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Structure-property relationship of castor oil based diol chain extended polyurethanes (PUs)

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A series of 1,4-butane diol and 1,6-hexane diol based chain extended polyurethanes (PUs) have been prepared using castor oil with different diisocyanates such as methylene bis (phenyl isocyanate) (MDI), toluene-2,4-diisocyanate (TDI) and hexa methylene diisocyanate (HMDI) as crosslinkers. The prepared aliphatic diol based chain extended PU's have been characterised for physico-mechanical properties such as density, tensile strength, percentage elongation at break, tensile modulus and surface hardness; and optical properties like total transmittance and haze. The properties imparted by the chain extenders and diisocyanates on PUs have been explained on the basis of chemical structure. Effect of heat aging on mechanical properties of PUs have also studied. These changes have been interpreted quantitatively in terms of microcrystalline parameters computed using wide-angle X-ray scattering (WAXS) data.

1. Introduction

Recently the utilization of the renewable resources in polymers has become an increasing interest because of their potential use in substitution of petro-chemical derivatives. Several research articles are available on the use of natural polymers having more than two hydroxyl groups per molecule either as polyol or as crosslinker in the preparation of PU, by allowing them to react efficiently with the diisocyanates. Many authors [1–4] have used castor oil and variety of lignins for the synthesis of PUs, as the properties can be controlled by changing the hard and soft segment contents and these products are of great importance in biomedical industry.

Chain extended polyurethanes (PUs) have wide range of industrial applications such as coating, adhesives, biomedical applications, etc., and they are well known for their mechanical properties. PU elastomers were the first to be used to any significant degree and even today they account for the largest proportion of solid polyurethanes (PUs) [1]. The three important components of these elastomers are macrodiol, diisocyanate and chain extender. Thus PUs are linear alternating block copolymers of soft and hard segments. The characteristics of hard and soft segments are important factors for the properties [2, 3] of PU elastomers. It is well known and understood that hard and soft segments segregate into microphase domains separately and such phenomenon causes the polymers to exhibit excellent elastomeric properties [4–8].

The properties of PUs can be varied in numerous ways according to their demand. It was found that diols containing an even number of carbon atoms adopt a lowest energy, fully extended conformation, that allows hydrogen bonding in both the directions of the chain axis [9].

A thorough literature survey reveals the lack of literature on the systematic study of natural polyol (castor oil) based diol chain extended PUs. Hence, this kind of research work was taken, which would give some input to polymer engineers to select and design PUs for tailor made applications. In our earlier research articles, we have reported synthesis, physico-mechanical, optical thermal, microcrystalline parameters and swelling behaviour of chain extended PUs [10–12]. In this research article authors have reported the effect of aliphatic diols on physico-mechanical and optical properties of chain extended PUs. Effect of heat aging on chain extend PUs has also studied. Microcrystalline parameters such as crystal size ($\langle N \rangle$), and lattice distortion (g in %) were calculated using wide angle X-ray scattering (WAXS) study.

2. Experimental

2.1. Materials

Castor oil (CO) was obtained from the local market and having characteristic properties such as molecular weight (M_n)—930; hydroxyl number—160 to 168; acid value—2.45 and isocyanate equivalent—330.

Toluene-2-4-diisocyanate (TDI), 4,4′-methylenebis (phenyl isocyanate) (MDI), hexa methylene diisocyanate (HMDI) and dibutyl dilaurate (DBTL) were obtained from Sigma, USA and they were used as received. Chain extenders like 1,4-butane diol and 1,6-hexane diol were obtained from Fluka, Switzerland. Solvents such as toluene and methyl ethyl ketone (MEK) of AR grade were distilled prior to use.

2.2. Synthesis of chain extended polyurethanes

Castor oil (0.001 mol) was dissolved in 50 ml methyl ethyl ketone (MEK). This was reacted with diisocyanate (0.0022 mol) using 2–3 drops of DBTL as catalyst. The contents in the 250 ml three necked round bottom flask were stirred using magentic stirrer for about 1 hr at 60–70°C. The pre polyurethane so obtained was reacted with the equal molar ratio (0.001 mol) of diol dissolved in MEK. The mixture was stirred for about 15–20 min at the same temperature to form a uniform mixture. Then the mixture was poured into cleaned glass mould, and is kept in a preheated circulating air oven at 70°C for 24 hrs. The film thus formed, was cooled slowly and removed from the mould. Similar procedure was followed with different formulations [13]. The golden yellow coloured transparent and toughened diol chain extended PU films were obtained.

2.3. Techniques

The prepared diol based chain extended PUs were characterised for physical properties like density and surface hardness (Shore A) according to ASTM D 792-86 and ASTM D 785 methods respectively. Mechanical properties such as tensile strength, percentage elongation at break and tensile modulus have been measured as per ASTM D 368 using 4302 model Hounsfield universal testing machine (UTM). Minimum of five samples were tested at room temperature for each formulation and the average values are reported. Optical properties such as total percent transmittance of light, total diffuse, percent parallel and haze of grease and dust free chain extended PUs have been measured as per ASTM D-1003 using suga test hazemeter (model 206).

2.4. X-ray recording and profile analysis

X-ray diffraction data on powder samples was collected on a STOE/STADIP X-ray powder diffractometer with germanium monochromatic Cu K_α ($\lambda = 1.5406$ Å) radiation in a transmission mode, using a curved position sensitive detector (CPSD) in the 2θ range from 5 to 50° at step size of 0.03°. It is emphasized here that the X-ray profile broadening observed in these polymers is due to both (i) crystal size and (ii) lattice distortion (strain) present in the materials. Scherrer equation is an empirical relation is not used there because it does not consider the strain present in the samples and hence, leads to an over-estimated value. There are multiple order methods using Fourier analysis and also other techniques employing FWHM methods. Since we do not observe two orders of X-ray reflection from the same set of Bragg planes, we have used single order method, of Hall and Somashekar [14].

We have used generally applicable one-dimensional model based on distortion of the lattice [15] to obtain the average microstructural parameters like crystal size and lattice strain along different directions of the lattice employing individual (*hkl*) reflections [15–17]. The corrected experimental X-ray profile was matched with the simulated profile using the following equations;

$$I(s) = I_{N-1}(s) + I_N^1(s) \tag{1}$$

where, I_{N-1} (s) is computed using,

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

where, $v = 2ia^2s + d$ and $I = I_1(s) = \exp(-a^2s^2 + ids)$ with $a^2 = w^2/2$. $I''_N(s)$ is the modified intensity for the probability peak centre at $d(= nd_{hkl})$ and it has been shown that;

$$I_N^1(s) = \frac{2a_N}{\mathscr{T}(\pi)^{1/2}} \exp(i\,\mathscr{T}Ns)\left[1 - a_N s\left\{2\,\mathscr{T}(a_N s) + i(\pi)^{1/2}\exp\left(-a_N^2 s^2\right)\right\}\right] \tag{3}$$

where, $a_N^2 = N\omega^2/2$, ω is the standard deviation of nearest neighbour probability function [18] and $\mathscr{T}$ $(a_N s)$ is the Dawson's integral or the error function with purely complex argument and can be easily computed. The $\langle N \rangle$ is number of unit cell counted in a direction perpendicular to the (*hkl*) Bragg plane and d is the spacing of the (*hkl*) planes. Re refers to the real part of the expression, s is $\sin\theta/\lambda$, λ is the wavelength of X-ray used, a is related to the standard deviation and ω is lattice distribution function and D is the crystal size $(= \langle N \rangle\ d_{hkl})$. $I_N(s)$ is modified intensity for the probability peak centered at D. The experimental profile between s_0 and $s_0 + s_0/2$ (or s_0 and $s_0 + B/2d$, if there is a truncation of the profile $B < 1$) is matched with corresponding simulated reflection profile between s_0 and $s_0/2$ (s_0 and $s_0 + B/2d$) using a one-dimensional para crystalline model for various values of $\langle N \rangle$ and g to minimize the difference between calculated and experimental normalized intensity values. SIMPLEX, a multidimensional algorithm [19] was used for minimization. The estimated enthalpy α $(= N^{1/2}\ g)$ [19] which physically implies that the growth of the para crystals in a particular material is appreciably controlled by the level of g in the net plane structure. This is only an empirical deinition of enthalpy given by Hosemann in order to characterise the materials.

3. Results and discussion

3.1. Physico-mechanical properties

The measured physico-mechanical properties such as density, surface hardness, tensile strength, percentage elongation at break and tensile modulus of 1,4-butane diol and 1,6-hexane diol based chain extended PUs are shown in Table I.

TABLE I Physico-mechanical properties of both diol chain extended PUs

Samples	Density (g/cc)	Surface hardness ±2% Shore A	Surface hardness ±2% Shore D	Tensile strength (MPa) ±2%	Percentage elongation at break ±3%	Tensile modulus (MPa) ±2%
CO + TDI + 1,4-diol	1.058	70	46	1.25	156	6.7
CO + TDI + 1,6-diol	1.127	69	50	1.05	136	4.8
CO + MDI + 1,4-diol	1.041	76	48	1.29	162	5.0
CO + MDI + 1,6-diol	1.105	78	59	1.10	137	4.2
CO + HMDI + 1,4-diol	1.028	55	38	1.18	147	3.8
CO + HMDI + 1,6-diol	1.086	65	36	0.99	124	2.8

CO - Castor oil

The densities of chain extended PUs are greater than water, because they are cross-linked. The density of both diol based chain extended PUs lies in the range 1.028–1.127 g/cc and they are in the expected range. From Table I it is evident that lower density [19] values were observed for HMDI based PUs when compared to MDI and TDI based PUs. This is because the densities of PUs depend upon the ratio between hard and soft segments. 1,6-hexane diol chain extended PUs show higher density values compared to 1,4-butane diol chain extended PUs.

Surface hardness results reflects the resistance to local deformation, which is related to the degree of crystallinity, crosslink density and porosity of the polymer matrix. The surface hardness values of all PUs are recorded using both shore A and shore D tester and obtained data are given in Table I. The surface hardness values of both diol chain extended PUs lie in the range 55–78 Shore A and 36–59 Shore D respectively. From Table I, it was observed that higher surface hardness values are observed for 1,6-hexane diol chain extended PUs than 1,4-butane diol. This result reveals that 1,6-diol system yields higher dimensional stability, compared to 1,4-butane diol system.

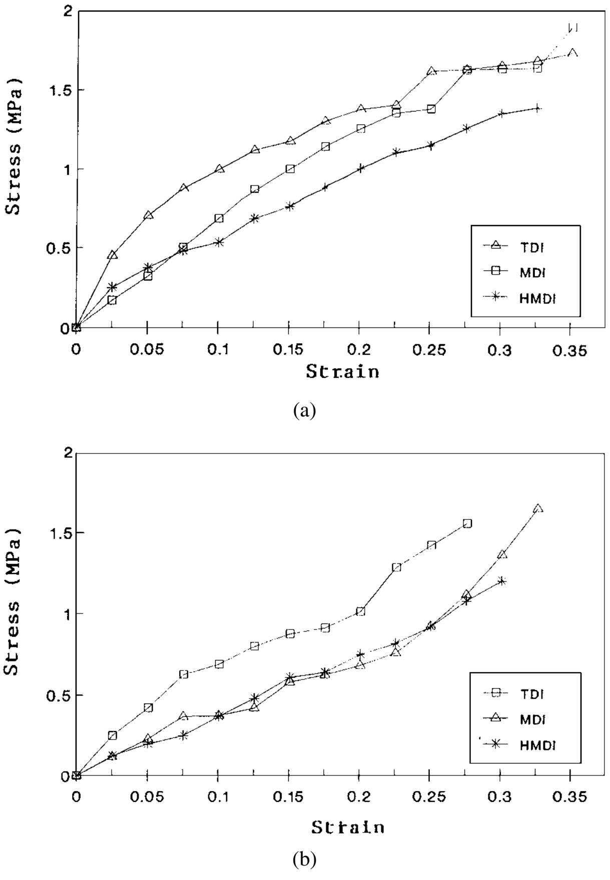
From Table I it can be observed that, there is a variation in the tensile strength with the nature of chain extender. Higher tensile strength value (1.18–1.29 MPa) was observed for 1,4-diol chain extended PUs than 1,6-diol based PUs [20]. Among diisocyanates, MDI based chain extended PUs show higher tensile strength of 1.10 and 1.29 MPa for 1,6-diol and 1,4-diol based PU systems respectively. The sequence of variation of tensile strength with respect to diisocyanates are in the order; MDI > TDI > HMDI.

From Table I, it was also observed that the percentage elongation at break lies in the range 124–162. Both the diol chain extended PUs show almost same amount of percentage elongation behaviour, but slightly higher values for MDI based PUs. 1,4-diol chain extended PUs show higher percentage elongation behaviour compared to 1,6-diol. Table I reveals there is a weak mechanical performance for HMDI based PUs. This is due to the presence of more flexible methylene (-CH_2-) groups in HMDI.

Tensile modulus of diol chain extended PUs lie in the range 2.8–6.7 MPa. Lowest tensile modulus of 2.8 MPa was observed for CO + HMDI + HD and highest for CO + TDI + BD. This result clearly indicates that the, HMDI systems show poor dimensional stability compared to other aromatic diisocyanates. 1,4-butane diol chain extended PUs show better tensile modulus compared to 1,6-hexane diol based PUs. From tensile behaviour, it can be concluded that 1,4-diol based PU systems show superior mechanical properties [9] than 1,6-diol chain extended PUs.

3.2. Effect of heat aging on mechanical behaviour

Diols chain extended PUs have been subjected to heat aging at 90°C, for 24 and 48 h. The effect of heat aging on mechanical properties such as tensile strength, percentage elongation at break and tensile modulus of PUs have been reported. The plots of stress verses strain curves for thermally treated chain extended Pus are shown in Fig. 1a and b and Fig. 2a and b for 24 and 48 h respectively. These plots represent the effect of heat aging on the deformation pattern of PUs. From these plots a slight reduction in the mechanical behaviour is noticed after heat aging. The sequence of stress verses strain curves variation with nature of diioscyanates are; TDI > MDI > HMDI.



(a)

(b)

Figure 1 Stress-strain plots of thermally treated diol chain extended PUs for 24 h: (a) Butane diol (b) Hexane diol.

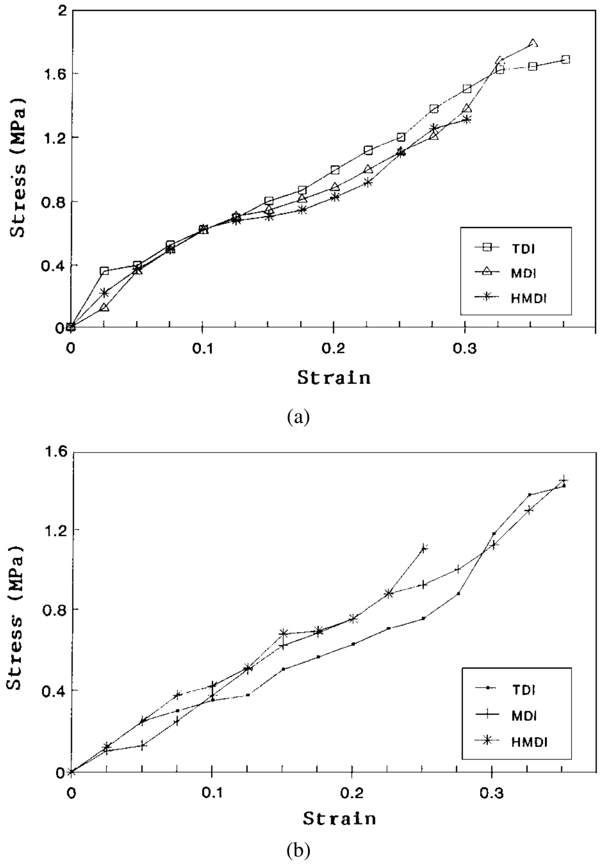


Figure 2 Stress-strain plots of thermally treated diol chain extended PUs for 48 h: (a) Butane diol (b) Hexane diol.

The measured tensile strength, percentage elongation and tensile modulus from stress verses strain plots are shown in Table II. From Table II, it is evident that there is a higher percentage of reduction in tensile strength for HMDI based PUs compared to other diisocyanates. From Table II, it is also noticed that increase in duration of heat aging, reduces the mechanical performance. This may be due to the decrosslinking of PUs or reduction in degree of interaction between different layers of PUs.

The variation in tensile strength with respect to heat aging is shown in Fig. 3. From this, the reduction in tensile strength with duration of heat aging is noticed. From these results it can be concluded that diol chain extended PUs will retain useful properties at low temperature [21]. One of the most outstanding properties of diol chain extended PUs are their performance at low temperature.

3.3. Optical properties

The recorded optical properties such as total percent transmittance, total diffuse, percent parallel and haze values of 1,4-diol and 1,6-diol chain extended PUs are given in Table III. These values are in expected range [14]. The total transmittance and haze values of diol chain extended PUs lie in the range 72.9–82% and

TABLE III Optical properties of diol chain extended PUs

Samples	Percent total transmittance	Total diffusion	Percent parallel	Haze
CO + TDI + 1,4-diol	82.0	38.4	43.6	28.6
CO + TDI + 1,6-diol	80.0	14.1	64.9	8.2
CO + MDI + 1,4-diol	73.7	64.0	13.7	9.7
CO + MDI + 1,6-diol	72.9	41.8	31.1	27.6
CO + HMDI + 1,4-diol	80.0	60.4	19.6	12.6
CO + HMDI + 1,6-diol	82.0	41.2	40.8	29.5

TABLE II Mechanical properties of both diol chain extended PUs after heat aging at 90°C

	Tensile strength (MPa) ±2%		Percentage elongation at break ±3%		Tensile modulus (MPa) ±2%	
Samples	24 hrs	48 hrs	24 hrs	48 hrs	24 hrs	48 hrs
CO + TDI + 1,4-diol	0.95	0.86	141.2	124.8	5.8	5.2
CO + TDI + 1,6-diol	1.05	1.02	106.0	105.5	4.2	3.8
CO + MDI + 1,4-diol	1.00	0.88	147.2	126.6	4.3	4.0
CO + MDI + 1,6-diol	1.15	1.08	122.2	114.8	3.7	3.5
CO + HMDI + 1,4-diol	0.78	0.67	116.2	95.5	3.2	3.0
CO + HMDI + 1,6-diol	0.84	0.79	87.6	82.3	2.2	1.9

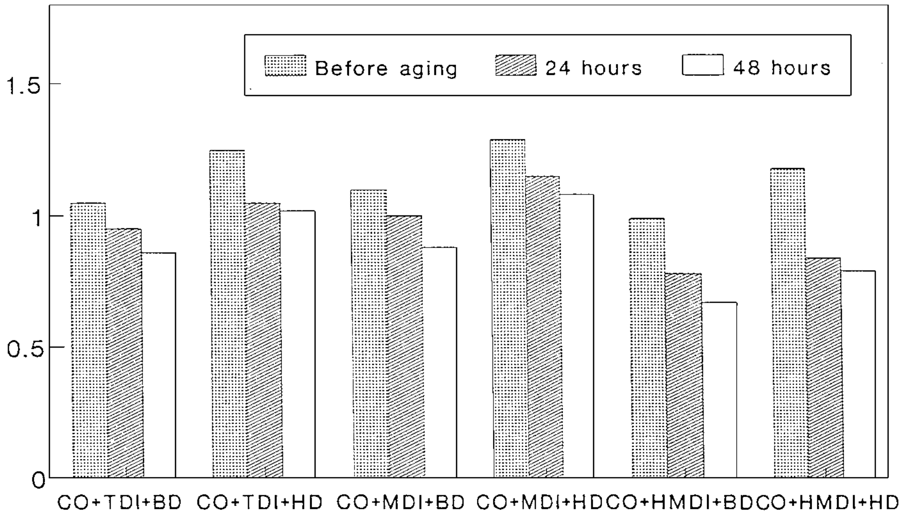


Figure 3 Comparison of tensile strength before and after heat aging of diol chain extended PUs.

8.2–29.5 respectively. From the table, it is observed that all chain extended PUs are good transparent films and their percent of transmittance is greater than 72.9. Higher percent transmittance value is observed for HMDI and TDI based PUs compared to MDI based PU systems. The percent transmittance of PU films depends on the levels of NCO/OH ratios, or ratios of hard/soft domains and morphology [22].

From Table III it is noticed that, there is no systematic variation in both percent transmittance and haze values with the nature of diols. This is due to the complicated chemical structure and morphology of chain extended PUs than simple PU. Diol chain extended PUs are good transparent and flexible films, and may be used in surface coating and paint industries.

3.4. X-ray profile analysis

X-ray diffractograms of all diol chain extended PUs are given in Fig. 4a–e. All these samples belong to the orthorhombic system. The X-ray diffractograms of all

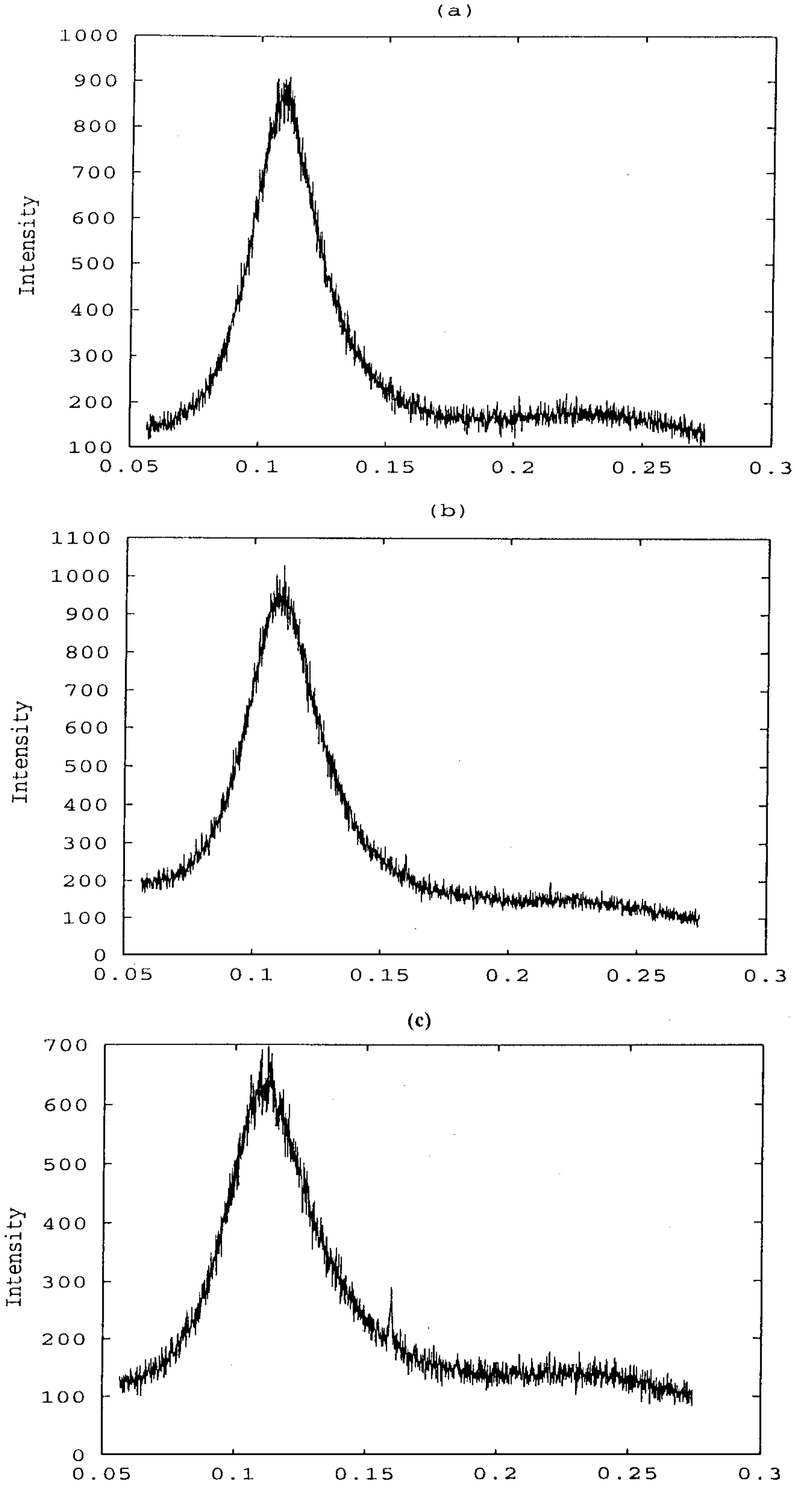


Figure 4 X-ray diffractrograms of diol chain extended PUs: (a) CO + TDI + BD (b) CO + TDI + HD (c) CO + MDI + BD (d) CO + MDI + HD (e) CO + HMDI + BD (f) CO + HMDI + HD. (*Continued.*)

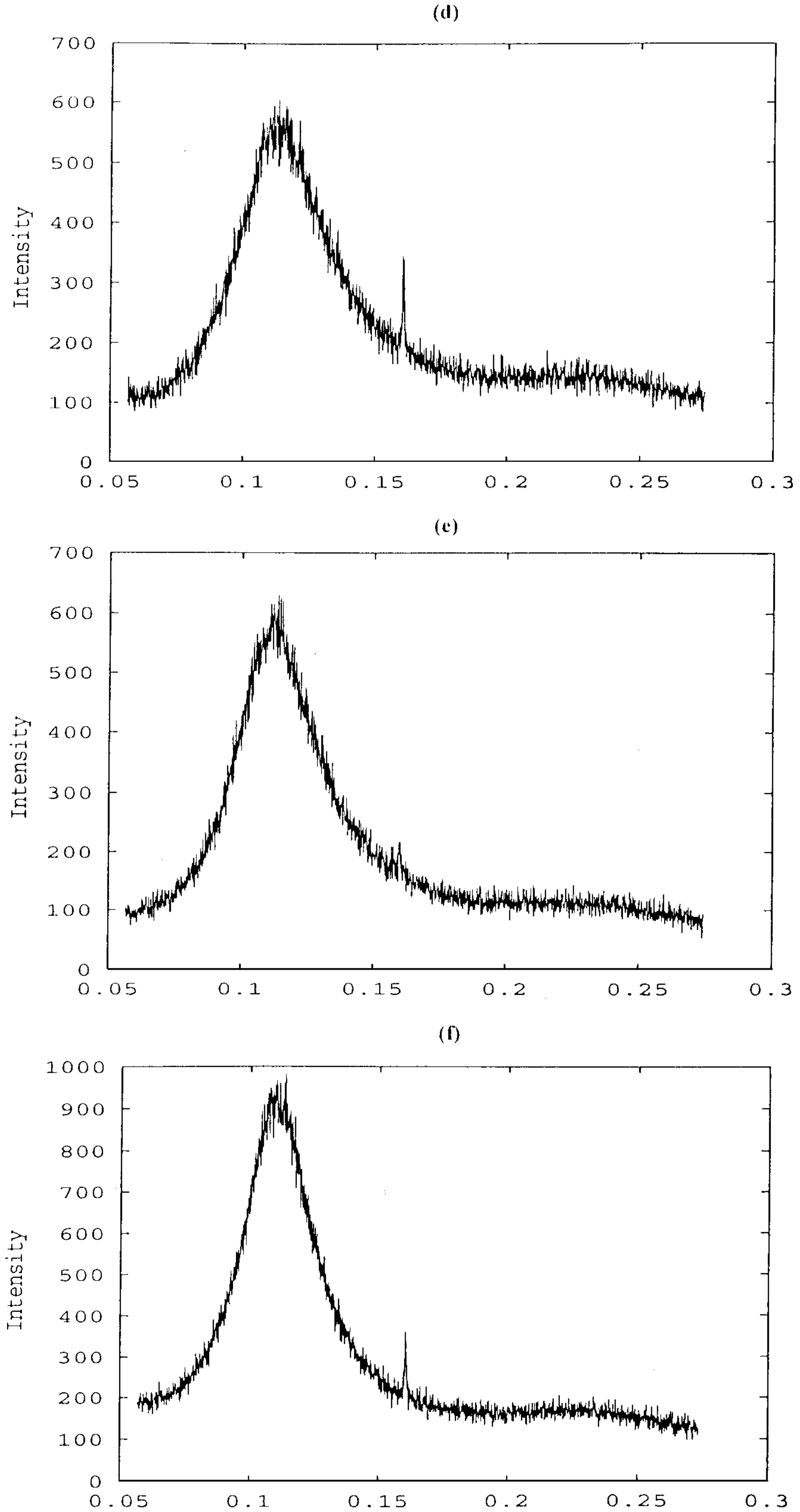


Figure 4 (*Continued*).

PU samples show, a small (at $2\theta = 28.5$) and a broad intense reflections ($2\theta = 19.57$). According to Warren [23], broadening in any polymer sample arises due to (i) crystal size ($\langle N \rangle$) and (ii) strain or lattice disorder (g in %). Microstructural parameters such as crystal size ($\langle N \rangle$), lattice strain (g in %), smallest crystal unit (p), crystal size distribution width (α), the enthalpy (α^*) and surface weighted crystal size (D_{Sur}) are calculated using the equations mentioned earlier [24] in the text, for both butane diol and hexane diol chain extended PUs and the results are given in Table IV. A physical interpretation of crystal imperfection parameters like, crystal size ($\langle N \rangle$) and lattice strain (g in %) [24] is essentially the percentage of deviation in the lattice for a distance of D in Å($=N d_{hkl}$) along the direction normal to Bragg (hkl) plane.

TABLE IV Microcrystalline parameters of diol chain extended PUs obtained by X-ray at $2\theta = 19.57$ Å

Samples	$\langle N \rangle$	g in %	α^*	P	D_s in Å	α
CO + TDI + 1,4-diol	2.56 ± 0.20	1.50 ± 0.11	0.02	1.68	11.29	1.13
CO + TDI + 1,6-diol	3.11 ± 0.24	1.00 ± 0.08	0.02	2.19	13.83	1.08
CO + MDI + 1,4-diol	2.64 ± 0.23	1.00 ± 0.09	0.02	1.63	11.61	0.99
CO + MDI + 1,6-diol	2.89 ± 0.19	1.50 ± 0.10	0.03	1.87	13.13	0.98
CO + HMDI + 1,4-diol	2.58 ± 0.15	0.50 ± 0.03	0.01	1.47	11.79	0.90
CO + HMDI + 1,6-diol	2.87 ± 0.18	1.00 ± 0.06	0.02	1.79	12.86	0.92

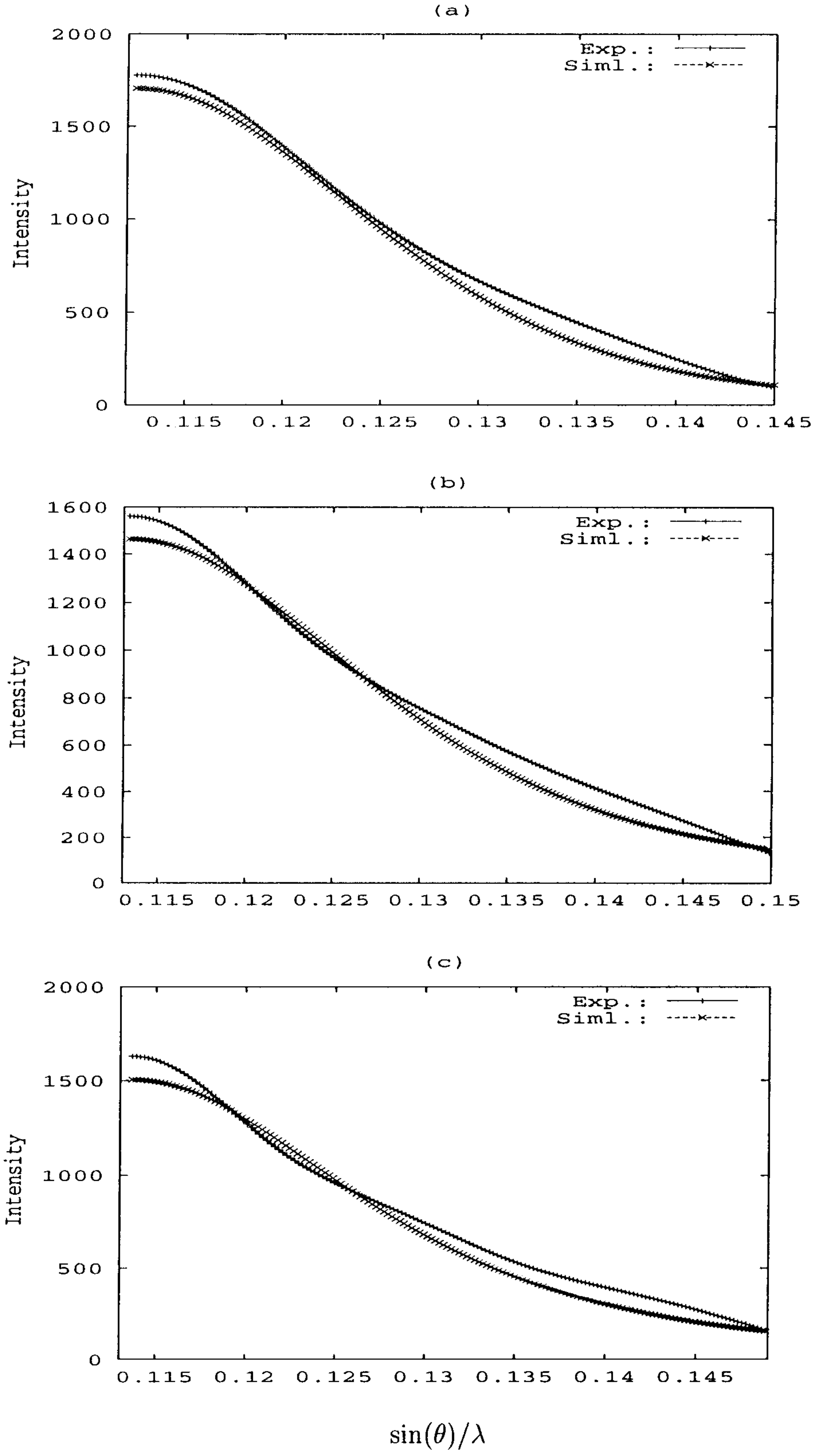


Figure 5 Simulated X-ray patterns for chain extended PUs: (a) CO + TDI + BD (b) CO + TDI + HD (c) CO + MDI + BD (d) CO + MDI + HD (e) CO + HMDI + BD (f) CO + HMDI + HD. (*Continued.*)

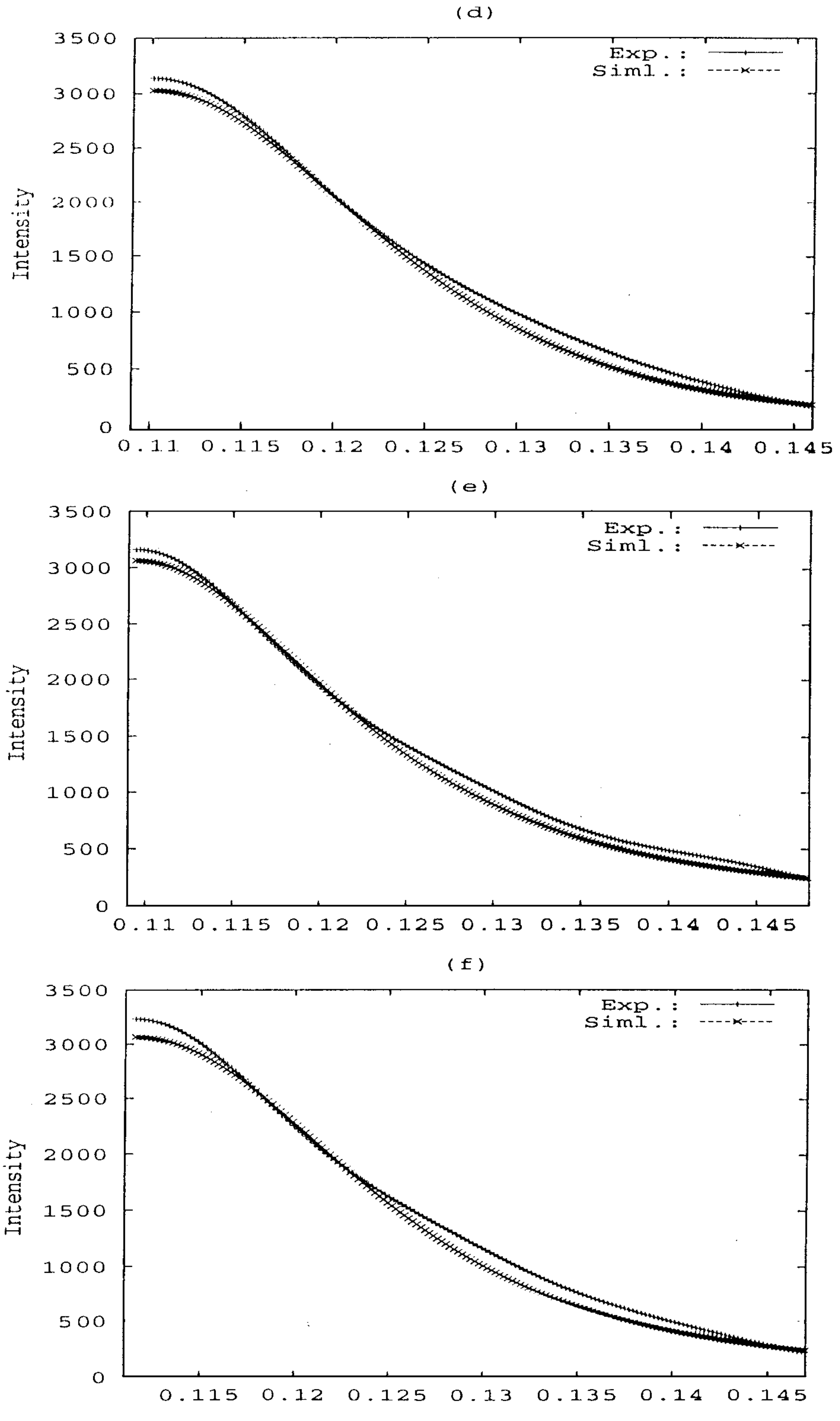
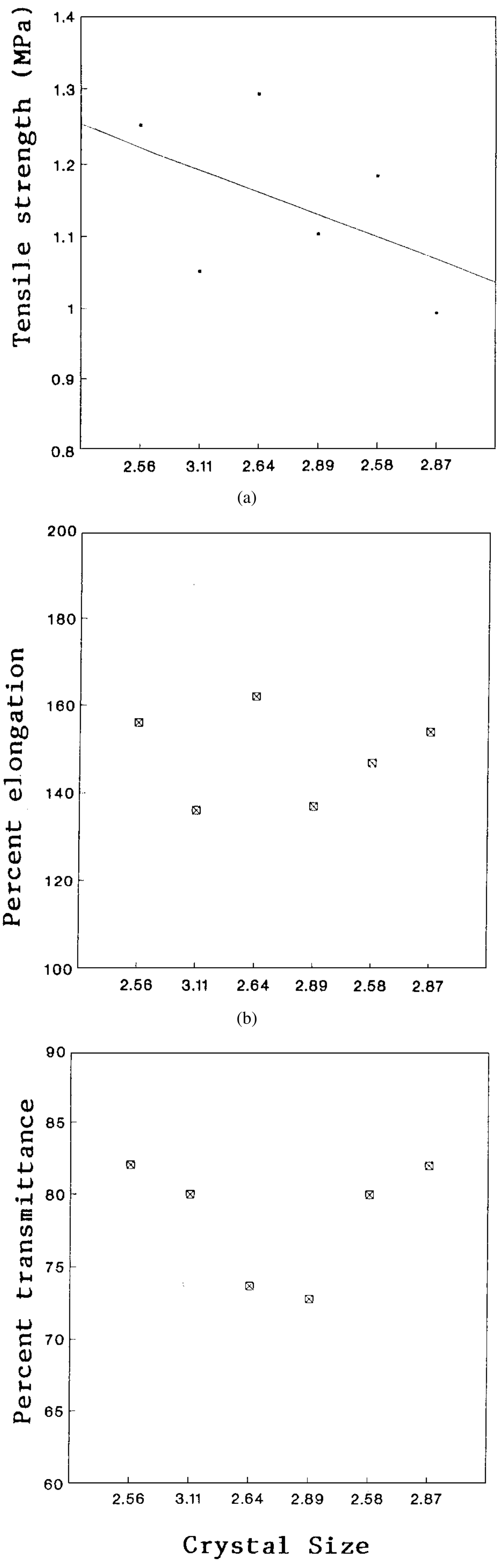


Figure 5 (*Continued*).

The phase stabilisation occurs in all diol chain extended PUs. This conclusion has been made on the basis of minimum value of α^* (0.01–0.03) calculated in these samples. As mentioned earlier in the text, Hosmann introduced the parameter to characterise various types of materials. Our observed values are in agreement with the ones reported for polymers. Using an exponential distribution function we have determined the surface weighted (D_s) crystal size (Table IV). The order of magnitude of the surface weighted crystal size clearly indicates the extent of crystallinity present in the materials. Higher values of crystal size, lattice strain, smallest cyrstal unit (P) and surface weighted (D_s) crystal size were observed for hexane diol chain extended PUs than butane-diol chain extended PUs. This increase in microstructural parameters are due to organisational change in 1.6-diol based PU polymer network. For the sake of completeness we have reproduced in Fig. 5a–e the simulated and experimental profiles of all chain extended PU systems. In fact the goodness of the fit was less than 2% in all the PU samples which justifies the model used here.



(a)

(b)

(c)

Figure 6 Variation of (a) tensile strength with crystal size (b) percentage elongation with crystal size (c) percentage transmittance with crystal size.

The physical properties like tensile strength, surface hardness, etc., of PUs show a marked improvement [25] when crystal size ($\langle N\rangle$) and D_{surf} values are low. The variation of tensile strength, percentage elongation at break and percentage transmittance with crystal size are given in Fig. 6 a-c. This is supported [26] by the crystal imperfection data (Table IV) obtained by X-ray profile analysis, which shows for a distance of 11 Å units along a direction normal to the Bragg plane at 19.57 Å (2θ) and there is a lattice distortion of 2%. This is true for both the PU series investigated here.

From the Table III and IV and also Fig. VI, we find that there is a significant change in crystal size value for blends with changes in the diols and hence resulting in non-linear variation of transmittance, diffusion and haze with the crystal size prameters. However, there is a linear variation of tensile strength with crystal size which is in agreement with the earlier studies [27]. Relatively the crystal size of MDI based PU 1,4-diol samples is lower compared to other samples.

4. Conclusions

Butane-1, 4-diol and hexane-1, 6-diol chain extended PUs were prepared using castor oil and different diisocyanates. Flexible, tough and transparent films of diol chain extended PUs are obtained for both the series. The total transmittance of all chain extended PUs are greater than 72. Higher mechanical and thermal properties were observed for MDI with 1,4-butane diol chain extended PUs. Heat aging studies reveal that, chain extended PUs shows outstanding performance at low temperature. All diol chain extended PUs behave as semicrystalline because chain extended PUs are made up of both soft and hard segments as confirmed from WAXS studies. We have quantified the changes observed from WAXS studies in chain extended PUs in terms of crystal imperfection parameters like crystal size ($\langle N\rangle$) and lattice strain (g in %). Eventhrough we have quantified the changes in these samples using X-ray profile analysis, we could only get an averaged picture of the relations between the physical properties of the samples with the crystalline structure wherein, a crystal size value may enhance most of properties like tensile strength, transmittance, haze and percentage elongation.

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