# Effect of Macroglycol Structure and Its Molecular Weight on Physicomechanical Properties of Polyurethanes

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## SYNOPSIS

The molecular weight of polyester polyol plays an important role in controlling mechanical and dynamic mechanical properties of polyurethanes. Two systems are studied for evaluation of these properties. Since the properties of polyurethanes are derived from the properties of various constituents involved in their synthesis, the magnitude of properties of polyurethanes are also studied. Dynamic mechanical properties are analyzed using a dynamic mechanical analyzer that employs the principle of compound resonance. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Cast polyurethanes (PUs) can be synthesized by employing a three-component system, viz., a polyol, diisocyanate, and chain extender; all these components exert their individual effect on the properties of PUs. Chain extenders have a profound effect on physicomechanical properties of PUs and significant research has been carried out on this topic.[1–4] In our earlier article, we reported on the effect of the diisocyanate structure on the viscoelastic, thermal, mechanical, and electric properties of cast PUs.[5] The present article deals with the effect of molecular weight and structure of polyol in PU. The polyols selected for the study include poly(ethylene adipate) (PEA), poly(ethylene-co-propylene adipate) (PEPA), and poly(hexamethylene-co-neopentylene adipate) (PHNA).

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## EXPERIMENTAL

### Materials

(a) Polyols required for this work were synthesized in our laboratory (Table I). (b) 2,4-Toluene diisocyanate (TDI) (80% 2,4- and 20% 2,6-isomeric mixture) was used as received (Koch Light, England). (c) Butanediol (BD) was used as received (BDH, England).

### Synthesis and Characterization of Poly(ester polyol)s and Polyurethanes

The details of the procedure were given in our earlier publication.[6]

## RESULTS AND DISCUSSION

### Effect of Molecular Weight of Polyol

Two polyol systems, PEA and PEPA, were selected for studying the effect of molecular weight. PUs

**Table I   Polyols and Their Characteristics Used for the Synthesis of PU Elastomers**

| Series No. | Polyol | Appearance | Acid No. | Hydroxyl No. | Molecular Weight by VPO | Molecular Weight by End Group |
|---|---|---|---|---|---|---|
| 1. | Poly(ethylene-co-propylene adipate) (PEPA-1) | Viseous liquid, light yellow | 2.24 | 53 ± 2 | 2200 | 2050 |
| 2. | Poly(ethylene-co-propylene adipate) (PEPA-2) | Viscous liquid, light yellow | 1.67 | 108 ± 2 | 985 | 1020 |
| 3. | Poly(ethylene adipate) (PEA-1) | White waxy, solid | 3.5 | 34 ± 1 | 3075 | 3200 |
| 4. | Poly(ethylene adipate) (PEA-2) | White waxy, solid | 3.8 | 180 ± 7 | 700 | 600 |
| 5. | Poly(hexamethylene-co-neopentylene adipate) (PHNA) | Viscous liquid, light yellow | < 2 | 105 | — | 1060 |

synthesized from low molecular weight polyol (PEPA-1) showed high moduli at various elongations, tensile strengths, hardness, and Young's moduli, while there was a decrease in the ultimate elongations by about 36%. Although a decrease in elongation implies the tendency of the material to be brittle, the decrease was much less compared to the improvement achieved in the other properties. The improvement in the mechanical properties can be attributed to the ratio of the softcore-to-hardcore segment in the synthesized PUs. PUs owe their properties to interchain hydrogen bonding. The higher the extent of H-bonding, the higher the magnitudes of the properties and the higher the contributions of the hardcore segments.[7,8] Low molecular weight polyol reduced the contribution of soft-core segment and, hence, relatively speaking, the proportion of the hard-core segment was more when the stoichiometry was kept the same.

### Effect of Poly(ester polyol) Structure

As the properties of PUs are derived from the properties of various constituents involved in the syn-

thesis, it was decided to study the influence of the polyester with respect to structure–property relationships (Table II). The magnitudes of tensile strength did not reveal any significant influence of the structure of the polyester. However, other properties such as modulus (100, 200, and 300%), elongation at break, and hardness showed the superiority of the PEPA backbone over the PHNA backbone. Higher modulus, as well as high hardness and lower elongation, indicated crystallinity in the PU. The crystallinity arises due to the inherent tendency of polyesters containing polyethylene units in the chain to crystallize. The higher elongation shown by PHNA-based PU is probably due to the hexamethylene moiety (in the polyester) by the virtue of its higher number of methylene groups. The lower glass transition temperature shown by PHNA-based PU is due to the restoration of symmetry of the monomeric units of the polymer backbone as well as to the increased number of methylene units in the polymer.

A useful parameter, which is a measure of the ratio of energy lost to energy stored, is the loss tangent: $\tan \delta = E'' / E'$, where $E'$ and $E''$ are the storage

**Table II   Mechanical Behavior of PUs[a]: Effect of Nature of Poly(ester polyol)**

| Base Polyol | MW (Av) | Modulus (MPa) 100% | Modulus (MPa) 200% | Modulus (MPa) 300% | Tensile Strength (MPa) | Elongation at Break (%) | Hardness Shore-A | Density (g/cc) | Glass Transition Temp ($T_g$ °C) |
|---|---|---|---|---|---|---|---|---|---|
| PEPA-2 | 1020 | 6.00 | 9.3 | 14.2 | 31.1 | 510 | 84 | 1.308 | +7.0 |
| PHNA | 1060 | 3.7 | 5.8 | 8.6 | 34.0 | 900 | 65 | 1.240 | −8.0 |

[a] Components: Poly(ester polyol) (1.0 mol); TDI (3.2 mol); butanediol (2.0 mol).
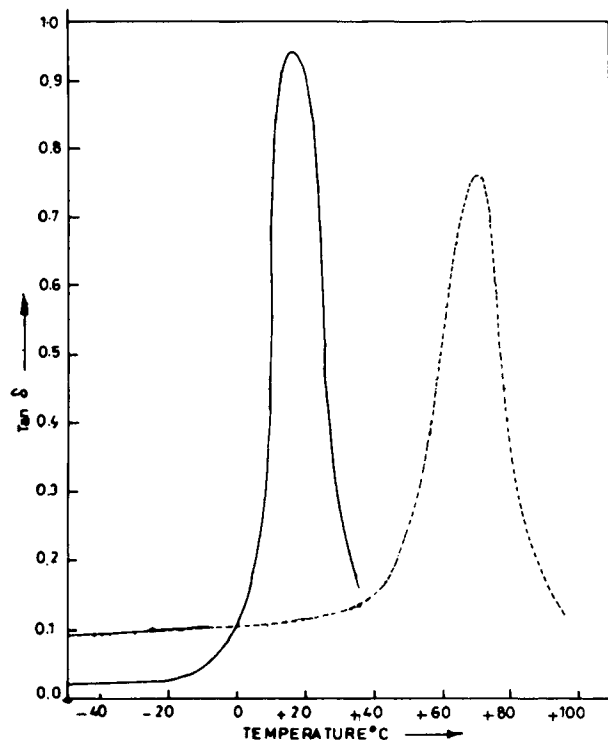
**Figure 1**   Tan $\delta$ as a function of temperature for PEPA-1/TDI/BD and PEPA-2/TDI/BD systems showing the effect of molecular weight of polyol on PUs.
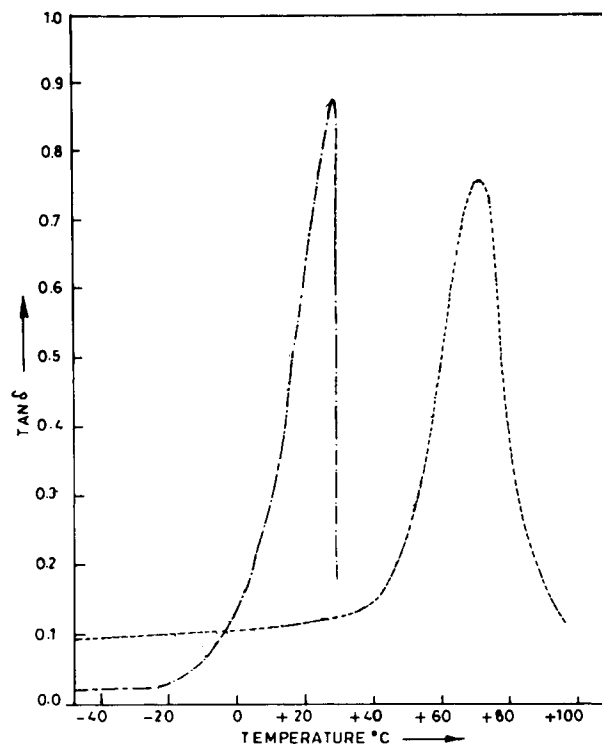


**Figure 2**   Tan $\delta$ as a function of temperature for PHNA/TDI/BD and PEPA-2/TDI/BD systems showing the effect of structure of polyol on PUs.

and the loss moduli, respectively (Fig. 1). The maximum magnitude of tan $\delta$ was found to occur at higher temperatures (70°C) for the PUs synthesized from low molecular weight polyol. At ambient conditions (temperature range 10–25°C), PU based on PEPA-1 showed higher magnitudes of tan $\delta$.

The effect of the nature of the polyol on the dynamic properties of PUs is represented in Figure 2, selecting PEPA-2 (MW = 1020) and PHNA (MW

= 1060). The glass transition temperature was much lower (23°C) for PHNA-based PU as compared to PEPA-2-based PU (71°C). Hence, it can be concluded that the former may behave as better shock-absorbing material.

Glass transition temperatures of PUs, as determined by TMA, are reported in Tables I and III. The experiments were designed to understand the relationship between the structure and molecular

**Table III   Mechanical Behavior of PUs[a]: Effect of Molecular Weight of Polyol**

| Polyol | MW (Av) | Modulus (MPa) | | | Tensile Strength (MPa) | Elongation at Break (%) | Hardness Shore-A | Density (g/cc) | Young's Modulus (MPa) | Glass Transition Temp ($T_g$ °C) |
| | | 100% | 200% | 300% | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| PEPA-1 | 2051 | 1.41 | 2.02 | 2.76 | 7.2 | 790 | 45 | 1.283 | 20.1 | −29.0 |
| PEPA-2 | 1020 | 6.00 | 9.3 | 14.2 | 31.1 | 510 | 84 | 1.308 | 32.0 | +07.0 |
| PEA-1 | 2700 | — | — | — | 5.8 | 70 | 90 | 1.285 | — | −29.0 |
| PEA-2 | 600 | 17.7 | 18.2 | 19.85 | 28.0 | 530 | 96 | 1.307 | — | — |

[a] Components: Poly(ester polyol) (1.0 mol); TDI (3.2 mol); glycol (2.0 mol). PEA, poly(ethylene adipate); PEPA, poly(ethylene-co-propylene adipate).

**Table IV    Thermal Behavior—Polyol/TDI/BD System**

| Polyol | idt (°C) | Temperature at (% Weight Loss) | | | | ipdt (°C) | % Residue at 500°C | E* (kcal) |
|---|---|---|---|---|---|---|---|---|
| | | 10% | 30% | 50% | 70% | | | |
| Molecular weight effect | | | | | | | | |
| PEPA-1 | 275 | 318 | 356 | 390 | 410 | 400 | 12 | 31.6 |
| PEPA-2 | 228 | 260 | 328 | 352 | 390 | 354 | — | 14.0 |
| Effect of Structure of polyol | | | | | | | | |
| PEPA-2 | 228 | 260 | 328 | 352 | 390 | 354 | — | 14.0 |
| PHNA | 240 | 315 | 342 | 370 | 395 | 382 | 50 | — |

weight of poly(ester polyol). The glass transition temperature decreased with increasing molecular weight of poly(ester polyol), due to additional flexibility imparted in PUs by higher molecular weight polyols. This trend was noted also in uncross-linked thermoplastic polycaprolactone[9,10] and adipate polyurethanes.[11]
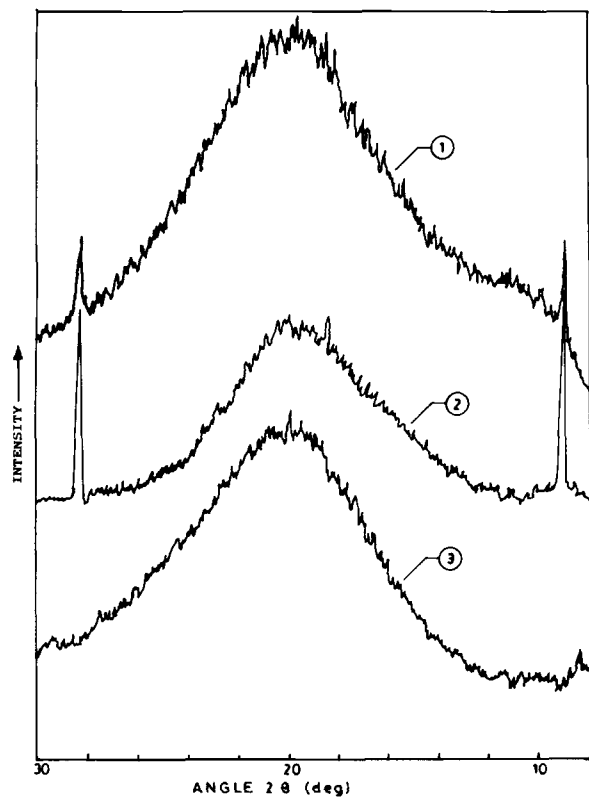


**Figure 3**    Diffraction intensity vs. angle $2\theta$ for PEPA-1/TDI/BD, PEPA-2/TDI/BD, and PHNA/TDI/BD systems.

Even though the molecular weights of the polyols PHNA and PEPA-2 are the same, the $T_g$ of PUs derived from these polyols have shown considerable difference. The $T_g$ value of PHNA-based PU can be accounted for by the higher flexibility imparted by hexanediol and neopentyl glycol.

PUs derived from higher molecular weight polyols showed better thermal stability, as evident from the results of the initial decomposition temperature (idt), integral procedural decomposition temperature[12] (ipdt), and energy of activation, $E^*$, reported in Table IV. The thermal stability of PHNA-based PU is found to be marginally higher.

The X-ray diffraction patterns (Fig. 3) consisted of one broad halo in the region between $2\theta = 10°$ to $28°$ and sharp peaks at about $9°$ and $28°$. The diffraction intensity of the polymers seemed to vary with the molecular weight of the polyol. Higher diffraction intensity, (i.e., higher crystallinity), is shown by PU derived from low molecular weight polyols. When comparing the polyol structures, PEPA-2-based PU showed higher crystallinity over PHNA based PU, which accounts for the higher mechanical properties of the former.

## CONCLUSIONS

Molecular heterogeneity of polyol plays an important role in deciding the properties of PUs. A decrease in molecular weight of poly(ester polyol) causes a substantial increase in modulus, tensile strength, and Young's modulus and a decrease in ultimate elongation of PUs synthesized using PEPA. Similar behavior is seen in the case of PEA except for the ultimate elongation.

The increase in hardness is comparatively more

than the decrease in elongation and indicates the role of the low molecular weight polyol. High-damping PUs in the desired temperature range can be formulated by adjusting the molecular weight of the polyol. The nature of the poly(ester polyol) also plays an important role in deciding the physicomechanical properties of PUs.

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