

**Property Difference of Polybutadiene-derived
Thermoplastic Polyurethanes Based on
Preparative Methods**

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ABSTRACT

Thermoplastic polyurethanes (TPUs) based on hydroxyl-terminated polybutadiene resins have different properties depending on if they were made by a one-shot or prepolymer method. The one-shot method with isocyanate index equal to about 1 in general yielded soluble products which are useful in solvent-based adhesives. The prepolymer method usually produced insoluble materials having slightly better mechanical properties. The difference may be attributed to the small amount of allophanate formation in the prepolymer procedure.

INTRODUCTION

Polyurethanes based on polybutadiene polyols are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties, and low-temperature flexibility [1-3]. However, until recently, the commercially available hydroxyl-terminated polybutadienes have been manufactured by a free-radical polymerization technology (e.g., the Poly bd[®] resins of Cray Valley). This technology yields polyols with functionalities higher than 2.0 that are not useful in TPU systems [4].

Krasol[®] LBH and LBH-P polybutadiene diols, manufactured by Cray Valley Co. are anionically polymerized products with very narrow molecular-weight distribution containing no species with functionality higher than 2.0 [5]. These diols are available in the molecular weight range from 2,000 to 10,000. The standard product Krasol[®] LBH resins are terminated by secondary OH groups and Krasol[®] LBH-P resins are terminated by primary OH groups. They are ideal candidates for making stable prepolymers [6] and also thermoplastic polyurethanes based on the work accomplished by MacKnight et al. [7].

However, during the commercial process studies, it was found that the prepolymer, i.e., two-step, process yielded polyurethanes which were still moldable, but insoluble in common organic solvents at room temperature. In contrast, the one-shot process with the same formulation generally produced soluble polyurethane. This paper explores the possible root causes.

EXPERIMENTAL

Preparation of Thermoplastic Polyurethanes

LAB PROCEDURE:

The synthesis of TPUs was performed in a one-liter glass reactor at normal pressure under a nitrogen blanket with vigorous agitation. The NCO/OH equivalent ratio (NCO index) of all formulations was specified, ranging from 0.95 to 1.05. In the case of the prepolymer procedure, Krasol[®] LBH diol was reacted with a diisocyanate at 80°C for one hour to yield a prepolymer. The prepolymer was mixed in the second step with a chain extender, 2-ethyl-1,3-hexanediol (EHD) at 100° C for 10 minutes. The resulting material was poured into a mold and left to cure at 100°C for 20 hours. Post-curing of the TPU proceeded at ambient temperature for seven days. Under these conditions, the addition of a catalyst was not necessary, but the catalyst dibutyltin dilaurate (DBTDL) was added sometimes to accelerate the curing.

In the case of the one-shot procedure, hydroxyl terminated polybutadiene resins were degassed and dehydrated in a resin kettle in vacuo (< 15 mmHg) at 90°C for 2 hours. Solid 4,4'-methylenebis(phenyl isocyanate) (4,4'-MDI) flakes were heated up to 60°C and melted under nitrogen purging with stirring. Warm (about 60°C) hydroxyl-terminated polybutadiene resins, EHD and melted MDI were charged into a plastic centrifuge cup. The mixture was thoroughly mixed in a speed mixer for 30 seconds at room temperature and then poured in a hot mold (100°C) for curing. All the samples were cured at 100°C for 5 hours and then at 70°C overnight. After 5 days post-cure at ambient temperature, the hardness of those samples was measured at room temperature. The solubility was tested by adding TPU (0.2 g) to a specified solvent (10g) at room temperature. After a week, the final solubility of the polyurethane sample was recorded.

The melt flow rate was determined with a Tinius Olsen Plastometer according to ASTM D 1238-04b procedure. The TPU material was dried for four hours at 88°C. The melt flow was measured out at 190°C with a load of 2.16 kg.

RESULTS AND DISCUSSION

Differences between One-Shot and Prepolymer-Based TPU

The TPU pellets were prepared commercially by reactive extrusion process from Krasol® LBH 2000, MDI and EHD, with 35% hard segment content. They were made initially using a one-shot process. Afterwards, it was decided to produce it using a two-step (prepolymer) procedure with the same formulation. However, the materials obtained from these two processes showed some interesting

differences, especially in hardness and melt flow (Table 1). It is apparent that the material derived from prepolymer process has slightly higher hardness and modulus and significantly lower melt flow than that derived from the one-shot procedure.

Further, the solubility profile of these two products also differed. The TPU material obtained from the one-shot process could be dissolved in a few common solvents, such as ethyl acetate, methyl ether ketone and THF (Table 2), but the TPU pellets from the prepolymer process failed to dissolve in any common solvents (Table 3).

Table 1. Property Differences for TPUs Made from One-Shot and Prepolymer Processes

Properties	One-Shot Process	Prepolymer Process
Elongation %	550	559
Hardness Shore A	80	82
Modulus @ 100%, MPa	5.6	6.6
Vicat Softening point, °C	-	52.2
Specific gravity @ 25 °C	0.96	0.995
Tensile strength @ break, MPa	14.0	11.9
Tg, °C	-35	-34
Melt Flow Rate, g/10min @ 190 °C, 21 N load	17	1.06

Table 2. Solubility Results of One-Shot TPU Pellets in Various Solvents at Room Temperature

Solvent	Solubility results	Appearance of mixture
Ethanol	Not soluble	Pellets nearly intact
n-Heptane	Not soluble	Pellets nearly intact
Methanol	Not soluble	Pellets nearly intact
Renoil 100 (mineral oil)	Not soluble	Pellets nearly intact
2-Propanol	Not soluble	Pellets nearly intact
Acetone	Not soluble	Hazy, two phases
Xylenes	Not soluble	Hazy, two phases
Dibutyl phthalate	Not soluble	Pellets swelled
Cyclohexane	Not soluble	Pellets slightly swelled
N,N-Dimethyl foramide	Soluble after a few days	hazy
Toluene	Soluble after a few days	lightly hazy
Ethyl acetate	Soluble	Slightly cloudy
Tetrahydrofuran	Soluble	Clear
Pyridine	Soluble	Clear
Methyl ethyl ketone	Soluble	Slightly cloudy
Dichloromethane	Soluble	Cloudy

Table 3. Solubility Results of Prepolymer-Based TPU Pellets in Various Solvents at Room Temperature

Solvent	Solubility results	Appearance of mixture
Ethanol	Not soluble	Pellets intact
n-Heptane	Not soluble	Pellets nearly intact
Methanol	Not soluble	Pellets intact
Renoil 100 (mineral oil)	Not soluble	Pellets intact
2-Propanol	Not soluble	Pellets intact
Acetone	Not soluble	Pellets nearly intact
Xylenes	Not soluble	Pellets swelled
Dibutyl phthalate	Not soluble	Pellets nearly intact
Cyclohexane	Not soluble	Pellets nearly intact
N,N-Dimethyl foramide	Not soluble	Pellets swelled
Toluene	Not soluble	Pellets swelled
Ethyl acetate	Not soluble	Pellets swelled
Tetrahydrofuran	Not soluble	Pellets swelled
Pyridine	Not soluble	Pellets swelled
Methyl ethyl ketone	Not soluble	Pellets nearly intact
Dichloromethane	Not soluble	Pellets swelled

INVESTIGATION OF ROOT CAUSES

Based on the data, the preparative method apparently plays a critical role in generating the structural disparity between these two TPUs. To gain further insights into the discrepancy, the effect of a few possible factors, including hard segment concentration, molecular weight of hydroxyl-terminated polybutadiene diols, and NCO index on solubility under either preparative procedure was examined. Maintaining the same NCO index at 1.0 as the commercial products, the hard segment concentration was varied from 32 to 45% in the lab sample preparation using the prepolymer method (Table 4, samples 1 and 2). Both polyurethane

samples were not soluble. This finding supports the premise that the insolubility has little to do with the reactive extrusion conditions which require larger amounts of catalyst and higher temperature than the lab procedure, as the mild laboratory synthesis also yielded insoluble products. The hard segment content might not be a critical factor either in the range of interest based on the results. To further support that the insolubility was not caused by 4,4'-MDI isomer in forming more orderly hard domains, Lupranate® MI (a mixture of 2,4'- and 4,4'-MDI isomers) was used. Similarly, the insoluble polyurethanes were generated (Table 4, samples 3 and 4)

Table 4. TPUs from Prepolymer Method

	1	2	3	4
Krasol® LBH 2000	100	100	100	100
EHD	6.48	12.96	18.12	38.82
4,4'-MDI	33.22	55.37	---	-----
Lupranate MI	----	----	33.27	55.47
T-12 (drop)	1	1	1	1
NCO Index	1.0	1.0	1.0	1.0
Equivalent ratio of LBH / MDI / EHD	1 / 3 / 2	1 / 5 / 4	1 / 3 / 2	1 / 5 / 4
Hard segment content (%)	31.58	44.81	31.6	44.84
Procedure of preparation	prepolymer			
Hardness (shore A/D) of sheet	83 / 30	95 / 50	77 / 28	94 / 50

Table 5. TPUs from Prepolymer Method

	1	2	3
Krasol® LBH 2000	100	100	100
EHD	12.95	13.35	13.76
MDI	33.25	33.25	33.25
T-12 (drop)	1	1	1
NCO Index	1.0	0.98	0.96
Equivalent ratio of LBH / MDI / EHD	1 / 3 / 2	1 / 3 / 2.06	1 / 3 / 2.13
Hard segment content (%)	31.6	31.8	32.0
Procedure of preparation	Prepolymer		

The NCO index was then reduced from 1.0 to 0.96 for the prepolymer method. The materials of 32% hard segment concentration became soluble when an NCO index of 0.96 was used (Table 5, sample 3). The other two samples (Table 5, samples 1 and 2) having higher NCO index were still not quite soluble. Interestingly,

when the hard segment concentration was increased to 38%, reducing the NCO index to 0.96, it did not make the resulting material soluble (Table 6, sample 3). It is conceivable that the amount of side reactions making the polyurethane insoluble increase with the concentration of hard segments.

Table 6. TPUs from Prepolymer Method

	1	2	3
Krasol® LBH 2000	100	100	100
EHD	18.13	18.64	19.16
MDI	42.12	42.12	42.12
T-12 (drop)	1	1	1
Index of NCO / OH	1.0	0.98	0.96
Eqs ratio of LBH / MDI / EHD	1 / 3.8 / 2.8	1 / 3.8 / 2.88	1 / 3.8 / 2.96
Hard segment content (%)	37.6	37.8	38.0
Procedure of preparation	Prepolymer		

The one-shot process was then studied. Four samples were prepared based on Krasol® resin of 3000 molecular weight (Table 7) using the one-shot method in the lab. With hard segment concentrations ranging from 27 to 61%, all the resulting materials were insoluble as long as the NCO index was maintained at 1.05. Similarly, using Krasol® resin of 2000 molecular weight, a series of polyurethanes with hard segment concentration ranging from 23 to 55% were

prepared (Table 8, samples 1-4). These elastomers were insoluble as well. Further, the only major difference between these materials (Table 8, samples 1-4) and the commercial one-shot product was the NCO index, namely, 1.05 versus 1.0, respectively, in addition to the concentration of hard segments. Indeed, once the NCO index was lowered to 1.0 (Table 8, sample 5), the material became soluble again.

Table 7. TPUs from One-Shot Method

	1	2	3	4
Krasol [®] LBH 3000	100	100	100	100
EHD	10.36	23.54	37.67	51.79
MDI	27.07	50.76	76.14	101.52
T-12 (drop)	1	1	1	1
Equivalent ratio of LBH / EHD / MDI	1 / 2.2 / 3.36	1 / 5 / 6.3	1 / 8 / 9.45	1 / 11 / 12.6
NCO Index	1.05	1.05	1.05	1.05
Hard segment content (%)	27.2	42.6	53.2	60.5
Hardness (shore A/D) of cured sheet	69/25	79/34	82/35	90/47

Table 8. TPUs from One-Shot Method

	1	2	3	4	5
Krasol [®] LBH 2000	100	100	100	100	100
EHD	6.47	12.94	18.12	38.82	12.95
MDI	23.25	34.88	44.18	81.39	33.25
T-12 (drop)	1	1	1	1	1
Equivalent ratio of LBH / EHD / MDI	1 / 1 / 2.1	1 / 2 / 3.15	1 / 2.8 / 3.99	1 / 6 / 7.35	1 / 2 / 3
NCO Index	1.05	1.05	1.05	1.05	1.0
Hard segment content (%)	22.9	32.4	38.0	54.6	31.6
Hardness (shore A/D) of cured sheet	67 / 22	83 / 33	88 / 40	94 / 56	79 / 30

As expected, when an NCO index of less than one was employed for the one-shot method, the materials were soluble (Table 9, samples 1-3). Moreover, as

the hard segment concentration was increased from 32 to 38% (Table 10), the resulting polyurethanes were still soluble as long as the NCO index was kept at one or less.

Table 9. TPUs from One-Shot Method

	1	2	3
Krasol [®] LBH 2000	100	100	100
EHD	12.95	13.35	13.76
MDI	33.25	33.25	33.25
T-12 (drop)	1	1	1
NCO Index	1.0	0.98	0.96
Equivalent ratio of LBH / MDI / EHD	1 / 3 / 2	1 / 3 / 2.06	1 / 3 / 2.13
Hard segment content (%)	31.6	31.79	31.97
Procedure of preparation	One shot		

Table 10. TPUs from One-Shot Method

	1	2	3
Krasol [®] LBH 2000	100	100	100
EHD	18.13	18.64	19.16
MDI	42.12	42.12	42.12
T-12 (drop)	1	1	1
NCO Index	1.0	0.98	0.96
Equivalent ratio of LBH / MDI / EHD	1 / 3.8 / 2.8	1 / 3.8 / 2.88	1 / 3.8 / 2.96
Hard segment content (%)	37.6	37.8	38.0
Procedure of preparation	One shot		

Correlating the melt flow property of the materials derived from either one-shot or two-step methods may shed some light to the structural differences among them, as the melt flow property is related to the molecular weight of the material. In the first set of five formulations (Table 11) the NCO index was varied from 0.95 to 1.05 and the polyurethanes were made through the prepolymer method. The second set of five formulations, having the same corresponding stoichiometry and NCO index as the first set, were prepared with the one-shot method. The two-step method generated plaques of higher hardness for every composition than the corresponding one obtained using the one-shot method (Tables 11 and 12). The solubility profile for each set of samples is also consistent with what we have observed previously based on the NCO

index of each formulation and preparation procedure. The melt flow data are also consistent with the NCO index for both sets of TPUs. When the NCO indices are less than 1.0, the high melt flow indicates that the materials having low molecular weight. Once the NCO indices are larger than 1.0, side reactions such as allophanate formation are likely to take place, causing the melt flow to decrease. In addition, the melt flow for the materials produced via the two-step process is in general lower than the corresponding product made from the one-shot process. The difference could also be accounted for by the higher amount of allophanate formation in the samples from prepolymer process (Table 11, samples 2-5) compared to the corresponding samples from the one-shot process (Table 12, samples 7-10). This conclusion is supported by the trend in solubility profile as well.

Table 11. TPUs from Prepolymer Method

Sample no. 595-133-	1	2	3	4	5
Krasol [®] LBH 2000	100	100	100	100	100
MDI	36.22	37.17	38.13	39.07	40.03
EHD	15.80	15.80	15.80	15.80	15.80
T-12 (drop)	1	1	1	1	1
NCO index	0.95	0.975	1.00	1.025	1.05
Hard segment content, wt%	34.2	34.6	35.0	35.4	35.8
Preparative method	Two step reaction (prepolymer procedure)				
Equivalent ratio of reactants	LBH 2000 /MDI / EHD = 1 / 3.44 / 2.44 for 1.0 index				
Hardness of cured sheet (Shore A)	84	86	87	88	89
Solubility in ethyl acetate	+	±	—	—	—
Solubility in THF	+	+	—	—	—
Melt flow (g/10 minutes)	102.1	15.96	5.317	2.098	1.654

Table 12. TPUs from One-Shot Method

Sample no. 595-133-	6	7	8	9	10
Krasol [®] LBH 2000	100	100	100	100	100
MDI	36.22	37.17	38.13	39.07	40.03
EHD	15.80	15.80	15.80	15.80	15.80
T-12 (drop)	1	1	1	1	1
NCO index	0.95	0.975	1.00	1.025	1.05
Hard segment content, wt%	34.22	34.63	35.04	35.43	35.83
Date sample prepared	5/23/06	5/23/06	5/24/06	5/24/06	5/25/06
Preparative method	One shot procedure				
Equivalent ratio of reactants	LBH 2000 /MDI / EHD = 1 / 3.44 / 2.44 for 1.0 index				
Hardness of cured sheet (Shore A)	78	81	82	83	81
Solubility in ethyl acetate	+	+	+	±	—
Solubility in THF	+	+	+	+	±
Melt flow (g/10 minutes)	67.05	44.74	6.072	4.614	3.689

CONCLUSIONS

The one-shot process generates soluble TPUs as long as the NCO index is maintained around 1.0 or lower. On the other hand, the two-shot or prepolymer process only yielded insoluble, but still moldable, TPUs, even if the NCO index was kept at 1.0 or slightly lower. This insolubility is attributed to the allophanate formation when the isocyanate functionality is in excess. The allophanate moiety can also be used to account for the relatively high hardness and low melt flow of the material generated from the prepolymer process.

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BIOGRAPHIES

Herbert Chao



Herbert Chao received his Ph.D. in Organic Chemistry from Massachusetts Institute of Technology. After graduation in 1980, he worked at Union Carbide Co. and then General Electric Co. on various aspects of engineering plastics. Since 2001, he has been with Cray Valley Co. as technical manager in charge of developing applications for polybutadiene materials.

