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New Approach to Recycling of Thermosets

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Abstract: The decrosslinking of thermosetting reaction injection molded (RIM) polyurethane-urea products with the smallest amounts of glycols was studied. The effects of the reaction conditions on the properties of liquid oligomers were determined. Successful scale-up studies and utilization of the resulting liquid oligomers for preparation of RIM products, coatings and adhesives are described.

INTRODUCTION

The increasing use of plastics in various industrial and consumer applications in the past few decades has created problems with their disposal. Various legislations as well as escalating landfill costs together with environmental pressures have directed the attention of the public to recycling of plastics. Melt-processing methods were successfully applied to thermoplastics but most thermosets, due to their crosslinked structure, are usually not recycled and are disposed of in landfills. Several methods have been proposed to recycle thermosets (Ref. 1-14) including pyrolysis and oxidative degradation (recovery of hydrocarbons or glass fibers in the case of composites), combustion (recovery of energy), granulation with use as filler and most recently chemical decrosslinking into reactive oligomers.

The most successful reuse of thermosets presently is in the production of carpet underlay using granulated recycled flexible

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polyurethane-urea (PUU) foams rebonded with isocyanate adhesive and in the sheet molding compound (SMC) process, where granulated SMC is used to replace part of the calcium carbonate filler.

Chemical decrosslinking is the most promising approach to the recycling of RIM (reaction injection molded) PUU elastomers and foams. It is much more cost-effective than pulverizing the scrap for use as alternative filler. In special cases, PU can be reprocessed by reactive molding (thermal dissociation of urethane groups and their recombination during cooling) but this process often results in products of inferior quality. PUU RIM elastomers and foams can be successfully decrosslinked into reactive liquid oligomers (LO) by the catalyzed transesterification reactions with low- molecular-weight diols (Ref. 1-14). The decrosslinking reaction is usually carried out using a large excess of diol in order to improve processing. This process is complicated by the formation of a two-phase reaction product and the need for the removal of the excess diol from the product by distillation. This affects the overall economy of the process. We have been studying transesterification of PUU RIM elastomers using a very low diol/PUU RIM ratio. This type of approach eliminates the need for recovery of the diol. The resulting LO contain OH and NH_2 groups which can be reacted with polyisocyanates or epoxides to form new products.

EXPERIMENTAL

Material and Procedures

The PUU RIM scrap material was supplied by the Micro RIM Co. in the form of bumpers which were ground to 2-3 mm particle size. This PUU RIM (N content 5.92%) was a reaction product of polyether triol, MDI (4,4'-diphenylmethane diisocyanate) prepolymer and the chain extender DETDA (diethyltoluenediamine isomers). The reaction procedures and transesterification techniques used to produce LO were described previously (Ref. 15-18).

RESULTS AND DISCUSSION

Transesterification of PUU RIM

In order to be competitive with virgin products, the chemical recycling of PUU RIM has to be simple and economical. Preferentially, the reaction must be short, using small amounts of diol and catalyst.

The transesterification of PUU RIM is a complex heterogeneous reaction involving interfacial phenomena such as diffusion of diol into particles, swelling and series of reactions in the PUU RIM particles. The swelling of PUU RIM particles in ethylene glycol (EG) and butane-1,4-diol (BD) were investigated at various temperatures (100, 120, 130 °C). It was found that the swelling of PUU RIM is relatively low and that swelling in 1,4-BD was higher than in EG. During these reactions (at 210 °C), solid particles visually changed into a paste and finally into a transparent, brown liquid. The changes in concentration of urethane, aromatic amine and urea groups in LO and solid residues were evaluated by measurement of the relative FTIR absorbances with time. With the progress of the reaction, the concentrations of urethane (1749 cm^{-1}) and amine groups (1624 cm^{-1}) in LO increased and finally leveled off at high conversion. In the LO, the urea peak (1647 cm^{-1}) was absent. This implies that the urea linkage in PUU RIM was broken to form amine groups:

$$\text{-NH-CO-NH-} + \text{HO-X-OH} \rightarrow \text{-NH-COO-X-OH} + H_2N\text{-}$$

On the other hand, the FTIR spectra of solid residues showed a steady increase in concentration of urethane groups with reaction time. Strong absorptions of urea groups were found in all solid residues. These results support the conclusion that the transesterification of PUU RIM particles started at the surface layer of the particles, not inside. During the transesterification, cleavage of urea and urethane groups occurs simultaneously and at the end of the reaction, cleavage of the urea groups has been completed.

The effects of reaction variables (such as type and concentration of catalyst, type of diol, glycol/RIM ratio) on yield and properties of LO prepared in a batch reactor were studied. The transesterification reaction proceeded very slowly below 200 °C; however, it was fast in the 210-220 °C range. Of a large number of evaluated catalysts, NaOH, KOH and Na acetate were found to be most active and were used in further studies. The efficiency of various glycols in transesterification of PUU RIM was studied. They included diols (EG, BD, diethylene glycol, triethylene glycol, poly(ethylene glycol) of MW 400, propane-1,3- diol, hexane-1,6-diol) and triols (glycerol and trimethylolpropane). It was found that with the increase in the molecular weight of glycols, the reaction rate decreased and the resulting LO had a high viscosity. Similarly, triols also produced LO with high viscosity. The lowest viscosity was obtained with EG. The effect of EG/RIM ratio on properties of LO showed that with increasing EG/RIM ratio, the reaction rate increased and the viscosities of the resulting LO decreased. At higher EG/RIM ratios, phase separation of LO was observed.

The transesterification of PUU RIM with EG was also studied using a co-rotating twin screw extruder. The effects of screw speed (rpm) on through-put and reaction conversion (% of insolubles) are summarized in Table 1. It was found that a reactive extrusion can be effectively used for transesterification of thermosets such as PUU RIM.

Table 1. Decrosslinking of PUU RIM in the twin screw extruder [a]

Speed (rpm)	Through-put (g/min)	Insolubles (%)
40	37	17.7
70	62	24.3
100	93	32.9
150	116	33.8

[a] Conditions: Berstoff ZE25; temperature(°C) in zones: *1* 180, *2* 200, *3* 240, *4* 230, *5* 230, die 220. RIM/EG/catalyst 84.5/5.0/0.5.

The decrosslinking reaction of PUU RIM was successfully scaled up at Lymtal International Inc. The LO were prepared using a 200-l reactor. The formulation and the results are summarized in Table 2. As can be seen, there was no significant difference between the laboratory and pilot plant samples.

Table 2. Characteristics of liquid oligomers

Properties	**Laboratory**	**Pilot plant, run 2**
Appearance	brown liquid	brown liquid
Viscosity (cps, 20 °C)	4225	4400
Density	1.06	1.06
Equivalent weight based on		
active H	156	168
OH	327	390
NH_2	298	306

CHARACTERIZATION OF LIQUID OLIGOMERS

The LO prepared in the laboratory batch reactor and in the pilot plant were characterized by FTIR, H^1 and C^{13} NMR, gel permeation chromatography and by determination of NH_2, OH and active-hydrogen equivalent weights. The molecular weight distribution curve was trimodal. Comparison of refractive index and UV-GPC curves indicated that the high-molecular-weight products of LO contained aromatic rings (urethane and chain extender groups). All these results supported the conclusion that the LO are mixtures of low-molecular-weight polyurethane polyols (based on MDI and poly(oxypropylene)diols, aromatic diamines (chain extenders) and small amounts of EG.

APPLICATION OF LIQUID OLIGOMERS

The LO resulting from the transesterification of PUU RIM contain both OH and amine groups. These functional groups can be reacted with isocyanates, epoxides, anhydrides and melamines to prepare adhesives, coatings, sealants, foams, RIM, composites, etc. Previously we had reported preparation of solvent and waterborne polyurethane coatings (Ref. 15).

The LO were also used for preparation of PUU RIM parts using commercial PUU RIM system (Bayflex 110-50, Bayer). The LO were blended with the polyol component at various ratios keeping the NCO index at 103.5. The mechanical properties of these LO-modified PUU RIM samples are shown in Table 3. Both modulus and hardness of LO-based PUU RIMs increased but the elongation decreased with increasing amounts of LO. By reformulating the polyol side (decrease in concentration of the chain extender, hard segment), it would be possible to increase the loading of LO in the RIM system and optimize the mechanical properties.

Table 3. Properties of PUU RIM based on liquid oligomers

Liquid oligomers wt.-%	Density g/cm^3	M_{100} MPa	M_{200} MPa	Tensile strength MPa	E %	Hardness Shore D
0	1.05	11.8	13.1	21.9	350	53
10	1.07	12.8	14.2	23.6	330	56
20	1.08	13.0	14.5	19.7	250	56
30	1.09	14.8	-	15.3	110	61

One-package urethane adhesives were prepared by mixing the acetoxime-blocked prepolymer (poly(oxytetramethylene)diol, MW 1000) and MDI (Isonate 143, Dow) with LO/BD blends as crosslinkers. The lap shear strength and peel strength were determined according to ASTM D-1002 and D-903, respectively. The results, presented in Figures 1 and 2, show excellent adhesive strengths.

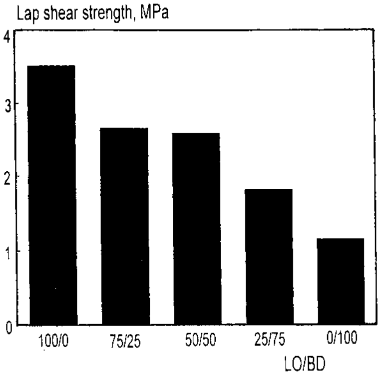

Fig.1 Effect of LO/BD ratio on the lap shear strength (steel/steel) of urethane adhesives

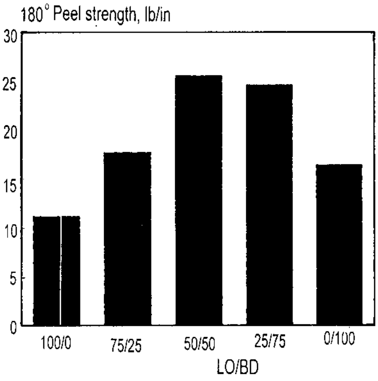

Fig.2 Effect of LO/BD ratio on the 180° peel strength (fabric/steel) of urethane adhesive

Liquid oligomers: equivalent weight 136, prepared by trans-esterification of PUU RIM with ethylene glycol

Similarly, epoxy structural adhesives were prepared from LO and epoxy resin (GY 6020, Ciba Geigy, equivalent weight 200) at various equivalent ratios and cured under different conditions. The results are shown in Figure 3. It is interesting to mention that the optimum equivalent ratio is in the range of 0.93 to 1.45 which is broader than the range for conventional epoxy curing agents (i.e., more forgiving system).

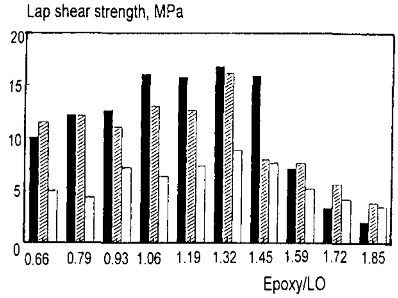

Fig.3 Effect of epoxy/LO ratio and curing conditions on the lap shear strength of epoxy adhesive (liquid oligomers from pilot run; Epoxy GY 6020, Ciba-Geigy)

■ 140 °C, 60 min
▨ 60 °C, 20 h
□ 20 °C, 20 days

CONCLUSIONS

The recycling of the PUU RIM by transesterification using low-molecular-weight diols was studied. It was determined that the transesterification of PUU RIM can be carried out at very low diol/RIM ratios. The resulting LO form single phase and can be economically utilized in various applications such as coatings, RIM and adhesives without special purification or recycling of diols.

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