

Blocked Isocyanates and Isocyanated Soybean Oil as New Chain Extenders for Unsaturated Polyesters

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ABSTRACT: Two different blocked isocyanates, diphenylmethane-bis-4,4'-ethyleneurea and diphenylmethane-bis-4,4'-carbamoil- ϵ -caprolactam, and isocyanated soybean oil were used as chain extenders for low-molecular-weight unsaturated polyesters. Oligomeric polyesters (molecular weight = 600–700), taken from a manufacturing process in the sixth hour of a 16-h polyesterification reaction, were reacted with these chain extenders, and the desired chain lengths (molecular weight = 1000–1500) were obtained in a very short time through the reaction of the chain extenders with the polyester end groups. The increase in the molecular weight was monitored with gel permeation chromatography. The obtained polymers were characterized with Fourier transform infrared and $^1\text{H-NMR}$ and with styrene

solubility and gel time measurements. After dilution with styrene, the polyesters were cured with a radical initiator. The thermal and mechanical properties of the cured polyesters were examined with dynamic mechanical analysis and thermogravimetric analysis tests and then compared to those of a commercially available reference unsaturated polyester. The results show that unsaturated polyesters can be chain-extended with these compounds to shorten the polyesterification time substantially without alterations of the styrene solubility or gel time of the polyesters. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1102–1110, 2011

Key words: crosslinking; mechanical properties; polyesters; renewable resources

INTRODUCTION

Unsaturated polyesters (UPEs) are very widely used in composite applications.¹ They are commonly employed in construction, transportation, and marine industries as composites with glass fibers. These low-molecular-weight polymers (molecular weight = 1500) are usually dissolved in vinyl monomers such as styrene to facilitate the molding or shaping of the resins into desired forms before they are cured into rigid solids. Typical applications include fiberglass-reinforced boat hulls, construction panels, pipes, automotive parts, sports equipment, and wind-generator blades.²

Industrial production of UPEs involves the condensation polymerization of phthalic anhydride and maleic anhydride with suitable diols.¹ Condensation polymerization needs to be pushed toward the products by the removal of water so that the desired molecular weight of approximately 1500 can be achieved. This requires long reaction times, high temperatures, and the application of vacuum. A reaction time of 16 h, 220°C, and 10 mmHg are commonly used conditions. The required removal of water reduces the yield of

the product. All these conditions contribute to the cost of manufacture, the discoloration of the product, and the loss of diol due to evaporation (with environmental problems), which constitute the main problems in the industrial production of UPEs.³ When the desired molecular weight of approximately 1500 is reached (usually determined by acid number analysis), the mixture is cooled, and the UPE is dissolved in the reactive diluent styrene. The molding process involves the introduction of fiber reinforcements such as glass fibers and a free-radical initiator, which crosslinks the polyester chains through polystyrene crosslink segments and yields a rigid, load-bearing thermoset resin.

The severe reaction conditions during polycondensation and the long reaction time could be avoided by the use of a chain extender able to increase the molecular weight of the polyester without a condensation reaction. Such a chain extender should be a low-molecular-weight monomer with at least two functional groups that can react with the end groups of the UPE oligomer. The polyester oligomeric chains would be extended, and this would lead to the desired molecular weight in a much shorter time versus the usual polycondensation reaction. The functional groups of the extender should be suitable for a fast reaction with both or either of the hydroxyl and carboxyl ends of the polyester, preferably without the production of byproducts. Chain extension by a chemical reaction that does not produce water as a byproduct would automatically increase the

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yield of the product. Reducing the reaction time and simultaneously increasing the yield of the final product would be a major advantage in industrial applications.

Various difunctional molecules, such as diisocyanates, diepoxides, dianhydrides, and bisoxazolines, have been shown to increase the molecular weight of poly(ethylene terephthalate) (PET) by reacting with its terminal groups.^{4,5} The practice is especially favored when recycled PET, which has been partially hydrolyzed, is to be spun as a fiber. Chain extenders are simply added to the polymer during extrusion, and high molecular weights are reached within very short periods. PET has a much higher molecular weight than UPEs, so a few extension reactions lead to large increases in the molecular weight. Partially hydrolyzed PET chains are long enough that even with a low quantity of an extender, regaining the desired molecular weight is not difficult. However, short-chain UPEs have much lower molecular weights and therefore have a higher concentration of end groups; this requires higher amounts of the chain extender to reach the desired molecular weight.

Three epoxy compounds—diglycidyl ether of bisphenol A; epoxidized soybean oil, and 1,2,7,8-diepoxyoctane—were investigated as chain extenders earlier in our laboratories.³ These extenders readily reacted with the carboxyl end groups of the polyester chains and showed promising results; therefore, their use in the manufacture of UPEs was proposed.

In this work, three new extenders were investigated for the same purpose: two aromatic blocked diisocyanates, diphenylmethane-bis-4,4'-ethyleneurea (MDI-E) and diphenylmethane-bis-4,4'-carbamoil- ϵ -caprolactam (MDI-C), and one plant-oil-based diisocyanate, isocyanated soybean oil (SONCO). The production of urethanes through the reaction of isocyanates with a hydroxyl group is well known. In fact, toluene diisocyanate has been used to increase the viscosity of commercially available UPE resins. However, here, the aim was not to shorten the reaction time; finished high molecular-weight UPE samples were used, and the viscosity of the final product was found to increase.⁶ The reaction of isocyanates with carboxylate groups has been subjected to less attention. Nevertheless, examples of isocyanate/carboxylic acid reactions yielding amides and carbon dioxide, as shown in Figure 1, can be found in the literature.⁷⁻⁹

Blocked isocyanates have widespread use in many types of coatings, such as automotive, maintenance, and industrial finishes. An excellent review of blocked isocyanates was provided by Wicks and Wicks.¹⁰

During the manufacture of UPEs, the acid number is generally used as a measure of the molecular weight, but in this study, the increase in the molecu-

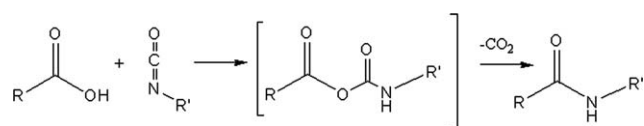


Figure 1 Reaction of carboxylic acids with isocyanates.

lar weight was followed by gel permeation chromatography (GPC). When extenders that react with carboxylic acid end groups are used, a decrease in the acid number will not necessarily mean a molecular weight increase. This is one important reason that the increase in the molecular weight was monitored with GPC rather than the acid number. Short-chain UPE oligomers (with an acid number of 80 and a molecular weight of 700) were used as the starting materials. Samples of low-molecular-weight UPEs were supplied by a major local UPE manufacturer and were taken from the reactor at the sixth hour of a 16-h polyesterification reaction. The sixth hour was chosen arbitrarily and was thought to be an appropriate time for the addition of the extender.

Even though chain extenders are usually used in small amounts, they can alter the solubility, the gel time, and finally the mechanical and thermal properties of UPEs. Therefore, the mechanical and thermal properties of the final crosslinked products were examined and compared to those of a reference commercial UPE. The reference UPE was obtained in the usual way by the continuation of the polycondensation to the 16th hour. Thus, the low-molecular-weight UPEs used in this work and the high-molecular-weight reference UPE had the same feed formulation. The chain extenders employed in this work and their reactions are shown in Figure 2.

The first two extenders, MDI-E and MDI-C, are commercially available and are mainly used as crosslinking agents to improve the bonding strength of various adhesives.^{11,12} They are sold as emulsions; however, in this study, they were precipitated from the emulsions and were used in a solid form.

The other chain extender used in this work, SONCO, was synthesized in our laboratories and had already been employed in some of the previous research projects of our group.¹³ The importance of SONCO as a chain extender lies in the fact that it originates from a plant oil, can easily be synthesized, and biodegrades easily.

EXPERIMENTAL

Materials

The starting materials for the chain-extension reactions were short-chain UPEs with an acid number of 80 and a molecular weight of approximately 600–700. These short-chain polyesters were taken from

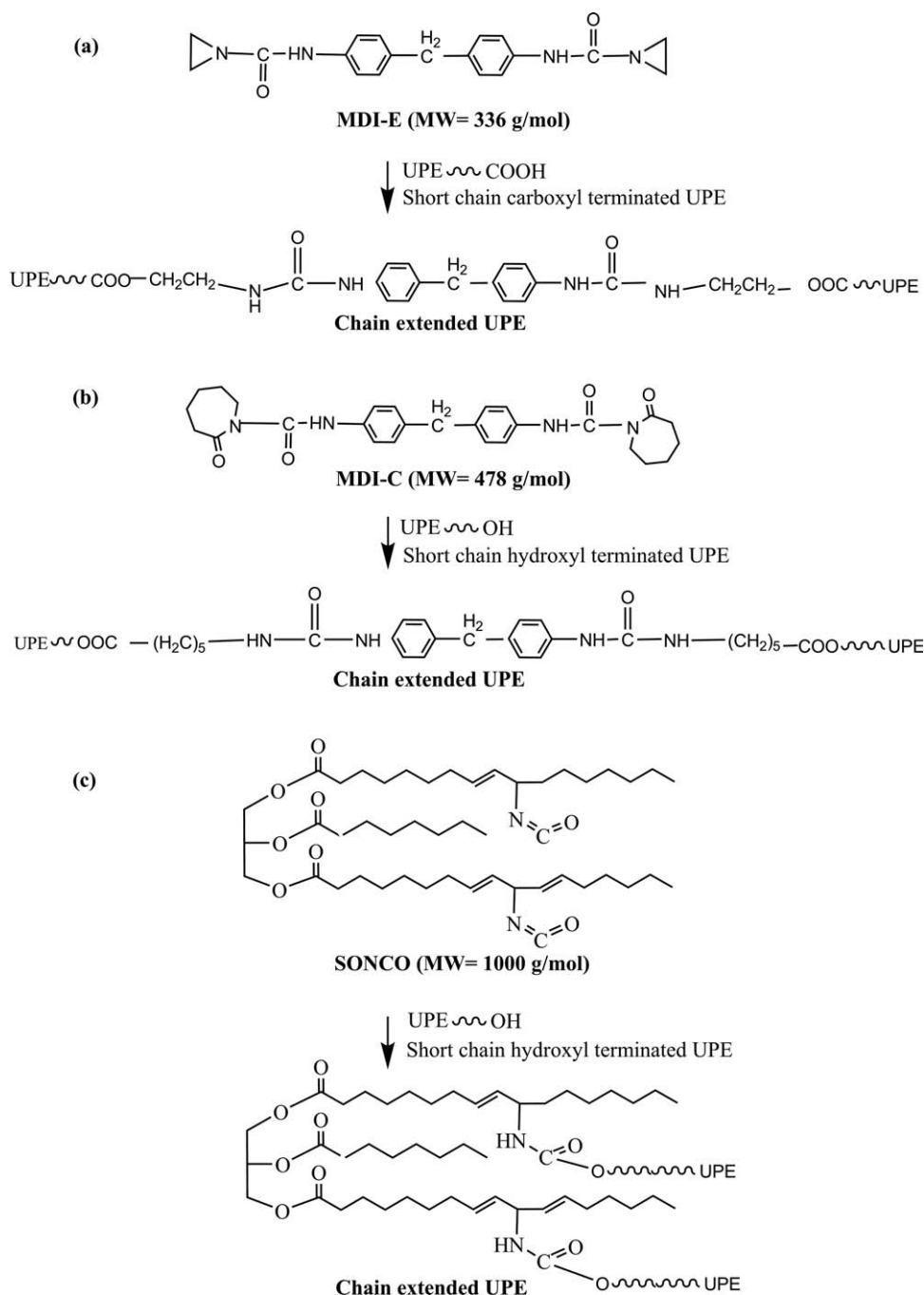


Figure 2 Blocked isocyanates and SONCO as chain extenders: (a) MDI-E, (b) MDI-C, and (c) SONCO.

the reactor in the sixth hour of a 16-h industrial UPE synthesis reaction. They were supplied by Cam Elyaf A.S. (Istanbul, Turkey) a major producer of polyesters in Turkey. MDI-E and MDI-C (water emulsions) were supplied by Meisei Chemical Works, Ltd. (Kyoto, Japan), and Organik Kimya A.S. (Istanbul, Turkey) with the commercial names SU-125F and DM 3031, respectively. The addition of a 10% CaCl_2 (aqueous) solution produced phase separation. Cen-

trifugation, decantation, and drying yielded the desired blocked isocyanate.

GPC samples were prepared by the dissolution of the UPE samples in tetrahydrofuran, which was bought from J. T. Baker (Deventer, Holland).

Synthesis of SONCO

SONCO was synthesized from allylic brominated soybean oil and AgCNO .¹³ $^1\text{H-NMR}$ analysis of the

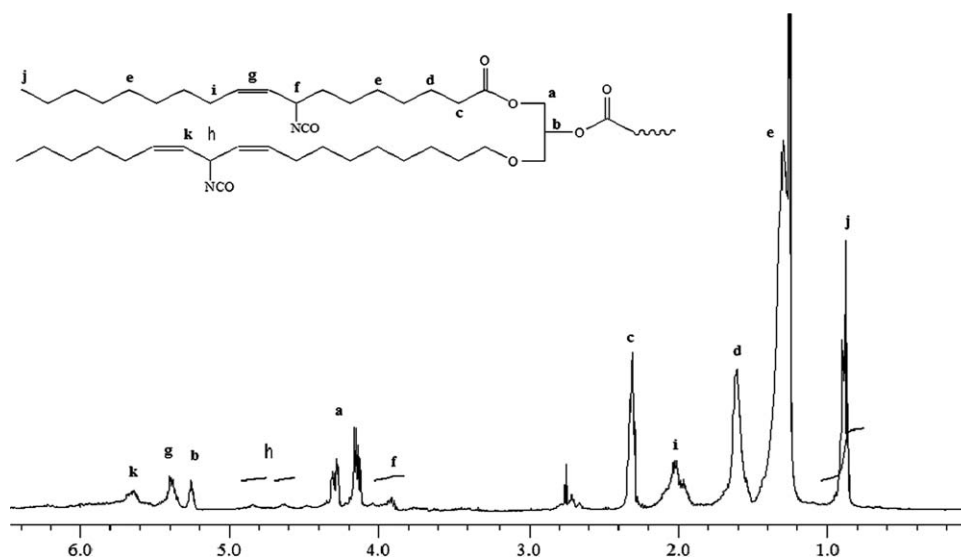


Figure 3 $^1\text{H-NMR}$ spectrum of SONCO.

product indicated the presence of 2.1 isocyanate groups on average per triglyceride molecule. This number was determined by the summation of 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 the double allylic α proton of the NCO group. The sum of these integration values was compared to the triglyceride CH_3 protons at 0.8 ppm (taken to be nine protons per triglyceride).

The peaks belonging to SONCO were as follows: 0.8 ($-\text{CH}_3$), 1 (triplet, $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$), 1.2–1.4 ($-\text{CH}_2-$), 1.6 [β to carbonyl group, $-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{OCH}_2-$], 2.25 [α to carbonyl group, $-\text{CH}_2-\text{C}(=\text{O})-\text{OCH}_2-$], 2.75 (double allylic position, $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$), 3.9 ($\text{CH}=\text{CH}-\text{CH}-\text{NCO}$), 4.1 and 4.3 (multiplet, glycerin protons, $-\text{O}-\text{CH}_2-$), 4.5 [broad, $-\text{CH}=\text{CH}-\text{CH}(\text{Br})$], 4.8 [$-\text{CH}=\text{CH}-\text{CH}(\text{NCO})-\text{CH}=\text{CH}-$], 5.25 (center proton of glycerin, $-\text{O}-\text{CH}_2-\text{CHO}-\text{CH}_2\text{O}-$), 5.4 [$\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}(\text{NCO})$], 5.8 [$-\text{CH}=\text{CH}-\text{CH}(\text{NCO})-\text{CH}=\text{CH}-$].

Chain-extension reactions

The chain-extension reactions of short-chain polyesters with the chain-extending reagent were run in bulk and under nitrogen at temperatures between 100 and 120°C with 0.05% 1,4-diazabicyclo[2.2.2]octane (DABCO) as the catalyst. Table I shows the weight ratios of the chain extenders to the UPEs investigated in this work.

At the end of the reactions, the obtained resins were cooled and dissolved in styrene to produce a 65% solid solution; finally, the resins were cured at room temperature with 2% methyl ethyl ketone peroxide and 0.25% cobalt naphthenate (a 6% solution

in dibutyl phthalate) and then postcured at 80°C for 3 h. Gel times were measured as the time of first gel formation at the ambient temperature according to ISO standard 2535 (2001).¹⁴

Instruments

The molecular weight increase was monitored by GPC with a VE-2001 (GPCmax) analysis system (Viscotek, Houston, TX) with a PLgel 5- μm mixed-C column that was calibrated against polystyrene standards.

THF was used as a solvent at room temperature with a flow rate of 1 mL/min. $^1\text{H-NMR}$ spectroscopy was performed with a Varian Mercury Vx 400-MHz NMR instrument (Varian Associates, Palo Alto, CA). Infrared (IR) characterization of the compounds was performed with a Thermo Nicolet 380 Fourier transform infrared spectrometer (Thermo Fischer Scientific, Waltham, MA) with the diamond attenuated total reflection accessory. The dynamic mechanical analysis tests were conducted between 20 and 180°C on $40 \times 12 \times 2 \text{ mm}^3$ samples with a TA Instruments Q800 dynamic mechanical analyzer (New Castle, DE) in a single-cantilever mode at a frequency of 1 Hz and at 25°C with a heating rate of 3°C/min. The

TABLE I
Weight Ratios for the Extenders

Run	Extender	Extender (wt %)	Temperature (°C)	M_n at 120 min
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

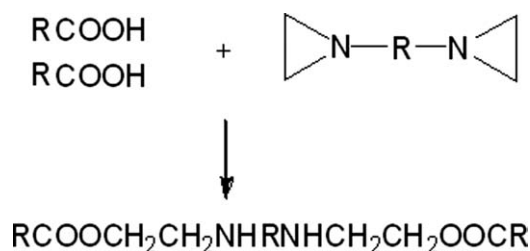


Figure 4 Reaction of MDI-E with carboxylic end groups by aziridine ring opening.

measurements range was room temperature to 155°C. Thermogravimetric analysis (TGA) was carried out with a TA Instruments Q50 thermal analyzer (TA Instruments, New Castle, DE) with a heating rate of 10°/min from room temperature to 600°C; nitrogen gas was purged at a rate of 60 mL/min.

RESULTS AND DISCUSSION

Chain-extension reactions and GPC results

Chain extension with MDI-E

At 100°C, aziridine-blocked crosslinkers such as MDI-E react through the ring opening of the aziridine group¹¹ by hydroxyl or carboxyl end groups of the UPE chain, but above 130°C, they deblock to produce methylene diphenyl diisocyanate and free aziridine, which is a low-boiling-point, toxic liquid. Figure 4 illustrates the reaction of carboxylic end groups by aziridine ring opening.

The chain-extension reactions were run at 120°C, at which the ring-opening mechanism dominated, and the reactions proceeded without liberation of byproducts. A dry sample of MDI-E was kept at 120°C for 2 h, and no weight loss was observed; this

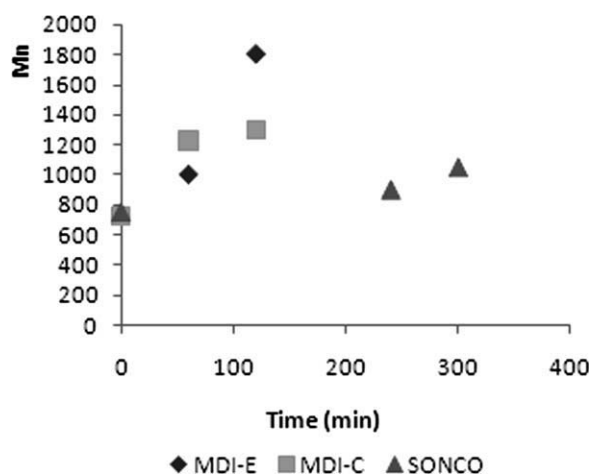


Figure 5 Molecular weight increase in UPEs with the three extenders.

TABLE II
Increasing M_n Values of the Three Polyesters

	M_n				
	0 min	60 min	120 min	240 min	300 min
MDI-E	725	1000	1800	—	—
MDI-C	730	1230	1300	—	—
SONCO	750	—	—	900	1050

meant that spontaneous decomposition to the isocyanate and aziridine did not take place.

Initially, for the chain-extension reactions, different amounts of MDI-E were tried, and a satisfactory molecular weight increase was obtained with the stoichiometric amount of the extender per carboxyl end group in the UPE. To investigate the effect of the amounts of the extenders, various weight ratios were tried, as shown in Table I.

The amount of the chain extender was progressively reduced, and a 5 % of the MDI-E or MDI-C chain extender was also found to yield the desired molecular weight within the same reaction time. As the aim was to use a minimal amount of the chain extender, only samples made with these chain extenders at a 5% were examined further. Figure 5 and Table II show the rapid increase in the molecular weight with 5% MDI-E at 120°C together with the other extenders.

At 120°C, the number-average molecular weight (M_n) increased from 725 to 1800 within 2 h. At the end of the 16-h industrial process, the standard commercial UPE reaches a molecular weight of approximately 1500; therefore, an M_n value 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 versus the standard polyesterification method.

Chain extension with MDI-C

MDI-C is a caprolactam-blocked methylene diphenyl diisocyanate used to promote the adhesion of rubber and other elastomers to textile fibers and cords such as polyester.¹² Caprolactam-blocked isocyanates do not deblock to methylene diphenyl diisocyanate and caprolactam at temperatures lower than 150–160°C.¹⁵ Therefore, at 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 (a or b),¹⁶ as shown in Figure 6.

Path (a) proceeds through the opening of the caprolactam ring and does not produce any byproducts, but path b produces free caprolactam. Any caprolactam that can be produced by path (b) will remain in the final product. As caprolactam is not a common

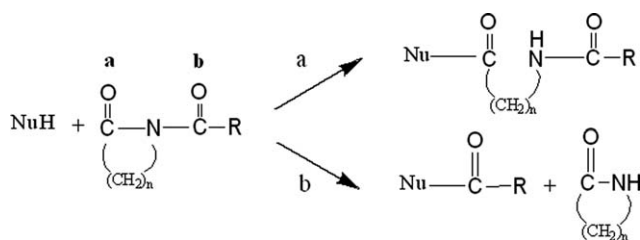


Figure 6 Reaction mechanisms of a caprolactam-blocked isocyanate with a nucleophile.

plasticizer for UPEs, there is no published work on its effect on the mechanical properties of UPEs. In this work, there was no evidence of plasticization because the thermal and mechanical properties of the MDI-C-chain-extended polyester remained close to those of the commercial polyester. Used in a 5% weight ratio, this chain extender increased the molecular weight from 730 to 1300 in 2 h at 120°C. These results are shown in Figure 5 and in Table II.

Chain extension with SONCO

SONCO obtained from soybeans is thought to be a promising candidate as a chain extender for UPEs. Other triglyceride-containing polymers synthesized in our laboratory biodegraded easily as shown by soil burial tests.¹⁷ SONCO has a molecular weight of approximately 1000 and contains an average of 2.1 isocyanate groups per triglyceride. In one of our earlier studies, SONCO successfully reacted with diols to yield polyurethanes.¹³

With only 2.1 isocyanate groups for every large triglyceride molecule, one has to use considerably more SONCO weightwise (vs the blocked isocyanates) to obtain reasonable chain extension. In the chain-extension reactions, SONCO was used in a weight ratio of 20% at 85–120°C. The use of 1,4-diazabicyclo[2.2.2]octane as the catalyst increased the reaction rate of the reaction as expected. M_n increased from 750 to 1050 within 5 h.

In our earlier work, epoxidized soybean oil, another soybean-oil-based renewable extender with 4.2 epoxy groups per triglyceride, produced a better molecular weight increase when it was used in the same weight ratio.³ Therefore, instead of adding more SONCO to the UPE, if the isocyanate number of SONCO (the number of isocyanate groups per triglycerides) could be increased, more effective chain extension could be expected. The molecular weight increase obtained with SONCO chain extension is shown in Figure 5 and in Table II.

Characterization

Although the initial feed composition of the monomers for the UPE used in this study was not dis-

closed by the producer, ¹H-NMR analysis indicated that the following monomers exist in the polymer: phthalic anhydride, maleic anhydride, propylene glycol, and ethylene glycol. The ¹H-NMR spectra of the chain-extended polyesters are shown in Figure 7. (The $-\text{CH}_3-$ protons arising from propylene glycol appear at 1.2 ppm; $-\text{CH}_2-$ protons of ethylene glycol and propylene glycol appear at 4.4 ppm; the $-\text{CH}-$ proton of propylene glycol appears at 5.3 ppm; fumarate vinyl protons appear at 6.8 ppm; and finally, the phthalate aryl protons appear at ca. 7 ppm in the aromatic region.) In UPE samples in which SONCO was used as an extender, peaks at 0.9 ppm belonging to the terminal methyl groups of SONCO could be identified. The fatty acid methylenes of SONCO gave rise to the large peak at 1.4 ppm, the small peak at 1.8 ppm was due to the protons β to the carbonyl, and the peak at 2.4 ppm was due to the protons α 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 contributed mostly aromatic protons, which fell in the same region as the polyester phthalate protons in the ¹H-NMR spectrum. Besides, in these cases, the extender amounts were so low that peaks arising from them could not be identified in the ¹H-NMR spectra.

The reference polyester and the chain-extended products were also characterized with IR spectroscopy. In all the IR spectra, the ester carbonyl could be identified at 1720 cm^{-1} . In the case of SONCO as the 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 was relatively high in comparison with the two blocked isocyanate extenders. The spectra are shown in Figure 8.

To be industrially applicable, a chain-extended UPE needs to have the same styrene solubility and the same gel time as commercial UPE. Therefore, in

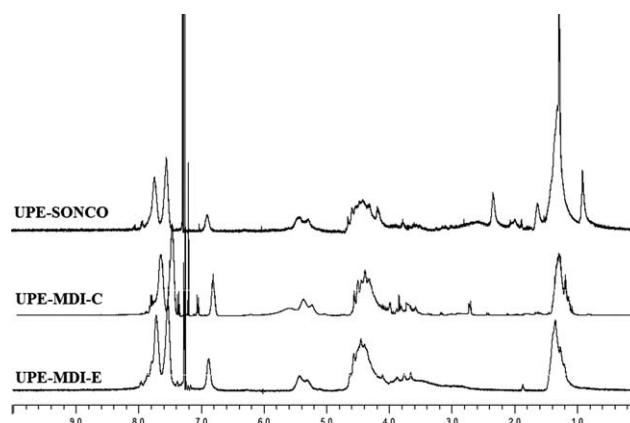


Figure 7 ¹H-NMR spectra of the chain-extended polyesters.

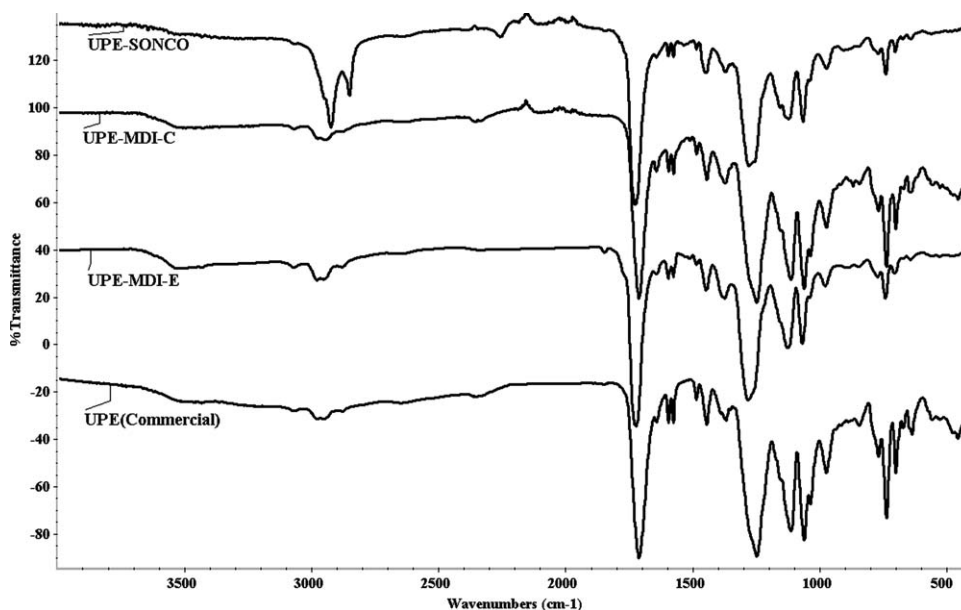


Figure 8 Fourier transform infrared spectra of the commercial and chain-extended polyesters.

each case, the styrene solubility and gel time were compared to those of a commercial reference product. Adhering to the industrially accepted ratio of 35% styrene, we first dissolved the polyester in styrene at 40°C and then stirred the mixture further at room temperature until a clear solution was obtained. The resin had a viscosity of approximately 600 cps, which was very similar to that of the commercial UPE. The measured gel times for the commercial product and the chain-extended polyesters can be seen in Table III. Gel time measurements gave a reproducibility of ± 2 min. Besides, the differences in the gel times for different UPEs obtained with different extenders were attributed to the various numbers of moles of extenders in the chains.

Mechanical and thermal analysis

Tan δ plots of commercial and chain-extended polyesters are shown in Figure 9. The actual values are shown in Table III.

The glass-transition temperatures (T_g 's) were taken as the maxima of the tan δ curves. The MDI-C-extended polyester exhibited T_g of 84°C and a stor-

age modulus 3250 MPa that were very close to those of the commercial polyester. For the commercial polyester, these values were 88°C and 3000 MPa, respectively. In the case of chain extension with MDI-E, lower values were found ($T_g = 73^\circ\text{C}$, 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. T_g and storage modulus differences between the commercial UPE and the chain-extended polyesters of this work can be attributed to this fact. In the case of chain extension with SONCO, T_g dropped to 65°C. A similar trend was observed when its storage modulus was measured. The SONCO-chain-extended UPE showed a lower storage modulus (1500 MPa) than that of the commercial product. These decreases in the T_g and storage modulus values were attributed to the higher weight ratio and plasticizing effect of SONCO. The introduction of long alkyl chains by the triglyceride should plasticize the final product just as dioctyl and dinonyl phthalates do.¹⁸ In addition, in one of our earlier works, UPEs were found to be plasticized

TABLE III
Final M_n , T_g , and Storage Modulus Values, TGA Data, and Gel Times for the Commercial and Chain-Extended Polyesters

UPE	Final M_n	T_g (°C)	Storage modulus (MPa)	Temperature at 5% weight loss (°C)	Gel time (min)
Commercial UPE	1500	88	3000	272	12–15
UPE extended with MDI-E	1800	73	2400	204	7–8
UPE extended with MDI-C	1300	84	3250	202	10–15
UPE extended with SONCO	1050	65	1500	188	7–8

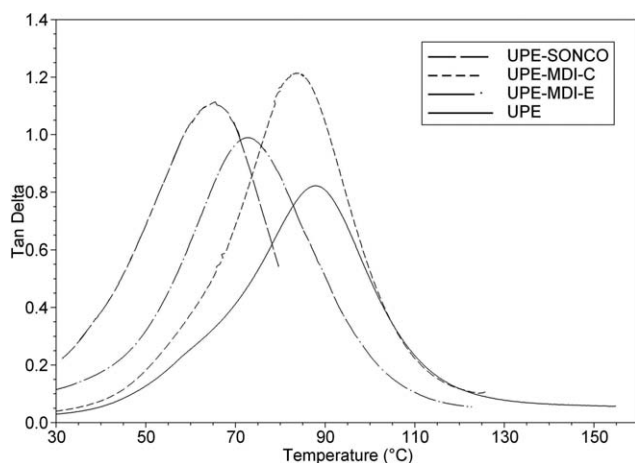


Figure 9 Tan δ plots of the commercial and chain-extended polyesters.

upon the introduction of long alkyl chains of epoxidized soybean oil.³ In the case of MDI-C, in which some caprolactam was expected to be liberated, a similar plasticizing effect was not observed because the T_g values and mechanical properties of the chain-extended UPE were found to be very close to those of the commercial sample. Thus, in the case of MDI-C, the advantages obtained by chain extension were a dramatically reduced reaction time without the thermal and mechanical properties of the product being compromised. The storage modulus curves of all the polyesters are shown in Figure 10. The actual values are shown in Table III.

Thermal stability tests were also performed for the chain-extended polyesters and the reference product. The results are shown in Figure 11. The final M_n , T_g , storage modulus, and TGA values are summarized for comparison in Table III.

The TGA results of the chain-extended polyesters showed that the temperatures corresponding to 5% weight loss were around 190–200°C. This value was

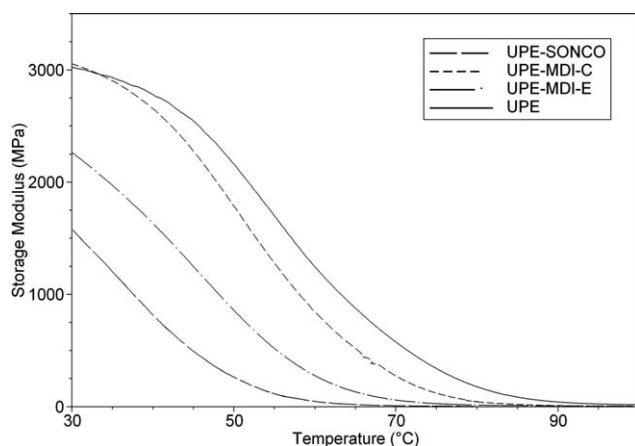


Figure 10 Storage modulus curves of the commercial and chain-extended polyesters at 25°C.

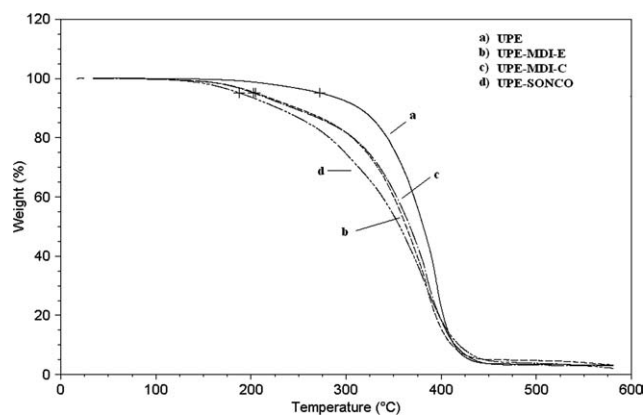


Figure 11 TGA thermograms of the commercial and chain-extended polyesters (temperature at 5% weight loss).

272°C for the commercial UPE. The difference reflected the lower thermal stability of the introduced linkages versus the ester linkage. In the 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°C.¹⁹ Similarly, in the case of chain extension with SONCO, urethane linkages were introduced to the polyester backbone. As the urethane bond is unstable above 170°C,²⁰ again, in comparison with the commercial UPE, the decrease observed in the thermal stability was expected. Therefore, it is concluded that the SONCO-extended UPE would be suitable only for applications in which high T_g and modulus values and high thermal stability are not required, but fast biodegradability is.

MDI-E-extended and MDI-C-extended polyesters have, in principle, different chain-extending groups at temperatures lower than 160°C, so the variations in the molecular weight at a given reaction time and the variations in the thermal and mechanical properties are not surprising.

The MDI-E-extended and MDI-C-extended UPEs exhibited thermal and mechanical properties that were perfectly suitable for industrial use. As mentioned in the introduction, the production of UPEs requires a long reaction time and severe conditions. When we think in terms of industrial production, the benefits imparted by the extenders, such as shortened reaction times, reduced energy use, and increased yields, present a major advantage. Starting with the UPE oligomers used in this work, which have an M_n value of 700, and continuing the polycondensation reaction to reach an M_n value of 1800 would result in a 2% weight loss due to the water that needs to be separated. This was calculated from the decrease in the acid number. The actual loss in practice is probably much higher because of the

azeotropic loss of diols along with water. With the chain-extension method described in this work, there is a 5% increase in the weight of the product. The total increase in the polymer yield is therefore at least 7%, 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.

CONCLUSIONS

In this work, UPE oligomers ($M_n = 600\text{--}700$) were chain-extended (with M_n values up to 1800) with two blocked diisocyanates and one renewable-source diisocyanate. Solubilities, gel times, and mechanical and thermal properties of the chain-extended polyesters were examined and compared to those of a commercial product. The aziridine- and caprolactam-blocked isocyanates (MDI-E and MDI-C, respectively) were successfully used to increase the molecular weights of UPEs in a short time. As they primarily react through a ring-opening addition route at 120°C , the disadvantage of byproduct generation is eliminated. Decreasing the production time and increasing the yield of polyesters in industrial applications are of utmost importance. The chain extension can be carried out directly in the polyesterification reactor after a reduction of the temperature. The diol loss due to evaporation that is usually encountered in the late stages of commercial UPE manufacture is also eliminated, and this provides economies in raw materials and minimizes pollution. The use of these extenders decreases the production time and increases the yield of the polyester substantially without alteration of the styrene solubility or gel time of the polyester. This work will be continued through the examination and characterization of other chain extenders, including renewable-source ones that seem to be promising in scientific

and/or industrial applications. The biodegradability of SONCO-chain-extended polyesters is now under investigation.

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