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PHYSICO-MECHANICAL, OPTICAL, AND WAXS STUDIES ON CHAIN EXTENDED POLYURETHANE

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ABSTRACT

Thermoset polyurethane (PU) elastomers were prepared using castor oil, 4,4'-methylenebis(phenyl isocyanate) (MDI), and toluene-2,4-diisocyanate (TDI). The effect of aromatic diamines on the physico-mechanical and optical properties of chain extended polyurethane prepared using castor oil has been investigated. Tensile strength and percent elongation lies in the range 13-24 MPa and 76-32, respectively. Higher tensile strength was observed for 4,4'-diaminodiphenylsulphone (DDS) than the 4,4'-diaminodiphenylmethane (DDM) chain extender. The properties imparted by the extenders are explained on the basis of the

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groups present in the diamines. These changes have been interpreted quantitatively in terms of microcrystalline parameters computed using wide-angle X-ray scattering data.

INTRODUCTION

Chain extended polyurethane (PU) elastomers have a wide range of industrial applications and are well known for their mechanical properties. The three main ingredients of these elastomers are a long chain polyol, a diisocyanate and a chain extender in the form of diamine. The structure and amount of chain extender used causes a significant variation in the mechanical properties of elastomers [1-5].

The present work describes the effect of two aromatic diamines on physico-mechanical and optical properties of polyurethane prepared using castor oil. PU synthesized using aromatic diamine chain extenders shows superior mechanical and thermal properties compared to the diols [3, 4]. These changes have been explained in terms of microstructural parameters obtained from wide angle X-ray scattering (WAXS) studies.

EXPERIMENTAL

Materials

Castor oil was obtained from the local market. Its molecular weight (\overline{M}_n) is 930 and 2.24 hydroxyl group per molecule. Toluene-2,4-diisocyanate (TDI), 4,4'-methylenebis(phenyl isocyanate) (MDI), and dibutyltin dilaurate were used as received. Chain extenders, 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulphone (DDS) were obtained from Sigma. Solvents, toluene and tetrahydrofuran of AR grade were distilled.

Synthesis of Polyurethanes

Castor oil (0.001 mol) was dissolved in 50 ml of toluene. This was reacted with TDI (0.0022 mol) using 2-3 drops of dibutyltin dilaurate as catalyst. The contents of the flask were stirred mechanically for about 1 hour at 60-70°C. The prepolymer obtained was reacted with the equal molar ratio (0.001 mol) of diamine dissolved in dry tetrahydrofuran. The mixture was stirred for about 30 minutes at the same temperature. Then, the mixture was poured into molds and

left to dry at room temperature. One percent of cobalt acetyl acetonate (CAA) chelating agent was incorporated as a filler to two formulations.

Tensile Properties

Tensile properties were determined according to ASTM D 638 using a Hounsfield universal testing machine, model 4302, UK (at ambient condition), and with dumbbell-shaped specimens. The specimens were prepared with the help of a punching die, (165 mm × 14 mm). The edges of the specimens were polished using very fine sandpaper. The specimens were conditioned according to the standard before testing. A minimum of 6 (six) samples were tested for each composition and the average was taken.

X-ray Recording and Profile Analysis

X-ray diffraction data on powder samples were collected on a STOE/STADI-P X-ray powder diffractometer with germanium monochromated $\text{CuK}\alpha$, ($\lambda = 1.5406 \text{ \AA}$) radiation in a transmission mode, using a curved position sensitive detector (CPSD) in the 2θ range from 5 to 53° at step sizes of 0.03° . The trial and error indexing program TREOR [7] was used in determining the unit cell parameters. All these samples belong to the orthorhombic system and the lattice parameters are $a = 10.567$, $b = 10.567$ and $c = 13.10$ in \AA . X-ray diffractogram of all the samples are given in Figures 1 (a-f). It is evident from the Figures 1(a-f) that there is a broadening which arises due to two main factors. According to Warren [8] these are due to a decrease in (i) crystal size (N), and an increase in (ii) strain (lattice disorder) (g in %) present in the samples.

We have estimated these parameters by simulating the profile employing the procedure described earlier [9-12] and a Bragg reflection at $2\theta = 18.9^\circ$. The following equations [9, 13] have been used to simulate X-ray reflection;

$$I(s) = I_{N-1}(s) + I'_N(s) \quad (1)$$

where

$$I_N(s) = 2 * \text{Re} \left[\frac{(1 - I^{N+1})}{(1 - I)} + \frac{Iv}{d(1 - I)^2} \left\{ I^N(N(1 - I) + 1) - 1 \right\} \right]^{-1} \quad (2)$$

where

$v = 2ia^2s + d$ and $I = I_1(s) = \exp(-a^2s^2 + ids)$; $a^2 = \omega^2/2$. Also,

$$I'_N(s) = \frac{2a_N}{D(\pi)^{1/2}} \exp(iDs) \left[1 - a_N s \{ 2D(a_N s) + i(\pi)^{1/2} \exp(-a_N^2 s^2) \} \right] \quad (3)$$

with $a_N^2 = N\omega^2/2$, ω is the standard deviation of the nearest neighbor probability function, $D(a_N s)$ is the Dawson's integral or the error function with complex argument and can be computed. $\langle N \rangle$ is the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane, d is the spacing of the (hkl) planes, 'Re' refers to real part of the expression, s is $\sin\theta/\lambda$, λ is the wavelength of X-rays used, a is related to the standard deviation ω of lattice distribution function and D is the crystal size ($= \langle N \rangle d_{hkl}$). $I'_N(s)$ is the modified intensity for the probability peak centered at D .

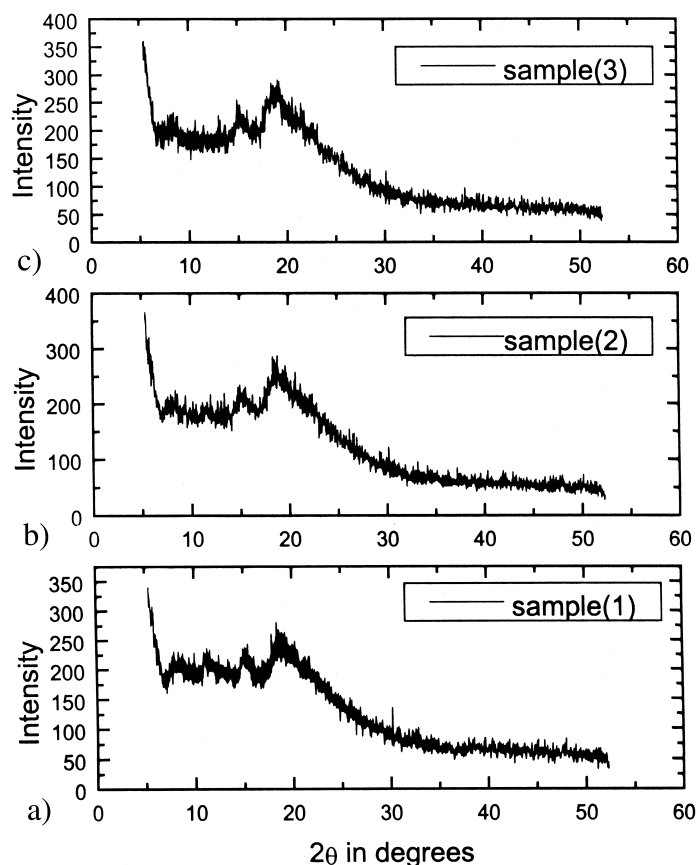


Figure 1. Wide angle X-ray scattering patterns for (a) sample(1)-(CO+TDI+DDS+CAA), (b) sample(2)-(CO+TDI+DDS), (c) sample(3)-(CO+TDI+DDM+CAA), (d) sample(4)-(CO+TDI+DDM), (e) sample(5)-(CO+MDI+DDS), and (f) sample(6)-(CO+MDI+DDM).

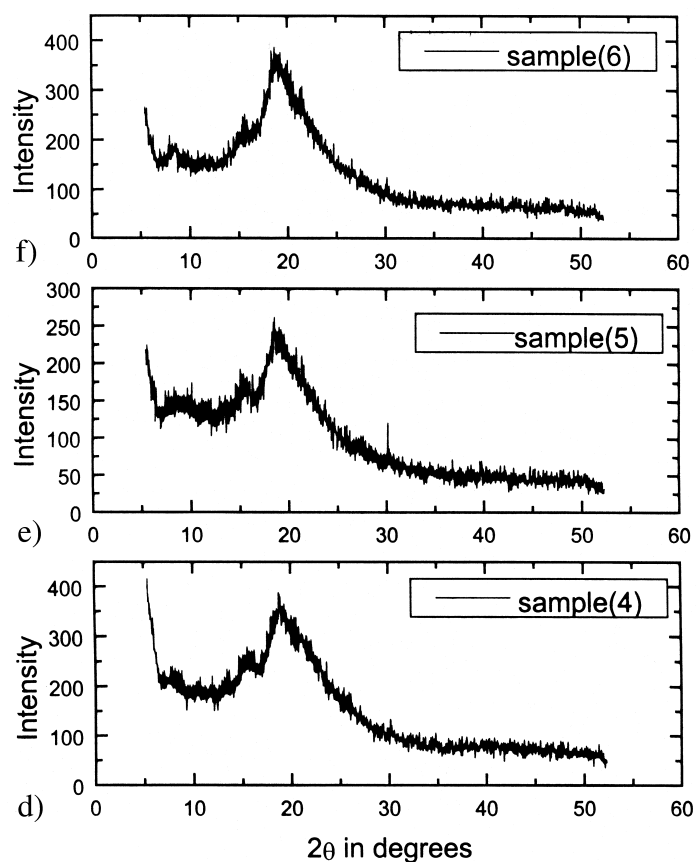


Figure 1. Continued.

For the sake of completeness, we have reproduced in Figures 2 (a, b), the simulated and experimental profiles for the samples (a) CO+TDI+DDS+CAA and (b) CO+MDI+DDM. In fact, the goodness of the fit was less than 5% in all the samples.

RESULTS AND DISCUSSION

The physico-mechanical and optical (total light transmittance, diffuse light and haze) properties of chain extended polyurethane are given in Table 1. From the Table 1, it is observed that percent of transmittance of light was very good in all chain extended polyurethanes and in the range of 75-90%. Incorporation of CAA to chain extended PU decreases the transmittance and

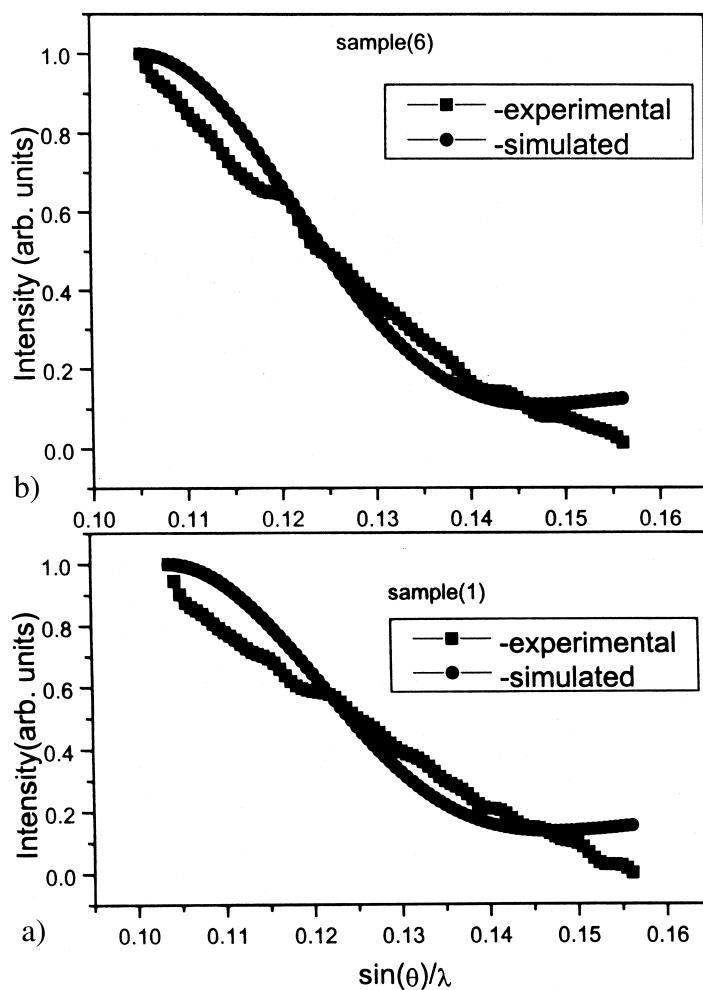


Figure 2. Experimental and simulated X-ray profile for sample (1) and sample (6).

increases percent haze [14]. Among the polyurethane chain extended with diamines it is found that, the higher mechanical properties are observed for DDS systems compared to DDM. This is understandable, since as we move from DDM to DDS the ease of formation of hydrogen bonding increases due to the presence of O_2 atoms (i.e, DDS has S group). In DDS hydrogen, bonding will be even greater, due to the presence of two O_2 atoms and the system becomes more stabilized and tensile strength increases. Therefore, in the case of DDS chain extended PU systems tensile strength increases, elongation decreases, and hardness increases. Hence, PU extended with DDS becomes more stabilized with

TABLE 1. Optical and Mechanical Properties of Chain Extended PU Samples

Samples	% of Transmittance	Total Diffuse	Haze	Surface Hardness (Shore A)	Tensile Strength (MPa)	% of Elongation
CO+TDI+DDS+CAA	80	10	25	94±3	24±1	32±1
CO+TDI+DDS	89	5.7	6.3	85±3	21±1	39±1
CO+TDI+DDM+CAA	75	13.4	27	92±3	18±1	46±1
CO+TDI+DDM	90	11.9	13	81±3	15±1	61±2
CO+MDI+DDS	81	23.4	19	91±3	18±1	46±1
CO+MDI+DDM	85	29.5	30.5	89±3	13±1	76±2

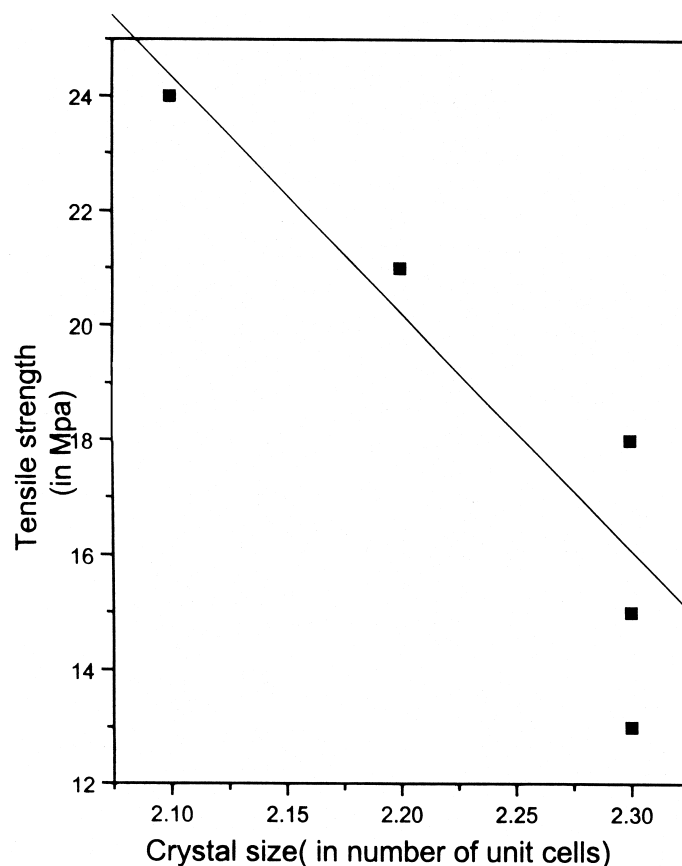


Figure 3. Variation of tensile strength with crystal size observed in chain extended polyurethane.

TABLE 2. The Microcrystalline Parameters of Chain Extended PU Samples Using Bragg Reflection Observed at $2\theta = 18.9^\circ$

Sample	$\langle N \rangle$	g in %	α^*
CO+TDI+DDS+CAA	2.1 ± 0.1	8.2 ± 0.1	0.12
CO+TDI+DDS	2.2 ± 0.1	6.3 ± 0.1	0.09
CO+TDI+DDM+CAA	2.3 ± 0.1	7.5 ± 0.1	0.11
CO+TDI+DDM	2.3 ± 0.1	8.4 ± 0.1	0.13
CO+MDI+DDS	2.3 ± 0.1	6.6 ± 0.1	0.10
CO+MDI+DDM	2.3 ± 0.1	6.8 ± 0.1	0.10

highly improved tensile property [3, 6]. These results are further justified by X-ray profile analysis wherein the crystal size and lattice disorder (or strain g in %) values are comparatively low in DDS samples. In fact, α^* the enthalpy of DDS chain extended samples are of the order 0.12, indicating phase stabilization of these samples. With different chain extenders, even though crystal size increases, there is an additional increase in lattice disorder leading to a decrease in physical properties of the samples.

In fact, Figure 3 shows that tensile strength decreases with increase in crystal size estimated in different chain extenders [15]. An increase of a 1% in the values of crystal size, shows a reduction of 10% in the values of tensile strength of these samples.

It is evident from Table 2 that, microstructure parameters does not show significant changes in TDI and MDI systems. This implies that the shape of the crystallite ellipsoid does not vary so much in these samples. MDI based PU systems show higher tensile strength when compared to TDI based PU systems. This is due to the presence of 2 aromatic rings (presence of phenyl stiffening groups along the chain) in MDI.

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