

Poly bd[®] Resins With Low Hydroxyl Functionality

Abstract

Poly bd[®] resins with lower hydroxyl functionality than the standard R45HTLO have been developed by Cray Valley Company. These novel products, LF-1, -2, and -3, provide urethane prepolymers with lower viscosity and better storage stability compared with those derived from the standard product R45HTLO at the same NCO index. Further, by employing low-functionality Poly bd resins, polyurethanes, with and without chain-extenders, were prepared via two-step and one-step syntheses, respectively. As anticipated, more thermoplastic properties were observed for the polyurethanes derived from Poly bd[®] resins with low hydroxyl functionality.

Introduction

Poly bd[®] resin, a hydroxyl-terminated polybutadiene liquid, has been widely used in adhesives, sealants, and electrical applications owing to its low glass transition temperature (-75°C), superior hydrophobicity and acid-base resistance, and excellent dielectric properties. As a hydrocarbon-based polyol, Poly bd[®] resin has been widely used in polyurethane and polyester formulations by reacting with polyisocyanates or carboxylic acid derivatives, respectively. In contrast to polyester or polyether polyols, Poly bd[®] resin-based thermoset resins having low surface tension can easily accommodate a large quantity of inorganic fillers or hydrocarbon plasticizers, such as bitumen and soybean oil. The fillers and plasticizers can improve mechanical properties of the final products and lower raw material cost.

Although Poly bd[®] resin have a predominantly linear backbone structure, they also contain a small

portion of branched polymer resulted from the radical polymerization manufacture process. Thus, the commercial product has a hydroxyl functionality of 2.4-2.6 per chain on average. This branched structure occasionally imposes limitations on customers' processes or product performance especially when they seek design flexibility between thermoplastic and thermoset properties. To offer more choices and flexibility in the Poly bd[®] product line, three new grades LF-1, -2, and -3 with lower hydroxyl functionality of 2.30, 2.15 and 2.00 are introduced.

Results and Discussion

Gumstock Properties Derived from Low Functionality Poly bd[®] Resins

Since Poly bd[®] R45HTLO has an average hydroxyl functionality of 2.4-2.6 per chain, the viscosity during the prepolymer preparation sometimes becomes undesirably high. Adding more isocyanate to dilute the system increases the cost and handling concerns. Worse yet, the final material properties with more isocyanate in the system might not meet specifications. Thus, three Poly bd[®] resins with lower hydroxyl functionality, ranging from 2.3 to 2.0 were designed. Those grades are designated as Poly bd[®] LF-1, LF-2 and LF-3. The concentration of the hydroxyl end groups, along with the properties of the polyurethane gumstock derived from them are listed in Tables 1 and 2, respectively. It is observed that the tensile strength, elongation at break and tear strength of the gumstocks increase as the hydroxyl functionality decreases. At the same time, the modulus decreases, as less crosslinking takes place in gumstocks from low functionality Poly bd[®] resins. In other words, more thermoplastic properties are displayed in gumstocks as the OH functionality of the Poly bd[®] resins becomes lower.

Table 1. Properties of Poly bd[®] Resins

| | Poly bd [®] R45HTLO | LF-1 | LF-2 | LF-3 |
|--|------------------------------|------|------|------|
| Average hydroxyl functionality per chain | 2.50 | 2.33 | 2.15 | 1.98 |
| Hydroxyl value (meq/g) | 0.85 | 0.87 | 0.89 | 0.90 |
| Hydroxyl number, mg KOH/g | 47.6 | 48.7 | 49.8 | 50.4 |

Table 2. Physical Properties of Polyurethanes Derived from Poly bd[®] Resins with Regular and Reduced Functionality

| Formulation (pbw) | | | | |
|--|-------|-------|-------|-------|
| R45HTLO | 100 | | | |
| LF-1 | | 100 | | |
| LF-2 | | | 100 | |
| LF-3 | | | | 100 |
| Isonate 143L | 12.79 | 13.11 | 13.44 | 13.76 |
| Physical properties of elastomers | | | | |
| Tensile strength at break (psi) | 97.8 | 165.7 | 172.4 | 211.7 |
| Elongation at break (%) | 58.5 | 117.9 | 178.0 | 408.5 |
| Modulus (psi) | 264.1 | 309.3 | 252.0 | 188.5 |
| Tear strength (lbf/in) | 23.6 | 33.2 | 54.7 | 63.8 |
| Hardness, Shore A | 49 | 52 | 51 | 48 |

Prepolymer Viscosity from Poly bd[®] Resins with Regular and Low Functionality

Polyurethane prepolymers made from modified MDI (Isonate 143L) and low functionality Poly bd[®] resins, namely, LF-1, -2, and -3, have lower viscosity than those from Poly bd[®] R45HTLO of the same NCO index (Figure 1). With a NCO index of 2.5, the viscosity of the prepolymers made from Poly bd[®] R45HTLO and LF-1 are too high to measure. For higher NCO indices, the prepolymer viscosity decreases as the hydroxyl functionality per chain in the polyols decreases. These results are expected, as less branch points in the low functionality Poly bd[®] resins render their prepolymers less gel-like. Thus, the usage of isocyanate monomer can be reduced with low functionality Poly bd[®] resin in preparing prepolymers that have a workable viscosity.

Stability of Prepolymer Viscosity from Poly bd[®] R45HTLO And LF Materials

Prepolymers prepared from Poly bd[®] R45HTLO require a large excess of MDI to keep the viscosity of the prepolymer at a workable level. The viscosity of the final prepolymer is determined by the NCO/OH ratio, the molecular weight, and the functionality of the polyol and MDI used under the assumption that the reaction is carried out to completion. However, it was also known that the viscosity of a prepolymer increases during storage owing to water contaminants or various side reactions. Thus, the prepolymers prepared above were stored for a month to monitor their stability.

The results from the stability study are shown in Figure 2. Although the viscosity increased somewhat for all prepolymer compositions after storage at room temperature for a month, the one derived from the lowest functionality, LF-3, was still the most “stable” prepolymer composition.

Prepolymer Viscosity

Prepolymer viscosity with regular and LF materials

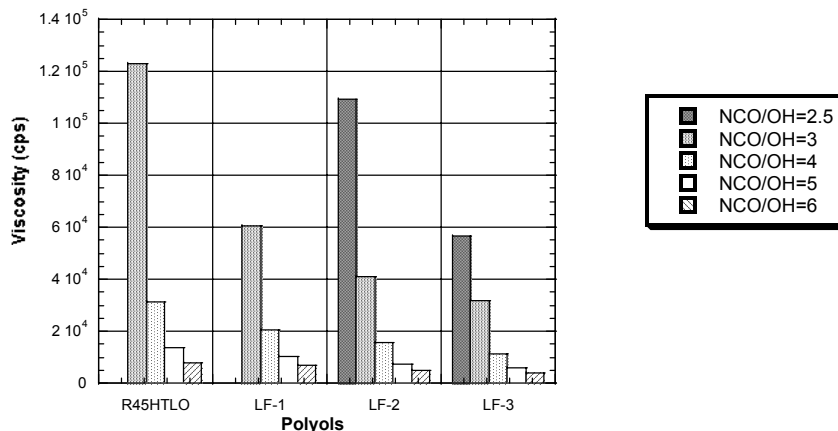


Figure 1. Viscosity of prepolymers made from Poly bd[®] resins and Isonate 143L.

Prepolymer Viscosity

Prepolymer viscosity with regular and LF materials

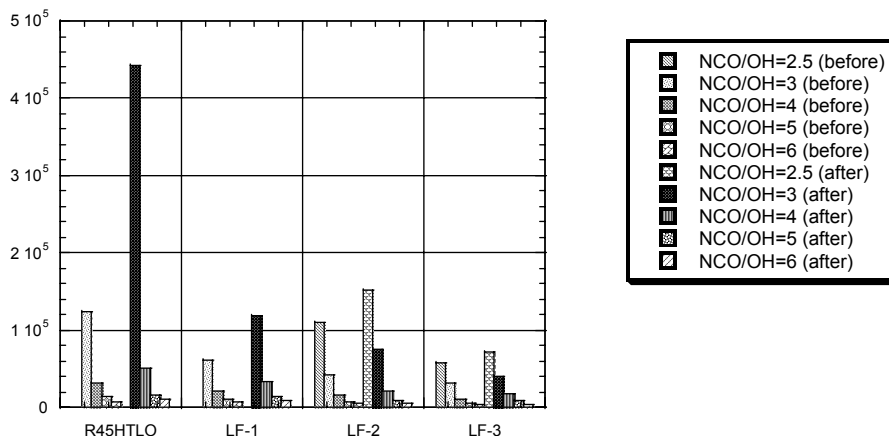


Figure 2. Viscosity of prepolymer before and after one-month storage at room temperature.

Two-Step Urethane Elastomer from Prepolymers and 2-Ethyl-1,3-Hexandiol

The prepolymers prepared from Poly bd[®] resins and Isonate 143L were chain-extended with 2-ethyl-1,3-hexandiol to complete curing. The physical properties of those cured polyurethane sheets with and without dibutyltin dilaurate (DBTDL) catalyst were also compared. The “thermoplastic” properties of those urethane elastomers were

strongly enhanced by the content of non-branched component (prepolymers from LF-2 and LF-3), especially for those derived from the prepolymers of relatively low NCO index. In general, the modulus was decreased, and the tensile strength and elongation at break were increased in the cured urethane sheets as the polyol with decreasing hydroxyl functionality in the prepolymer formulations was used. However, the trend became

less distinctive as more Isonate 143L was used in the prepolymer preparation. It is conceivable that having more isocyanate in the prepolymer requires more chain extender to maintain the NCO index for final curing. As a result, the increase of the hard segments offset the effect manifested by the branched and non-branched polybutadiene soft segments.

The mechanical properties of the cured polyurethane sheets (Tables 3-10) follow a predictable trend depending on the relative amount of short-chain diol, i.e., extender, and ratio of branched and linear components in the polyol mixtures.

Table 3. Two-Step Urethane Elastomers from Poly bd[®] R-45 HTLO/Isonate 143L Prepolymer and 2-Ethyl-1,3-Hexandiol (EHD) with DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|----------|----------|----------|----------|
| % Free NCO of prepolymer | 5.07 | 6.08 | 7.00 | 8.64 |
| NCO / OH index for elastomer | 1.05 | | | |
| Formulation (pbw) | | | | |
| R-45 HTLO prepolymer | 100 | 100 | 100 | 100 |
| EHD | 8.67 | 10.39 | 11.97 | 14.77 |
| Dibutyltin dilaurate (DBTDL), (drops) | 1 | 1 | 1 | 1 |
| Physical properties of elastomer | | | | |
| Tensile strength (psi) | 1233 | 1703 | 2169 | 2360 |
| Modulus (psi) | 2971 | 6710 | 12039 | 22193 |
| Elongation (%) | 252 | 252 | 258 | 185 |
| Tear resistance (lbf/in) | 209 | 283 | 330 | 406 |
| Hardness, Shore D | 36 | 44 | 48 | 56 |
| Hardness, Shore A | 86 | 92 | 94 | 98 |

Table 4. Two-Step Urethane Elastomers from Poly bd[®] R-45 HTLO/Isonate 143L Prepolymer and 2-Ethyl-1,3-hexandiol (EHD) without DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|----------|----------|----------|----------|
| % Free NCO of prepolymer | 5.07 | 6.08 | 7.00 | 8.64 |
| NCO / OH index for elastomer | 1.05 | | | |
| Formulation (pbw) | | | | |
| R-45 HTLO prepolymer | 100 | 100 | 100 | 100 |
| EHD | 8.67 | 10.39 | 11.97 | 14.77 |
| Dibutyltin dilaurate (DBTDL), (drops) | None | | | |
| Physical properties of elastomer | | | | |
| Tensile strength (psi) | 1536 | 1778 | 2279 | 3160 |
| Modulus (psi) | 2481 | 4909 | 8399 | 15950 |
| Elongation (%) | 296 | 256 | 268 | 272 |
| Tear resistance (lbf/in) | 226 | 278 | 324 | 393 |
| Hardness, Shore D | 35 | 45 | 48 | 56 |
| Hardness, Shore A | 87 | 92 | 95 | 98 |

Table 5. Two-Step Urethane Elastomers from Poly bd[®] LF-1/Isonate 143L Prepolymer and 2-Ethyl-1,3-Hexandiol (EHD) with DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|----------|----------|----------|----------|
| % Free NCO of prepolymer | 5.20 | 6.22 | 7.16 | 8.81 |
| NCO / OH index | 1.05 | | | |
| Formulation (pbw) | | | | |
| LF-1 prepolymer | 100 | 100 | 100 | 100 |
| EHD | 8.89 | 10.63 | 12.24 | 15.05 |
| Dibutyltin dilaurate (DBTDL), (drops) | 1 | 1 | 1 | 1 |
| Physical properties of elastomer | | | | |
| Tensile strength, (psi) | 1570 | 1857 | 2579 | 2944 |
| Modulus, (psi) | 2370 | 4636 | 8052 | 21544 |
| Elongation, (%) | 344 | 286 | 345 | 302 |
| Tear resistance, (lbf/in) | 206 | 288 | 320 | 465 |
| Hardness, Shore D | 38 | 46 | 49 | 60 |
| Hardness, Shore A | 84 | 91 | 94 | 97 |

Table 6. Two-Step Urethane Elastomers from Poly bd[®] LF-1/Isonate 143L Prepolymer and 2-Ethyl-1,3-hexandiol (EHD) without DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|----------|----------|----------|----------|
| % Free NCO of prepolymer | 5.20 | 6.22 | 7.16 | 8.81 |
| NCO / OH index | 1.05 | | | |
| Formulation (pbw) | | | | |
| LF-1 prepolymer | 100 | 100 | 100 | 100 |
| EHD | 8.89 | 10.63 | 12.24 | 15.05 |
| Dibutyltin dilaurate (DBTDL), (drops) | None | | | |
| Physical properties of elastomer | | | | |
| Tensile strength (psi) | 1632 | 1913 | 2615 | 2944 |
| Modulus (psi) | 2019 | 3704 | 5716 | 15747 |
| Elongation (%) | 340 | 293 | 341 | 256 |
| Tear resistance (lbf/in) | 216 | 273 | 324 | 401 |
| Hardness, Shore D | 40 | 49 | 49 | 57 |
| Hardness, Shore A | 86 | 91 | 94 | 94 |

Table 7. Two-Step Urethane Elastomers from Poly bd[®] LF-2/Isonate 143L Prepolymer and 2-Ethyl-1,3-Hexandiol (EHD) with DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|------|-------|-------|-------|
| % Free NCO of prepolymer | 5.32 | 6.36 | 7.31 | 8.99 |
| NCO / OH index | 1.05 | | | |
| Formulation (pbw) | | | | |
| LF-2 prepolymer | 100 | 100 | 100 | 100 |
| EHD | 9.09 | 10.88 | 12.49 | 15.36 |
| Dibutyltin dilaurate (DBTDL), (drops) | 1 | 1 | 1 | 1 |
| Physical properties of elastomer | | | | |
| Tensile strength (psi) | 1586 | 2591 | 2619 | 3093 |
| Modulus (psi) | 2498 | 3943 | 8163 | 18670 |
| Elongation (%) | 298 | 396 | 301 | 260 |
| Tear resistance (lbf/in) | 227 | 286 | 362 | 450 |
| Hardness, Shore D | 42 | 47 | 50 | 60 |
| Hardness, Shore A | 87 | 91 | 94 | 99 |

Table 8. Two-Step Urethane Elastomers from Poly bd[®] LF-2/Isonate 143L Prepolymer and 2-Ethyl-1,3-Hexandiol (EHD) without DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|------|-------|-------|-------|
| % Free NCO of prepolymer | 5.32 | 6.36 | 7.31 | 8.99 |
| NCO / OH index | 1.05 | | | |
| Formulation (pbw) | | | | |
| LF-2 prepolymer | 100 | 100 | 100 | 100 |
| EHD | 9.09 | 10.88 | 12.49 | 15.36 |
| Dibutyltin dilaurate (DBTDL), (drops) | None | | | |
| Physical properties of elastomer | | | | |
| Tensile strength (psi) | 1766 | 2103 | 2751 | 3292 |
| Modulus (psi) | 1922 | 3042 | 5921 | 13440 |
| Elongation (%) | 337 | 309 | 307 | 277 |
| Tear resistance (lbf/in) | 220 | 279 | 334 | 427 |
| Hardness, Shore D | 40 | 46 | 53 | 57 |
| Hardness, Shore A | 86 | 91 | 94 | 98 |

Table 9. Two-Step Urethane Elastomers from Poly bd[®] LF-3/Isonate 143L Prepolymer and 2-Ethyl-1,3-Hexandiol (EHD) with DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|------|------|-------|-------|
| % Free NCO of prepolymer | 4.27 | 5.43 | 7.44 | 9.14 |
| NCO / OH index | 1.05 | | | |
| Formulation (pbw) | | | | |
| LF-3 prepolymer | 100 | 100 | 100 | 100 |
| EHD | 7.30 | 9.27 | 12.72 | 15.62 |
| Dibutyltin dilaurate (DBTDL), (drops) | 1 | 1 | 1 | 1 |
| Physical properties of elastomer | | | | |
| Tensile strength (psi) | 1725 | 2328 | 3317 | 3742 |
| Modulus (psi) | 849 | 2192 | 9148 | 22797 |
| Elongation, (%) | 424 | 406 | 337 | 281 |
| Tear resistance (lbf/in) | 190 | 250 | 366 | 470 |
| Hardness, Shore D | 36 | 40 | 53 | 59 |
| Hardness, Shore A | 83 | 88 | 96 | 97 |

Table 10. Two-Step Urethane Elastomers Derived from Poly bd[®] LF-3/Isonate 143L Prepolymer and 2-Ethyl-1,3-Hexandiol (EHD) without DBTDL

| Sample no. | 1 | 2 | 3 | 4 |
|---|------|------|-------|-------|
| % Free NCO of prepolymer | 4.27 | 5.43 | 7.44 | 9.14 |
| NCO / OH index | 1.05 | | | |
| Formulation (pbw) | | | | |
| LF-3 prepolymer | 100 | 100 | 100 | 100 |
| EHD | 7.30 | 9.27 | 12.72 | 15.62 |
| Dibutyltin dilaurate (DBTDL), (drops) | None | | | |
| Physical properties of elastomer | | | | |
| Tensile strength, (psi) | 2232 | 2511 | 2802 | 3655 |
| Modulus (psi) | 767 | 1710 | 7027 | 14281 |
| Elongation, (%) | 506 | 413 | 280 | 291 |
| Tear resistance, (lbf/in) | 208 | 249 | 330 | 424 |
| Hardness, Shore D | 36 | 36 | 41 | 55 |
| Hardness, Shore A | 86 | 83 | 85 | 97 |

EXPERIMENTALS

General

Poly bd[®] resins, R45HTLO, LF-1, LF-2, and LF-3, are supplied by Cray Valley Company. Isonate 143L, a modified MDI, was obtained from Dow Chemical. Dibutyltin dilaurate was purchased from Atofina Chemicals. Chain extender 2-ethyl-1,3-hexanediol was obtained from either Kyowa Hakko U.S. A., Inc. or Dixie Chemical.

Mechanical Testing

The cured samples were further aged for a week at ambient temperature before being tested. Instron automated materials tester (model 4301) was used for measuring the physical properties of polyurethane sheets at 73° F and 50% humidity. Tensile strength, elongation and Young's modulus were obtained by following the ASTM D638 protocol. Tear resistance was measured using Rubber Tear Test – US Customary Units. The

crosshead pulling speed during the test was set at 2.0 in/min. For each sample, 4 or 5 specimens were tested and the average values reported. Hardness of sample was determined with a Durometer Type A or Type D at room temperature.

Viscosity Measurement

A Brookfield viscometer was used and the viscosity was measured at a specified temperature.

Gumstock Properties Derived from Regular and Low Functionality Poly bd[®] Resins

Preparation of polyurethane sheets. Polyurethane mixtures were prepared by adding Isonate 143L to vacuum-degassed Poly bd[®] R45HTLO or reduced functionality Poly bd[®] resins. The molar ratio of NCO to OH was maintained at 1.05 for all the mixtures. Polyurethane sheets were then made by spreading the mixture in a 10”x 5”x 1/8” open mold. The polyurethane materials made with the reduced functionality polyols were compared with those derived from the standard Poly bd[®] R45HTLO. All the samples were prepared without catalyst.

Prepolymer Viscosity from Low Functionality Poly bd[®] Resins

Prepolymer preparation from Poly bd[®] R45HTLO (2.5 hydroxyl functionality per chain).

| Components | Weight (g) | | | | |
|------------------------------------|------------|---------|--------|--------|-------|
| R45HTLO | 100 | 100 | 100 | 100 | 100 |
| BHT* | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Isonate 143L | 30.45 | 36.55 | 48.72 | 60.9 | 73.11 |
| Index | 2.5 | 3.0 | 4.0 | 5.0 | 6.0 |
| Free NCO% in product (In theory) | 4.04 | 5.15 | 7.10 | 8.75 | 10.16 |
| Prepolymer viscosity at 40°C (cps) | - | 123,000 | 31,200 | 13,600 | 7,600 |

*2,6-Di-tert-butyl-4-methylphenol (BHT)

Prepolymer preparation from LF-1 (2.32 hydroxyl functionality per chain).

| Component | Weight (g) | | | | |
|------------------------------------|------------|--------|--------|--------|-------|
| LF-1 | 100 | 100 | 100 | 100 | 100 |
| BHT | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Isonate 143L | 31.26 | 37.51 | 50.02 | 62.52 | 75.03 |
| Index | 2.5 | 3.0 | 4.0 | 5.0 | 6.0 |
| Free NCO% in product (In theory) | 4.12 | 5.25 | 7.22 | 8.89 | 10.32 |
| Prepolymer viscosity at 40°C (cps) | - | 60,400 | 20,600 | 10,400 | 6800 |

Prepolymer preparation from LF-2 (2.14 hydroxyl functionality per chain).

| Component | Weight (g) | | | | |
|------------------------------------|------------|--------|--------|-------|-------|
| LF-2 | 100 | 100 | 100 | 100 | 100 |
| BHT | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Isonate 143L | 32.06 | 38.47 | 51.30 | 64.12 | 76.94 |
| Index | 2.5 | 3.0 | 4.0 | 5.0 | 6.0 |
| Free NCO% in product (In theory) | 4.20 | 5.35 | 7.34 | 9.03 | 10.47 |
| Prepolymer viscosity at 40°C (cps) | 109,500 | 41,200 | 15,700 | 7,400 | 4,900 |

Prepolymer preparation from LF-3 (1.98 hydroxyl functionality per chain).

| Component | Weight (g) | | | | |
|------------------------------------|------------|--------|--------|-------|-------|
| | | | | | |
| LF-3 | 100 | 100 | 100 | 100 | 100 |
| BHT | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Isonate 143L | 32.86 | 39.43 | 52.57 | 65.71 | 78.86 |
| Index | 2.5 | 3.0 | 4.0 | 5.0 | 6.0 |
| Free NCO% in product (in theory) | 4.28 | 5.44 | 7.46 | 9.16 | 10.61 |
| Prepolymer viscosity at 40°C (cps) | 56,800 | 31,800 | 11,400 | 5,800 | 3,800 |

Procedures of preparing prepolymers.

- To a one-liter resin kettle were charged polyol(s) and BHT. The mixture was degassed and dehydrated *in vacuo* (< 10 mm Hg) for 0.75 hr at 100°C with stirring.
- The system was cooled, and then vented with nitrogen purge.
- Isonate 143L was added to the flask at 40 ± 5 °C under N₂. The resulting mixture was stirred at 40°C for 20 minutes and then at 70°C for 4 hrs to complete the reaction.
- After cooling, the prepolymer was placed in a sealed jar under nitrogen.
- The viscosity of the prepolymer was determined at 40°C after the prepolymer was thermally equilibrated in an oven of 40°C for 3 hours.

Stability of Prepolymer Viscosity from Poly Bd® R45HTLO and LF Materials

Brookfield viscosity (cps) of prepolymers at 40°C before and after one-month storage at room temperature.

| Composition of polyol(s) | NCO/OH | Viscosity (cps) | |
|--------------------------|--------|-----------------|--------------|
| | | 40°C (before) | 40°C (after) |
| R45HTLO | 3.0 | 123,000 | 442,400 |
| | 4.0 | 31,200 | 50,000 |
| | 5.0 | 13,600 | 15,400 |
| | 6.0 | 7,600 | 10,600 |
| LF-1 | 3.0 | 60,400 | 118,400 |
| | 4.0 | 20,600 | 32,800 |
| | 5.0 | 10,400 | 14,200 |
| | 6.0 | 6,800 | 8,400 |
| LF-2 | 2.5 | 109,500 | 151,400 |
| | 3.0 | 41,200 | 74,200 |
| | 4.0 | 15,700 | 21,400 |
| | 5.0 | 7,400 | 9,100 |
| | 6.0 | 4,900 | 5,400 |
| LF-3 | 2.5 | 56,800 | 71,400 |
| | 3.0 | 31,800 | 40,800 |
| | 4.0 | 11,400 | 17,200 |
| | 5.0 | 5,800 | 8,200 |
| | 6.0 | 3,800 | 4,300 |

Two-Step Urethane Elastomer from Prepolymers and 2-Ethyl-1,3-Hexandiol

Formulations of prepolymer from Poly bd[®] R-45 HTLO.

| Sample no. | NCO Index | NCO % | Reactant wt. Ratio R-45HTLO | Isonate 143L |
|------------|-----------|-------|-----------------------------|--------------|
| 1 | 3.0 | 5.07 | 100 | 35.66 |
| 2 | 3.5 | 6.08 | 100 | 41.60 |
| 3 | 4.0 | 7.00 | 100 | 47.54 |
| 4 | 5.0 | 8.64 | 100 | 59.43 |

Formulations of prepolymer from LF-1.

| Sample no. | NCO/OH Index | NCO % | Wt. ratio of reactants LF-1 | Isonate 143L |
|------------|--------------|-------|-----------------------------|--------------|
| 1 | 3.0 | 5.20 | 100 | 36.83 |
| 2 | 3.5 | 6.22 | 100 | 42.97 |
| 3 | 4.0 | 7.16 | 100 | 49.11 |
| 4 | 5.0 | 8.81 | 100 | 61.39 |

Formulations of prepolymer from LF-2.

| Sample no. | NCO/OH Index | NCO % | Wt. ratio of reactants LF-2 | Isonate 143L |
|------------|--------------|-------|-----------------------------|--------------|
| 1 | 3.0 | 5.32 | 100 | 38.02 |
| 2 | 3.5 | 6.36 | 100 | 44.36 |
| 3 | 4.0 | 7.31 | 100 | 50.70 |
| 4 | 5.0 | 8.99 | 100 | 63.37 |

Formulations of prepolymer from LF-3.

| Sample no. | NCO/OH Index | NCO % | Wt. ratio of reactants LF-3 | Isonate 143L |
|------------|--------------|-------|-----------------------------|--------------|
| 1 | 2.5 | 4.27 | 100 | 32.57 |
| 2 | 3.0 | 5.43 | 100 | 39.08 |
| 3 | 4.0 | 7.44 | 100 | 52.11 |
| 4 | 5.0 | 9.14 | 100 | 65.14 |

Procedures for preparing urethanes via two-step process.

1. Poly bd[®] R45HTLO was charged to a resin kettle, followed by degassing and dehydrating in *vacuo* (< 10 mm Hg) at 80 °C with stirring for 1.5 h.
2. Isonate 143L was added to the kettle at 45 °C with stirring. Reaction was maintained for 3 hrs at 75 °C under N₂. After the reaction was finished, the resulting prepolymer was degassed in *vacuo*.
3. To a centrifuge cup were charged the degassed prepolymer and 2-ethyl-1,3-hexandiol, according to the ratio in the formulations listed in the text above.
4. The mixture was mixed with a speed-mixer for 50s at 1200 rpm.
5. DBTDL (1 drop, about 0.003g) was added to the cup, and then the mixture was mixed by the speed-mixer for 15s at 1200 rpm. The final mixture was poured onto a warm (ca.50 °C) mold (10" x 5" x 1/8") and cured

at 75 °C for 2.5 h, then at 50 °C for overnight. All the samples were aged at least one week at room temperature before being tested for physical properties.

Conclusions

Polyurethanes derived from Poly bd[®] resins with reduced hydroxyl functionality (2.3-2.0) possessed increased thermoplastic properties compared with those made from Poly bd[®] R45HTLO. For example, the elongation at break increases from 59 to 409%

and the tear strength improves from 24 to 64 lb f/in when Poly bd[®] R45HTLO in polyurethane gumstock is replaced with low functionality Poly bd[®] LF-3. Prepolymers made from liquid modified MDI and the reduced functionality polyols also showed reduced viscosity and improved storage stability as anticipated. Representative examples of using 2-ethyl-1,3-hexanediol as a chain extender in the two-step synthesis are only one example of the wide range of material properties that the low functionality Poly bd[®] resin can offer.