

Soybean Oil Based Polyisocyanurate Cast Resins

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ABSTRACT: Two series of polyisocyanurates were prepared from polymeric 4,4'-diphenylmethane diisocyanate (MDI) and soy-based or polypropylene oxide polyols by varying isocyanate indexes from 105 to 350. Increasing isocyanate index gave polyisocyanurates with increased thermal stability, flame resistance, tensile strength, modulus, and glass transition. Impact was lower. Soy-based polyisocyanurates displayed better thermal stability, higher rigidity

(modulus), and higher strength than those based on the propylene oxide polyols of the same molecular weight and functionality. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3333–3337, 2003

Key words: soy oil; polyol; polyisocyanurate; structure; property

INTRODUCTION

Polyisocyanurates are heat-resistant materials obtained by polycyclotrimerization of diisocyanates or isocyanate-terminated prepolymers.¹ They consist of rigid and thermally stable six-member isocyanate rings. If only polyisocyanates are used as reactants, the reaction product is a polymeric material with a highly crosslinked structure. A disadvantage of these materials is their fragility. It can be decreased by modification with polyols attached to isocyanurate rings via urethane groups, as in this work. An illustration of the modified structure is depicted in Figure 1. The preparation of these polymers involves the simultaneous formation of urethane and isocyanurate groups, which is promoted by specific catalysts, such as ammonium² and amino-based compounds, potassium salts of fatty acids.³ Polyisocyanurates are used in applications where the material is exposed for extended periods of time to elevated temperatures. The maximum service temperature of polyisocyanurates is 150–220°C. Modified polyisocyanurates are produced as foams⁴ or cast resins.⁵ The unfoamed polyisocyanurate grades may be processed by standard casting techniques, such as reaction injection molding (RIM) or by reinforced reaction injection molding (RRIM).

The properties of these polyisocyanurate materials depend on the type of isocyanate and polyol and the NCO/OH molar ratio, the so-called isocyanate index. By varying these three parameters, it is possible to regulate the properties of modified polyisocyanurates to reach desirable properties.⁶ One of the most impor-

tant parameters is isocyanate index. At higher isocyanate indices (higher molar ratios of isocyanate to polyol), higher content of isocyanurates is formed and the polymer is more thermally stable but more rigid and fragile.

Polyols derived from soybean oil, being new raw materials from renewable resources, are potentially interesting materials for polyisocyanurate modification. With isocyanates, they produce polyurethanes (PU) that can compete in many aspects with ones derived from petrochemical polyols. Thermal and oxidative stability of the polyurethanes from soybean oil is better than that of the ones from polypropylene oxide.⁷ Soybean oil is highly hydrophobic, and an excellent weather stability of the derived polyurethanes can be expected. They can be used in production of polyurethane, elastomers,⁸ coatings,⁷ foams,⁹ etc. It is expected that their impact on polyurethane chemistry will be significant.

The objective of this work was to investigate the effect of the polyol structure and isocyanate index on modified polyisocyanurate foam properties. The effects of a soybean oil based polyol were compared with the polyether-based one. Both polyols were of the same molecular weight of about 1000 and the same functionality of 3. Isocyanate index varied from 105 to 350. Isocyanate index 100 corresponds to the equimolar ratio of NCO and OH groups, whereas higher indices characterize an excess of isocyanate.

EXPERIMENTAL

Materials

The polyol components were soybean oil based polyol, designated as Soypolyol 173, and polypropylene oxide based polyether polyol Arcol LG 168,

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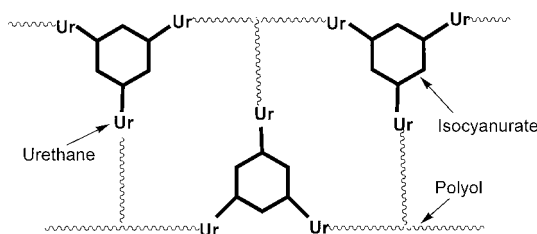


Figure 1 Schematic representation of the polyisocyanurate structure.

designated PPO 168. Hydroxyl numbers of Soypolyol 173 and PPO 168 were 173 and 168 mg KOH/g, respectively. Soypolyol 173 was prepared according to the proprietary procedure¹⁰ and PPO 168 was supplied by ARCO Chemical Co. Mondur 489, a polymeric isocyanate supplied by Bayer, had isocyanate content of 31.5% and functionality of 3. Polycat 41, supplied by Air Products, was used as the trimerization catalyst.

Methods

The samples were prepared by mixing 30 g (0.09 g equivalent) of polyol, catalyst, and a proper amount of isocyanate, poured in the mold, and cured at 130°C for 48 h, until the disappearance of NCO groups as measured by a Perkin–Elmer Spectrum 1000 Fourier transform infrared (FTIR) spectrometer. The isocyanate indices were 105, 150, 200, 250, 300, and 350.

Density was measured by immersion in water according to ASTM 792. A thermal analyst system from TA Instruments, consisting of the Controller 3100 with DSC 2910 module and TGA 2050 Thermogravimetric Analyzer, was used to measure glass transition and thermal stability. Dynamic mechanical tests were carried out on DMA 2980 from TA Instruments. Heating

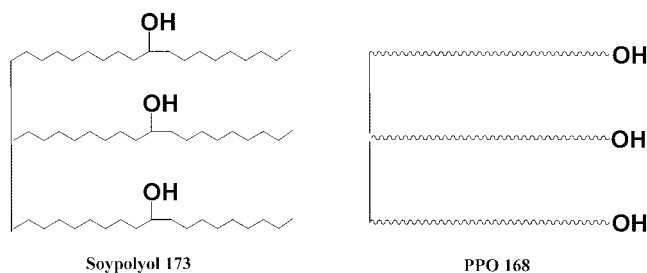


Figure 2 Schematic representation of the polyol structure.

rate with DMA and TMA was 3°C/min and with DSC was 10°C/min. Tensile properties were measured on Qtest-2 Tensile Tester from MTS, according to ASTM D882-97.

RESULTS AND DISCUSSION

The two polyols had the same hydroxyl number, functionality, and molecular weight, but significant structural differences. PPO 168 had terminal OH groups and after reacting with isocyanate complete polyether chain was part of the polyisocyanurate network (Fig. 2). Soypolyol 173 had internal hydroxyl groups positioned in the middle of the fatty acid chain, giving higher crosslinking density of the polyisocyanurate network. Hydroxyl groups can be located on 9th or 10th and 12th or 13th carbon atom in a fatty acid. Thus, when crosslinking was completed, a portion of the chains was not included in the network and was left dangling, increasing the free volume in the polymer network and acting as a plasticizer.¹¹ Thus, the density of the polyisocyanurate samples (Table 1) from Soypolyol 173 were slightly lower than the density of the samples from PPO 168. However, swelling in toluene of soy-based samples was less than that of the PPO-based ones (Table 1). Swelling was measured

TABLE I
Physical Properties of the Cast Polyisocyanurate Samples

Sample	Index	Density (g/cm ³)	Swelling in toluene, 30 days (%)	DSC T _g (°C)	DMA, °C	
					β-Transition	T _g
PPO-105	105	1.1560	62	7	-55	11
PPO-150	150	1.1724	42	28	-62	32
PPO-200	200	1.1728	30	41	-67	42
PPO-250	250	1.1768	20	52	-65	56
PPO-300	300	1.1722	4	N.A.	-64	59
PPO-350	350	1.1884	-2	N.A.	-63	64
SOY-105	105	1.1130	47	45	-64	71
SOY-150	150	1.1308	32	55	-71	83
SOY-200	200	1.1388	18	N.A.	-68	98
SOY-250	250	1.1421	5	N.A.	-66	91
SOY-300	300	1.1545	2	N.A.	-66	87
SOY-350	350	1.1727	0	N.A.	-72	89

N.A., Not available. The material did not show presence of any T_g.

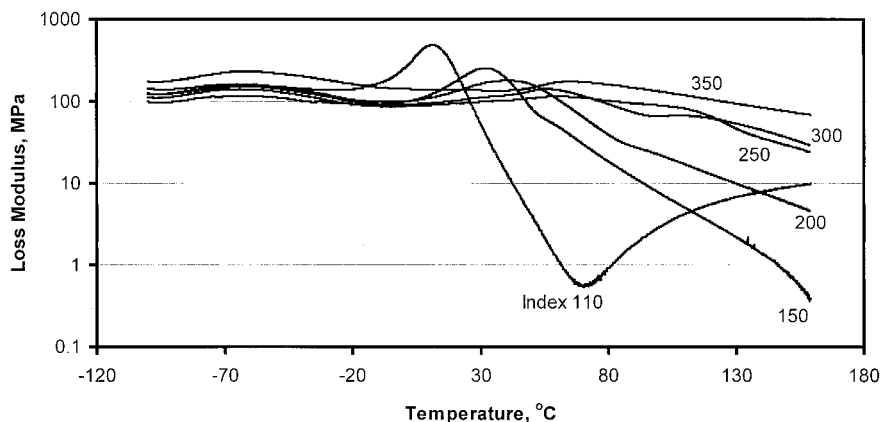


Figure 3 Loss modulus-temperature curves of PPO 168 based polyisocyanurates.

after 30 days when the equilibrium state was reached. Better resistance to the solvent swelling of the soy polyol based samples comes from the higher crosslinking density. Both series of samples showed lower swelling and increased density when the isocyanate index was increased.

Glass transition temperature, T_g , measured by DSC, increased for both series with the increase of the isocyanate index (Table 1). The samples based on soy polyol had T_g higher by about 30°C because of higher crosslinking density and lower flexibility of paraffinic chains in comparison with polyether chains. T_g was not noticeable at indices higher than 200 because soft segment was not detectable as a separate phase at the high isocyanurate content. Glass transition temperature measured by DMA of the PPO 168 based samples was between 11 and 64°C (Table 1 and Fig. 3), and for Soypolyol 173 based, it was between 71 and 89°C

(Table 1 and Fig. 4). On average, T_g of PPO-based samples was 20–30°C lower than T_g of the soy polyol based ones. All samples displayed a β -transition at about -60 to -70°C that was associated with the rotation of shorter segments in the fatty acid chains. The soy polyol based samples with isocyanate indices of 150 and higher showed very little change of modulus because of high rigidity of the polyisocyanurate network.

Tensile strength of the soy polyol based samples was considerably higher than tensile strength of the PPO-based samples (Fig. 5). The higher strength can be assigned to the higher crosslinking density. Tensile tangent modulus was much higher with Soypolyol 173 based samples below an index of 250 (Table 2). The moduli were quite similar for higher indices because the polyol concentration was relatively small, and the structure of a polyol did not have any significant effect

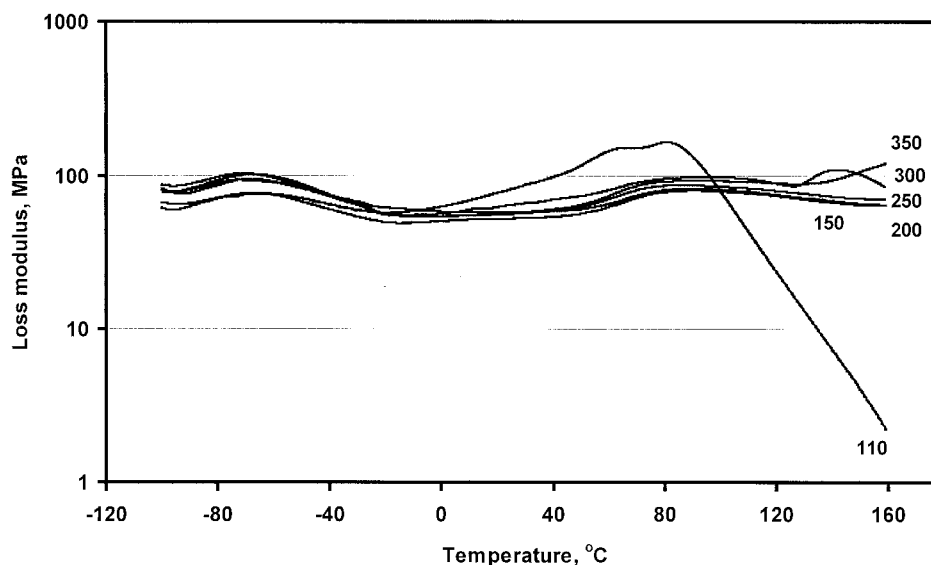


Figure 4 Loss modulus-temperature curves of Soypolyol 173 based polyisocyanurates.

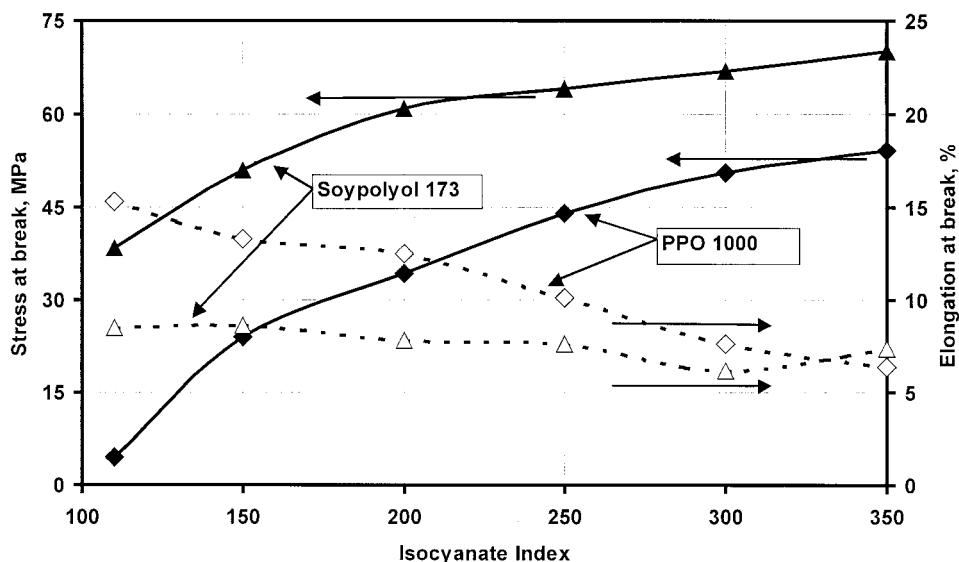


Figure 5 Tensile strengths and elongations at break of polyisocyanurates.

on the modulus. Flexural modulus followed the same trend as tangent modulus. Izod impact was higher for the samples from PPO 168 for indices lower than 200 because of higher flexibility of the polyol chain but for higher indices impact was almost the same (Table 2).

Thermal degradation of modified polyisocyanurate resins started with decomposition of urethane bonds and continued through the breakup of polyol chains and finally triisocyanurate groups. The urethane groups and isocyanurate rings are present in both types of resins in equal concentrations, and the differences in stability between polyisocyanurates from PPO 168 and those from Soypolyol 173 are due to the differences of the polyol structure. Polypropylene oxide based polyols have tertiary C-atoms bonded to ether oxygen that are susceptible to oxidation to ketones, unlike soy polyol, which consists of more stable paraffinic chains and ester

groups. Differential thermogravimetric analysis (DTGA) of pure PPO 168 and pure Soypolyol 173 showed significant differences (Fig. 6). The decomposition of PPO 168 in air occurred in a narrow temperature region with the highest rate at 235°C, whereas the maximum rate of the soy polyol decomposition was at 370°C (i.e., 135°C higher). The soy polyol decomposition peak was followed by several peaks, and the final decomposition peak was at 530°C. The soypolyol 173 decomposition maximum in nitrogen was at 425°C, or 125°C higher than PPO polyol decomposition maximum. The higher thermal stability of the soy polyol had a profound effect on the stability of the derived polyisocyanurates. The highest weight loss in PPO 168 based samples was mostly at 350°C (Fig. 7), and completed degradation was mostly at 450°C. Soypolyol 173 based samples showed several distinctive decomposition ranges (Fig. 8). Their degradation started

TABLE 2
Mechanical Properties and Residue at TGA of Polyisocyanurates

Sample	Index	Tangent modulus (MPa)	Flexural modulus (MPa)	Izod impact (KJ/m ²)	Residue at TGA in air (%)	Residue at TGA in N ₂ (%)
PPO-105	105	157	111	8359	25	15
PPO-150	150	565	524	3829	30	23
PPO-200	200	1017	2228	1839	30	26
PPO-250	250	1186	3313	1596	36	29
PPO-300	300	1257	3146	1375	37	32
PPO-350	350	1188	3264	1104	41	34
SOY-105	105	898	1880	4008	30	19
SOY-150	150	1009	3358	2413	34	24
SOY-200	200	1200	3327	1661	37	29
SOY-250	250	1160	3311	1456	40	32
SOY-300	300	1326	3195	1181	43	33
SOY-350	350	1195	3484	1005	43	35

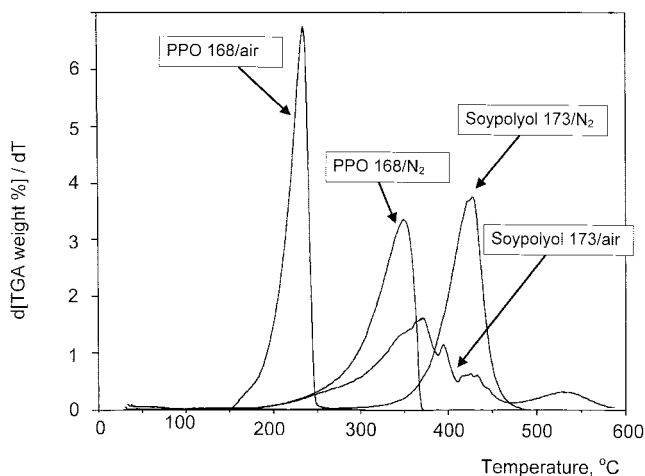


Figure 6 TGA curves in air and nitrogen of polyols.

at 330°C, but the dominant degradation peak was at 480°C, probably because of degradation of the soy polyol along with the degradation of isocyanurate rings. Decomposition of polyisocyanurates in nitrogen proceeded in a similar way as it was in air. The PPO 168 based samples were decomposed mainly at 380°C, with a small final degradation peak at around 500°C. The samples from Soyopolyol 173 were partially degraded in nitrogen in the region between 380 and 400°C with the second strong decomposition peak at 480–500°C. At higher isocyanate indices, this peak was larger than the peak at 380°C, indicating that the decomposition of the isocyanurate rings along with the soy polyol molecule took place. That was quite opposite than with the PPO-based samples. The decomposition of the soy polyol based samples was delayed to the higher temperatures because

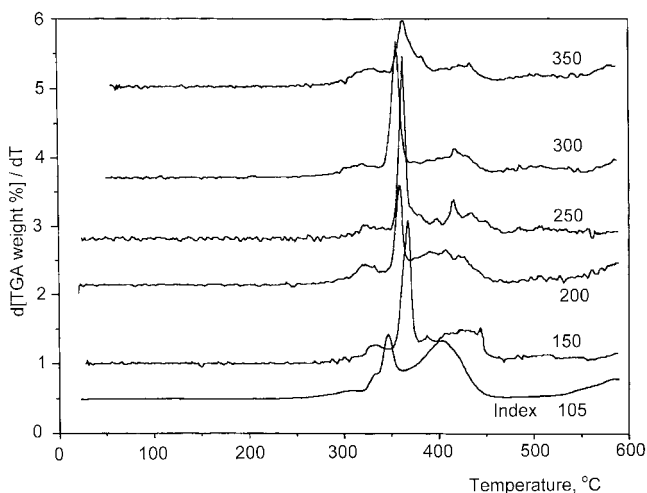


Figure 7 Derivative TGA curves in air of polyisocyanurates from PPO 168 polyol.

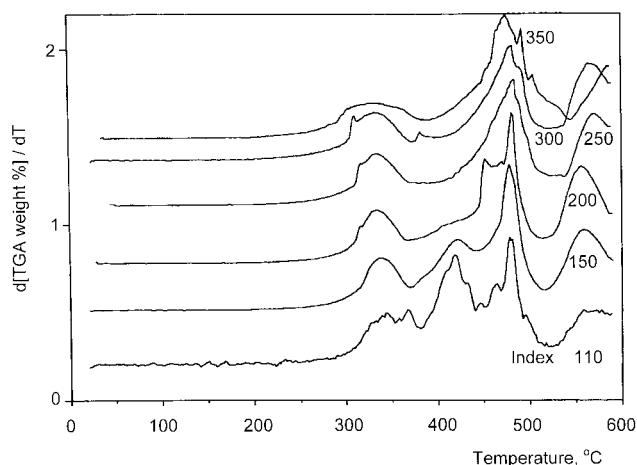


Figure 8 Derivative TGA curves in air of polyisocyanurates from Soyopolyol 173.

of better stability of the polyol, resulting in improved *flammability* characteristics and mechanical properties at elevated temperatures. The materials with slower degradation retain more of their mechanical strength at higher temperatures. The residue for the TGA analysis was higher for the soy polyol samples as well (Table 2).

CONCLUSION

Soybean oil based polyisocyanurates are high-value materials that can be used in foams, elastomers, and coatings. They display better resistance to swelling in toluene than polyisocyanurates from polypropylene oxide polyols of the same molecular weight and functionality. Also they have higher tensile strength, glass transition, and thermal stability.

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