TECHNICAL UPDATE

CRAY VALLEY
Hydrocarbon Specialty Chemicals

Krasol® Polybutadiene-Derived Thermoplastic Polyurethanes

Yield Differential Properties Based On One-Shot and Prepolymer Methods

Benefits

- Exceptional hydrolytic and chemical resistance
- Excellent hydrophobicity
- Enhanced electrical insulation properties
- Excellent low-temperature flexibility
- Excellent compatibility with polyolefins

Applications

- Adhesives, including tie layers between polar and non-polar surfaces
- Sealants
- Polymer/rubber modification
- Hose and tube
- Wire and cable
- Footwear
- Film and sheet

Additional Information

MSDS/TDS: Krasol® LBH 2000

Description

Krasol® LBH and LBH-P polybutadiene diols are anionically polymerized products with very narrow molecular-weight distribution and containing no species with functionality higher than 2.0. These diols are available in a molecular weight range from 2,000 to 10,000. The standard 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 and also thermoplastic polyurethanes (TPUs). Thermoplastic polyurethanes based on Krasol resins have different properties depending on whether they were made by a one-shot or prepolymer method. The one-shot method, with isocyanate index equal to about 1, yielded soluble products that are useful in solvent-based adhesives. The prepolymer method usually produced insoluble, but still moldable materials, having slightly better mechanical properties.

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TPU Preparation and Testing

As shown below, the following raw materials were used to prepare TPUs:

Polyol – Krasol LBH 2000
Diisocyanate – 4,4' methylenebis(phenyl isocyanate) (4,4'-MDI)
Chain extender – 2-ethyl-1,3-hexanediol (EHD)
Catalyst – dibutyltindilaurate (DBTDL)

Thermoplastic elastomer samples were synthesized in the laboratory adopting a prepolymer method (Table I) or a one-shot procedure (Table II); their mechanical and thermal properties were measured.

In the first set of five formulations (Table I), 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 (Table II).

Table I
Prepolymer Method

Formulation No. Preparation	1	2	3	4	5
Krasol LBH 2000 (g)	100	100	100	100	100
MDI (g)	36.22	37.17	38.13	39.07	40.03
EHD (g)	15.80	15.80	15.80	15.80	15.80
DBTDL (drop)	1	1	1	1	1
Formulation Characteristics					
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
Properties					
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
Tensile strength, psi	1615	2427	2666	2590	3111
Modulus at 50% strain, psi	702	764	805	842	869
Elongation at break, %	492	504	442	373	412
Tear resistance, lbf/in	392	405	411	356	386

+ = soluble
± = partially soluble
— = insoluble

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Table II
One-Shot Method

Formulation No. Preparation	6	7	8	9	10
Krasol LBH 2000 (g)	100	100	100	100	100
MDI (g)	36.22	37.17	38.13	39.07	40.03
EHD (g)	15.80	15.80	15.80	15.80	15.80
DBTDL (drop)	1	1	1	1	1
Formulation Characteristics					
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
Properties					
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
Tensile strength, psi	1226	1691	1449	1287	1339
Modulus at 50% strain, psi	443	537	568	615	611
Elongation at break, %	358	343	222	171	175
Tear resistance, lbf/in	351	354	301	301	311

+ = soluble
± = partially soluble
— = insoluble

Structural/Physical Properties Discussion

Comparing the melt flow results for the materials derived from either one-shot or prepolymer methods may shed some light on the structural differences among them, as the melt flow property is related to the molecular weight of the material. The solubility profile for each set of samples is also reported. 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. 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 have 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 prepolymer process is generally 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 1, samples 2-5) compared to the corresponding samples from the one-shot process (Table 2, samples 7-10). This conclusion is supported by the trend in solubility profile as well.

Mechanical Properties Discussion

Mechanical properties were determined for all the plaques generated in the investigation. The prepolymer method yielded plaques of higher hardness than the one-shot method for all the compositions examined (Tables I and II). Surprisingly, other properties, including tensile strength, modulus, elongation, and tear of those materials derived from the prepolymer method, are also much better than those from the one-shot method. Such a large discrepancy in mechanical properties was not observed between the injection molded plaques of PRO7840 and Poly bd 2035 TPU produced by the one-shot and prepolymer methods, respectively, via reactive extrusion. Different thermal exposure between the lab and commercial samples may have induced significant changes in microstructures between them.

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