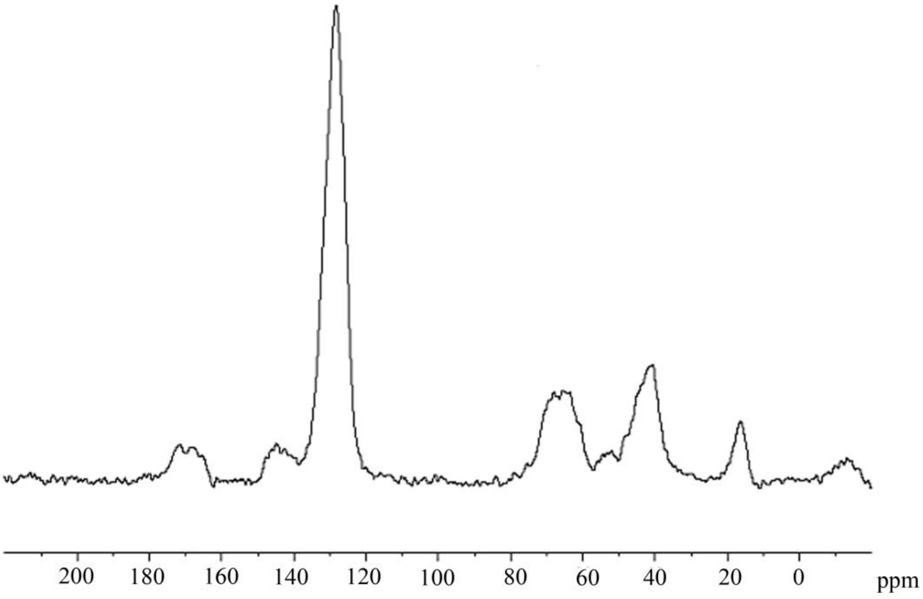


Figure 4.9. The ^{13}C CP/MAS NMR spectrum of the reference UPE after cure

The overlay of the ^{13}C CP/MAS NMR spectra of the chain extended samples is shown in Figure 4.10.

4.1.3. Styrene Solubility and Gel Time of Diepoxide Extended Polyesters

In industrial applications, styrene is frequently used as comonomer for UPE resins and the obtained polymer is commonly dissolved in 35 per cent styrene by weight to give a 65:35 (UPE:styrene ratio by weight). Variations in the styrene content affect the resulting properties of the final material. Following each chain extension, styrene solubility and gel times of the extended polyesters were compared to a commercial reference product to make sure that physical and chemical properties remain unchanged upon chain extension.

The polyester was dissolved in styrene first at 40 °C and then was stirred further at room temperature until a clear solution was obtained.

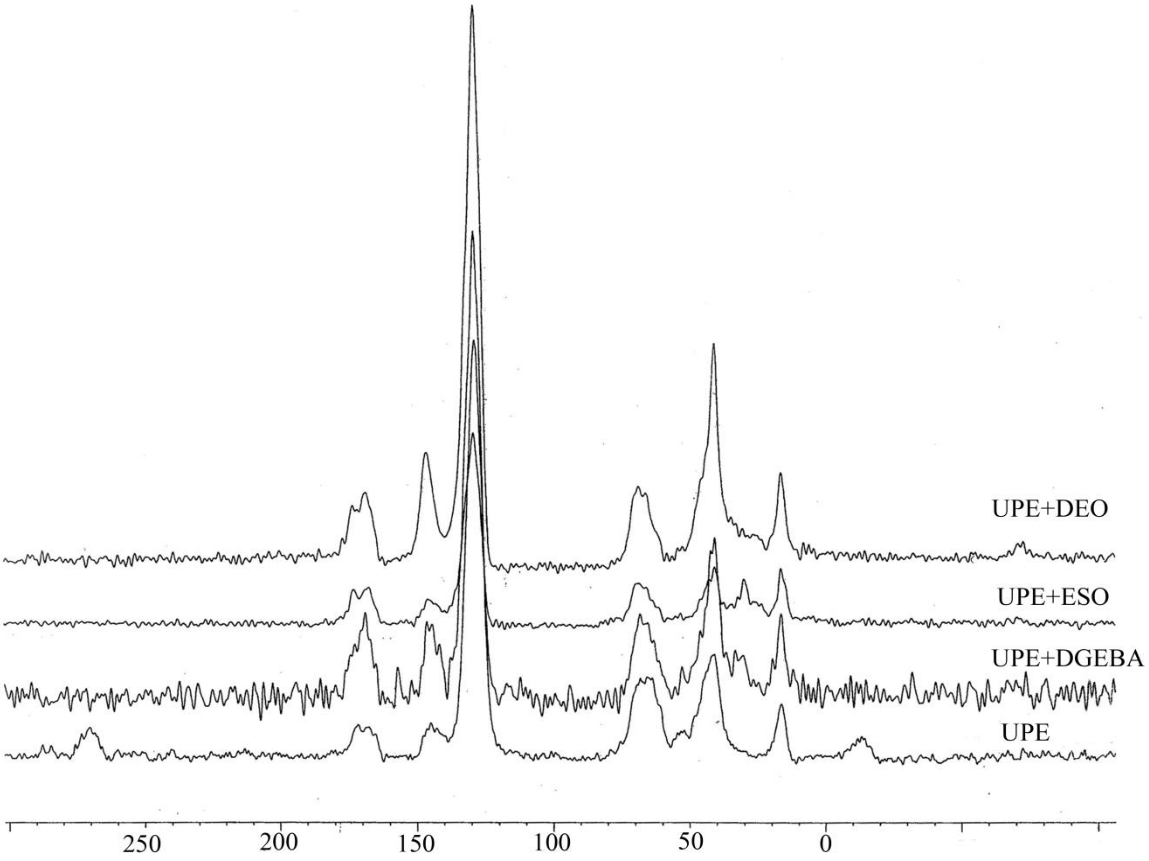


Figure 4.10. Overlay of ^{13}C CP/MAS NMR spectra for the chain extended and reference samples after cure

All diepoxide chain extended polymer showed very similar solubility in styrene when compared with the commercial UPE. Solubility was considered achieved upon formation of a clear solution. Then the obtained viscous resins were cured with 2 per cent Methyl ethyl ketone peroxide (MEKP) and 0.25 per cent cobalt naphthenate (6 per cent solution in dibutyl phthallate). When these standard amounts [7] of initiator and accelerator were used, the measured gel times were close to the gel time of 12-15 minutes for the commercial product. The gel times are listed in Table 4.2. The cured polymers were postcured in an oven at 80 °C for 3 hours and then examined thermally and mechanically.

Table 4.2. Gel times of UPEs chain extended with various epoxy extenders

UPE extended with	**Gel time (min)**
Blank	12-15
DGEBA	10-12
ESO	6-7
DEO	12-14

The lower gel time for the case of ESO was related to the higher concentration of this extender in the polyester. AMC-2 catalyst may also have an effect on the earlier gel times as claimed by the producer. [28]

4.1.4. Mechanical and Thermal Analysis of Diepoxide Extended Polyesters

As this project aims to create a benefit for industrial practice, one of the major objectives was to measure mechanical and thermal properties of the chain extended polymers to make sure that they remained unaltered when compared to the standard commercial polyester. Therefore following each chain extension, the final crosslinked polyester was tested and compared to the standard reference product, produced in a real 20 hours polyesterification reaction.

As a general trend, the introduction of an extender molecule to the polymer chain is expected to alter mechanical and thermal properties of the final product. Phenyl rings should increase rigidity and long alkyl groups should give plasticizing properties. In each case when the thermal stability of the introduced linkage is lower than that of the ester linkage, the polyester should be expected to exhibit weight loss at earlier temperatures.

Mechanical properties of the final polyesters were measured with the help of a dynamic mechanical analyzer, therefore the T_g values obtained are dynamic T_g values and should be expected to divert to a certain extent from the ones measured by differential scanning calorimetry (DSC). In fact, when DSC was used to determine the glass transition temperature of the reference product a value of about 60 ^{o}C was found lower compared to the dynamic value of 88 ^{o}C. This result is shown in Figure 4.11.

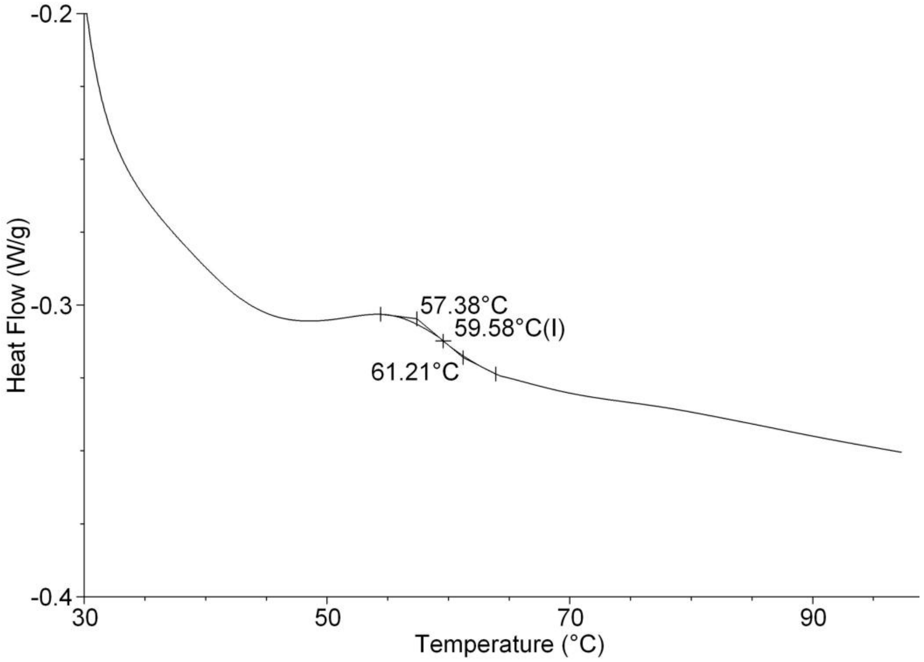


Figure 4.11. DSC of the reference UPE

The glass transition temperature for the polyester extended with DGEBA was found to be 74 ^{o}C (Figure 4.12). This value is comparable with the T_g value of the commercial polyester (88 ^{o}C). The decrease in T_g is due to the addition of the extender molecules to the chain, which possibly increases flexibility. The storage modulus was 2650 MPa, very close to that of commercial UPE.

The glass transition temperature for the ESO extended polyester was found to be 66 ^{o}C (Figure 4.12). Here the decrease in T_g from 88 ^{o}C (for the commercial polyester) to 66 ^{o}C could be attributed to the plasticizing effect of ESO. The storage modulus of the ESO chain extended polyester also decreased to a value of 1650 MPa from 3000 MPa for the commercial polyester (Figure 4.13).

The glass transition temperature for the polyester extended with DEO was found to be 89 ^{o}C (Figure 4.12). This value is very close to the T_g of the commercial polyester. In fact in the case of this extender only additional methylene groups are added to the polymer chain, which do not really alter the glass transition temperature of the polyester. The storage modulus was found to be 2875 MPa (Figure 4.13), which is very close to that of commercial UPE. These values are summarized in Table 4.3.

T_g values are measured as the maxima of the tan delta curves as shown in Figure 4.12.

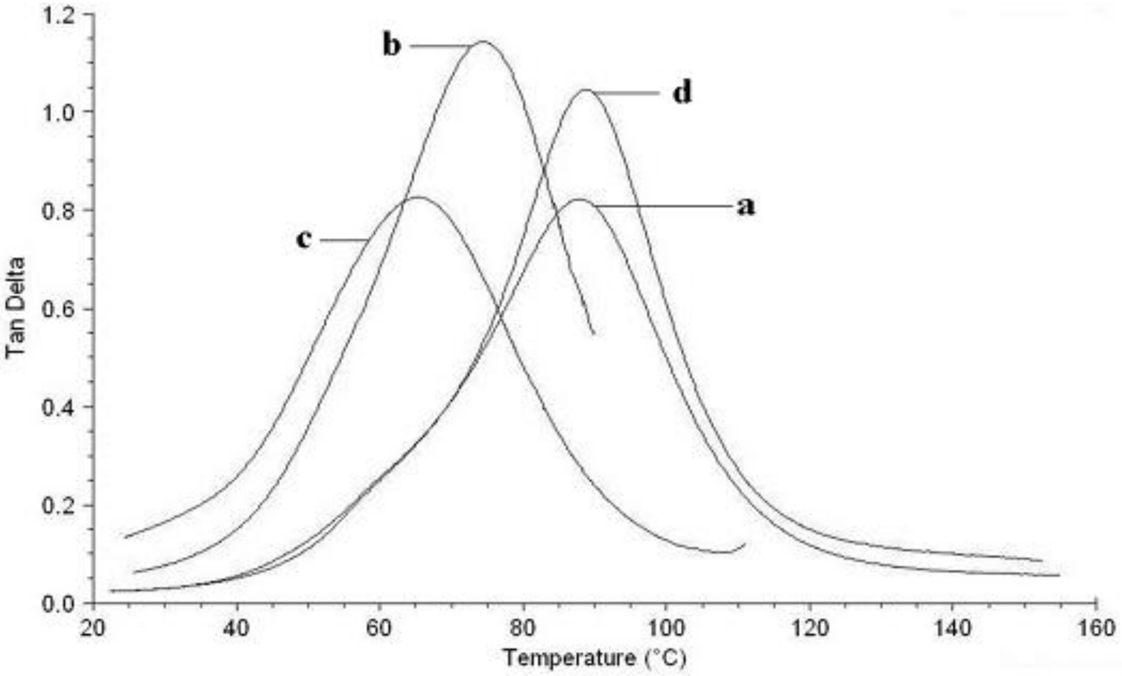


Figure 4.12. Tan delta curves of the chain extended polyesters
(a) Commercial UPE; (b) UPE extended with DGEBA; (c) UPE extended with ESO;
(d) UPE extended with DEO

In the case of DEO the tan delta curve was identical to the reference polyester exhibiting increased toughness.

The storage modulus values of the chain extended polymers exhibited the expected behavior. For UPEs chain extended with DGEBA and DEO the measured storage modulus values were very comparable to that of the commercial polyester. However, ESO extended UPE showed a lower storage modulus value and a lower glass transition temperature. The storage modulus plots of the four UPEs can be seen in Figure 4.13.

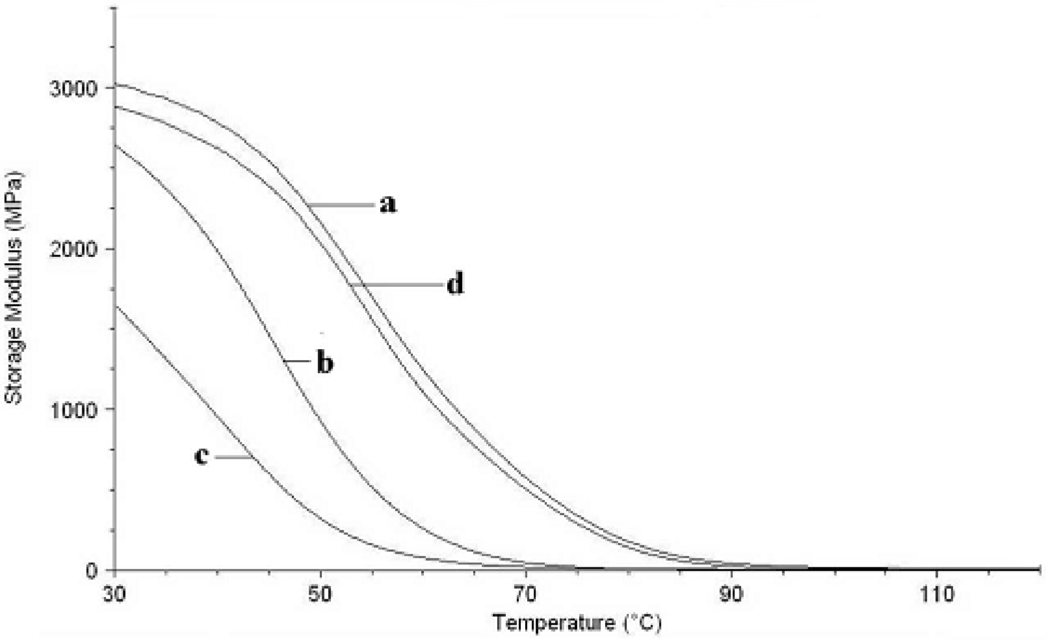


Figure 4.13. Storage Modulus curves of the chain extended polyesters
(a) Commercial UPE; (b) UPE extended with DGEBA; (c) UPE extended with ESO;
(d) UPE extended with DEO

T_g and storage modulus values are summarized for comparison in Table 4.3. Thermal stability tests were performed for the chain extended polymers. Figure 4.14 illustrates the obtained results. The values measured at 5 per cent weight loss are shown in Table 4.3 together with T_g, storage modulus and gel time values.

In conclusion, UPE oligomers were chain extended using di- or multifunctional epoxy compounds. Different extender weight ratios and different temperatures were tried and solubilities, gel times, and mechanical and thermal properties of the chain extended polyesters were examined and compared to a commercial product. The study has shown that difunctional (or multifunctional) epoxy compounds are effective chain extenders for UPE. The use of these extenders decreases the production time and increases the yield of the polyester substantially, without compromising its solubility in styrene or from its mechanical and thermal properties.

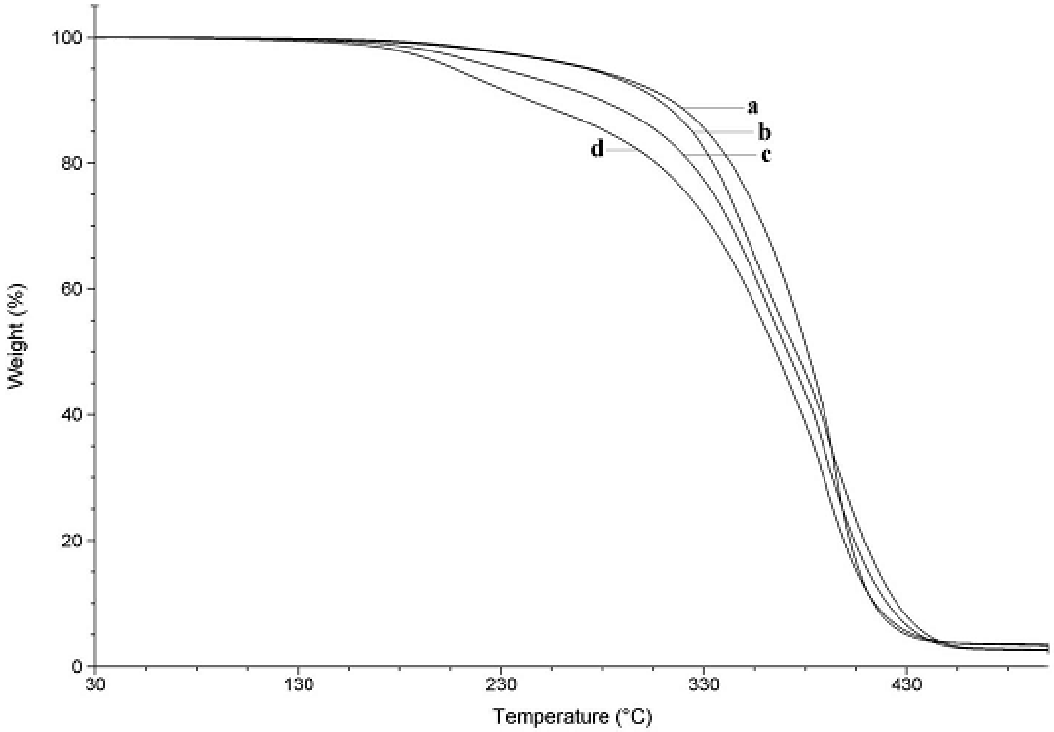


Figure 4.14. TGA thermograms of commercial and chain extended polyesters (Temperature at 5 per cent weight loss)

(a) Commercial UPE; (b) UPE extended with DEO; (c) UPE extended with ESO; (d) UPE extended with DGEBA

Table 4.3. Final $\overline{M}_n$, T_g, storage modulus, TGA data and gel times of commercial and chain extended polyesters

UPE	**Final $\overline{M}_n$**	**T_g (^oC)**	**Storage Modulus* (MPa)**	**Temperature at 5 per cent weight loss (^oC)**	**Gel time (min)**
Commercial UPE	1500	88	3000	272	12-15
Extended with DGEBA	1920	74	2650	208	10-12
Extended with ESO	1015	66	1650	230	6-7
Extended with DEO	1970	89	2875	273	12-14

*Storage modulus value at 30 ^oC

4.2. Isocyanate Chain Extenders

4.2.1. Chain Extension Reactions with Blocked Isocyanates and Isocyanated Soybean Oil

4.2.1.1. Chain Extension with Diphenylmethane-bis-4,4'-N,N'-ethyleneurea (MDI-E)

Diphenylmethane-bis-4,4'-N,N'-ethyleneurea (Molecular weight: 336 g/mol) is a blocked isocyanate frequently used as an adhesion promoter in textile industry. It is claimed to improve the bonding strength of various binders and adhesives especially with functional groups such as carboxyl or hydroxyl nucleophiles or radicals [44].

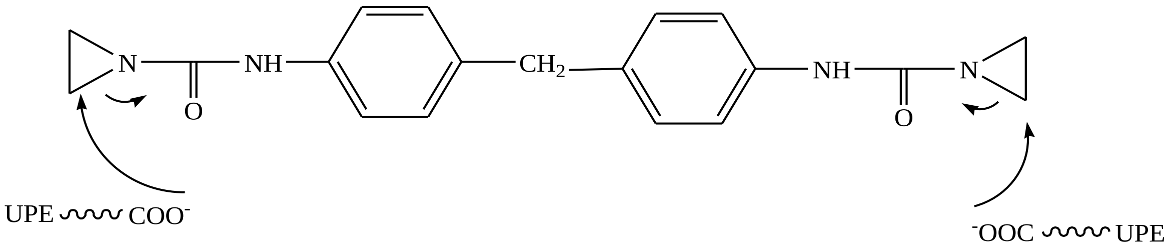


Figure 4.15. Diphenylmethane-bis-4,4'-N,N'-ethyleneurea (MDI-E)

The terminal ethylene imine (aziridine) groups in MDI-E readily react with nucleophiles by ring opening of the aziridine group [45] and above the deblocking temperature of 130 °C the compound rearranges to MDI, liberating free aziridine which is a low boiling toxic liquid.

Blocked isocyanates are frequently employed when the isocyanate groups need to be protected to prevent early reactions with other functional groups [46]. Many compounds have been employed as blocking groups to decrease the deblocking temperature and to comply with the stricter laws in environmental legislation for the prevention of the emission of volatile masking agents.

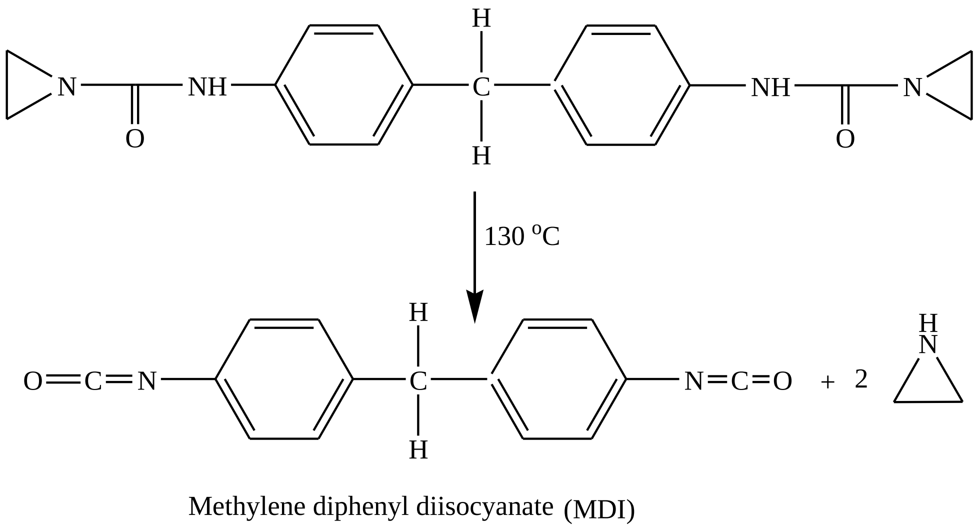
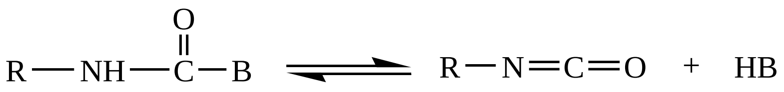


Figure 4.16. Deblocking of MDI-E to MDI

In general, the deblocking reaction results in with free isocyanate groups and the blocking agent as shown in Figure 4.17.



$$R-NH-\overset{\overset{O}{\|}}{C}-B \rightleftharpoons R-N=C=O + HB$$

Figure 4.17. Deblocking to isocyanates

In the case of aziridine blocked chain extender, the reactions were run at 120 °C, where the ring opening mechanism (shown in Figure 1.23) dominates and the reaction proceeds without liberation of aziridine. In case of MDI-E since the blocking agent is a volatile compound, the weight loss was considered an indication of deblocking to free isocyanate and aziridine. A dry sample of MDI-E was kept at 120 °C for two hours and no weight loss was observed, meaning that spontaneous decomposition to the isocyanate and aziridine at that temperature did not take place.

For the chain extension reactions, the stoichiometric amount of the extender per carboxyl end group in the UPE gave the desired molecular weight increase. In order to investigate the effect of the amount of the extenders, lower weight ratios were tried as shown in Table 3.2 under the “Experimental” section. It was found that 5 per cent MDI-E chain extender gave the desired molecular weight within 120 minutes at 120 ^{o}C. As the aim is to use the minimal amount of chain extender, only samples made by using 5 per cent of these chain extenders were examined later in mechanical and thermal tests. Figure 4.18 shows the rapid increase of the molecular weight with 5 per cent MDI-E at 120 ^{o}C.

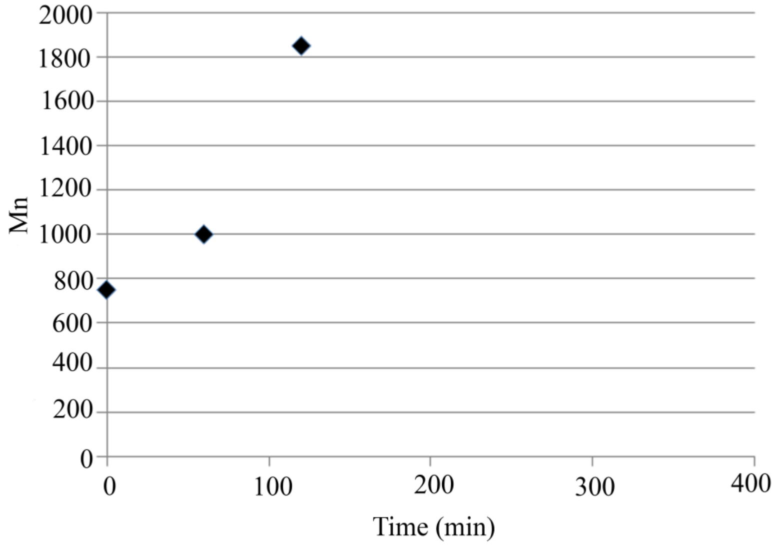


Figure 4.18. Molecular weight increase of UPE with MDI-E at 120 ^{o}C

At 120 ^{o}C the number average molecular weight increased from 725 to 1800 within two hours. At the end of the 16 hour industrial production, standard commercial UPE reaches a molecular weight of about 1500; therefore a number average molecular weight of 1800 is already above the desired molecular weight. This demonstrates that, in an industrial production process the desired molecular weight would be reached much earlier with this extender compared to the standard polyesterification method.

4.2.1.2. Chain Extension with Diphenylmethane-bis-4,4’-carbamoyl-Є-caprolactam (MDI-C)

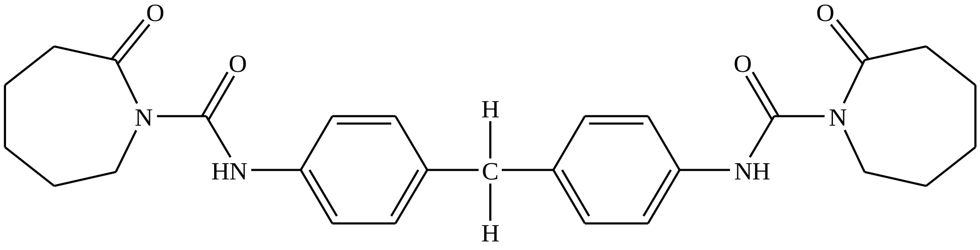


Figure 4.19. Diphenylmethane-bis-4,4’-carbamoyl-Є-caprolactam (MDI-C)

MDI-C is a caproplactam blocked MDI, used as an adhesion promoter for rubber and other elastomers to textile fibers and cords such as polyester. Caprolactam blocked isocyanates deblock to MDI at temperatures above 150-160 °C [47].

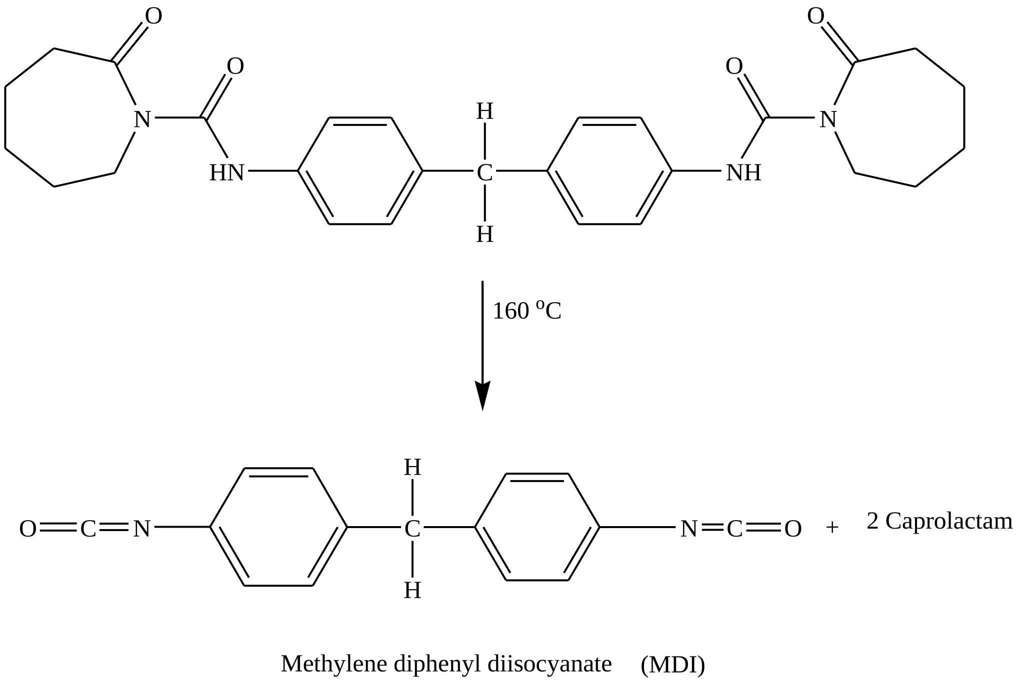


Figure 4.20. Deblocking of MDI-C to MDI

At 120 °C deblocking does not take place; but caprolactam blocked isocyanates react by the addition of a nucleophile (in this case the hydroxyl ends of the polyester chain) to either of the carbonyl groups [35] (a or b) as shown in Figure 4.21. Path (a) proceeds through opening of the caprolactam ring and does not produce any by-products, but path (b) produces free caprolactam.

The reaction of the caprolactam ring with nucleophiles has been used in industrial applications. 1,1'-Carbonyl bis caprolactam (CBC) has been used as chain extender for PET and has been reported to lead to higher molecular weight polyesters with better mechanical properties [48].

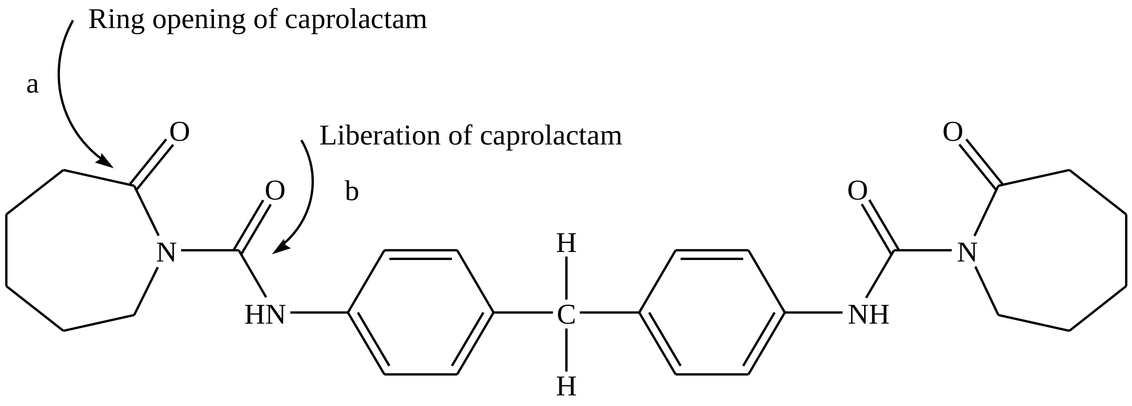


Figure 4.21. Reaction of MDI-C with nucleophiles

It couples two hydroxyl end groups according to the following mechanism in which both (a) and (b) operate. Urethane linkages are introduced to the polyester and some caprolactam is liberated. The viscosity increase is adjusted by the amount of CBC and in practice for PET about 0.5 per cent (by weight) CBC is used.

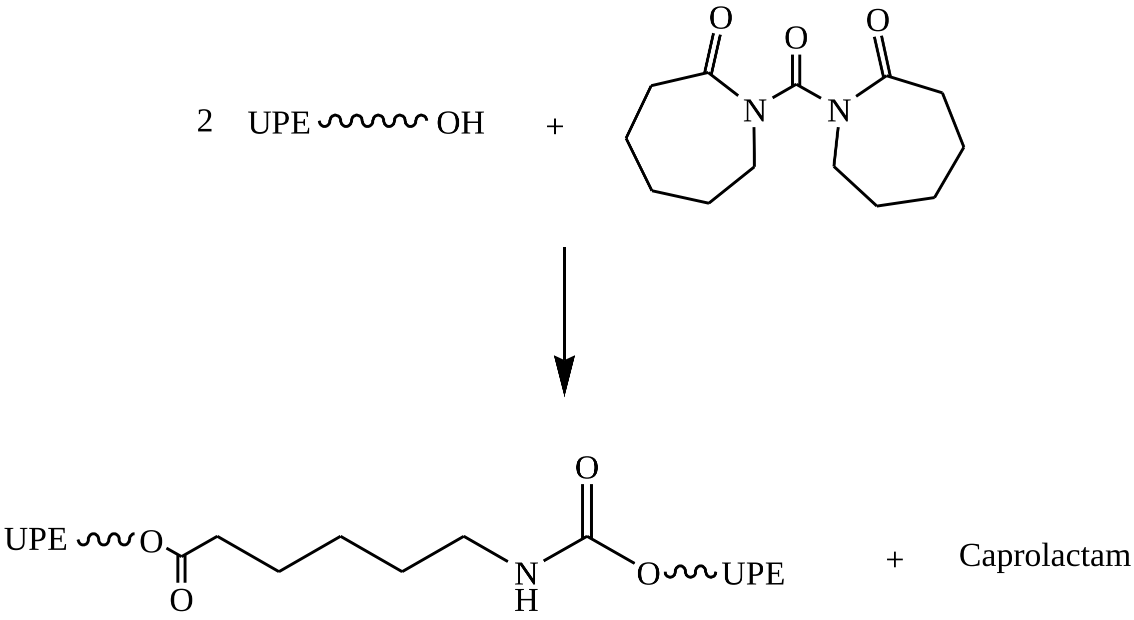


Figure 4.22. Reaction of hydroxyl end groups with caprolactam carbonyl groups

In case of chain extension of unsaturated polyesters, any caprolactam that may be produced by path (b) will remain in the final product. As caprolactam is not a common plasticizer for UPE, there is no published work on its effect on the mechanical properties of

UPE. In this work there was no evidence of plasticization as the thermal and mechanical properties of the MDI-C chain extended polyester remained close to the commercial polyester. When used in 5 per cent weight ratio this chain extender gave an increase in molecular weight from 730 to 1300 in two hours at 120 ^{o}C. These results are shown in Figure 4.23.

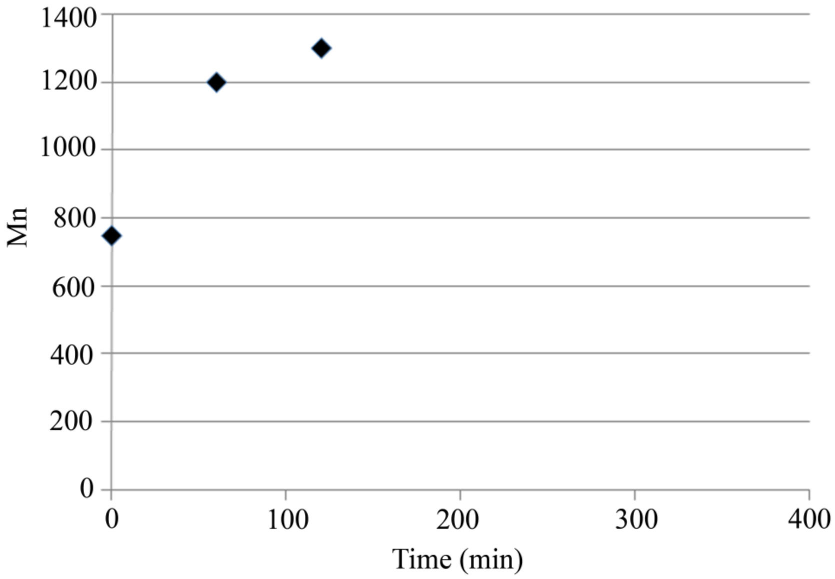


Figure 4.23. Molecular weight increase of UPE with MDI-C at 120 ^{o}C

4.2.1.3. Chain Extension with Isocyanated Soybean Oil (SONCO)

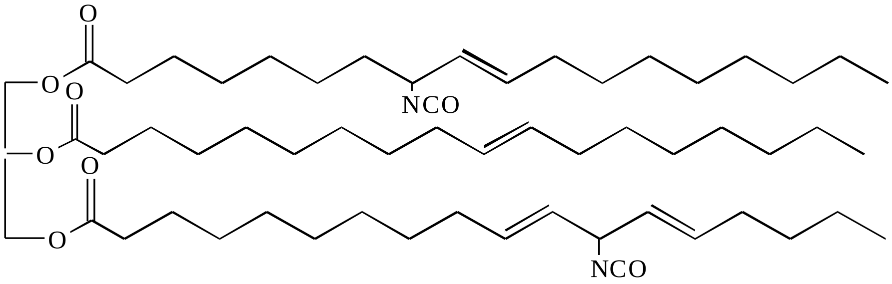


Figure 4.24. Isocyanated soybean oil (SONCO)

Isocyanated soybean oil (Molecular Weight: 900 g/mole) obtained from soybean oil is a promising candidate as chain extender for unsaturated polyesters. Other triglyceride containing polymers synthesized earlier in our laboratory biodegraded easily as shown by soil burial tests [36]. In another study of our group, SONCO successfully reacted with diols to yield polyurethanes [41]. The synthesized SONCO contains an average number of 2.1 isocyanate groups per triglyceride as determined by ^{1}H-NMR analysis as explained in the “Experimental” section.

With only 2.1 isocyanate for every triglyceride molecule and a molecular weight of 900, one has to use considerably more SONCO weight wise (compared to the blocked isocyanates), to obtain a reasonable chain extension. In the chain extension reactions SONCO was used in a weight ratio of 20 per cent at 85-120 ^{o}C. Use of 1,4-diazabicyclo[2.2.2]octane (DABCO) as catalyst increased the reaction rate of the reaction as expected. $\overline{M}_n$ value increased from 750 to 1050 within five hours.

In one of our earlier projects, epoxidized soybean oil, another soybean oil based renewable extender with 4.2 epoxy groups per triglyceride, gave a better molecular weight increase when used in the same weight ratio [49]. Therefore instead of adding more SONCO into the unsaturated polyester, if the isocyanate number of SONCO (the number of isocyanate groups per triglyceride) is increased, more effective chain extension can be expected. Therefore, as a future work, synthesis of SONCO with a higher number of isocyanate groups per triglyceride is planned.

The molecular weight increase obtained with SONCO chain extension is shown in Figure 4.25.

4.2.2. Characterization of Polyesters Extended with Blocked Isocyanates and SONCO

4.2.2.1. ^{1}H-NMR Characterization. The ^{1}H-NMR spectra of the chain extended polyesters are shown in Figure 4.26. (The -C$\mathbf{H_3}$ protons arising from propylene glycol appear at 1.2 ppm; -C$\mathbf{H_2}$- protons of ethylene glycol and propylene glycol at 4.4 ppm; the -C**H**- proton of propylene glycol at 5.3 ppm; fumarate vinyl protons at 6.8 ppm and finally the phthalate aryl protons at about 7 ppm in the aromatic region.) In UPE samples where SONCO is used as extender peaks at 0.9 ppm belonging to the terminal methyl groups of SONCO could be identified.

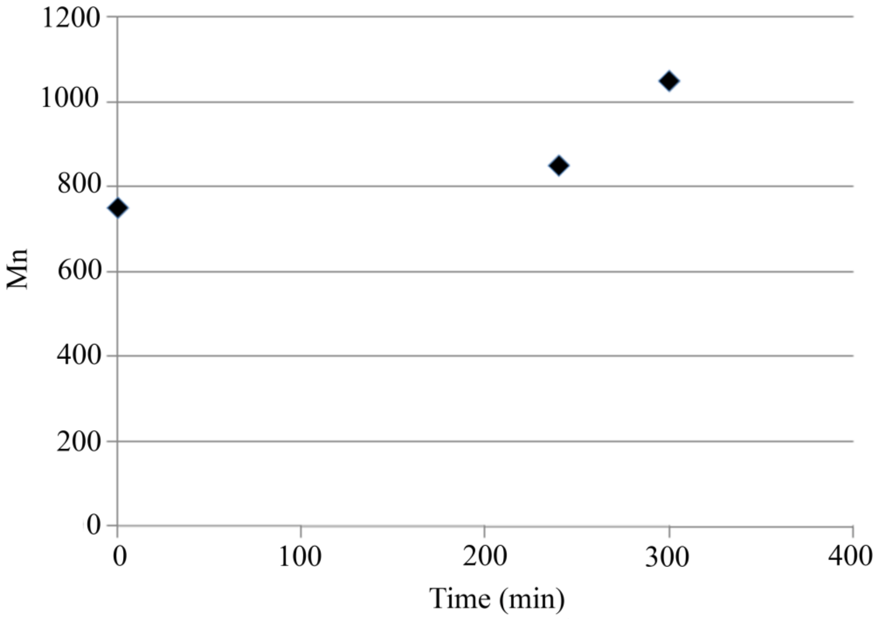


Figure 4.25. Molecular weight increase of UPE with SONCO

The fatty acid methylenes of SONCO gave rise to the large peak at 1.4 ppm; and the small peak at 1.8 ppm is due to the protons beta to the carbonyl and the peak at 2.4 ppm alfa to the carbonyl groups in SONCO. Finally, the peaks at 4.0-4.4 ppm originated from the glycerol group. Both, MDI-E and MDI-C contribute mostly with aromatic protons, which fall in the same region as the polyester phthalate protons in the ^{1}H-NMR spectrum. Besides, in these cases the extender amounts were so low, that peaks arising from them could not be identified in the ^{1}H-NMR spectra.

4.2.2.2. IR Characterization. The reference polyester and the chain extended products were also characterized by infrared spectroscopy. In all of the FTIR spectra the ester carbonyl could be identified at 1720 cm^{-1}. In the case of SONCO chain extender, triglyceride fatty alkyl chains could easily be detected at 3000 cm^{-1}. This was expected as the amount of SONCO used in chain extension is relatively high compared to the two blocked isocyanate extenders. The spectra are shown in Figure 4.27.

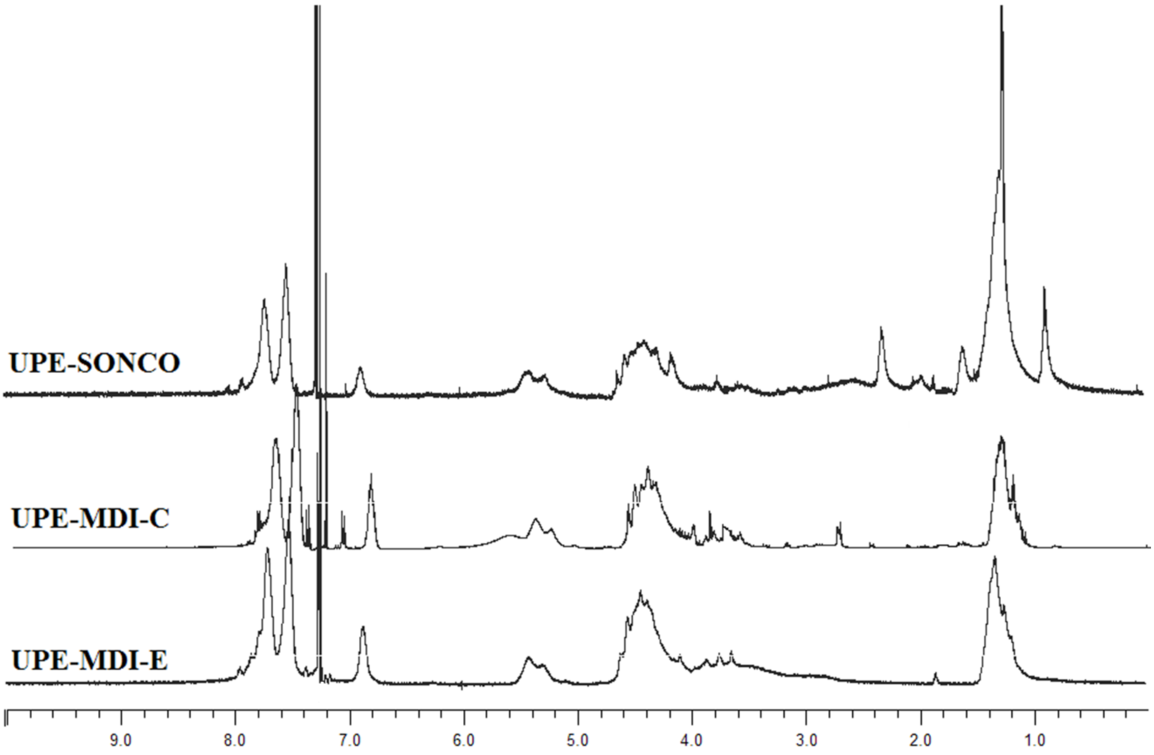


Figure 4.26. ^{1}H-NMR spectra of the chain extended polyesters

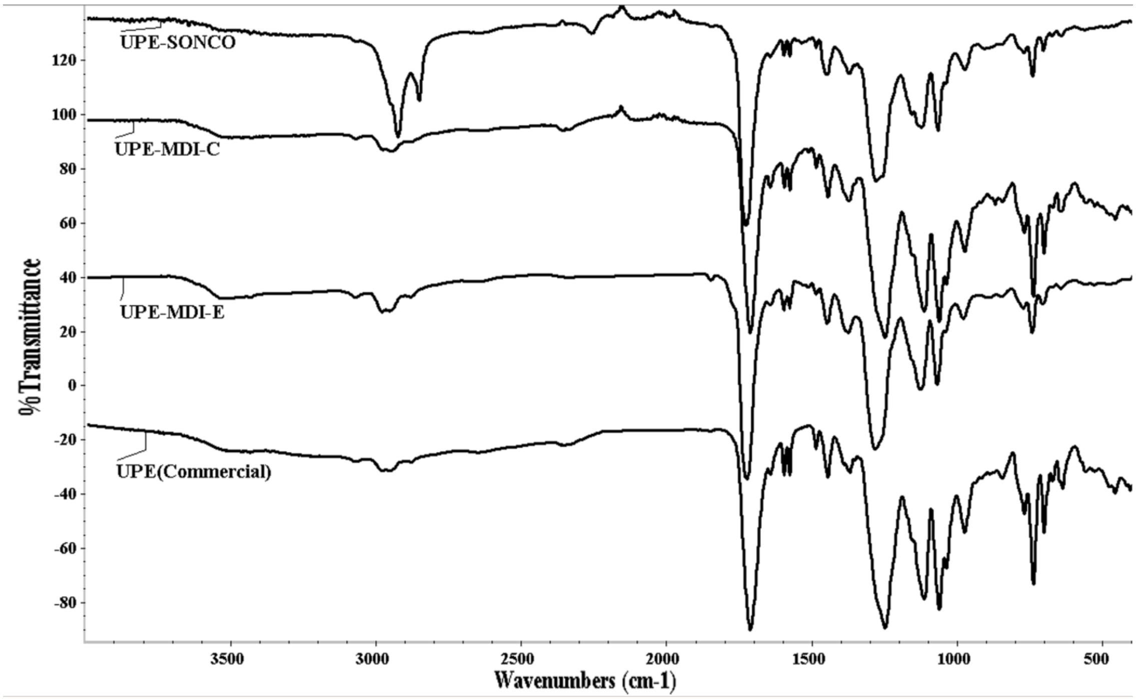


Figure 4.27. FTIR spectra of commercial and chain extended polyesters

4.2.3. Styrene Solubility and Gel Time of Isocyanate Extended Polyesters

To be industrially applicable, the isocyanate extended UPE needs to have the same styrene solubility and the same gel time as commercial UPE. Therefore in each case, styrene solubility and gel time were compared to a commercial reference product. Adhering to the industrially accepted ratio of 35 per cent styrene, the polyester was dissolved in styrene first at 40 ^{o}C and then was stirred further at room temperature until a clear solution was obtained. The resin obtained had a viscosity of approximately 600 cps, very similar to that of commercial UPE. The measured gel times for the commercial product and the chain extended polyesters can be seen in Table 4.4. The differences in gel times for different UPEs obtained with different extenders were attributed to the different number of moles of extenders in the chains.

Table 4.4. Gel times of UPEs chain extended with various isocyanate extenders

UPE extended with	Gel time (min)
Blank	12-15
MDI-E	7-8
MDI-C	10-15
SONCO	7-8

4.2.4. Mechanical and Thermal Analysis of Isocyanate Extended Polyesters

Tan delta plots of commercial and chain extended polyesters are shown in Figure 4.28 and the actual values are listed in Table 4.6.

The glass transition temperatures were taken as the maxima of tan delta curves. MDI-C extended polyester exhibited T_g and storage modulus values that were very close to that of commercial polyester (T_g = 84 ^{o}C and the storage modulus = 3250 MPa). For the commercial polyester these values are 88 ^{o}C and 3000 MPa, respectively. In case of chain extension with MDI-E lower values were found (T_g = 73 ^{o}C and the storage modulus = 2400 MPa). In chain extension reactions, in most cases, the fraction of the used chain extender that reacts at only one end of the polyester cannot be determined. For different chain extenders this ratio is expected to be different.

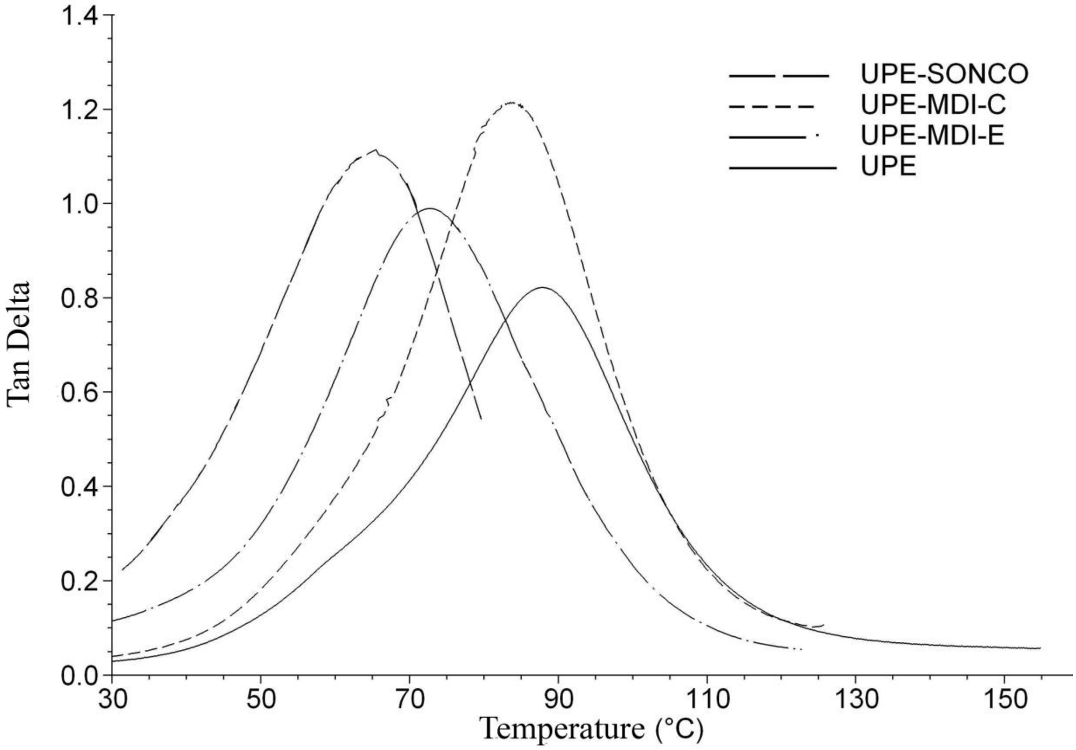


Figure 4.28. Tan delta plots of commercial and chain extended polyesters

T_g and storage modulus differences between commercial UPE and the chain extended polyesters can be attributed to this fact. In case of chain extension with SONCO the glass transition temperature dropped to 65 °C. A similar trend was observed when its storage modulus was measured. SONCO chain extended UPE showed a lower storage modulus (1500 MPa) than that of commercial product. These decreases in T_g and storage modulus values were attributed to the higher weight ratio and to the plasticizing effect of SONCO. Introduction of long alkyl chains by the triglyceride should plasticize the final product just like dioctyl and dinonyl phthallates do act as plasticizers [50]. In addition, in one of our earlier work, UPEs were found to be plasticized upon introduction of long alkyl chains of epoxidized soybean oil [49]. In case of MDI-C where some caprolactam is expected to be liberated, a similar plasticizing effect was not observed, as the T_g and mechanical properties of the chain extended UPE were found to be very close to that of the commercial sample. Thus in case of MDI-C the advantages obtained by chain extension were dramatically reduced reaction time without compromising the thermal and mechanical properties of the product. The storage modulus curves of all the polyesters are shown in Figure 4.29. The actual values are listed in Table 4.6.

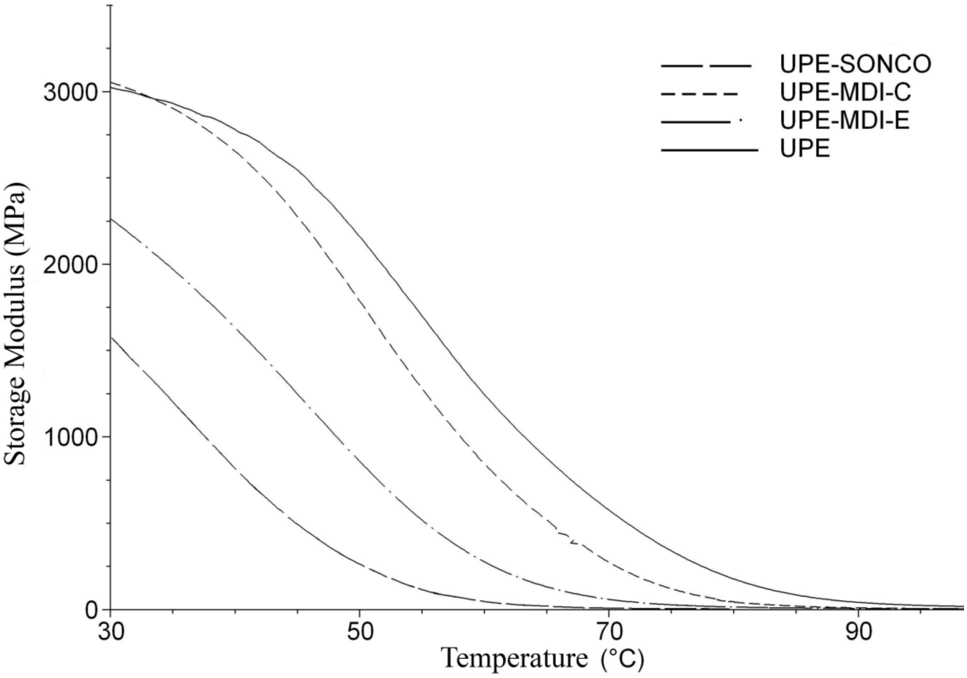


Figure 4.29. Storage modulus curves of commercial and chain extended UPEs at 25 ^{o}C

Thermal stability tests were also performed for the chain extended polyesters and the reference product. The results are shown in Figure 4.30. The final number average molecular weight, glass transition temperature, storage modulus, TGA data and gel times are summarized for comparison in Table 4.5.

Table 4.5. Final $\overline{M}_n$, T_g, Storage Modulus, TGA data and Gel times of commercial and chain extended polyesters

UPE	**Final $\overline{M}_n$**	**T_g (^{o}C)**	**Storage Modulus (MPa)**	**Temperature at 5 per cent weight loss (^{o}C)**	**Gel time (min)**
Commercial UPE	1500	88	3000	272	12-15
Extended with MDI-E	1800	73	2400	204	7-8
Extended with MDI-C	1300	84	3250	202	10-15
Extended with SONCO	1050	65	1500	188	7-8

TGA results of the chain extended polyesters show that the temperatures corresponding to 5 per cent weight loss are around 190-200 ^oC. This value is 272 ^oC for commercial UPE. The difference reflects the lower thermal stability of the introduced linkages compared to the ester linkage. In case of MDI-E and MDI-C, the chain extension created urea linkages in the backbone, which have lower thermal stability than ester groups. For example, N-alkyl-N'-phenylureas are known to decompose at temperatures as low as 185 ^oC [51]. Similarly, in case of chain extension with SONCO, urethane linkages were introduced to the polyester backbone. As the urethane bond is unstable above 170 ^oC [52], again when compared to commercial UPE, the decrease observed in thermal stability was expected. Therefore, it was concluded that SONCO extended UPE would only be suitable for applications where high T_g, high modulus and high thermal stability are not required, but a fast biodegradability is. TGA thermograms of commercial and chain extended polyesters for the temperature at 5 per cent weight loss are shown in Figure 4.30.

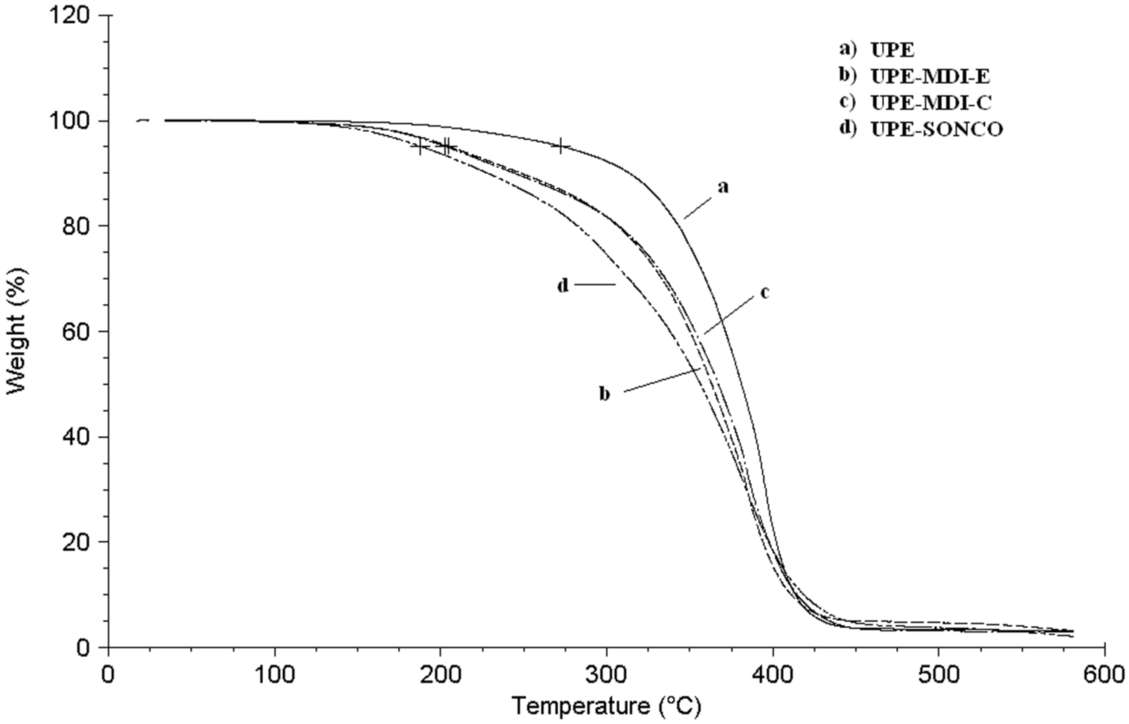


Figure 4.30. TGA thermograms of commercial and chain extended polyesters (Temperature at 5 per cent weight loss)

In conclusion, MDI-E and MDI-C extended polyesters have, in principle, different chain extending groups at temperatures lower than 160 ^{o}C, therefore variations in molecular weight at a given reaction time and variations in thermal and mechanical properties are not surprising.

MDI-E and MDI-C extended unsaturated polyesters exhibit thermal and mechanical properties that are perfectly suitable for industrial use. As mentioned in the "Introduction", production of unsaturated polyesters requires a long reaction time and severe conditions. When thought in terms of industrial production, the benefits brought on by the extenders such as shortened reaction time, reduced energy use or increased yield present a major advantage. Starting with the UPE oligomers used in this work which have a $\overline{M}_n$ of 700, and continuing the polycondensation reaction to reach a $\overline{M}_n$ of 1800, would result in a 2 per cent weight loss due to the water that needs to be separated. This was calculated from the decrease in acid number. The actual loss in practice is probably much higher due to the azeotropic loss of diols along with water. Using the chain extension method described in this part there is a 5 per cent increase in the weight of the product. The total increase in polymer yield is therefore at least 7 per cent which is an attractive number for a UPE producer and the price gain would offset the price of the extender that needs to be used.

4.3. Bisoxazoline Chain Extenders

4.3.1. Chain Extension Reactions with Bisoxazolines

4.3.1.1. Chain Extension with 1,3-phenylene-bis-oxazoline (1,3-PBO)

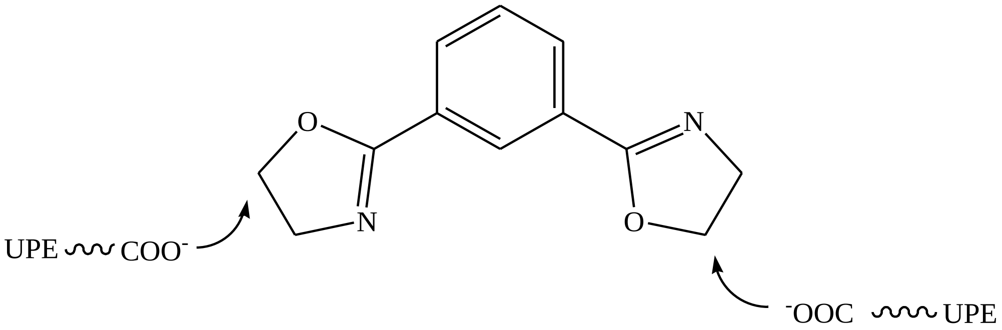


Figure 4.31. 1,3-phenylene-bis-oxazoline (1,3-PBO)

1,3-phenylene bis oxazoline (1,3-PBO) and 1,4-phenylene bis oxazoline (1,4-PBO) have effectively been used in chain extension of PET [53]. The reaction proceeds with the attack of the carboxylic end groups of polymeric chains to the oxazoline ring and poly (ester-amides) are produced as shown in Figure 4.32.

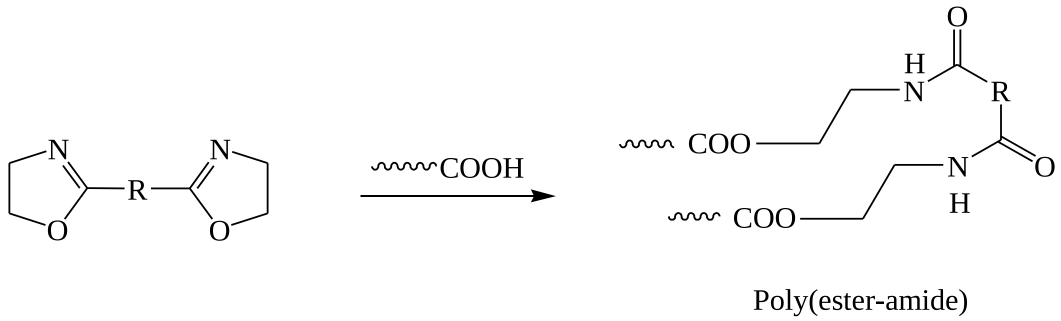


Figure 4.32. Formation of poly (ester-amides) from bisoxazolines

Effective concentrations of PBO for PET are in the range of 0.5-1.5 per cent by weight. Typical reaction conditions are 240 ^{o}C for 1-3 minutes [53]. However in case of unsaturated polyesters as the polymer end group concentration is higher, higher concentrations such as 1-5 per cent are needed.

In industrial applications PBO also acts as a carboxyl group scavenger and this way an increase in the hydrolytic stability of PET can be obtained. 0.5 per cent PBO can reduce the carboxyl content from 45 to 20 mmol/kg [54].

Karayannidis et. al. [53] studied the effect of PBO on the intrinsic viscosity increase of PET during extrusion. These authors observed enhanced results when phthalic anhydride was added to the initial sample before the addition of PBO. This way the hydroxyl end groups were consumed first and PBO acted as a more effective chain extender.

In a similar way, PBO has been used in combination with carbonyl-bis-caprolactam, an extender employed in PET chain extension. Carbonyl-bis-caprolactam reacts with the hydroxyl end groups of polyester chains to form mainly urethane linkages. In order to increase the effect of chain extension it has been used in combination with PBO, which reacts with the carboxylic end groups of polyester chains [55].

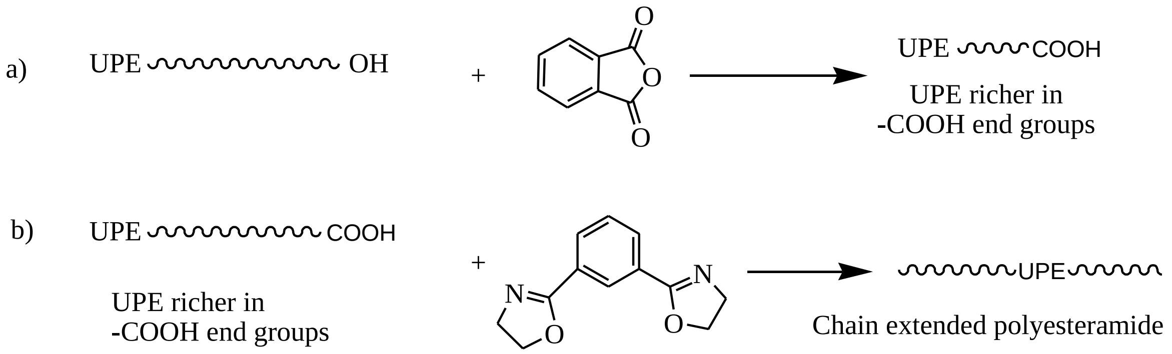


Figure 4.33. Chain extension with phthalic anhydride and PBO

In the present study, 1,3-phenylene-bis-oxazoline (Molecular Weight= 216 g/mol) was examined for its efficacy in chain extension of unsaturated polyesters. The stoichiometric amount of 1,3-PBO was calculated from the acid number of the short chain UPE as 15 per cent by weight. Using this theoretical amount at 160 ^{o}C, the molecular weight increased from 1030 to 1700 within 5 minutes. Then the extender concentration was gradually decreased and 3 per cent of extender was found to give the desired molecular weight increase. Table 3.3 shows the results of stoichiometric and optimum weight ratios of this extender together with 2,2'-bis(2-oxazoline) and the $\overline{M}_n$ values obtained during the reactions. In all cases even within 5 minutes the molecular weight of the unsaturated polyester reached 1400. However the reaction was continued up to 30-60 minutes, in order to check the reversibility of reactions at 160 ^{o}C. At the processing temperatures as high as 250-300 ^{o}C, the reaction of bis(2-oxazoline)s with carboxylic groups were shown to be reversible [35]. However, at 160 ^{o}C, in most of the runs the molecular weight of UPE continued to increase indicating further coupling reactions.

In Table 3.3, the results of a control (blank) run, (where the short chain UPE was heated at the reaction conditions without a chain extender, to investigate if polycondensation also contributes to the molecular weight increase) and the polydispersity index values are listed together with the molecular weight increase due to the extender. In the case, where no extender was present, the molecular weight did not increase.

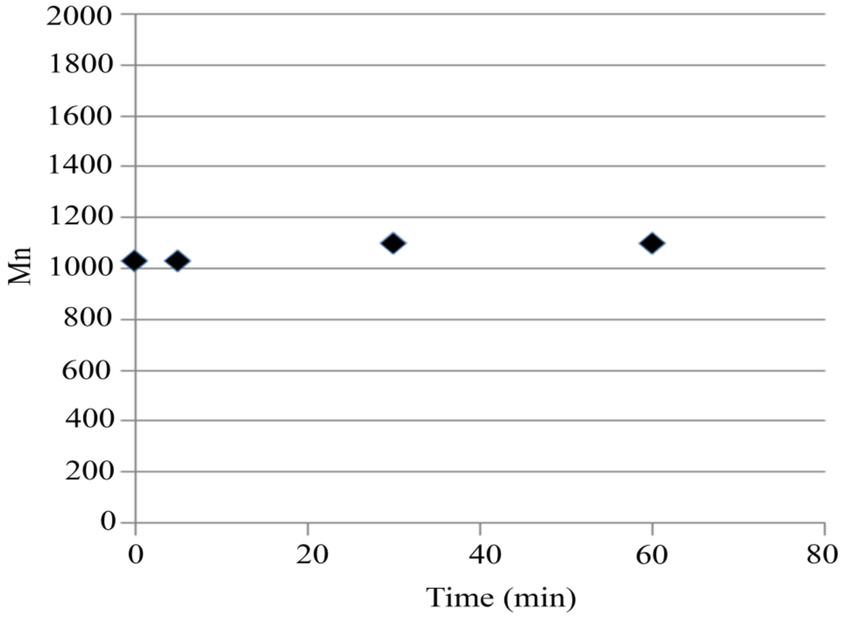


Figure 4.34. Blank run (without extender) for commercial UPE at 160 ^{o}C

During the chain extension reactions, polydispersity index values were found to increase. This was expected, because chain coupling reactions are random and cause production of different length chains in the reaction medium.

The molecular weight increase of UPE caused by 1,3-PBO is shown in Figure 4.35. The values are listed in Table 3.1 under the "Experimental"section. When compared to Figure 4.34, the rapid increase in molecular weight of the polyester can be seen. The $\overline{M}_n$ value reached 1500-1600 (the $\overline{M}_n$ value of the commercial reference polyester) in 30-60 minutes when 1,3-PBO was added to the reaction medium at 160 ^{o}C.

<u>4.3.1.2. Chain Extension with 2,2'-bis(2-oxazoline) (BO)</u>. 2,2′-bis(2-oxazoline) has been investigated for its influence on mechanical and thermal properties of PET. In a recent study BO was found to react with PET to form linear chain-extended polymers without branching. As to thermal stabilities, unreacted oxazoline remaining in the polymer was reported to act as a heat stabilizer by further reacting with carboxyl terminals of the polymers and by preventing decrease in the molecular weight even in the solid state.

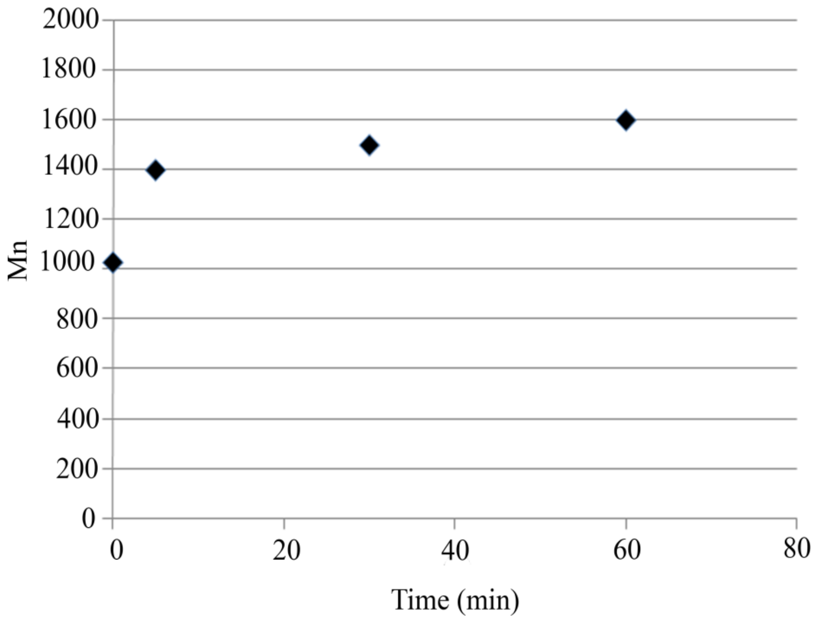


Figure 4.35. Molecular weight increase of UPE with 1,3-PBO at 160 ^{o}C

On the other hand, the BO unit incorporated into the polyester chain was found to be relatively thermally unstable compared with the ordinary polyester chain, especially under the polyester melt conditions. The PET treated with BO exhibited a lower carboxyl content, and considerable improvement in the hydrolytic stability [56].

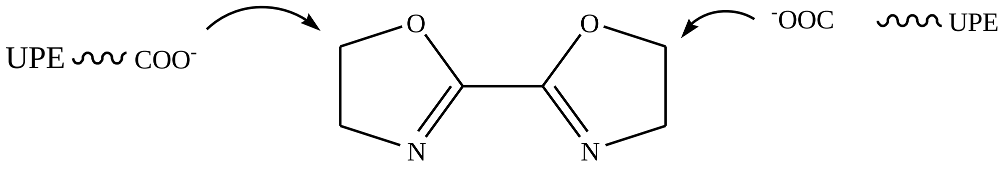


Figure 4.36. 2,2'-bis(2-oxazoline)

In this study, 2,2'-bis(2-oxazoline) (Molecular Weight: 140 g/mol) was investigated for its efficiency in chain extension of unsaturated polyesters. Various amounts of chain extender were employed to investigate the optimum amount of BO. The stoichiometric amount of the extender calculated from the acid number of the short chain UPE was 10 per cent. For this amount a high molecular weight increase ($\overline{M}_n$= 1500) was found within 5 minutes. Then this amount was decreased gradually and 4 per cent of extender was found to give the desired molecular weight increase. Table 3.3 shows the results of stoichiometric and optimum weight ratios of this extender together with 1,3-PBO and the $\overline{M}_n$ values obtained during the reactions. In all cases even within 5 minutes the molecular weight of the unsaturated polyester reached 1400.

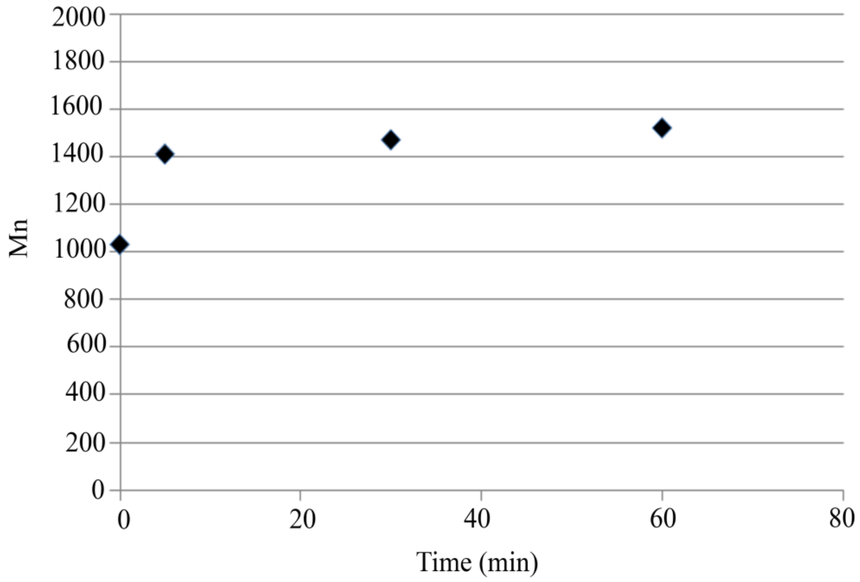


Figure 4.37. Molecular weight increase of UPE with BO at 160 ^oC

The molecular weight increase of UPE caused by BO is shown in Figure 4.37. The $\overline{M}_n$ value reached 1500 (the $\overline{M}_n$ value of the commercial reference polyester) in 30-60 minutes when BO was added to the reaction medium at 160 ^oC.

As verified by Figure 4.34, at 160 ^oC, polycondensation did not take place. Besides, at or below 200 ^oC, the ester-amide bond formed in the reaction between bis(2-oxazoline)s and carboxylic groups is known to be stable [35]. . Thus 160 ^oC was found to be a rational reaction temperature at which polycondensation of acidic and hydroxyl groups does not take place and the formed ester-amide bond is stable.

Quarternary ammonium salts, quarternary phosphonium salts and tertiary phosphines were reported to catalyze the reaction of bis(2-oxazolines)s with carboxylic groups [38] but in this work no catalyst was needed or used.

4.3.2. Characterization of Bisoxazoline Extended Polyesters

The poly(ester-amides) obtained following chain extension were characterized by ^{1}H-NMR and FTIR spectroscopy. An example ^{1}H-NMR spectrum of UPE extended with 1,3-PBO is shown in Figure 4.38.

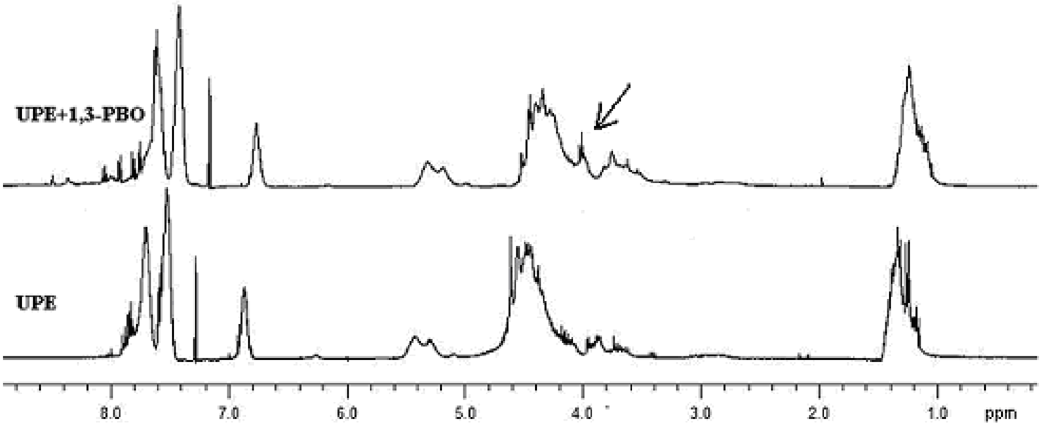


Figure 4.38. ^{1}H-NMR spectrum of 1,3-PBO chain extended UPE

In the unsaturated polyester, the -C**H**$_3$ protons arising from propylene glycol appear at 1.2 ppm; -C**H**$_2$- protons of ethylene glycol and propylene glycol at 4.4 ppm; the -C**H**- proton of propylene glycol at 5.3 ppm; fumarate vinyl protons arising from the thermal isomerisation of maleate groups appear at 6.8 ppm and finally the phthalate aryl protons at about 7 ppm in the aromatic region.

Bisoxazolines show characteristic peaks at 3.9 and 4.3 ppm arising from protons on the oxazoline carbons alpha to oxygen and nitrogen. Following chain extension with bisoxazolines, these peaks originating from the methylene groups between amide and ester bonds were identified in the ^{1}H-NMR spectrum of the chain extended UPE at about 4.0 ppm. When considered together with rapid molecular weight increase, this NMR signal is an indication of chain extension.

The chain extended unsaturated polyesters were also identified by FTIR. In case of chain extension, a new amide bond was introduced to the polyester chain. This amide stretch was detected at 1540 cm^{-1} and at 1750 cm^{-1}. This region of the IR spectrum is illustrated in Figure 4.39 for unmodified UPE and 1,3-PBO chain extended UPE.

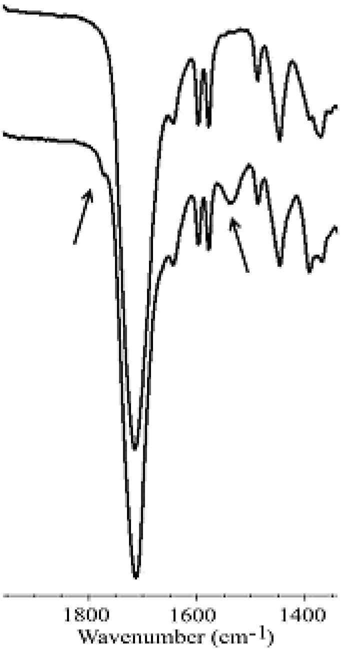


Figure 4.39. FTIR spectra of unmodified and chain extended UPEs

4.3.3. Styrene Solubility and Gel Time of Bisoxazoline Extended Polyesters

The styrene solubility and gel times of the bisoxazoline chain extended polyesters were also compared to the commercial reference product. Following the chain extension the polyesters were dissolved in styrene to give a clear solution containing 35 per cent styrene. The solubilities were found to be the same as the reference polyester. Gel times for chain extended polyesters were measured as 8-10 minutes, which is very comparable to the reference polyester. The measured gel times are given in Table 4.6.

4.3.4. Mechanical and Thermal Analysis of Bisoxazoline Extended Polyesters

The chain extended and cured polyesters were examined further for their thermal and mechanical behavior. Bisoxazoline chain extenders introduced new amide linkages to the polymer chain, which would be expected to increase the T_g of the cured polyester.

Table 4.6. Gel times of polyesters extended with bisoxazolines

UPE extended with	Gel time (min)
Blank	12-15
1,3-PBO	9-10
BO	8-9

The commercial reference polyester has a T_g of 88 ^oC as determined by the maximum of tan delta curve and a storage modulus of 3000 MPa as determined by DMA analysis.

1,3-PBO extended polyester exhibited a T_g at 88 ^oC and a storage modulus of 3200 MPa. Thus, the T_g remained unaltered with respect to the commercial polyester and the storage modulus is slightly above the reference value of 3000 MPa. In case of BO chain extension a T_g of 75 ^oC and a storage modulus of 2875 MPa were found. The higher values obtained with 1,3-PBO is attributed to the rigidity introduced by the phenyl ring. The tan delta and storage modulus curves of all the polyesters are shown in Figure 4.40.

Thermal stability tests were also performed for the chain extended polyesters and the reference product. The results are shown in Figure 4.41. The final number average molecular weight, glass transition temperature, storage modulus, TGA data and gel times are summarized for comparison in Table 4.7.

TGA results of the chain extended polyesters show that the temperatures corresponding to 5 per cent weight loss are around 250 ^oC. This value is 272 ^oC for commercial UPE. The difference reflects the lower thermal stability [35] of the introduced amide linkage compared to the ester linkage. However, this small decrease in thermal stability should not be detrimental in practice as unsaturated polyesters usually are not used in high temperature applications. Bisoxazoline extended unsaturated polyesters exhibit thermal and mechanical properties that are perfectly suitable for industrial use.

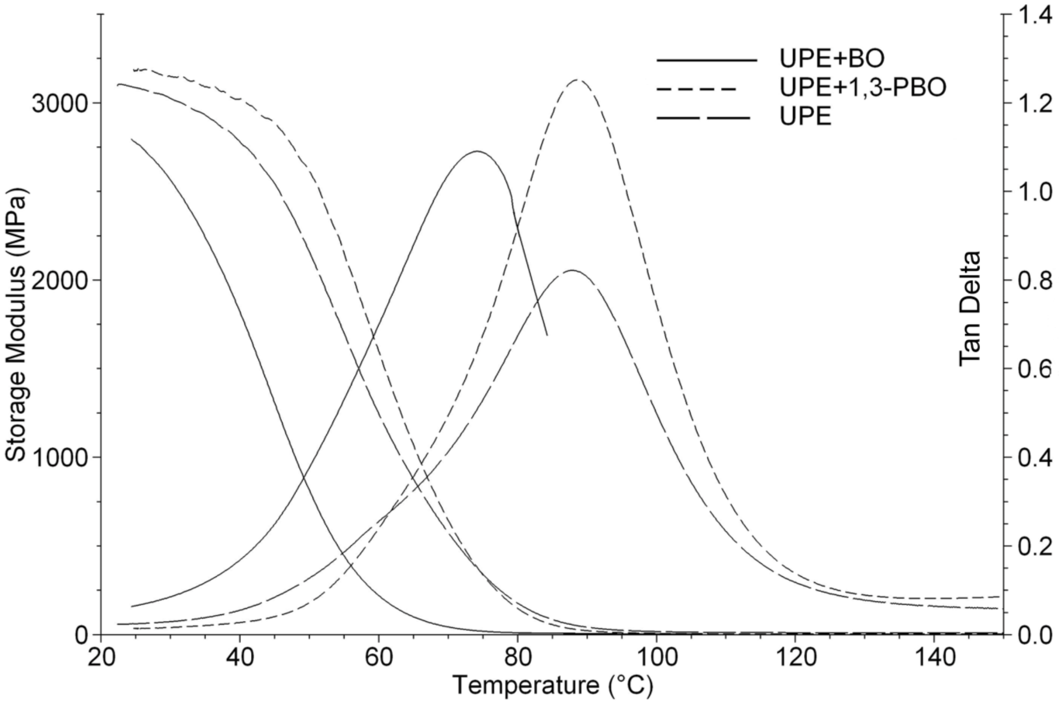


Figure 4.40. Tan delta and storage modulus curves of commercial and chain extended UPEs at 25 ^{o}C

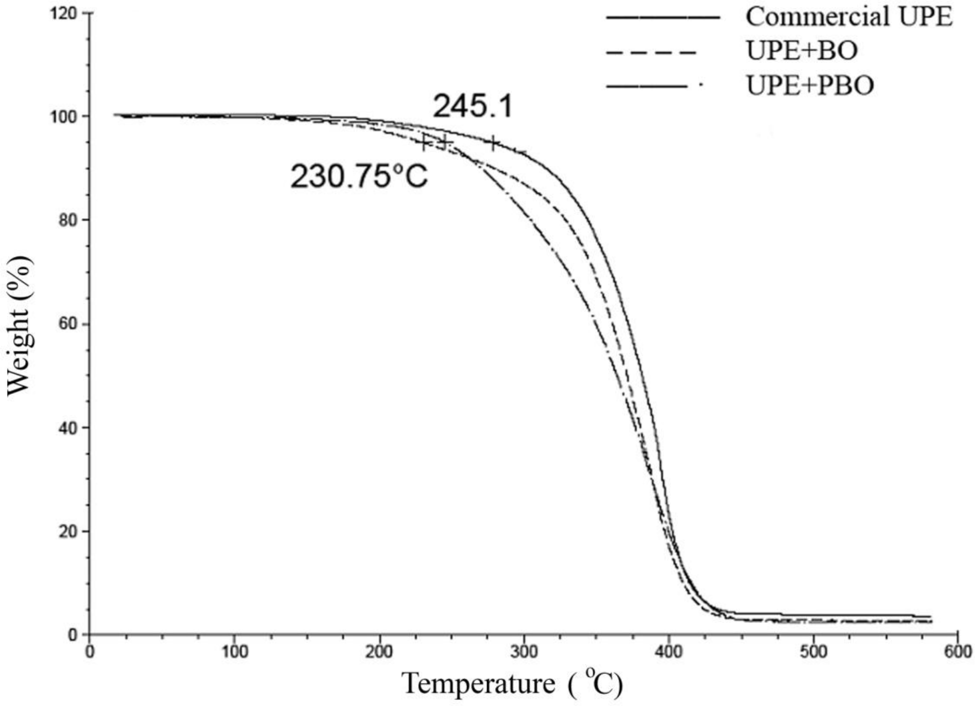


Figure 4.41. TGA thermograms of commercial and chain extended polyesters (Temperature at 5 per cent weight loss)

Table 4.7. Final $\overline{M}_n$, T_g, storage modulus, TGA data and gel times of commercial and chain extended polyesters

UPE	**Final $\overline{M}_n$**	**T_g (°C)**	**Storage Modulus (MPa)**	**Temperature at 5 per cent weight loss (°C)**	**Gel time (min)**
Commercial UPE	1500	88	3000	278	10-12
Extended with 3 per cent 1,3-PBO	1600	88	3200	245	9-10
Extended with 4 per cent BO	1520	75	2875	231	8-9

4.4. Comparison of the Chain Extenders

The chain extenders employed in this study belong to various chemical families. A must for a chain extender to be effective is the capability of giving fast reaction with the polymeric end groups. Besides, the extender preferably should not produce by-products and finally, the extender which introduces new linkages to the polymer should not alter mechanical and thermal properties of the final crosslinked product in an undesirable way. Therefore in this study each time final crosslinked products were compared to a commercial reference product.

4.4.1. Comparison of Introduced Linkages

Epoxide extenders reacted readily with carboxylic ends of the polyester chains introducing –OH groups to the polymer chain.

The new –OH groups are expected to increase the polarity of the polyester, thus rendering changes in its solubility. Besides, the hydrolytic stability is expected to be lower.

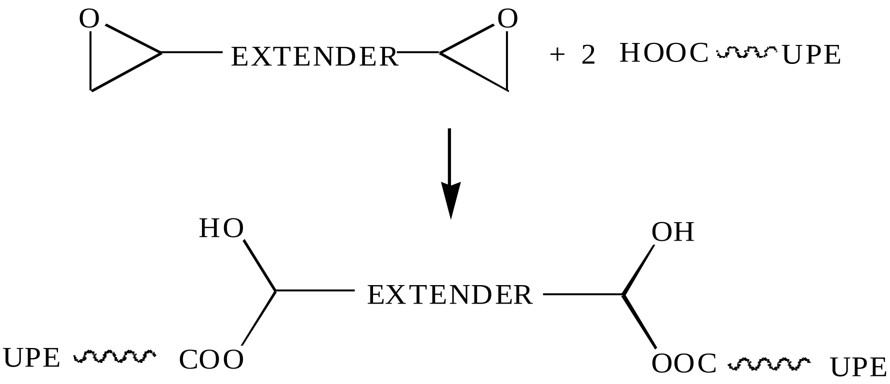


Figure 4.42. The reaction with epoxide extenders

Isocyanate extenders or blocked isocyanate extenders react with the hydroxyl as well as the carboxyl end groups of the polymer chains and introduce urethane or urea linkages to the polyester chain.

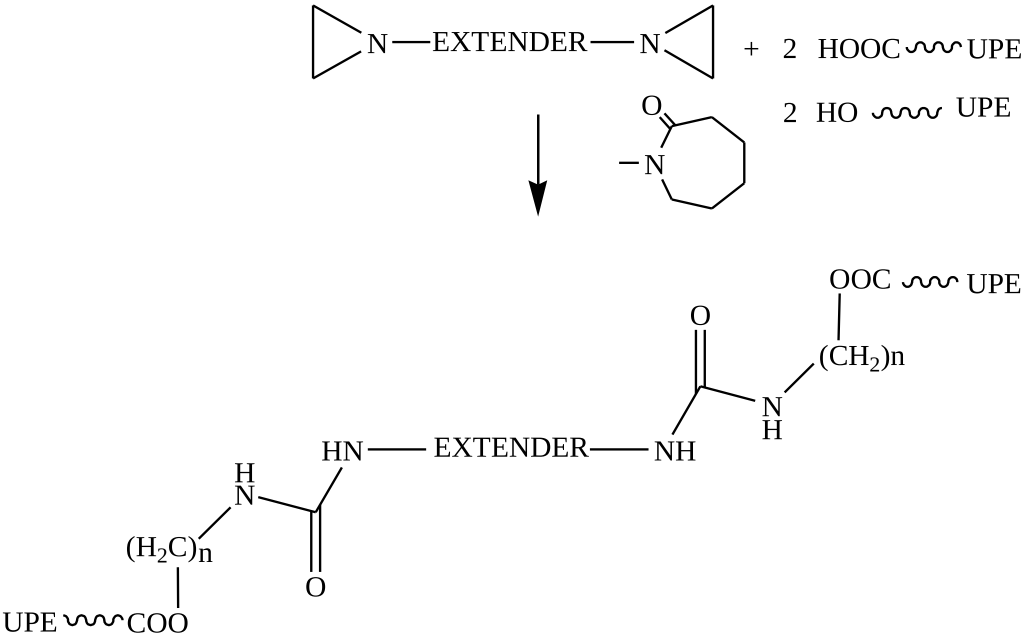


Figure 4.43. The reaction with blocked isocyanate extenders

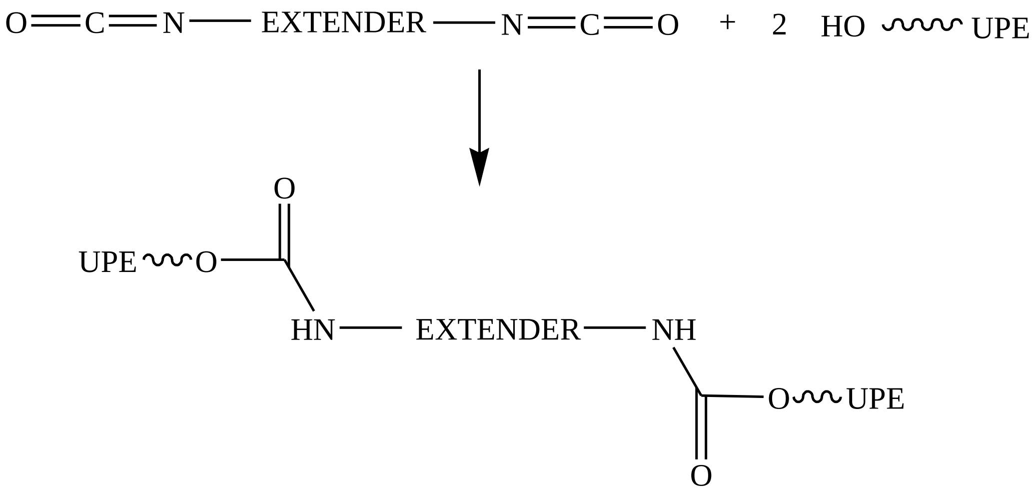


Figure 4.44. The reaction with isocyanate extenders

As detailed under “Results and Discussion” the introduced linkages have lower thermal stability than the ester linkage. Therefore it was not surprising to observe lower temperatures for 5 per cent weight loss whenever urea or urethane linkages were in the polymer chain. N-alkyl-N’-phenylureas are known to decompose at temperatures as low as 185 ^{o}C and the urethane bond is unstable above 170 ^{o}C. Bisoxazolines gave polyesteramides as shown in Figure 4.45.

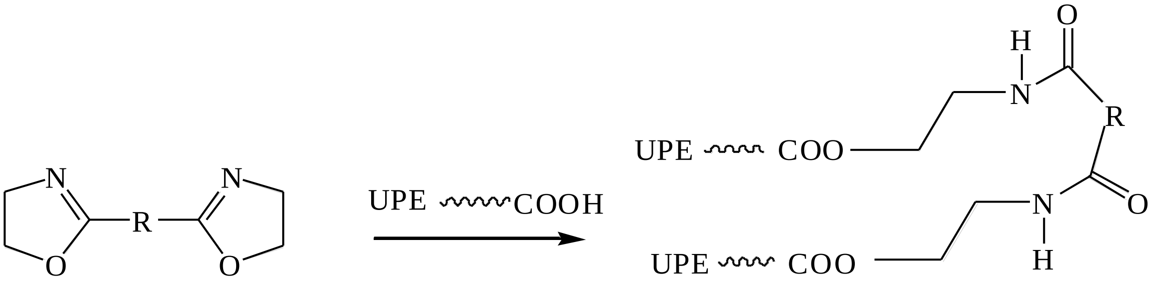


Figure 4.45. The reaction with bisoxazoline extenders

As discussed under “Results and Discussion” part, the amide bond incorporated into the polyester chain is relatively thermally unstable, and thus it decreased the 5 per cent weight loss temperature. However, it has also been reported that unreacted oxazoline remaining in the sample acts as a heat stabilizer by further reacting with carboxyl end groups and by preventing decrease in the molecular weight of polyesters when molten [56].

4.4.2. Comparison of Reaction Times

When compared with respect to reaction times bisoxazolines gave the fastest reactions and gave the desired molecular weight within minutes. The extenders where the functional site is not readily accesible gave the slowest results. This was the case in epoxidized soybean oil and isocyanated soybean oil. The epoxide extenders with terminal epoxy groups gave satisfying results, as did the two blocked isocyanates. The molecular weight of the chain extenders used in this study varied between 140-900 g/mol. Therefore the needed theoretical amounts and the calculated optimum weight percentages of extenders showed differences. Besides, different reaction temperatures were employed, again depending on the varying reactivities. As a result, comparison of reaction times based on standard parameters does not turn out to be meaningful. But the reaction times for all of the extenders for its optimum conditions and at which the desired molecular weight has been reached are summarized in Table 4.8, which should give an idea for the effective application of extenders especially in industrial practice.

Table 4.8. Comparison of reaction times at which the desired $\overline{M}_n$ is reached

Extender	**Extender**	**Reaction time***	**Reaction temperature**	$\overline{M}_n$ **reached**
	wt per cent	**(min)**	**(^{o}C)**	
DGEBA	12	60	160	1700
ESO	20	120	160	1015
DEO	10	120	140	1970
MDI-E	5	120	120	1800
MDI-C	5	120	120	1300
SONCO	20	300	120	1050
1,3-PBO	3	60	160	1600
BO	4	60	160	1520

*Reaction times at which the desired $\overline{M}_n$ is reached

4.4.3. Comparison of Solubility and Gel Times

To be industrially applicable, the chain extended UPE needs to have the same styrene solubility and gel time as the commercial reference polymer. Adhering to the industrially accepted ratio of 35 per cent styrene, in each case the chain extended linear polyester was dissolved in styrene first at 40 ^oC and then was stirred further at room temperature until a clear solution was obtained. All chain extended resins exhibited comparable solubilities in styrene and the obtained resins had viscosities about 600 cps, very similar to that of the commercial polyester.

Table 4.9. Comparison of gel times obtained with different extenders

Extender	**Gel Time (min)**
Blank	10-15
DGEBA	10-12
ESO	6-7
DEO	12-14
MDI-E	7-8
MDI-C	10-15
SONCO	7-8
1,3-PBO	9-10
BO	8-9

The gel times are compared in Table 4.9. Gel time measurements gave a reproducibility of +/- 2 minutes. Besides, the differences in gel times for different UPEs obtained with different extenders were attributed to varying number of moles of extenders in the chains.

4.4.4. Comparison of Mechanical and Thermal Properties

The newly introduced linkages or groups are expected to alter the mechanical and thermal properties of polymers. As a general trend, long alkyl chains increase elasticity and phenyl rings render rigidity. In general these trends were followed in chain extension reactions. For instance, epoxidized soybean oil extended UPE exhibited the properties of a plasticized material due to the presence of the long alkyl groups, 1,2;7,8-diepoxyoctane gave the smallest change in thermal and mechanical properties as in this case just ethylene groups were introduced. In all cases the introduced linkages had lower thermal stability compared to the polyester and therefore the measured temperatures at 5 per cent weight loss were lower compared to the unmodified reference product. Glass transition temperature, storage modulus and thermogravimetric analysis results are shown in Table 4.10.

Table 4.10. Comparison of mechanical and thermal properties of polyesters extended with different extenders

Extender	**T_g (^oC)**	**Storage Modulus (MPa)**	**Temperature at 5 per cent wt loss (^oC)**
Blank	88	3000	275
DGEBA	74	2650	208
ESO	66	1650	230
DEO	89	2875	273
MDI-E	73	2400	204
MDI-C	84	3250	202
SONCO	65	1500	188
1,3-PBO	88	3200	245
BO	75	2875	231

5. CONCLUSION

The world market of thermoset resins today has a growing trend and the annual consumption exceeds twenty million tons [3]. Newer and finely tailored materials enter the market every day, the challenge being the production of light weight, high performance and high quality products. Among the thermoset liquid molding resins unsaturated polyesters are the most commonly employed resin as the matrix for glass fiber reinforced composite materials.

Even though the basic chemistry of the manufacture of unsaturated polyesters has not been changed since its fast development in the 1950’s, in the last sixty years many methods to facilitate their production have been developed. Further process steps have been added to the manufacture in order to increase molecular weight of polyesters, thus obtaining stronger mechanical properties. Solid state post-condensation being the most commonly employed technique suffers from certain drawbacks like expensive equipment, complicated logistics, introduction of an additional process step, time consumption and requirement of high energy and vacuum.

In the present project, chain extension is proposed as an alternative method to obtain high molecular weight unsaturated polyesters in relatively short reaction times. Chain extenders can simply be added to the reactor during the polycondensation and the desired chain lengths are reached within very short times. This way, no additional processing step is needed and system costs are reduced.

In this study, various groups of chain extenders like di- or multi epoxides, di- or multi isocyanates and bisoxazolines have been employed in chain extension reactions of unsaturated polyesters.

(i) Di- or multifunctional epoxy compounds reacted readily with the carboxylic end groups of the polyester chains. Different weight ratios were tried and solubilities, gel times, and mechanical and thermal properties of the chain extended polyesters were examined and compared to a commercial reference product. The study showed that difunctional (or multifunctional) epoxy compounds are effective chain extenders for unsaturated polyesters. The use of these extenders decreases the production time and increases the yield of the polyester substantially, without compromising its solubility in styrene or from its mechanical and thermal properties. The chain extension can be carried out in the polyesterification reactor and proceeds without by-products.

(ii) Two blocked isocyanates and one renewable source isocyanate were reacted with unsaturated polyesters. Their solubilities, gel times and mechanical and thermal properties were found to be comparable to a commercial reference unsaturated polyester. It was concluded that aziridine and caprolactam blocked isocyanates are promising candidates for increasing molecular weights of unsaturated polyesters in a short time. They offer the benefit of reacting below the deblocking temperature as their blocking groups are also reactive with polyester end groups at these relatively low temperatures. Alternatively, unsaturated polyesters can be initially reacted with these blocked isocyanates at relatively low temperatures and then the reaction can further be continued at the deblocking temperature, to promote the reaction of remaining end groups with isocyanates. The renewable source isocyanate SONCO was found to introduce some elasticity to unsaturated polyesters and is proposed to be used particularly in such applications, where increased toughness and biodegradability offers an advantage. The use of these extenders decreases the production time and increases the yield of the polyester substantially.

(iii) Two different bisoxazolines were searched and found to be effective in chain extension for unsaturated polyesters. Bisoxazolines present the advantage of very fast reaction with the carboxylic end groups of the polyester chains at relatively lower temperatures compared to that of polycondensation. Solubilities, gel times and mechanical and thermal properties of the chain extended polyesters were examined and found to be very similar to a commercial reference polyester. Bisoxazolines also offer the advantage of very fast reaction without significant decrease in thermal stability.

In industrial applications, the chain extension can be carried out directly in the polyesterification reactor after a reduction in temperature. The diol loss due to evaporation that is usually encountered in the late stages of commercial UPE manufacture is also eliminated, giving economies in raw material and minimizing pollution. Standard industrial production of unsaturated polyesters requires a long reaction time and severe conditions. When thought in terms of industrial production, the benefits brought on by the extenders such as shortened reaction time, reduced energy use and increased yield present a major advantage. Starting with short chain polyesters of molecular weight about 1000, and continuing the polycondensation reaction to a molecular weight above 1500, would result in a 2-5 per cent weight loss due to the water that needs to be separated. This can be easily calculated from the decrease in acid number. The actual loss in practice is probably much higher due to the azeotropic loss of diols along with water. Using the chain extension method described in this work there is also an increase in the weight of the product. The total polymer yield therefore increases in favor of the producer and the price gain would offset the price of the extender that needs to be used. The reduction in labor and energy costs when the overall reaction time is reduced from 20 hours to 6-7 hours will depend on the actual scale of the reaction and the design of the reactor.

As a conclusion of this work, the chain extension concept is proposed to be applied to the manufacture of unsaturated polyesters. Decreasing the production time and increasing the yield of the polyester in industrial applications is of utmost importance. Renewable source extenders seem to be promising in scientific and/or industrial applications.

The outlook of this project is in designing and proposing new chain extenders which will add positive aspects to the manufacture and tailoring of unsaturated polyesters in order to better respond to the challenging demands of our rapidly developing industry as well as to the environmental threats our planet faces today.

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