

Incorporation of Carbon Dioxide into Soybean Oil and Subsequent Preparation and Studies of Nonisocyanate Polyurethane Networks

B. Tamami,¹ S. Sohn, G. L. Wilkes

Polymer Materials Interface Laboratory, Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

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ABSTRACT: Epoxidized soybean oil was effectively converted to carbonated soybean oil (CSBO) containing five-membered cyclic carbonates by reaction with carbon dioxide in the presence of tetrabutylammonium bromide as catalyst at 110°C in high yield. CSBO could easily react with di- or tri-primary amines to give the corresponding nonisocyanate polyurethane networks (NIPUs). A model reaction between CSBO and *n*-butylamine showed the effective ring opening of five-membered cyclic carbonate moieties in the triglyceride molecules by the amine to form β -hydroxyurethane systems. NIPUs were further characterized by the three

techniques of solvent extraction, dynamical mechanical analysis, and limited tensile testing. The data from these methods confirmed the network character of all materials and also showed how the levels of extractables, T_g , and mechanical properties varied with type of amine and, in the case of ethylenediamine, the effect of stoichiometry. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 883–891, 2004

Key words: nonisocyanate; polyurethane; soybean oil; networks

INTRODUCTION

Polymers prepared from renewable natural resources have become increasingly important because of their low cost, ready availability, and possible biodegradability.¹ Vegetable oils are renewable triglyceride oils based on different fatty acids with varying degrees of unsaturation. Their conversion to useful intermediates for polymeric materials is significant scientifically, economically, and environmentally.

Soybean oil (SBO) is the most readily available and one of the lowest cost vegetable oils in the world.^{2,3} In the past decade much effort has been dedicated to producing SBO-based polymeric materials. Recently, Wool and coworkers, as well as others,^{4,5} have reported the use of SBO and other triglyceride oils to synthesize several different types of monomers which can promote polymeric networks with a wide range of physical properties. The generation of these monomers was possible by the use of different functionalities present in the triglyceride molecules, i.e., double bond, the allylic carbon, the ester group and the car-

bon α to the ester group, which can be transformed into other reactive polymerizable moieties.

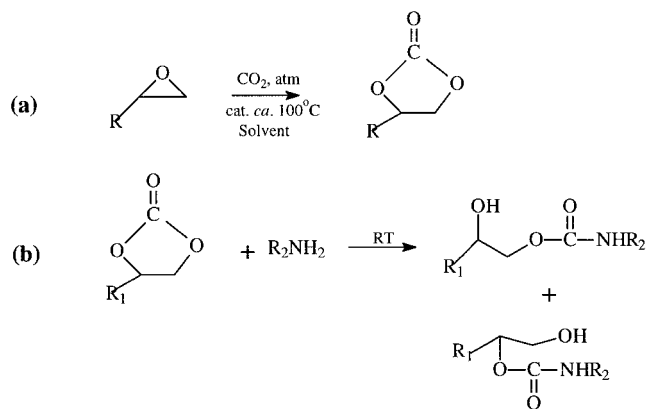
One of the major interests of other researchers has been investigation into the possibility of converting SBO into polyols for use in the polyurethane industry. Petrovic and coworkers^{6–12} have used epoxidized soybean oil (ESBO) to develop a range of polyols which can then be reacted with isocyanates to produce polyurethanes with useful properties. ESBO is the result of epoxidation of the double bonds of the SBO triglycerides with hydrogen peroxide, either in acetic acid or in formic acid,^{13–15} and it is industrially available in large volumes at a reasonable cost.

Much attention has also been paid to CO₂ as the most inexpensive and readily available carbon resource,¹⁶ and active investigation of the incorporation of CO₂ into organic molecules has been carried out from an economical and environmental point of view. Among many studies of chemical CO₂ fixation, the reaction of oxiranes and CO₂ to provide the five-membered cyclic carbonate has received much attention because of its simple reaction, high yield, and harmless nature of the reagents.^{17,18} The reaction can be performed with the help of a catalyst under atmospheric pressure at about 100°C (Scheme 1a). A large number of catalyst systems have been reported in the literature for this reaction; among them the alkali metal halides, quaternary ammonium halides, and polystyrene bound quaternary ammonium salts are the most effective.^{17–19}

Correspondence to: G. L. Wilkes (gwilkes@vt.edu).

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¹On sabbatical from Shiraz University, Iran.



Scheme 1 Schematics of the reaction of oxirane with CO_2 (a)¹⁷ and the reaction of five-membered cyclic carbonate with primary aliphatic amine (b).²²

As has been demonstrated,^{20–23} five-membered cyclic carbonates readily react with primary amines at room temperature to yield 2-hydroxyethylurethane quantitatively (Scheme 1b). Furthermore, recently Endo and coworkers, as well as others,^{24–31} have reported the polyaddition reaction of bifunctional cyclic carbonates with aliphatic diamines to give polyhydroxyurethanes, often commonly called “nonisocyanate polyurethanes” (NIPUs). They showed that one of the advantageous features of this polyaddition was its high chemoselectivity, i.e., it could be prepared in the presence of water, alcohol, and esters.

Considering the above facts, in this work we report the preparation of a new monomeric functionalized SBO and its subsequent polymerization to obtain a polyurethane network. Therefore, the synthesis of SBO containing cyclic carbonate moieties, named carbonated soybean oil (CSBO), its reaction with two specific diamines and one triamine to obtain the nonisocyanate polyurethane networks, and a limited study of some of their physical properties are described.

EXPERIMENTAL

Materials

Epoxidized soybean oil (Paraplex G-62) with a molecular weight of ca. 1000 g/mol and an oxygen content of 6.8% (~4.2 epoxy groups per triglyceride molecule) was provided courtesy of C.P. Hall Co. Carbon dioxide was purchased from Air Products and was used after passage through a Drierite column. Tetrabutylammonium bromide (TBAB), sodium iodide, lithium bromide, benzyltrimethylammonium bromide, Amberlit IR 400(Cl), ethylenediamine (ED), hexamethylenediamine (HMD), and tris(2-aminoethyl)amine (TA) were purchased from Aldrich. Amines were used as received or distilled over KOH prior to use. FTIR

spectra were recorded on a Nicolet 510 FT-IR spectrometer. ^1H - and ^{13}C -NMR spectra were recorded on a Varian Inova 400 (400 MHz) spectrophotometer using tetramethylsilane as an internal standard. GPC profiles were obtained with a Waters SEC equipped with an autosampler 410 RI detector eluted with THF at 40°C calibrated by polystyrene standards. Viscosity measurements were made at ambient temperature using cone and plate geometry over a shear rate range of 0 to 75 s^{-1} using an AR-1000 Rheometer from TA Instruments. Thermal stabilities of ESBO and CSBO were characterized using TGA (Model SSC 5200, Seiko) while air purging using a heating rate of 3°C/min over the temperature range of ca. ambient to 500°C.

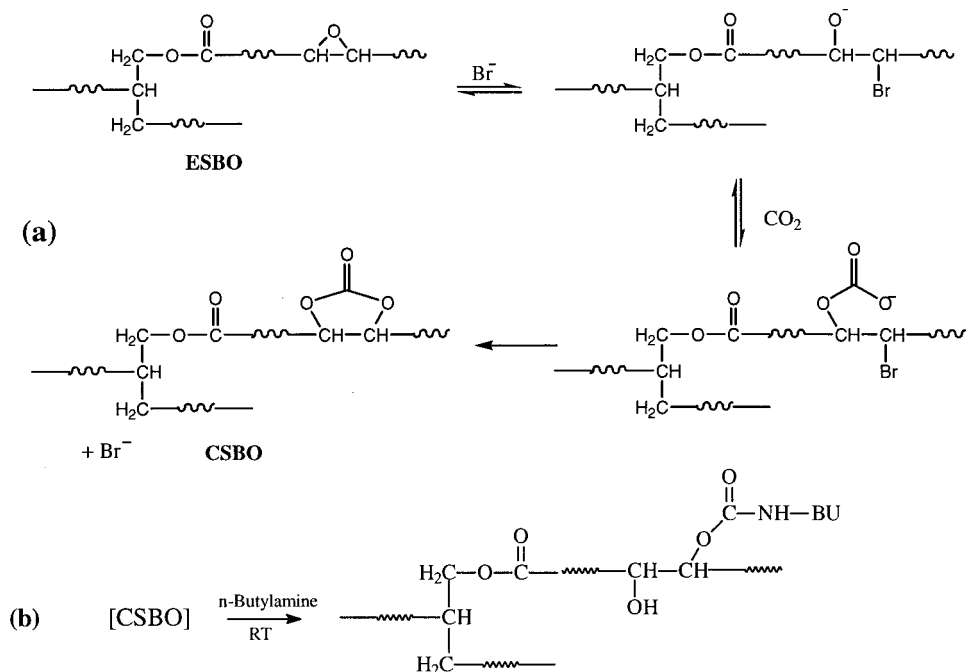
Synthesis

Reaction of epoxidized soybean oil with carbon dioxide

ESBO (200 g) and dried tetrabutylammonium bromide (13.52 g; 5 mol% with respect to epoxy groups) was placed in a 500-mL flask equipped with a gas dispersion inlet tube and an outlet. The reaction mixture, while stirred magnetically, was heated to ~110°C, at which point almost all of the catalyst dissolved. A medium flow of CO_2 was then introduced. While the temperature and CO_2 flow were maintained, the level of reaction was monitored by IR spectroscopy of small aliquots taken at 5-h intervals. As the absorbance band due to formation of the cyclic carbonate moiety appeared and increased in intensity at 1805 cm^{-1} , the oxirane C–O twin bands at 823 and 845 cm^{-1} decreased and disappeared. The reaction was complete in about 70 h. The catalyst was completely removed by dissolving the reaction mixture in ethyl acetate and extracting twice with water. The organic layer was then dried over molecular sieves and the solvent was evaporated to give 221 g (94% yield) of the clear light-brown carbonated soybean oil with a viscosity of 13,200 cps at 25°C.

Reaction of carbonated soybean oil with *n*-butylamine (model reaction)

n-Butylamine (5.85 g) was added to CSBO (11.76 g) dissolved in THF (8 mL). The solution was stirred at room temperature and the extent of reaction was followed by IR spectroscopy. While the absorbance band due to cyclic carbonate moiety at 1805 cm^{-1} diminished and finally disappeared, new bands due to the urethane –C=O, –NH, and –OH groups appeared at 1704, 1545, and 3332 cm^{-1} , respectively. The reaction was complete after 12 h. The mixture was then dissolved in chloroform and extracted twice with slightly acidic aqueous solution. The organic layer was sepa-



Scheme 2 Schematics of the reaction of epoxidized soybean oil (ESBO) with CO_2 to form carbonated soybean oil (CSBO) (a) and model reaction of CSBO with *n*-butylamine (b).

rated and dried, and the solvent was evaporated to give 13.5 g (92% yield) of an olive-oil-colored product.

Preparation of nonisocyanate polyurethanes

CSBO (11.76 g) was placed in a small beaker and was heated to 60°C in a constant-temperature oven. ED (1.20 g) was then added and mixed thoroughly. The viscous solution was poured into a small mold, covered, and heated at 70°C for 10 h and then at 100°C for 3 h to give a light-brown, transparent, and flexible polymeric material of 4 mm thickness. The same procedure was followed for experiments utilizing different ratios of CSBO/ED and also when HMD or TA was used as a di- or trifunctional amine, respectively.

Characterization of nonisocyanate polyurethanes

Solvent extraction

Thin sliced samples were extracted using toluene as a solvent at room temperature for 24 h. Equilibrium swelling was achieved under these conditions. Drying of the extracted sample was performed under vacuum (30 mmHg) at 100°C for 12 h. Sol fraction, the mass difference before and after solvent extraction, was expressed in weight percentage normalized to the original dry sample mass. Three samples were used for each test and the results were averaged.

Dynamical mechanical analysis

Dynamical mechanical analysis (DMA) operated in the tensile mode was carried out using a Seiko DMA 210 model over the temperature range of -110 to ca. 200°C . Data were obtained at a heating rate of $3^\circ\text{C}/\text{min}$ at 1 Hz. In all cases, the cross-sectional areas of samples were maintained as $3.0 \pm 0.5 \text{ mm}^2$. The grip-to-grip distance was 10 mm.

Tensile tests

For mechanical property testing, the samples were cut with a die into 2.54-mm-wide dog-bone-shape-strips. The grip-to-grip distance was 10 mm, and the thickness of samples was maintained at ca. 4.0 mm. Tests were made at ambient temperature using a constant crosshead speed (5.0 mm/min) on an Instron (Model 4400R) device with a load capacity of 100 N. The samples were gripped with pneumatically operated clamps.

RESULTS AND DISCUSSION

Reaction of ESBO with carbon dioxide

Epoxidized soybean oil (Paraplex G-62) with an average epoxy content of 4.2 per triglyceride molecule was used for the reaction with carbon dioxide. The reaction (Scheme 2a) was performed neat at $\sim 110^\circ\text{C}$ with different types of catalysts such as NaI, LiBr, benzyltri-

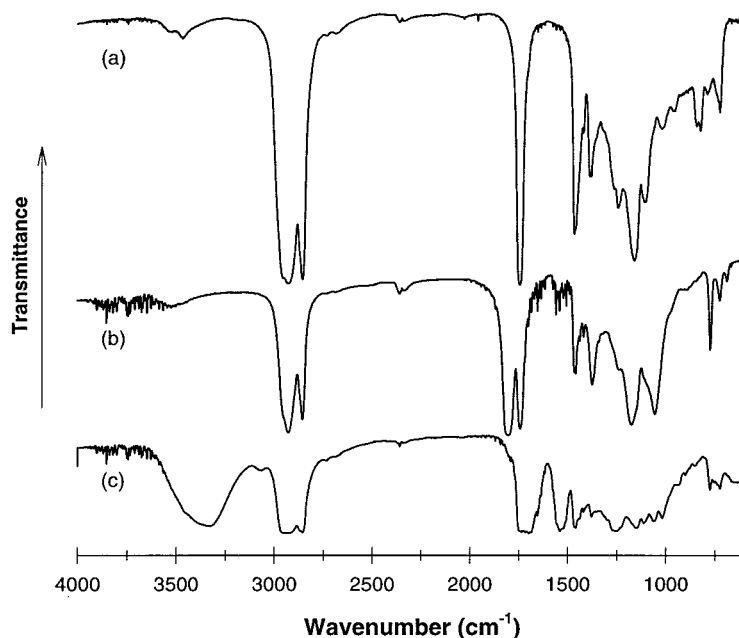


Figure 1 FT-IR spectra of (a) epoxidized soy bean oil (ESBO), (b) carbonated soybean oil (CSBO), and (c) reaction product of CSBO and *n*-butylamine.

methylammonium bromide, Amberlit IR 400(Cl), and TBAB. Of the catalysts employed, very high conversion of ESBO to carbonated soybean oil was particularly facilitated when a 5% molar concentration of TBAB with respect to epoxy content was used. The other catalysts, being insoluble or only partially soluble, resulted in very low to medium conversions.

The extent of the reaction was followed using IR spectroscopy by focusing on the appearance of a new peak at 1805 cm^{-1} due to the carbonyl of the cyclic carbonate moieties and the disappearance of the twin epoxy bands at 845 and 823 cm^{-1} (Figure 1a and b). Scheme 2a provides the proposed mechanism for this reaction. It is similar to that given for the reaction of oxiranes with carbon dioxide.^{17,18} In addition, the appearance of a new peak at 153.8 ppm in the ^{13}C -NMR of the product due to the $\text{C}=\text{O}$ of the cyclic carbonate confirmed the conversion of epoxy groups. The conversion was almost quantitative (94%) after about 70 h. The percentage conversion could be evaluated by ^1H -NMR considering the signals at about $2.70\text{--}3.00\text{ ppm}$ arising from the $-\text{CH}$ groups of the epoxy rings in ESBO and CSBO. The viscosity of the product at 25°C was 13200 cP compared to the much lower value of 450 cP for ESBO. The high value of viscosity is believed to be due to the presence of the polar cyclic carbonate groups causing enhanced intermolecular interactions. However, to check that no intermolecular reactions occurred resulting in oligomerization or polymerization, during conversion GPC was performed on both ESBO and CSBO. Figure 2 shows the GPC profiles and, as seen, no significant change in polydis-

persity of the product was observed; however, its molecular weight (M_n 1755 g/mol) was slightly higher than that of ESBO (M_n 1414 g/mol) as estimated by using polystyrene standards.

It is also of interest to briefly mention the relative thermal stabilities of ESBO and CSBO in light of their potential applications. Figure 3, in which the percentage mass decrease with temperature is provided, contrasts the thermal behavior of the two modified soy oils as obtained by TGA. While there is a slight in-

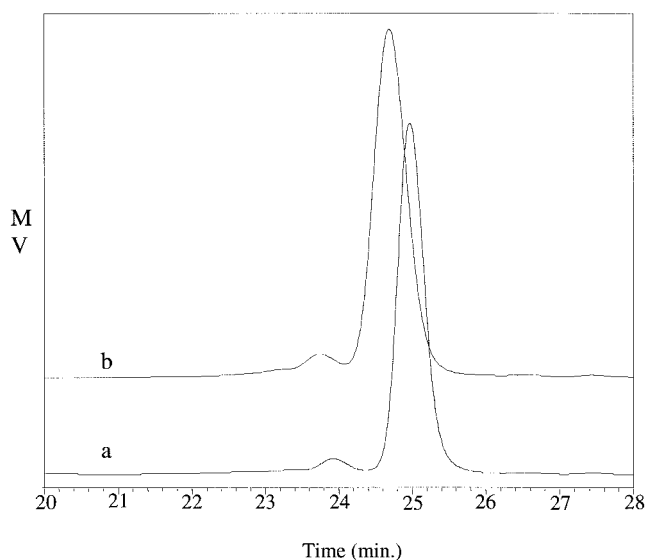


Figure 2 GPC profile of (a) epoxidized soy bean oil (ESBO) and (b) carbonated soybean oil.

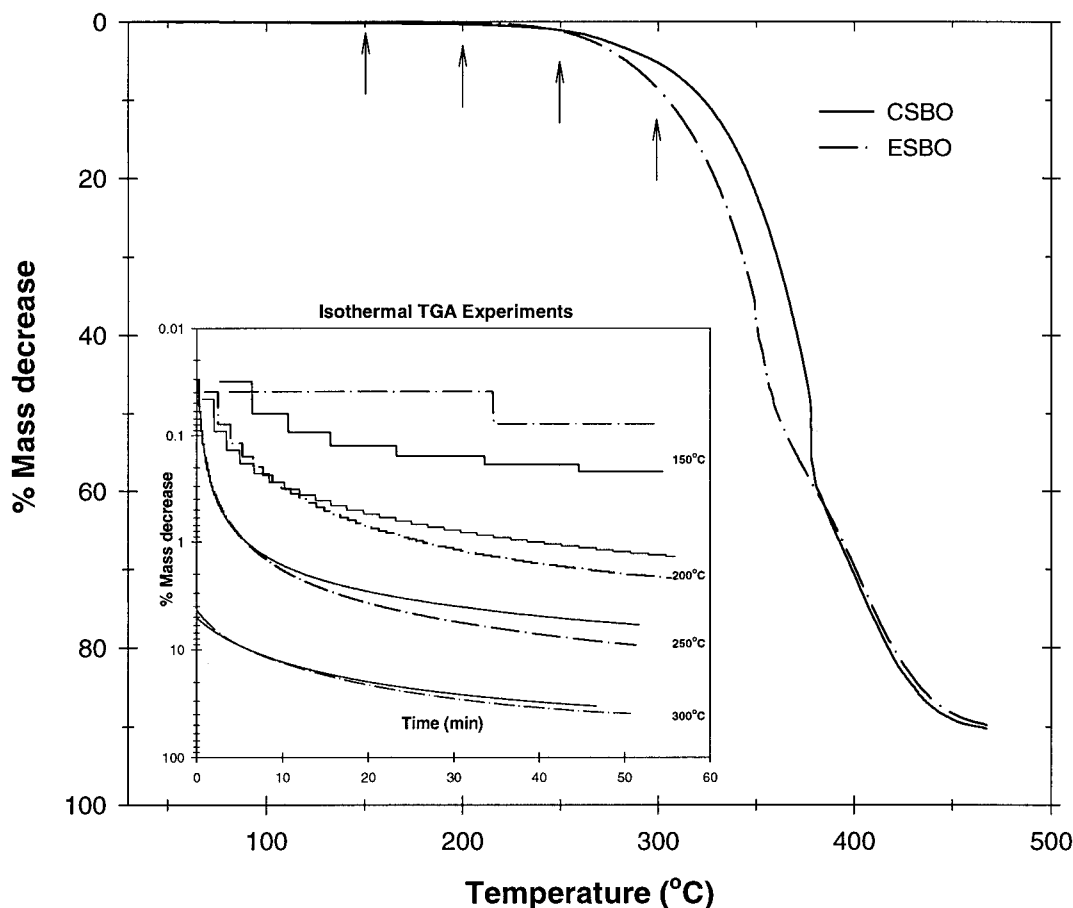


Figure 3 TGA profiles of mass loss with temperature for epoxidized soybean oil (ESBO) and carbonated soybean oil (CSBO).

crease in mass when converting the ESBO to that of the CSBO, which could influence their respective vapor pressures, the TGA profiles of these two materials suggest that CSBO is more thermally stable than ESBO—particularly in the range of approximately 250–375°C. In addition, the Figure 3 (inset) also shows some isothermal TGA experiments carried out at four different temperatures between 150 and 300°C at 50°C intervals (note that the Y-scale of the inset is in logarithmic scale). It is noted that at 150°C, the temporal mass decrease is quite insignificant for both modified soy oils, being on the order of 0.1% for the time interval studied. However, for the high temperature range, there is a more significant mass decrease in the same time interval with ESBO than for CSBO.

Reaction of CSBO with carbon *n*-butylamine (model reaction)

As a model, the reaction of CSBO with *n*-butylamine was performed to show the ring opening of cyclic carbonate moieties and the formation of β -hydroxyurethane systems on the triglyceride molecule (recall Scheme 2b). The extent of reaction was monitored by IR spectroscopy (Fig. 1c). The formation of

new bands at 1704 and 1545 cm^{-1} due to urethane linkages as well as a band at 3332 cm^{-1} due to hydroxyl groups and disappearance of the peak at 1805 cm^{-1} of cyclic carbonate moieties confirmed the conversion of cyclic carbonate into the β -hydroxyurethane systems in the triglyceride molecule. It is to be noted that absorbance bands due to the ester and urethane groups overlap to some extent. It should be mentioned that no amide I band was observed in the IR spectrum of the product, which showed that no transamidation reaction occurred. This was in accordance with what Endo and coworkers reported for the formation of polyhydroxyurethanes.^{24,26} In addition, the disappearance of the peak at 153.8 ppm in the ^{13}C -NMR spectrum of the product due to the C=O of the cyclic carbonate and the appearance of a new peak at 157 ppm of the C=O of the urethane groups also confirmed the formation of the urethane moieties.

Preparation of nonisocyanate polyurethane networks

Preparation of nonisocyanate polyurethane network materials was easily performed by thoroughly mixing the equivalent weights of CSBO and ED, HMD, or TA

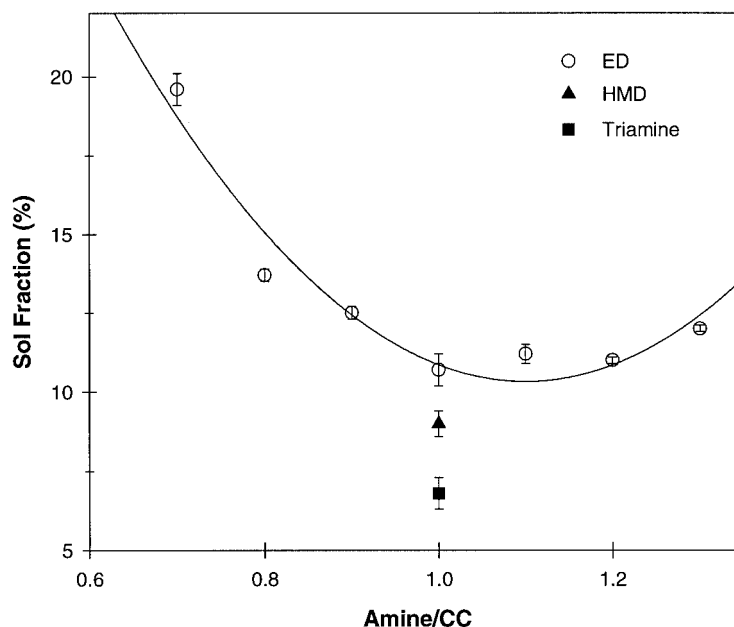


Figure 4 The variation of sol fraction as a function of the mass ratio of amine functionality to cyclic carbonate.

at 60°C, pouring the viscous solution into a small mold, and subsequently curing it as described in the Experimental section. However, CSBO had to be heated up to about 60°C to reduce the viscosity to an extent that mixing became possible.

Characterization of nonisocyanate polyurethane networks

Solvent extraction experiments

Sol fraction, as a function of the molar ratio of the amine functionality of ED to cyclic carbonate, is shown in Figure 4. Also included are two other data points which arise from the networks made from an equal molar ratio of the amine functionality to cyclic carbonate for either HMD or TA. Throughout the swelling tests, all samples maintained their shape integrity, indicating that the network reaction had distinctly achieved the gel point. It is clear that the sol fraction decreases at first, with the addition of ED and reaches a minimum at the stoichiometric balance, as might be expected. With further increases in ED content, the sol fraction again increases since there is a further offset again in stoichiometry. From this, it can be inferred, and was expected, that at the stoichiometric balance, the corresponding nonisocyanate polyurethane network provides the "best" network structure possessing the least amount of solubles and dangling chain ends.

The higher functionality amine, TA, shows an even lower amount of sol fraction at the stoichiometric balance point, which is readily understood from the fact that TA will contribute to promote a tighter network

structure than the equivalent diamine moieties. This result, and its consequences, will be further discussed later with those data obtained from DMA and tensile tests. The longer chain and more flexible diamine, HMD, exhibited a slightly lower sol fraction compared with ED.

DMA results

In Figure 5 a and b, the DMA parameters of $\tan \delta$ and E' are shown as a function of temperature, respectively. The principal peak temperature, which is obvious in the $\tan \delta$ results, is distinctly assigned to the glass transition of the corresponding network. For the series with varying ED content, it is noted that T_g systematically increases with ED addition, up to the stoichiometric balance, but then again decreases with further ED concentration. The overall thermal window of T_g variation with ED content is also noted to be about 20°C.

In addressing the two remaining data points associated with the triamine, TA, as well as the second diamine HMD, it is noted that the TA-based network provided the highest T_g value of approximately 43°C, whereas the HMD network exhibited the lowest T_g at stoichiometric balance at approximately 18°C. For clarity, the variation of the T_g 's, as determined by $\tan \delta$, are presented in the Figure 5a (inset) for all samples. These results regarding T_g are clearly consistent with respect to the earlier sol fraction behavior in that, as expected, the nearer the stoichiometric balance, the higher the T_g will be for those systems with varying ED, and in addition, the triamine, TA, again provides

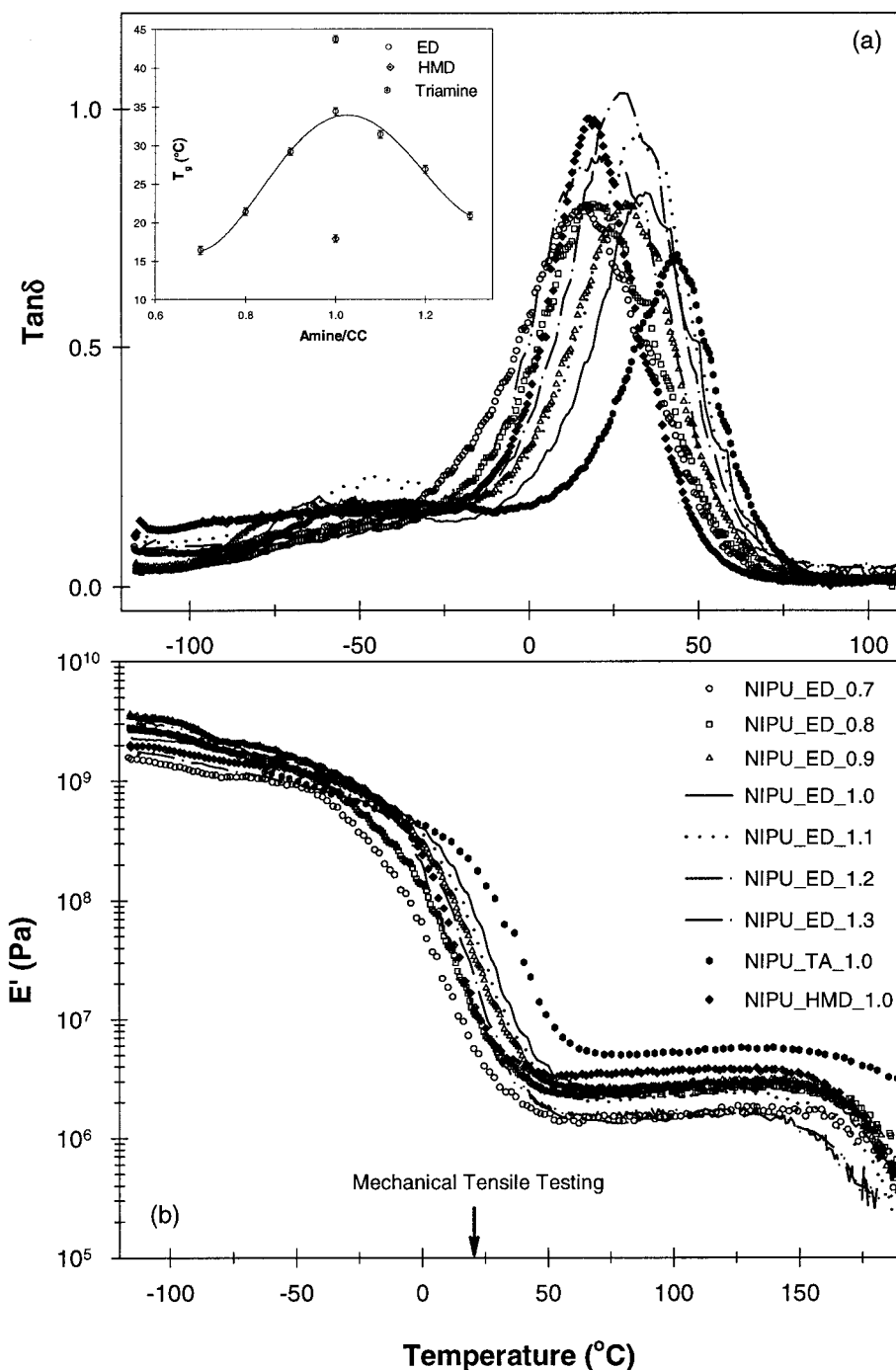


Figure 5 Dynamic mechanical analysis for various NIPU samples: (a) temperature versus $\tan \delta$ and (b) temperature versus storage modulus (E').

the highest glass transition temperature, indicative of the fact that it has a tighter network than that of either the ethylene or the hexamethylene diamine-based networks. Of note is also the fact that the HMD-based network gives a somewhat lower T_g than the corresponding ED containing sample, which is not necessarily surprising in view of the higher level of flexibility of the HMD moiety. Finally, another interesting observation relating to the T_g behavior is that the

intensity of the glass transition, as denoted by the $\tan \delta$ value at its peak decreases in the order of HMD > ED > TA. This ordering is of course the reverse of the ordering of the T_g 's of these same respective three stoichiometrically balanced samples.

In passing, it is also noted that, in Figure 5b, there is a relatively broad and weak secondary loss peak that occurs at about -50°C for some of the samples. To be sure that the nature of this peak is real, we used the

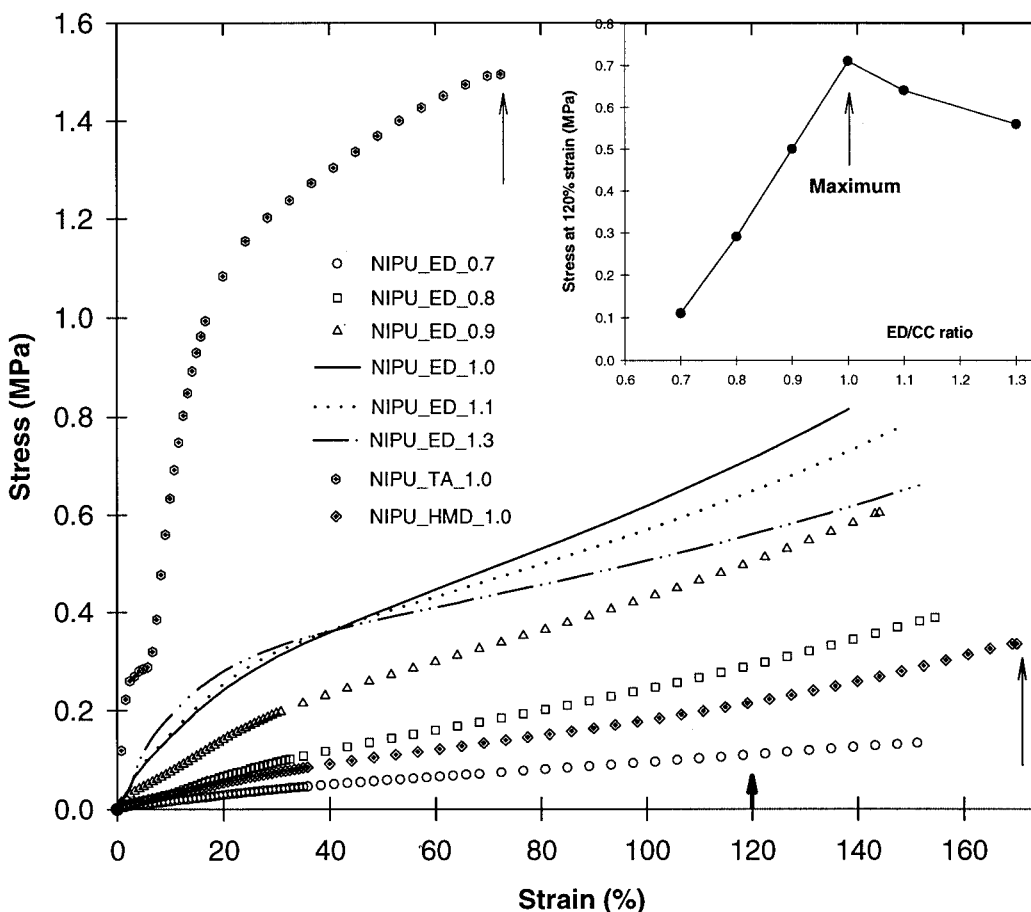


Figure 6 Tensile stress experiments performed on NIPU samples at ambient.

HMD sample and collected three independent DMA runs (results not shown). We found that only one of the runs distinctly carried the lower temperature relaxation, but the other two sets of data did not. Based on this we tentatively conclude that the nature of this small relaxation peak may not be real but rather is associated with instrumental artifacts.

In addressing the storage modulus data given in Figure 5b, it is noted that its behavior above the respective T_g of a given sample shows that the TA-based urethane network displays the highest rubbery plateau modulus, as would be expected based on its higher level of cross-link density (lowest solubles) as well as its higher T_g . The samples showing the variation in ED content illustrate once again that the highest rubbery modulus occurs at stoichiometric balance as would be expected and is lower for any other composition irrelevant of whether it is the diamine or the cyclic carbonate moiety that is in excess. The HMD-based network exhibited the second highest rubbery plateau modulus relative to all other networks studied. Specifically, it was below the network made from TA but above all of those based on ED. While it was noted earlier that the more flexible HMD gave rise to a lower T_g than the stoichiometrically

balanced networks based on TA and ED, its rubbery plateau modulus need not necessarily be the lowest of the three. In fact, it is noted that the ordering of the rubbery plateau moduli for the three stoichiometrically balanced networks is inversely related to the sol fraction, which might well be expected.

Tensile testing results

The results of the limited tensile experiments performed under room conditions are noted in Figure 6. In view of the data already discussed, one would anticipate that the TA-based network would display the highest level of stress for a given strain when compared against the other two stoichiometric balanced materials formulated with either ED or HMD. Indeed, this is true as can be discerned from the results presented. In addition, the HMD-based network displays the lower modulus of the same three systems even though the rubbery plateau modulus of the HMD network is intermediate to that of the TA and ED networks. This result is simply due to the fact that the HMD material possesses the lower T_g , which promotes a lower modulus at ambient temperature where

the tensile tests were conducted (recall Fig. 5b). Finally, it is particularly noted that, for the stoichiometric balance of ED with the CSBO moiety, the stress-strain behavior is higher than for all other compositions of ED with the results being in parallel and expected in light of the solubles data obtained by extraction and the DMA glass transition results (see also the Figure 6 (inset), which shows the levels of stress at 120% strain for the samples containing ED). It is interesting, however, that the strain at break for all of the ED-based networks is nearly constant at approximately 150%, thereby showing no systematic dependence on the ratio of ED to that of CSBO. In contrast, the strain at break for the tighter network TA-based material is distinctly lower (approximately 70%) and therefore well below that of any of the ED- or HMD- (170%) based urethanes.

SUMMARY

Reaction of epoxidized soybean oil with carbon dioxide under atmospheric pressure using tetrabutylammonium bromide as a catalyst to prepare carbonated soybean oil was demonstrated. Furthermore, CSBO could easily react with di- or triamines to produce nonisocyanate polyurethane networks.

Extractables characterization from the various NIPUs made from the three different amines confirmed that all network reactions had easily reached the gel point, since sample integrity was maintained for all materials of equilibrium swelling in toluene. DMA and tensile tests were in harmony with the extractable results in that, as extractable level increased for a given type of amine reactant, T_g and stress at a given strain increased. By varying the stoichiometric balance of the reactant ED with that of the cyclic carbonate moiety, it was confirmed that, as the stoichiometric balance was approached, the level of extractables decreased, while the stress at a given strain and the corresponding network T_g increased. Very consistently, and regardless of the type of the tests employed, the samples made from triamine showed the lowest soluble fraction (6.8%), the smallest strain at break, ϵ_b , (70%), and the highest T_g (ca. 43°C) and the highest level of stress for a given strain. In contrast, the sample containing HMD exhibited the lowest T_g (ca. 18°C), the lowest level of stress, and the highest ϵ_b (170%). When the amount of ED was varied among samples, the equivalent weight sample carried the lowest soluble fraction (10.7%), the highest T_g (ca. 34°C), and the highest level of stress among them-

selves. Strain at break for the samples made from ED were approximately constant regardless of the amount of ED (ca. 150%).

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