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APPLICATION BULLETIN

# *Novel Polybutadiene Diols for Thermoplastic Polyurethanes*


## Abstract

Krasol® polybutadiene diols are anionically polymerized products characterized by very narrow molecular weight distribution, linear structure of polymer chains and the absence of species with functionality higher than 0.2. These unique features make them suitable as hydrophobic polyol components for use in thermoplastic polyurethanes (TPUs).

Various TPU formulations were developed using polybutadiene diols with either primary (Krasol LBH-P) or secondary terminal OH groups (Krasol® LBH), adopting a one-shot or prepolymer procedure. The TPU elastomers thus obtained may be classified as soft grade TPUs. The elastomers were characterized by measuring their physical and mechanical properties.

Special attention was focused on the hydrolytic and chemical resistance of these TPUs. A hydrolysis study was performed in aqueous media (acetic acid, sulfuric acid, nitric acid, caustic soda), in methanol and ethanol. Contrary to a TPU based on a conventional polyether polyol, which was tested simultaneously, the stability of polybutadiene TPUs was outstanding even in very aggressive solutions of inorganic acids.

TPUs manufactured from Krasol® polybutadiene diols have excellent electrical properties. The measurements of volume and surface resistivity of the polybutadiene-urethanes showed values several orders higher than those of polyether based TPUs.

Based on their mechanical, chemical and electrical properties, polybuladiene TPUs have great potential for applications where excellent moisture resistance, chemical stability and electrical insulation characteristics are required.


## Introduction

Thermoplastic polyurethanes (TPUs) are formed by linear polymeric chains of segmented structure. They are prepared by the addition reaction of bifunctional isocyanates, chain extenders and long-chain polyols. Most of conventional TPUs are based either on polyester or polyether polyols, 4,4-diphenylmethane diisocyanate (MDI) as an isocyanate component and 1,4-butanediol (BDO) as a chain extender[1].

Development of soft grades of TPUs (having hardness about 70-85 Shore A) has been reported among the latest trends that are taking place in the TPU market. The main interest of researchers is focused on the polyol components[2].

Polyurethanes based on polybutadiene polyols could fall into this category. Moreover, they are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties and low-temperature elasticity[3-5]. However, most of the commercially available large-scale hydroxyl terminated polybutadienes are manufactured by a free radical polymerization technology, e.g. Poly bd®. This technology yields polyols with functionality exceeding the value 2.0, that are not applicable in TPU systems[6].

Polybutadiene polyols with a functionality of 2.0 designated Difol were developed by Amoco Chemicals several years ago[7]. These polybutadiene diols proved to be suitable components used for


Oaklands Corporate Center, 468 Thomas Jones Way, Suite 100, Exton, PA 19341
Toll Free 877-871-2729




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the preparation of TPU elastomers[8]. However, Difol polyols have not been commercialized.

Krasol® polybutadiene diols LBH are anionically polymerized products with very narrow molecular weight distribution containing no species with functionality higher than 2.0[9]. Krasol® LBH diols are available in molecular weight ranges from 2000 to 5000. The commercially manufactured products are terminated by secondary OH groups, however, developmental grades of Krasol® LBH-P with primary OH groups are also available in limited amounts.

To estimate the potential of Krasol® polyols in TPU applications, the first phase of the study was focused on the development of TPU formulations. Special attention was given to the evaluation of hydrolytic and chemical stability of the polybutadiene TPUs and to the measurements of their electrical insulation properties. The data thus obtained were compared with those of the polyether based TPU Pellethane® 2103-70A. This soft grade TPU is recommended for applications requiring very good hydrolytic resistance and excellent electrical properties[10].

## EXPERIMENTAL

### Materials

All chemicals used in this study are listed in Table 1 and were used as received from the suppliers unless otherwise stated. Chain extenders were checked for the content of moisture and, if necessary, dried under a vacuum until the content of water was below 0.03%. Pellethane 2103-70A was measured using a thermomechanical analysis method to determine its softening temperature, which was 145 °C.

### Preparation of Thermoplastic Polyurethanes

The synthesis of TPUs was performed in a one liter glass reactor at normal pressure, under nitrogen blanket and vigorous agitation. The NCO/OH ratio of all formulations was 1.03-1.05. In the case of the prepolymer procedure, Krasol® LBH diol was reacted with a diisocyanate at 80 °C for 1 hour to yield a prepolymer that was mixed in the second step with a chain extender 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 laboratory temperature for 7 days. Under these conditions the addition of catalyst was not necessary.

In the case of the one-shot procedure, the reaction vessel was charged with Krasol® LBH or LBH-P, chain extender and Tinuvin B75. The mixture was heated to 80-90 °C. Then, Suprasec MPR (preheated to about 45 °C) was added. After 3-5 minutes of the agitation the TPU was discharged into a mold and left to cure as previously described.

The polyurethane sheets thus prepared were used for the determination of mechanical and physical properties and for the resistance study.

**Table 1. Materials**

| Designation | Chemical Identification | Eq. Wt. | Supplier |
|---|---|---|---|
| **Krasol® LBH 3000** | Polybutadiene diol with secondary OH groups | 1320 | Kaucuk |
| **Krasol® LBH 2000** | Polybutadiene diol with secondary OH groups | 1110 | Kaucuk |
| **Krasol® LBH-P 3000** | Polybutadiene diol with primary OH groups | 1560 | Kaucuk |
| EHD | 2-Ethyl-1,3-hexanediol | 73.1 | Degussa-Huels |
| BDO | 1,4-Butanediol | 45.1 | Loba Chemie |
| Voranol RA 100 | N,N-Diisopropanol aniline (DIPA) | 104.6 | Dow Chemical |
| TMPD | 2,2,4-Trimethylpentane-1,3-diol | 73.1 | Chemopetrol |
| Suprasec MPR | 4,4'-Diphenylmethane diisocyanate (MDI) | 125.1 | Huntsman Corporation |
| Tinuvin B75 | Polyurethane stabilizer | - | Ciba Specialty Chemicals |
| Pellethane 2103-70A | Polyether based TPU | - | Dow Chemical Co. |

**Extrusion of Thermoplastic Elastomers**
Extrusion of the TPUs was carried out in a Goettfert extruder (Feinwerk Technik Buchen / Odenwald, Germany) with a screw diameter of 20 mm and three zones of electric heating adjusted to the temperatures 1/2/3=160/190/180 °C. The extruded strand was cooled by air and chopped to granules using a Scheer SGS-50-E machine.

**Evaluation of Elastomer Properties**
Physical and mechanical properties of polyurethane elastomers were evaluated by the following test methods:

- Shore hardness (ISO 868:1985)
- Tensile stress-strain properties (ISO 37:1994)
- Compression set (ISO 8 I 5: 199 1)
- Electrical properties, i.e. volume resistivity and surface resistivity (IEC 93), electrometer Keithley 616

The glass transition and the softening temperature values of the TPUs were measured by thermomechanical analysis (TMA).

The resistance of polyurethane elastomers was studied using aqueous solutions of $CH_3COOH$ (10%), $H_2SO_4$, (60%), $HN0_3$ (40%) and NaOH (50%), water steam, methanol and ethanol. The temperature of the media was 23 °C except for water steam, which was 100 °C. The time of exposure was 28 days, the retention of Shore hardness was determined. Swelling of polyurethanes in ethanol was monitored by measuring the volume change of the samples.

**Results and Discussion**

**Thermoplastic Polyurethanes Prepared by Prepolymer Procedure**
The following parameters of the formulation were tested in order to find out the structure-property relationship of the Krasol® based TPUs:

- Type of OH groups (primary or secondary) of the polybutadiene diol and its molecular weight
- Method of synthesis (one-shot or prepolymer procedure)
- Selection of the chain extender
- Hard segment content

The first syntheses were performed using Krasol® LBH 3000 secondary polyol and adopting the prepolymer approach. The formulation No. 1 - 4 in the Table 2 show the comparison of 2-ethyl-1,3-hexanediol (EHD), 2,2,4-trimethyl pentane-1,3-diot (TMPD), N,N-diisopropanol aniline (DIPA) and 1,4-batanediol (BDO) as chain extenders. EHD, DIPA and TMPD lead to polyurethanes with Shore hardness about 80 A that may be classified as soft grade TPUs. Their mechanical properties are comparable with those of good quality general purpose rubber materials.

The use of BDO as an extender in Krasol® based TPUs with 35% hard segment content cannot be recommended due to serious problems with demolding. It can be presumably caused by the limited miscibility of polybutadiene diols with 1,4-butanediol (BDO)[8]. However, successful syntheses of TPUs based on hydrocarbon polyols have been reported when using BDO at relatively low hard segment content (20-23%)[8,11]. This possibility for Krasol® based TPUs was verified later in one-shot formulations.

**Table 2. Characterization of Thermoplastic Polyurethanes Prepared by Prepolymer Procedure: Krasol® LBH 3000/MDI/extender**

| Formulation | 1 | 2 | 3 | 4[1] | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Extender | EHD | DIPA | TMPD | BDO | EHD | EHD | EHD | EHD |
| Hard segment (%)35 | 35 | 35 | 35 | 35 | 30 | 25 | 20 | 15 |
| Hardness (ShA) | 77 | 78 | 77 | - | 74 | 66 | 55 | - |
| Tensile strength (Mpa) | 18.2 | 17.2 | 17.5 | - | - | - | - | - |
| Elongation at break (%) | 410 | 490 | 400 | - | - | - | - | - |
| Softening temperature (°C) | 110 | 110 | 110 | - | 100 | 70 | 60 | 50 |
| Glass transition temperature (°C) | -42 | - | - | - | -43 | -43 | -42 | -40 |

[1] demolding of the sample after 20 hours cure at 100 °C was not possible

Regarding the thermal characteristics, the melting point of hard segments formed by MDI and non-linear chain extenders is significantly lower than that of MDI/BDO domains[12]. Therefore the softening temperature of TPUs in the Table 2 is relatively low. Glass transition temperature, on the other hand, corresponds to medium-vinyl type polybutadiene in the elastomer's soft segments.

The best results with good reproducibility were achieved with EHD and DIPA. The main difference between these two extenders is in processing - DIPA is solid at ambient temperature. Based on these data, EHD was chosen for further development.

In an attempt to obtain even softer TPUs, a series of samples with decreasing hard phase content was synthesized (Table 2, formulations 5-8). By decreasing the hard segment content it was possible to prepare a TPU with hardness as low as 55 Shore A. However, a weak point of TPUs containing EHD as a chain extender and having 25% or lower hard phase content is their poor heat resistance.

Preparations of the Krasol® LBH 3000/MDI/EHD with 35% hard segment content (according to Table 2, Formulation 1) were carried out repeatedly to check the reproducibility of the synthesis. The typical characteristics of the elastomer were as follows: Shore A hardness 78-82, tensile strength 15-18 MPa, elongation 500-700, compression set (70 °C, 22 hours) 50%, softening temperature about 110 °C, glass transition temperature from -39 to -43 °C.

Some of the batches were prepared with the addition (1.0%) of Tinuvin B75, a complex polyurethane stabilizer. The presence of the stabilizer is expected to reduce light-induced yellowing of the polyurethane (due to the presence of aromatic isocyanate) and to minimize possible oxidation processes in the double bonds of the polybutadiene backbone. The addition of Tinuvin B75 did not affect the measured elastomer properties.

**Thermoplastic Polyurethanes Prepared by One-Shot Procedure**

Krasol® LBH polybutadiene polyols, though having secondary OH groups, can be used with EHD as a chain extender for one-shot TPUs. The effect of the synthetic procedure on the elastomer properties is shown by comparing Formulation 1 in the Table 2 with No. 9 in the Table 3. One-shot TPUs based on LBH 3000 exhibited somewhat lower hardness as well as lower tensile properties compared with polyurethanes prepared by the prepolymer method. Thermal characteristics of both products were the same.

The role of polyol molecular weight and of the type of OH groups can also be seen from the Table 3 (No. 9 to 11). All these elastomers have similar properties, however, the use of LBH 2000 resulted in a small increase of Shore hardness and a slight change in softening and glass transition temperature.

As mentioned earlier, only limited amount of BDO can be added to the formulation. As a result, TPUs with hard segment content not exceeding about

25% can be prepared. Higher reactivity of BDO requires the use of more reactive Krasol® LBH-P in one-shot systems. A formulation with LBH-P 3000 and BDO yielded a very soft TPU product with hardness 60 Shore A, good elongation and relatively high softening temperature (Table 3, formulation 12).

**Processing Possibilities**

The processing possibilities were tested on TPUs composed of Krasol® LBH 3000 / MDI / EHD with 35% hard segment content. The TPUs can be hot-pressed at 140-150 °C and extruded at 160-190 °C.

The melting and recrystallization of the polyurethane hard segments was followed by changes in elastomer appearance. TPUs obtained after curing at 100 °C were white and not transparent. After hot-pressing at 140-150 °C the material became almost clear. Extrusion at temperatures 180-190 °C yielded a transparent product.

**Chemical and Hydrolytic Resistance**

Polybutadiene-urethanes No. 1, 10 and 12 (cf. Table 2 and 3) and a conventional TPU based on poly(tetramethylene ether) glycol (PTMEG) were included in the study.

The elastomers were tested for their resistance to aqueous solutions of a weak acid (10% $CH_3COOH$), strong mineral acid (60% $H_2SO_4$), oxidizing mineral acid (40% $HN0_3$) and strong alkaline solution (50% NaOH). All these tests were performed at ambient temperature.

**Table 3. Thermoplastic Polyurethanes Prepared by One-Shot Procedure**

| **Formulation** | **9** | **10** | **11** | **12** |
|---|---|---|---|---|
| **Composition** | | | | |
| **Krasol® LBH 3000 (pbw)** | 100 | - | - | - |
| **Krasol® LBH 2000 (pbw)** | - | 100 | - | - |
| **Krasol® LBH-P 3000 (pbw)** | - | - | 100 | 100 |
| EHD (pbw) | 16.5 | 15.1 | 17.0 | - |
| BDO (pbw) | - | - | - | 6.5 |
| Tinuvin B75 (pbw) | 1.6 | 1.6 | 1.6 | 1.3 |
| MDI (pbw) | 37.4 | 39.1 | 38.2 | 26.9 |
| Hard segment content (%) | 35 | 35 | 35 | 25 |
| **Physical Properties** | | | | |
| Hardness (Shore A) | 73 | 76 | 73 | 60 |
| Tensile strength (Mpa) | 14.4 | 15.2 | 15.9 | 6.8 |
| Modulus 100% (Mpa) | 7.0 | 6.5 | 8.7 | 2.6 |
| Elongation at break (%) | 390 | 460 | 470 | 890 |
| Softening temperature (°C) | 110 | 90 | 110 | 150 |
| Glass transition temperature (°C) | -40 | -35 | -41 | -44 |

No significant differences were found among Krasol® based TPUs with regards to their resistance to the individual media. Figure 1 compares the stability of the Krasol® LBH 3000 based TPU with one having the polyether polyol as the soft segments. Both TPUs were stable in acetic acid and NaOH. However, a dramatic difference was found after soaking the elastomers in solutions of sulfuric acid and nitric acid. In these media, the polyether based TPU corroded or dissolved after one day of immersion, while polybutadiene-urethane remained almost unaffected for 28 days.

Another series of measurements was carried out after immersion of elastomers in methanol and ethanol. Both polyether and polybutadiene based TPUs exhibited a considerable decrease in Shore hardness after 28 days immersion (Figure 1), which can be attributed to swelling. Remarkable differences between the TPUs were revealed by monitoring the volume change in the

course of the test in ethanol (Figure 2). Poiyether based TPU increased its volume within one day by about 90 %, and then remained without significant change till the end of exposure. The specimens withdrawn from alcohol after 28 days could be easily dried (24 hours at ambient temperature and normal pressure) to their original volume.

**Figure 1.**

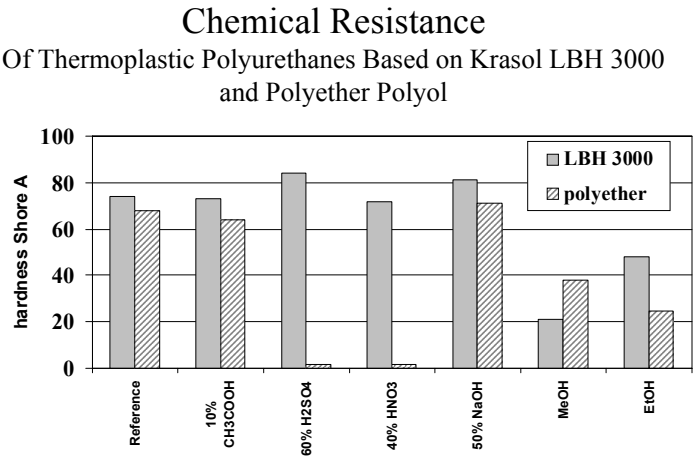


**Figure 2.**

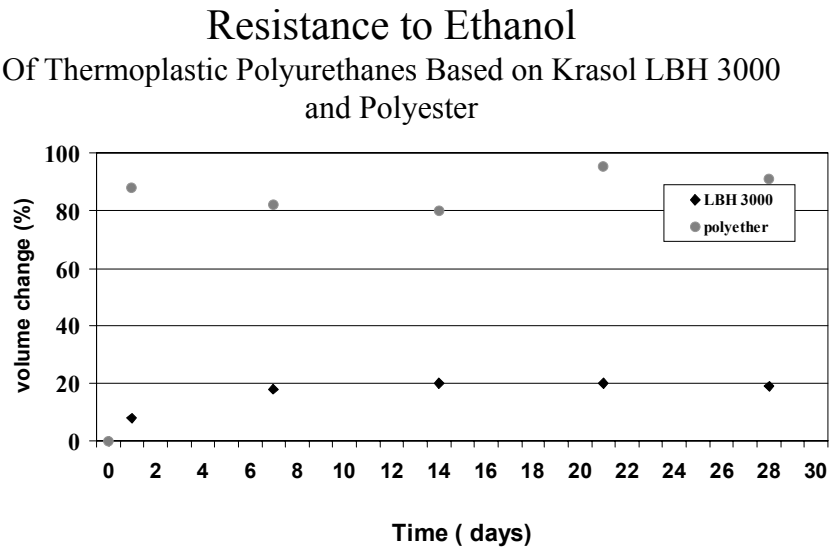


**Table 4. Resistance of Thermoplastic Polyurethanes to Water Steam at 100°C**

| No. | Composition | Hardness (Shore A) | |
|---|---|---|---|
| | | Initial | After 28 days |
| 1 | **Krasol® LBH 3000** / MDI / EHD | 73.0 | (deformation) |
| 12 | **Krasol® LBH-P 3000** / MDI / BDO | 59.0 | 37.0 |
| | Polyether based TPU | 68.0 | 40.5 |

Polybutadiene based material swelled slowly in ethanol reaching the maximum volume change (approx. 20%) after 14 days. By the drying after the exposure the solvent was removed only partially. These data suggest very slow diffusion of polar molecules of alcohol through the hydrophobic matrix of polybutadiene polyurethane both into and out of the sample.

The study of the hydrolytic resistance of polyurethanes was extended to testing their stability to water steam at 100 °C (Table 4). Under these conditions, polybutadiene-urethanes with hard segments formed by MDI and EHD suffered from their poor resistance upon heating. In this case, polybutadiene TPU with MDI/BDO hard segments was used for the comparison, since it has a similar softening temperature as the polyether elastomer. The data suggests that the resistance of Krasol® and polyether based TPUs to the water steam is comparable.

**Electrical Insulation Properties**

Volume resistivity and surface resistivity were measured for polybutadiene-urethanes of various compositions (Table 5). The data obtained were compared with those of PTMEG based Pellethane 2103-70A TPU, which is recommended for use in electrical insulation applications. The value of volume resistivity found for Pellethane corresponded to the published data[10].

The detailed composition of polybutadiene-urethanes had no significant effect on the measured parameters. Polybutadiene TPUs exhibited superior electrical insulation properties. Their values of volume resistivity and surface resistivity were by several orders higher than those of polyether TPU. These data indicate that polybutadiene based TPUs could be desirable materials for wire and cable jacketing applications.

**Table 5. Electrical Insulation Characteristics of Thermoplastic Polyurethanes**

| No. | Composition | Volume resistivity (Ω m) | Surface resistivity (Ω) |
|---|---|---|---|
| 1 | LBH 3000 / MDI / EHD | $3.040\ 10^{14}$ | $1.144\ 10^{16}$ |
| 10 | LBH 2000 / MDI / EHD | $1.029\ 10^{14}$ | $1.543\ 10^{16}$ |
| 12 | LBH-P 3000 / MDI / BDO | $3.814\ 10^{14}$ | $1.899\ 10^{16}$ |
| | Polyether based TPU | $5.484\ 10^{9}$ | $1.028\ 10^{13}$ |

**Conclusions**

Krasol® LBH polybutadiene diols (secondary OH groups) and LBH-P (primary OH groups) were used for the preparation of thermoplastic polyurethanes (TPUs) employing one-shot or prepolymer procedure.

2-Ethyl-1,3-hexanediol (EHD) was found to be a suitable chain extender for Krasol® based TPUs. 1,4-Butanediol can also be used in polybutadiene-urethanes provided that hard segment content of about 25% is not exceeded. Depending on the parameters of the formulation, the resulting TPUs exhibited hardness about 80 Shore A or lower, making them prospective materials falling into the category of the soft grade TPUs.

The polybutadiene backbone provides exceptional resistance against aqueous solutions of strong mineral acids (sulfuric acid, nitric acid), far superior to that of polyether based elastomers. The use of Krasol® polyols in TPU systems can open new applications in aggressive protic media or ensure long service in humid conditions.

Polybutadiene TPUs exhibited excellent electrical insulation properties suggesting great potential in wire and cable jacketing applications.

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