Chain Extension Reactions of Unsaturated Polyesters with Epoxy Compounds

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ABSTRACT: Unsaturated polyesters (UPE) were chain extended with three different epoxy group containing compounds. The molecular weight increase was monitored using gel permeation chromatography (GPC). The polymers obtained were characterized by FTIR and ^{1}H NMR, and styrene solubility and gel time. The polyesters were then diluted with styrene and cured with a radical initiator and compared with a commercial reference polyester. Thermal and mechanical properties of the cured polyesters were characterized by dynamic mechanical analysis (DMA) and thermal gravimetric analysis (TGA). The results show that UPE can be chain extended with epoxy containing compounds which substantially shortens the condensation polymerization during manufacture, without compromising their thermal and mechanical properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1184–1191, 2009

Key words: chain; crosslinking; mechanical properties, molecular weight distribution; polyesters

INTRODUCTION

Unsaturated polyesters (UPE) are the most widely used liquid resins in composite applications worldwide. They are commonly used in construction, transportation, and marine industries as composites with glass fiber. These low molecular weight polymers (M_W 1500–3000) are usually dissolved in vinyl monomers like styrene to facilitate molding or shaping of the resin into a desired form before curing to rigid solids. Typical applications are in fiberglass reinforced boat hulls, construction panels, pipes, automotive parts, sports equipment, and wind generator blades.[1]

Industrial manufacture of UPE involves the condensation polymerization of phthalic anhydride and maleic anhydride with suitable diols[2] (Fig. 1). Although the initial feed ratio of the monomers in the UPE used in this study was not disclosed by the producer, ^{1}H NMR analysis indicates the following monomer molar ratios: Phthallic anhydride, 1.0; maleic anhydride, 0.33; propylene glycol, 0.63; and ethylene glycol, 0.70.

Condensation polymerization needs to be pushed toward the products by the removal of water so that a reasonable molecular weight of around 1500 can be achieved. This requires long reaction times, high temperature, and application of vacuum. Sixteen hours of reaction time, 220°C and 10 mmHg are commonly used conditions. All of these contribute to the cost of manufacture, discoloration of the product, and loss of diol due to evaporation (with environmental problems) which constitute the main problems in industrial manufacture of UPE. The unsaturated polyester is then dissolved in the reactive diluent styrene. The molding process involves the introduction of fiber reinforcement such as glass fiber and a free radical initiator which crosslinks the polyester chains through polystyrene crosslink segments and gives a rigid, load bearing thermoset resin.

In terms of production cost and efficiency, methods that shorten the production time and provide milder reaction conditions would be valuable. Chain extension reactions are an effective way of shortening production times. In this strategy, the polyesterification is carried out to a lesser extent, and the oligomers obtained are chain extended with a suitable chain extender molecule to reach the desired molecular weight. As less water is removed by condensation, the yield of the final polyester is also increased.

For the same purpose, chain extension reactions are already used in nylon-6 and polyesters like polyethylene terephthalate (PET). This reaction is especially useful when recycled, partially hydrolyzed PET is used to spin fibers.[3] Chain extenders are preferably low molecular weight monomers with at least two functional groups which react with the end groups of the unsaturated polyester to reach high molecular weights within relatively short times. The functional groups of the extender should be suitable for a fast reaction with both or either of the hydroxyl
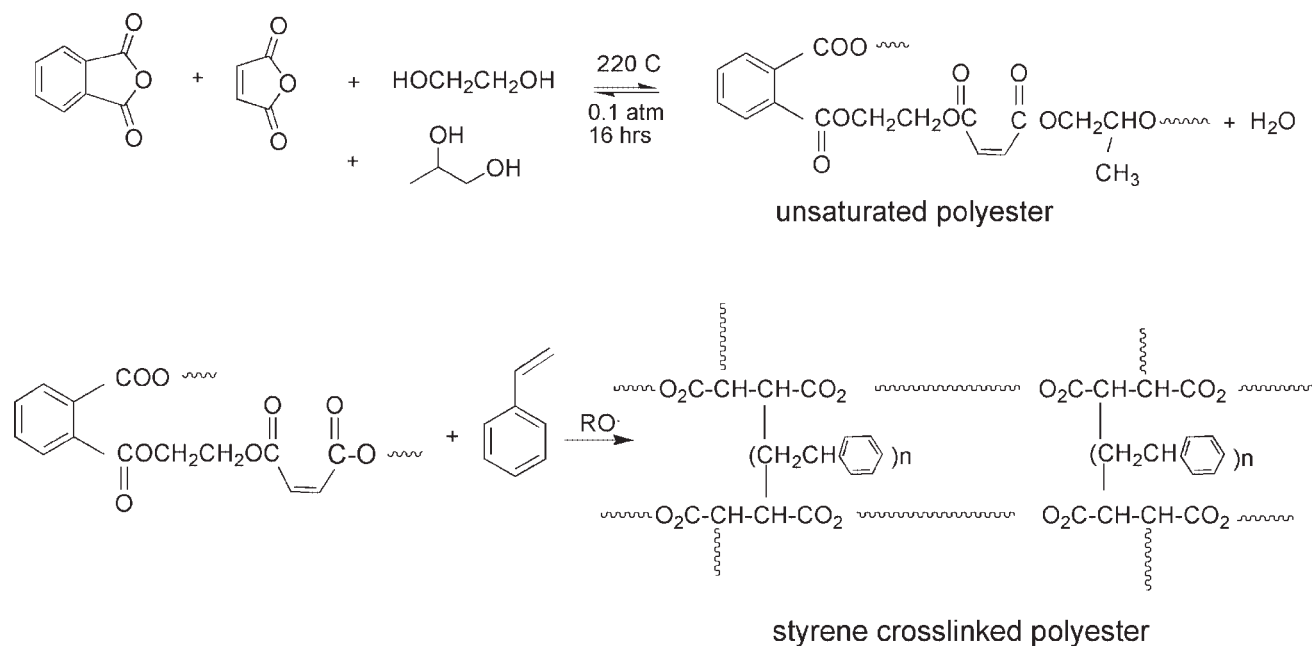
Figure 1 Synthesis and crosslinking of unsaturated polyesters.

and the carboxyl ends of the polyester, without producing by-products. Figure 2 shows the typical chain extension reaction.

In unsaturated polyester synthesis, acid number has been traditionally used as a measure of molecular weight. When chain extenders that react with the carboxylic end of the chains are used the relationship between acid number and chain length becomes meaningless. Therefore, another method of chain length measurement such as gel permeation chromatography is needed.

Difunctional molecules such as diepoxides, diisocyanates, dianhydrides, or bisoxazolines have been shown to increase the molecular weight of PET by reacting with its terminal groups.[4,5] Increasing the molecular weight of PET is also performed by solid state polycondensation; however, this method requires high vacuum and high temperatures for extended periods of time (12–20 h) leading to elevated production and capital costs.[5] Chain extenders are simply added to the polymer during extrusion and high molecular weights are reached within a short period. Diisocyanates like toluene diisocyanate have already been used on UPE to shorten reaction time.[6,7] The reaction of a commercial epoxide, diglycidylether of bisphenol A with UPE has been mentioned[8]; however, reaction time and molecular weight increase relations are not monitored. In this work, we carefully examined the correlation between chain extender amount, reaction time, reaction conditions, and the molecular weight increase.

Chain extenders, although present in small amounts, can alter solubilities, gel times and finally the thermal and mechanical properties of UPE. There-

fore, at the end of chain extension reactions, mechanical properties were examined and compared with a proven standard unsaturated polyester. The chain extenders employed are shown in Figure 3.

EXPERIMENTAL

Materials

Starting materials for chain extension reactions were short-chain UPE with an acid number of 80 and molecular weight of about 500–700. These short-chain oligomers were taken from the reactor at the 6th hour of a 16 h industrial UPE synthesis. These oligomers were supplied by Cam Elyaf A.Ş. (Istanbul, Turkey), a major producer of polyesters in Turkey. Diglycidyl ether of bisphenol A was a commercially available Epon 828 epoxy resin. 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). GPC samples
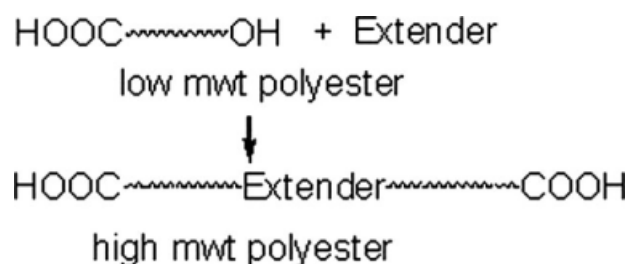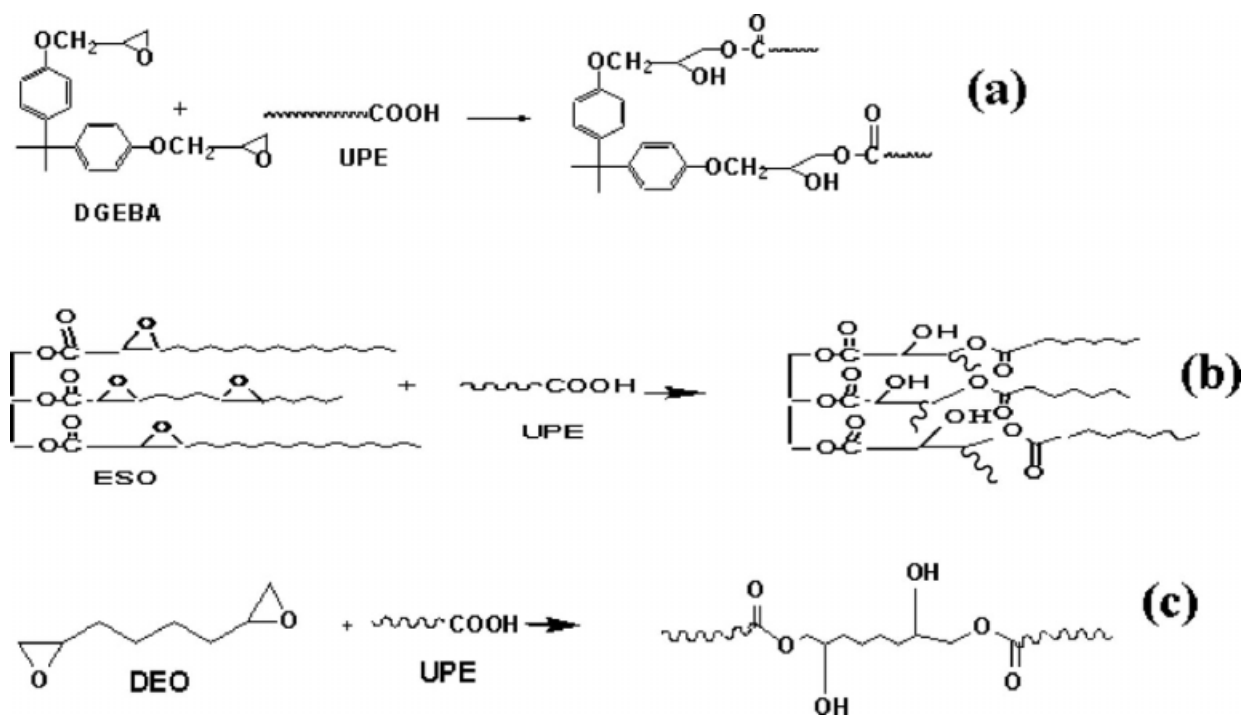

Figure 2 Typical chain extension reaction for an extender that reacts with hydroxyl end groups.

Figure 3 Diepoxy chain extenders (a) diglycidyl ether of bisphenol A (DGEBA, Epon 828), (b) epoxidized soybean oil (ESO), (c) 1,2;7,8-diepoxyoctane (DEO).

were prepared by dissolving the unsaturated polyester samples in tetrahydrofuran, bought from J. T. Baker.

Chain extension reactions

Typical reactions were done in bulk and at temperatures between 130 and 160°C. Short-chain UPE, diepoxide, and 1% AMC-2 catalyst were heated and stirred for a given time. The sample was cooled to 100°C and was dissolved in styrene to give a 65% solids solution. Finally this resin was molded and cured at room temperature using 2% MEKP and 0.25% Cobalt naphtanate (6% solution in dibutyl phtallate) to obtain the unsaturated polyester samples, to be used for thermal and mechanical investigations.

Instruments

In this work, the molecular weight increase was monitored utilizing gel permeation chromatography, a Viscotec VE-2001 (GPC max) Analysis system (Viscotek, Houston, TX) with a PL Gel 5 μm MIXED-C Column that was calibrated against polystyrene standards. ^{1}H NMR spectroscopy was run using Varian Mercury-Vx 400 MHz NMR Instrument (Varian Associates, Palo Alto, CA). The infrared spectroscopy was run using Perkin-Elmer 1600 Series FTIR instrument (Perkin–Elmer, Massachusetts, USA). The DMA tests were done using DMA Q800, TA Instruments (New Castle, DE) in single cantilever mode at a frequency of 1 Hz

and at a heating rate of 3°C/min. Thermal gravimetric analyses were carried out using "Thermal Analyses" Q-50 Instrument, TA Instruments (New Castle, DE) with a heating rate of 10°C/min starting from room temperature (25°C) to 600°C where nitrogen gas was purged at a rate of 60 mL/min.

Investigation of optimum weight ratios for the extenders

The investigation of optimum weight ratios for the extenders is discussed in the Table I.

TABLE I
Investigation of Optimum Weight Ratio for the extenders

Run	Extender	UPE/extender wt/wt ratio	Temperature (°C)	M_n reached in 120 min
1	DGEBA	4/1	100	1200
3	DGEBA	8/1	130	1300
4*	DGEBA	8/1	160	1920
5	DGEBA	12/1	130	625
6	ESO	2.2/1	130	Gelled
7	ESO	3/1	130	894
8	ESO	4/1	160	Gelled
9*	ESO	5/1	160	1015
10	DEO	10/1	160	1980
11*	DEO	10/1	140	1970

^{a}Run numbers 4, 9, and 11 were chosen as the best set of conditions.
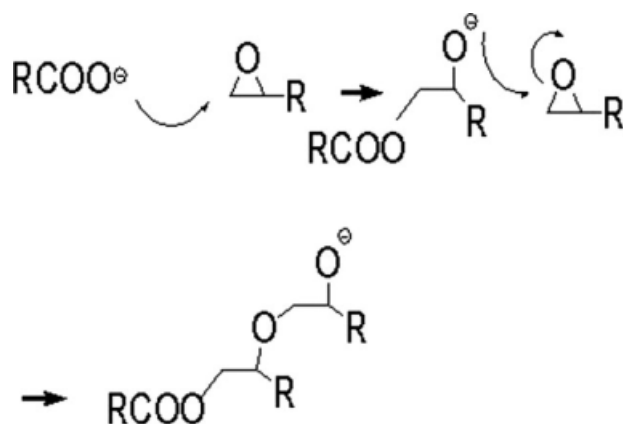
Figure 4 Polymerization of epoxide functionalities.

RESULTS AND DISCUSSION

Chain extension with diglycidylether of bisphenol A (DGEBA-UPE)

Diglycidylether of bisphenol A, has been used in chain extension of PET, where it gave satisfactory results by reactive blending.[9] Products were characterized by carboxylic end group analysis, intrinsic viscosity, and 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 diepoxide extenders used 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.[10–12]

The stoichiometric amount of the extender needed was calculated from the amount of the carboxylic acid end groups in the sample as determined by the acid number.

DGEBA led to a satisfactory molecular weight increase by using one equivalent of epoxy groups per carboxylic end groups of the UPE. However, we also wanted to go to lower DGEBA amounts with the aim of increasing the molecular weight of the polyester sufficiently in a short time by using the least possible amount of extender. Various weight ratios were examined and the optimum weight ratio was found as 12% extender by weight.

When PET is chain extended with DGEBA, very low amounts of DGEBA gave good results. PET has a much higher molecular weight than UPE, therefore in the case of PET 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 therefore higher amounts of chain extender are required to reach the desired molecular weight.

Epoxides are known to give an undesirable ring opening polymerization through epoxide functionalities as shown in Figure 4.

AMC-2 catalyst, a product of Aerojet Fine Chemicals, is claimed (1) to prevent homopolymerization of epoxy compounds and (2) to increase the rate of carboxylic acid-epoxy reactions. Therefore, AMC-2 catalyst was used in 1% weight ratio whenever diepoxy extenders were employed. Besides, to minimize possible polymerization through epoxy functionalities the extender was added to the reaction medium slowly within a period of 30 min. The reactions were done in bulk and samples were taken periodically.

Molecular weight increases of the UPE using DGEBA at 130 and 160°C are given in Table II ("Comparisons of the Three Chain Extended Polyesters" section) and Figure 5 shows the increase of the molecular weight of UPE with 12% DGEBA at 160°C.

At 130°C the number average molecular weight increased from 750 to 1300 within 2 h. However, when the reaction was repeated at 160°C, for the same sample the M_n value exceeded 1900 within 2 h; moreover, at the end of 1 h the M_n value was 1700 which coincides with a satisfactory chain length for commercial UPE. At the end of the 16 h 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. Figure 5 illustrates the rapid increase of molecular weight at 160°C. When the extender monomer is added to the reactor at the end of the 6th hour during manufacture, one should expect to go to the desired molecular weight within only one more hour. Thus the desired molecular weight would be obtained in seven instead of 16 h.

The ^{1}H NMR spectrum of the polymer was taken and compared with the spectrum of the standard, commercial polyester. Peaks due to phenyl groups of DGEBA (7 ppm); protons originating from fumaric acid (2 ppm) and peaks due to methyl groups of DGEBA (1.5 ppm) were observed. These peaks were of course in addition to the peaks of commercial unsaturated polyester: 7.5–8 ppm due to the phthalate; 4.3 ppm due to ethylene glycol; and 6.8 ppm due to

TABLE II
GPC Results Obtained with Three Different Extenders at Various Temperatures

| Time (min)	M_n extended with DGEBA 130°C	M_n extended with DGEBA 160°C	M_n extended with ESO 160°C	M_n extended with DEO 140°C
0	750	800	470	700
30	915	1360	–	–
60	1180	1700	810	–
90	1230	1960	–	–
120	1300	1920	1015	1970
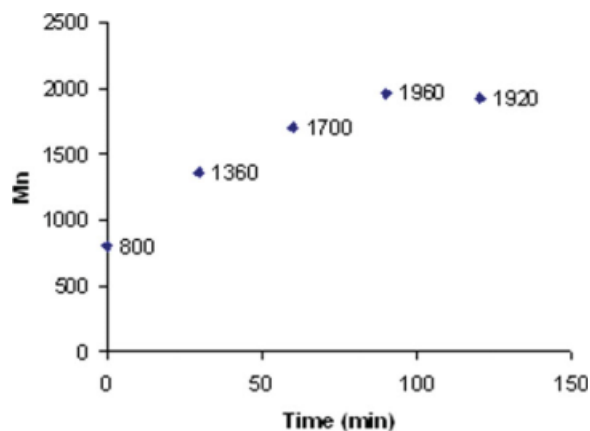
Figure 5 Molecular weight increase of UPE with DGEBA at 160°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the vinyl protons of the fumarate. Propylene glycol which is also present as the second diol gives rise to two types of peaks; they appear at 5.3 and 1.2 ppm. These results can be seen in Figure 8.

The chain extended polymer showed very similar solubility in styrene when compared with the commercial UPE. In industrial applications, UPE are dissolved in styrene in a 65 : 35 wt:wt ratio. Therefore, the chain extended samples were diluted with styrene to give a 65% solids solution and cured with MEK and cobalt naphtanate. The ease of solubility of the chain extended UPE in styrene allowed any desired final viscosity to be easily achieved. When standard amounts of initiator and accelerator were used the gel time was 10 min compared with the gel time of 15 min for the commercial product. The cured polymers were postcured in an oven at 80°C for 3 h and then examined thermally and mechanically.

The glass transition temperature for the polyester extended with DGEBA was found to be 74°C (Table III). This value is comparable with the T_g value of
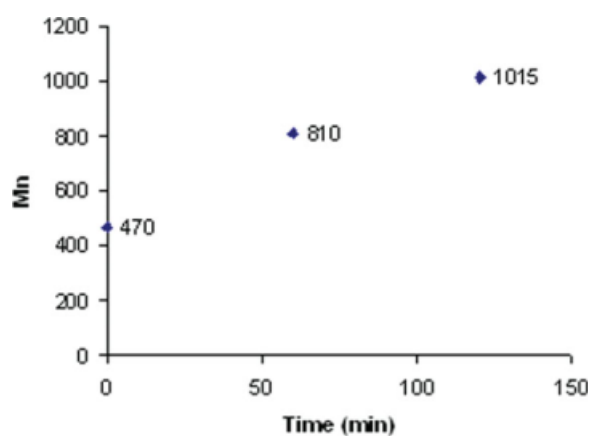
Figure 6 Molecular weight increase of UPE with ESO at 160°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the commercial polyester (88°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. Therefore, we concluded chain extension with DGEBA which gave satisfactory molecular weight increase without altering thermal and mechanical properties of the polyester.

Chain extension with epoxidized soybean oil (ESO-UPE)

ESO (M_W around 900) 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 therefore having environmental benefits. The ESO sample used in this work contains an average of 4.2 epoxy groups per triglyceride as determined by HI titration. Compared with difunctional epoxides like DGEBA and 1,2;7,8-diepoxyoctane, ESO can bring an advantage in chain extension reactions;[13–15] 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. In the case of ESO, the reaction must be run at a higher temperature because in ESO the epoxy groups are internal and therefore less reactive. Various weight ratios were tried and the optimum weight ratio was found to be 20%. The reaction was run at 160°C. ESO was added slowly to the reaction medium within 45 min, AMC-2 catalyst was added in 1% weight ratio.

The M_n value increased from 470 to 1015 within 2 h as shown in Figure 6.

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 h. 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.

TABLE III
Comparison of T_g and Storage Modulus Values of Chain Extended Unsaturated Polyesters as Obtained from DMA Tests

| UPE	T_g (°C)	Storage modulus (MPa)
Commercial UPE	88	3000
Extended with DGEBA	74	2650
Extended with ESO	66	1650
Extended with DEO	89	2875
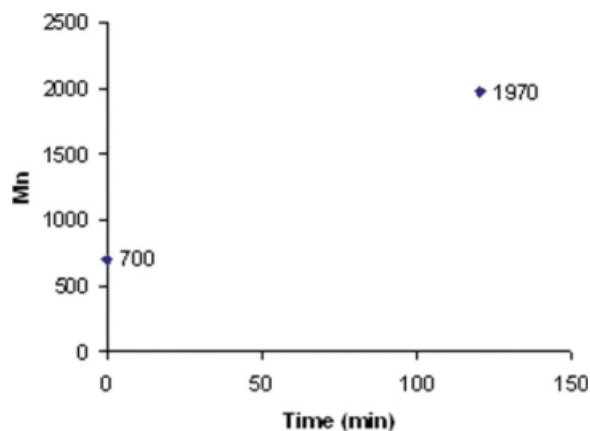
Figure 7 Molecular weight increase of UPE with DEO at 140°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In the ^{1}H NMR spectrum of the 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. These results can be seen in Figure 8.

Styrene solubility of the ESO-chain extended polymer was similar to the commercial unsaturated polyester. When this unsaturated polyester resin was cured using MEKP and Cobalt naphtanate the gel time was measured as 6 min. The cured polymers were postcured in oven at 80°C for 3 h and thermal and mechanical tests were carried out.

The glass transition temperature for the ESO extended polyester was found to be 66°C (Table III).
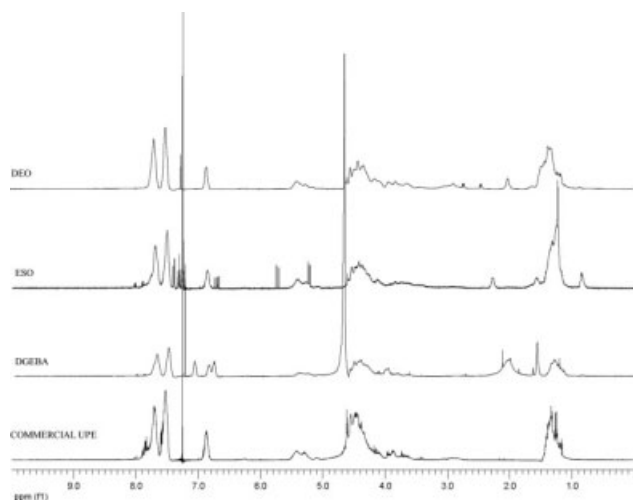
Here the decrease in T_g from 88°C (for the commercial polyester) to 66°C could be attributed to the plasticizing effect of ESO. The storage modulus of the ESO chain extended polyester decreased to a value of 1650 MPa from 3000 MPa for the commercial polyester (Fig. 9).

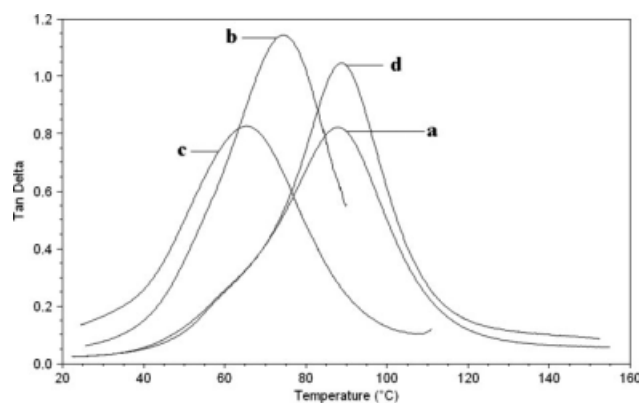## Chain extension with 1,2;7,8-diepoxyoctane (DEO-UPE)

The advantage of this extender is its relatively small molecular weight, which allows a lower weight percentage to be used. However, its high price is a burden in commercial applications.

AMC-2 catalyst was employed in a 1% weight ratio. DEO was used in 10% weight ratio and the reaction was run at 140°C. The molecular weight increase was examined using GPC. Within 2 h the M_n value increased from 700 to 1970 (Fig. 7). This is the highest increase among all extenders examined at the end of 2 h at 140°C. These results are illustrated in Table II.

In the ^{1}H NMR spectrum of the chain extended polyester in addition to the usual polyester peaks, peaks due to the CH$_2$ groups of diepoxyoctane were observed at 2.5 ppm (Fig. 8).

The polymer extended with DEO was also found to be soluble in styrene and this unsaturated polyester resin was also cured using MEKP and Cobalt naphtanate. The gel time was measured as 12 min. The cured polymers were postcured at 80°C for 3 h and tested for thermal and mechanical properties.

The glass transition temperature for the polyester extended with diepoxyoctane was found to be 89°C (Table III). 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

Figure 8 ^{1}H NMR spectra of commercial and chain extended polyesters.

Figure 9 T_g and tan delta values of the three chain extended polyesters and the commercial polyester (a) commercial UPE $T_g = 88$°C, (b) extended with DGEBA $T_g = 74$°C, (c) extended with ESO $T_g = 66$°C, (d) extended with 1,2;7,8-diepoxyoctane $T_g = 89$°C.

storage modulus was found to be 2875 MPa (Fig. 9), which is very close to that of commercial UPE.

Comparisons of the three chain extended polyesters

Table II shows the molecular weight increase of the UPE extended with three different extenders at various temperatures. The M_n of commercial UPE, manufactured by a 16 h condensation reaction is 1500.

In each chain extension reaction, the addition of the extender to the polyester chain is verified with ^{1}H NMR spectroscopy. These results can be seen in Figure 8.

The glass transition temperature values were obtained from DMA tests for the three chain-extended polyesters and the commercial polyester. These values are compared in Figure 9.

The storage modulus values of the chain extended polymers showed the expected behavior. UPE chain extended with DGEBA and DEO exhibited similar storage modulus values to that of the commercial polyester. However, the UPE chain extended using ESO 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 10.
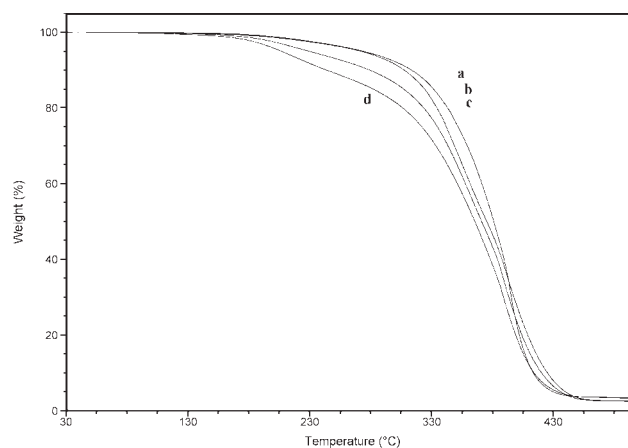
T_g and storage modulus values are summarized and compared in Table III.

Thermal stability tests were performed for the chain extended polymers. Figure 11 illustrates the obtained results.

TGA results show that the temperatures corresponding to 5% weight loss is 274.5 and 272.4 for the commercial UPE and the UPE extended with diepoxyoctane, respectively. For the other two chain extended polyesters, this value dropped to 229.98°C (ESO) and 207.54°C (DGEBA). As shown in Figure 3 use of epoxides as chain extenders inevitably intro-
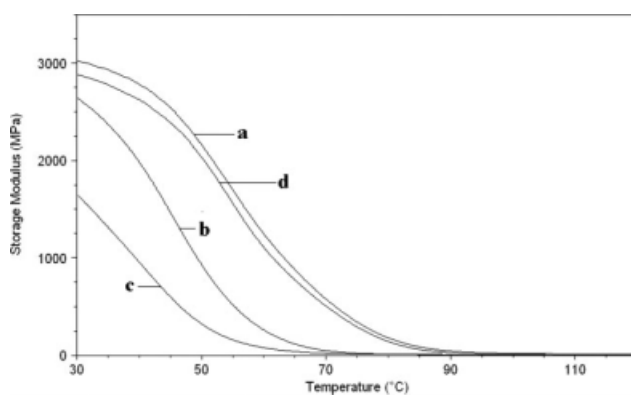
Figure 11 TGA thermograms of unsaturated polyesters (temperature of 5% weight loss) (a) commercial UPE (274.50°C), (b) extended with DEO (272.40°C), (c) Extended with ESO (229.98°C), (d) extended with DGEBA (207.54°C).

duces a hydroxyl group on the polymer backbone. The hydroxyl group enables the chain to decompose through a dehydration route. Therefore, in the TGA results the chain extended samples show a weight loss at a slightly lower temperature than the commercial UPE, which does not have hydroxyl groups on the backbone. For all chain extended UPEs the onset of this decomposition is around 200°C, a temperature which an unsaturated UPE finished part is very unlikely to experience.

CONCLUSIONS

In this work, UPE were chain extended using di- or multifunctional epoxy compounds. 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 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. The chain extension can be carried out in the polyesterification reactor and proceeds without by-products. 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. These results are beneficial in industrial applications.

Figure 10 Storage modulus values of the three chain extended polyesters and the commercial polyester (a) commercial UPE, (b) extended with DGEBA, (c) extended with ESO, (d) extended with diepoxyoctane.

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