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CAST POLYURETHANES: EFFECT OF CHAIN EXTENDERS ON THERMAL, MECHANICAL, AND DYNAMIC MECHANICAL PROPERTIES

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ABSTRACT

Effects of various diol chain extenders on thermal, mechanical, and viscoelastic properties of polyurethanes are discussed. Elastomers were prepared by using polyester (polyethylene-*co*-propylene adipate), toluene-2,4-diisocyanate, and α,ω-aliphatic diols. The properties imparted by the extenders are explained on the basis of the number of methylene carbons in the extenders. Butanediol-extended polymer showed superior properties, which are ascribed to regularity in the backbone chain of the polymer and ease of formation of hydrogen bonds.

INTRODUCTION

Solid polyurethane elastomers are now widely utilized as engineering materials and are well known for their outstanding mechanical properties. Millable and cast elastomers are the two main classes of polyurethane elastomers.

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Chain extenders have a profound effect on the mechanical properties of polyurethanes, and significant research has been carried out on this topic [1-4], prompted primarily by the search for a suitable replacement for diamines which present regulatory and handling problems. Therefore, we report here on the elastomeric properties obtained with diol curatives. Diols are more acceptable because of their low toxicity, ease of handling, ready availability, and low cost. Although mechanical properties of polyurethanes based on diol chain extenders and polyesters, like polyethylene adipate and polytetramethylene adipate, have been reported, the dynamic mechanical properties have not been studied.

The present work describes the effect of several aliphatic diols on thermal, viscoelastic, and mechanical properties of polyester-urethanes. Poly(ethylene-*co*-propylene adipate) was synthesized as the polyol component for this work. The viscoelastic properties are studied by the resonance vibration technique.

EXPERIMENTAL

Materials

(a) Hydroxy-terminated poly(ethylene-*co*-propylene adipate) (PEPA) was synthesized in our laboratory (see below) (Table 1). (b) 2,4-Toluenediisocyanate (80% 2,4- and 20% 2,6-isomeric mixture) (Koch Light, England) was used as received. (c) The following diols were used as chain extenders. Ethylene glycol (Merck, India); 1,2-propanediol (Sarabhai, India); 1,4-butanediol (BDH, England); and 1,5-pentanediol (Fluka AG, Switzerland). Diols were vacuum distilled before use.

Synthesis of Polyester Polyol

PEPA was synthesized [5] by reacting 1.0 mol of adipic acid with 0.71 mol of ethylene glycol and 0.48 mol of 1,2-propanediol. The monomers were heated under N_2 with continuous stirring. Initially the reaction was carried out at 140°C for 6 to 8 h; at this stage, elimination of water of condensation takes place. The pot material was analyzed for acid number every 2 h till the acid number decreased to 4 or less. The pressure was then slowly reduced to 1 torr, and the temperature was raised to 180-190°C so that excess glycol was removed. The mixture was cooled under N_2 to give a colorless, viscous liquid.

TABLE 1. Characteristics of Polyethylene Propylene Adipate (PEPA)

Appearance	Colorless viscous liquid
Acid number	1.67
Hydroxyl number	108 ± 2
Molecular weight by endgroup analysis	1000
Molecular weight by VPO	985

Characterization of Polyol

The acid number was determined by the usual titrimetric method using 0.2 *N* alcoholic KOH. The hydroxyl number was determined by acetylating the –OH groups of the ester and then titrating the free acetic acid with 0.2 *N* alcoholic KOH. Molecular weights were obtained by using a Knauer vapor-pressure osmometer (MEK solvent) and also by endgroup analysis.

Synthesis of Polyurethanes

One mol of polyester (PEPA) was reacted with 3.2 mol of toluene diisocyanate at 50°C to give isocyanate-terminated prepolymer. The reaction was carried out under N_2. The isocyanate was injected with a hypodermic syringe under continuous stirring. This prepolymer was reacted with 2.0 mol of diol chain extender. This mixture was degassed and then cast [6] into molds and cured at 100°C for 24 h in an oven to give polyurethane elastomers. Silicone compound was applied to the molds for easy removal of sheets.

Characterization of Polyurethanes

Dynamic mechanical measurements were carried out on a dynamic mechanical analyzer (DMA-981, Du Pont) coupled with a thermal analyzer (TA-990, Du Pont) comprised of a temperature programmer, controller, and a flat-bed X-Y,Y' recorder. DMA works on the principle of compound resonance and measures dynamic modulus (both storage and loss modulus) and damping of a specimen under oscillatory load as a function of temperature. The resonant frequency is related to the elongation storage modulus, E', of the sample, while the extra energy needed to keep the system oscillating at a constant amplitude is a measure of damping. All samples in the present investigation were clamped vertically between the two arms of the instrument. The oscillation amplitude was kept at 0.2 mm. The readings were taken from -90 to +90°C with a programmed heating rate of 10°C/min. Liquid nitrogen was used to achieve subambient temperatures. To ensure uniformity of temperature around the specimen, nitrogen gas was purged through the system at the rate of 2.5 L/min. The plot gave the oscillation frequency and the damping in the specimen as a function of temperature. Mechanical loss factor tan δ and storage modulus E' were calculated with a microcomputer from the primary plots at several closely spaced temperatures. In this method, sample frequency varies with temperature; at the glass transition temperature it falls suddenly, giving an inflection point. At the same point the damping passes through a maximum.

Mechanical properties such as Young's modulus, tensile strength, elongation at break, and stress at 100%, 200%, and 300% were measured on a universal testing machine (Instron) with a cross-head speed of 500 mm/min, according to ASTM D-412. Dumbbell-shaped specimens about 2 mm thick were cut with a "C"-type die. Hardness was measured with a Durometer on the Shore A scale. Abrasion resistance was studied by determining abrasion loss (g/1000 cycles) on a Du Pont abrader. The densities of the samples were determined by the water displacement method.

Thermomechanical analysis was carried out to determine the glass transition temperature (T_g) of the polymers. The sample was cooled to -70°C with liquid N_2. A penetration probe was rested on the sample, and the sample was heated at a uniform rate of 8°C/min. Differential thermal analysis (DTA) was carried out at a heating rate of 8°C/min under an oxidative atmosphere. ΔT against temperature was recorded from ambient to 400°C.

X-ray diffraction (XRD) was carried out by using a Philips PW 1140 diffractometer at a scanning rate of 2°/min, from $2\theta = 4$ to 35°. The transition was CuK$_\alpha$.

RESULTS AND DISCUSSION

Dynamic Mechanical Analysis

DMA is an important tool for the characterization of polymers [7-10]. Dynamic mechanical behavior, Figs. 1 and 2, shows the effect of the number of carbon atoms in the extender. For even-numbered diols, the glass transition temperature (as measured by the tan δ maximum) was found to be higher by 18°C than that for the odd-numbered diols (see Fig. 1). Butanediol did not give lower tan δ than the other polymers although the mechanical

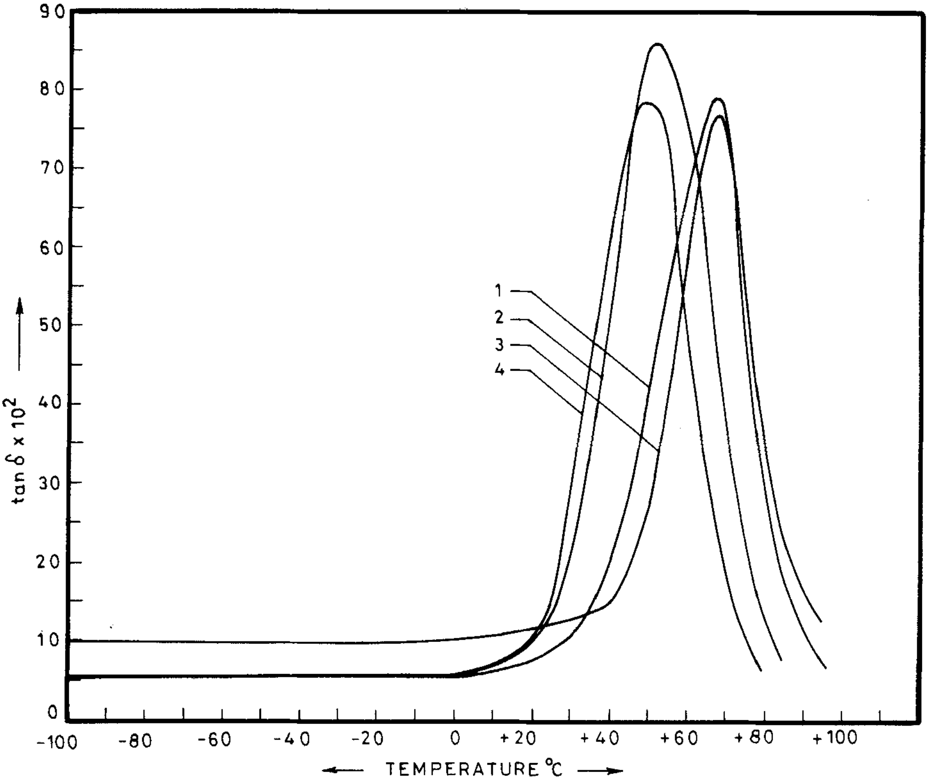

FIG. 1. Tan δ as a function of temperature: (1) ethanediol, (2) propanediol, (3) butanediol, (4) pentanediol.

properties showed significantly higher values of the moduli. In other words, butanediol offers a unique set of properties compared to other extenders.

Storage modulus E' and tan δ as functions of temperature can be studied together to predict performance of a material. As there are large changes in the storage modulus near T_g, E' is plotted on logarithmic scale (Fig. 2). The inflection point, which is associated with the glass-rubber transition, is observed at higher temperatures for the polymers extended by even-numbered diols (as illustrated in Fig. 2). This implies that the applicability of these polyurethanes is wider than that of their counterparts containing odd-numbered diols which have lower $\log E'$ above room temperature.

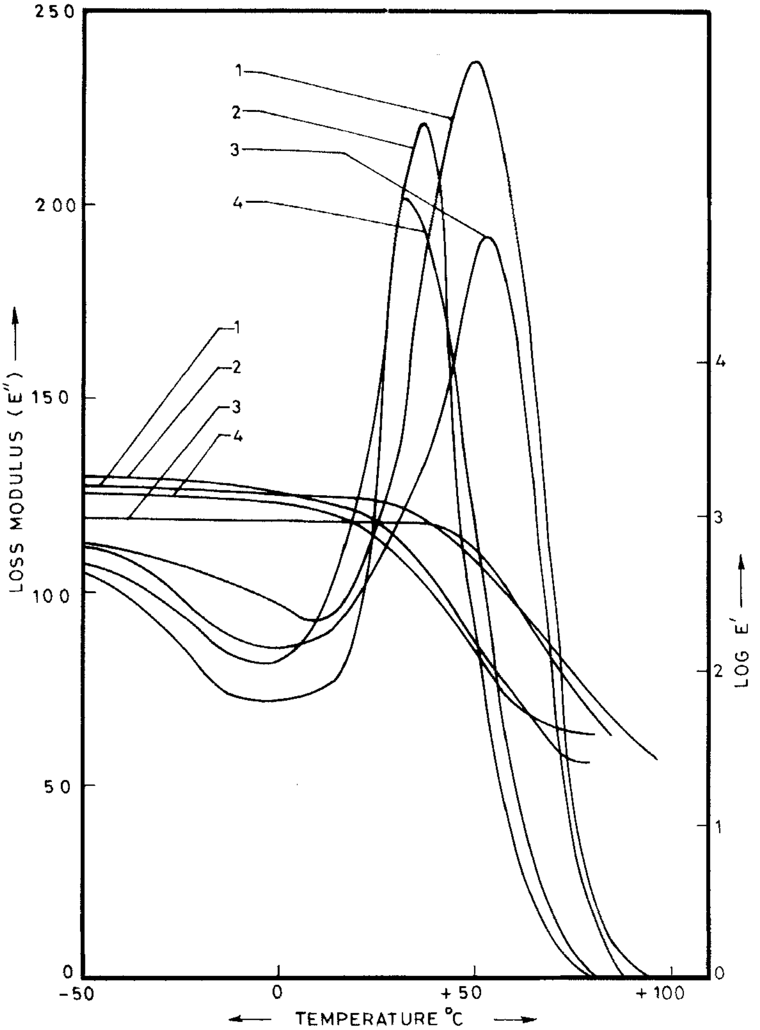

FIG. 2. Logarithm of storage modulus E' and loss modulus E'' as a function of temperature: (1) ethanediol, (2) propanediol, (3) butanediol, (4) pentanediol.

The loss modulus E'' shows basically a trend similar to the mechanical loss factor, tan δ. Peaks obtained in log E''-temperature curves (Fig. 2) are at temperatures lower than those in tan δ curves (Fig. 1) since tan δ is the ratio of the loss modulus to the storage modulus. As E'' increases, tan δ should increase, unless E' drops more than E''.

Mechanical Properties

Stress (also termed modulus) at 100%, 200%, and 300% elongation is shown in Fig. 3. The stress values for butanediol are significantly higher than those for the other diols, which differ very little. Tensile strength changes insignificantly for extenders other than 1,4-butanediol (Table 2). A similar trend is observed for Young's modulus (Table 2), while the elongation at break shows insignificant effect of the extenders. Ethanediol- and butanediol-extended polyurethanes have higher hardness than propanediol- and pentanediol-extended polyurethanes. Abrasion loss varies inversely with hardness.

The higher values for butanediol-extended elastomers can be explained on the basis of chain conformation. For extenders having an even number of carbon atoms, H-bonding is possible at a configuration of the lowest energy, while for extenders with an odd number of carbon atoms, H-bonding is not favored because higher energy is required. However, ethylene glycol does not show a significant effect because it adopts a contracted unstaggered structure [4]. The higher stresses for butanediol can also be accounted for on the basis of structural regularity offered by butanediol and the acid component of the polyol, both of which contain the C_4 moiety.

The density of polyurethanes from a chain extender with an even number of carbon atoms is higher than that of odd-numbered diols, presumably because of closer packing of the molecules.

Thermal Properties

As the number of carbon atoms in the chain extender increases, T_g decreases (Table 3). DTA thermograms gave exothermic peaks which correspond to the decomposition temperature of the polymer (see Table 3).

X-Ray Diffraction

Figure 4 depicts x-ray diffraction patterns of the polymers, consisting of one broad halo in the region $2\theta = 10\text{-}28°$ and sharp peaks at 9 and 28.2°.

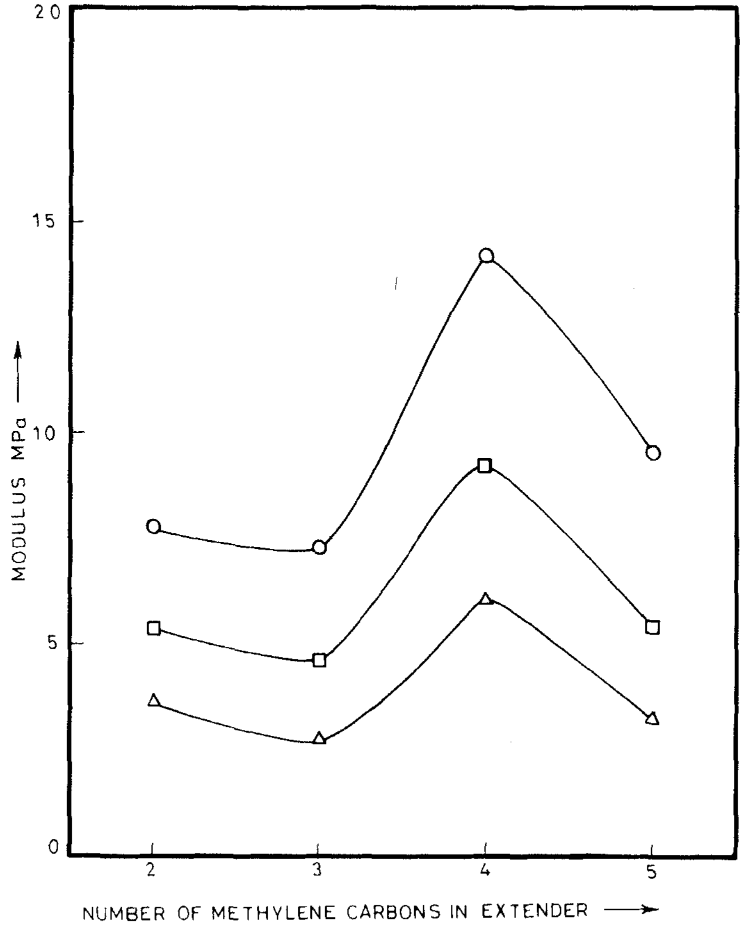

FIG. 3. Effect of number of methylene carbons on stress at various extensions: (△) 100%, (□) 200%, (○) 300%.

The diffraction intensity, a measure of crystallinity, seemed to vary with the nature of the diols [2]. The diffraction intensity for butanediol-extended polymer, and hence the crystallinity, was the highest.

TABLE 2. Mechanical Properties of Polyurethanes

Diol chain extender	Stress, MPa			Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %	Hardness Shore A	Abrasion loss, g/1000 cycles	Density g/mL
	100%	200%	300%						
Ethanediol	3.7	5.4	7.6	16	21.7	660	77	0.43	1.291
1,2-Propanediol	2.8	4.7	7.5	10	18.9	490	70	0.42	1.280
1,4-Butanediol	6.0	9.3	14.2	32	31.1	510	84	0.40	1.308
1,5-Pentanediol	3.2	5.4	9.6	11	21.8	480	71	0.45	1.264

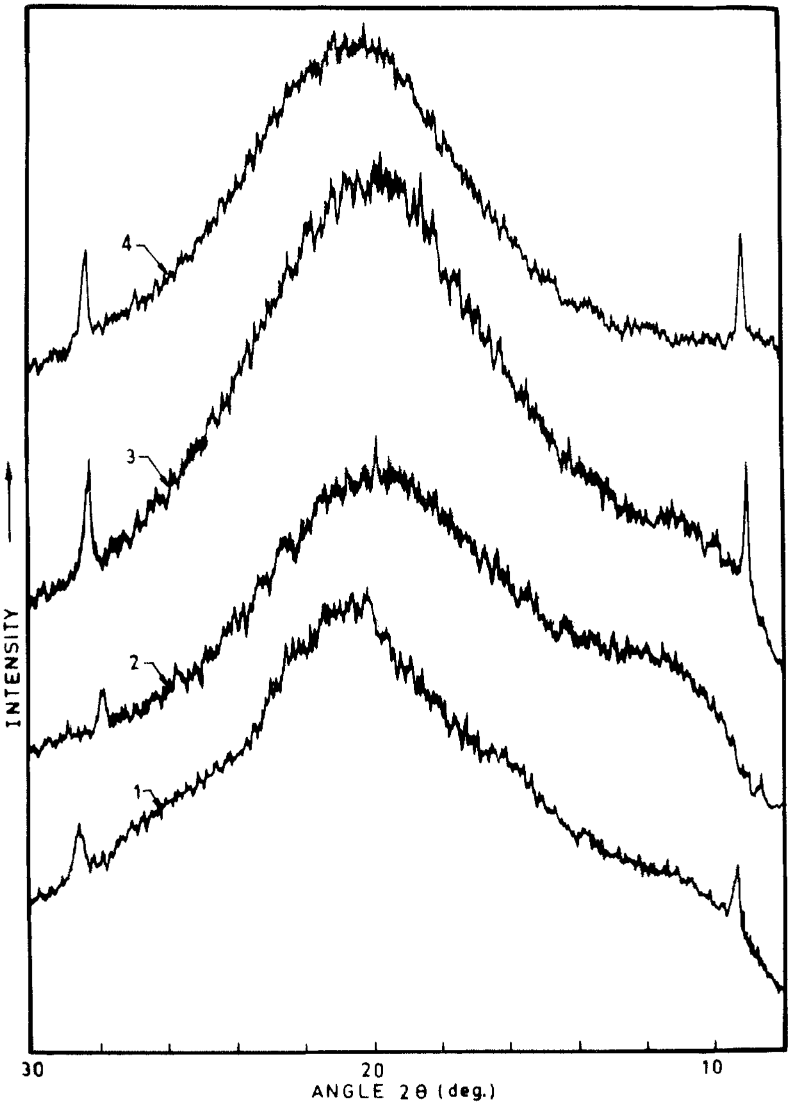

FIG. 4. Effect of methylene carbons on diffraction intensity: (1) ethanediol, (2) propanediol, (3) butanediol, (4) pentanediol.

TABLE 3. Thermal Properties of Polyurethanes

Diol chain extender	T_g, °C[a]	Decomposition temperature, °C
Ethanediol	10.5	294.5
1,2-Propanediol	8.5	296.0
1,4-Butanediol	7.0	310.0
1,5-Pentanediol	2.0	310.0

[a] Measured by TMA.

CONCLUSION

Among the chain extenders studied, butanediol gave properties superior to other extenders. This accounted for higher tensile strength, stress at various elongations, hardness, abrasion resistance, etc. The dynamic loss factor tan δ for butanediol-extended polymer was the lowest, implying lower heat dissipation. The superior performance of butanediol as an extender can be explained on the basis of structural regularity formed by the acid component in the polyester (4 carbon atoms). This is supported by x-ray diffraction, which shows higher diffraction intensity.

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