Studies on Physico-Mechanical and Optical Properties, and WAXS of Castor Oil Based Polyurethane/Polyacrylates Interpenetrating Polymer Networks

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ABSTRACT: Interpenetrating polymer networks (IPNs) of polyurethane (PU)/polyacrylates have been synthesized by sequential polymerization of castor oil, methylene diisocyanate (MDI), and acrylate monomers such as methyl acrylate (MA), methyl methacrylate (MMA), and ethyl acrylate (EA); with benzoyl peroxide (BPO) and ethylene glycol dimethyl acrylate (EGDM) as an initiator and crosslinker, respectively. The physico-mechanical properties, such as density, surface hardness, tensile strength, percentage elongation at break, and tear strength; and the optical properties, like total transmittance and haze, of PU/polyacrylate IPNs have been reported. Microcrystalline parameters of IPNs have been computed by using wide angle X-ray scattering (WAXS) recordings. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 764–773, 2005

Key words: polyurethane; polyacrylates; interpenetrating polymer networks; mechanical properties; microcrystalline parameters

INTRODUCTION

Interpenetrating polymer networks (IPNs) exhibit a variety of interesting properties and have been the subject of recent reviews.[1–6] IPNs typically consist of flexible elastomer and one or more rigid, high modulus component. Interpenetration plays a significant role in enhancing the intermixing of the polymer components through a physical interlocking. This exhibits further phase separation when the polymerization proceeds after the gel point is reached.[7] Improvement in polymer properties may be achieved by the formation of heterogeneous systems in which one polymer exists above its glass transition temperature (T_g), whereas the toughness exists below its T_g at room temperature by varying the relative amounts of the other polymer in the IPN.[8–14] By this procedure, tailor-made properties of IPNs can be created. But these are dependent mainly upon the material that forms the continuous phase. Thus, the product may range from a reinforced rubber to a high impact plastic.

PU is a versatile polymer with a unique chemistry and excellent mechanical and optical properties, but lacks in low temperature stability, whereas acrylates have excellent (1) solvent and oil resistance, (2) low temperature properties, and (3) good optical and adhesive nature. Also, PU and polyacrylates are polar polymers. Hence, IPNs of these two polymers are likely to produce a material having excellent dimensional, optical, and thermal stability, with oil and solvent resistant properties. Recently we have published some research articles on castor oil based PU IPNs.[15–17] In the present research article, one of the most naturally occurring vegetable oils (castor oil) is used for the synthesis of novel IPNs with different polyacrylates. From a thorough literature survey, it is evident that the structure-property relationship of PU/polyacrylates has been less studied. This research article reports the effect of the nature of acrylates on physico-mechanical properties, optical properties, structure-property relationship, and surface morphology of PU/polyacrylates.

EXPERIMENTAL

Materials

Castor oil was obtained from the local market. Its characteristic properties, such as hydroxyl No. 160–168, acid value 2.45, and isocyanate equivalent value 330, were estimated according to the literature.[15] 4,4′-diphenyl methane diisocyanate (MDI) obtained from Fluka, Switzerland; and ethylene glycol dimethyl methacrylate (EGDM) and benzoyl peroxide obtained from Aldrich, USA, were used without further purification. The acrylate monomers like methyl acrylate

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TABLE I
Data on Feed Composition of Individual IPNs

Sample code	Vinyl monomer	Contents of pre-polyurethane (wt %)	Contents of vinyl monomer (wt %)
IPN1	MMA	80	20
IPN2	MMA	60	40
IPN3	MMA	50	50
IPN4	MMA	40	60
IPN5	MMA	20	80
IPN6	MA	80	20
IPN7	MA	60	40
IPN8	MA	50	50
IPN9	MA	40	60
IPN10	MA	20	80
IPN11	EA	80	20
IPN12	EA	60	40
IPN13	EA	50	50
IPN14	EA	40	60
IPN15	EA	20	80

(MA), methyl methacrylate (MMA), and ethyl acrylate (EA) obtained from Schuchardt M, Germany, were freed from stabilizer prior to use.

Synthesis of IPNs

A series of castor oil based PU and polyacrylates (PU/polyacrylate (wt/wt) -80/20, 60/40, 50/50, 40/60, and 20/80) IPNs were synthesized as per the procedure reported in the literature.[16,17] Three series of PU/polyacrylate (PU/PMA, PU/PMMA, and PU/PEA) IPNs were synthesized by the polycondensation (sequential) method. Castor oil was mixed with MDI (NCO/OH ratio 1.4) at room temperature with continuous stirring for 2 h to produce isocyanate terminated prepolyurethane. Then prepolyurethane in different proportions was charged into a 250 mL three necked round bottom flask. To this mixture, a calculated amount of acrylate monomer, 0.5% benzoyl peroxide (BPO), 1% EGDM, and 0.5% dibutyl tin dilaurate (DBTL) were added. The mixture was stirred at room temperature for 15 min to form a homogeneous solution. Then it was poured into a clean glass mold sprayed with the releasing agent. The reaction was kept for 12 h at room temperature to allow polymerization of the PU. The temperature was slowly raised to 80°C, to initiate acrylate polymerization, and kept for 4 h at 100°C. The golden yellow transparent PU/polyacrylate IPNs of each series thus formed were cooled slowly and removed from the mold. Similarly, different IPNs were synthesized by varying the composition of different monomers of acrylate and PU (Table I).

TECHNIQUES

The prepared IPNs were characterized for physical properties like density and surface hardness (Shore A) according to ASTM 792–86 and ASTM D785, respectively. Mechanical properties such as tensile properties and tear strength were measured using a 4302 model Hounsfield Universal testing machine (UTM) as per ASTM D368 and ASTM D1922, respectively. A minimum of six samples were tested at room temperature for each composition, and the average value was reported. The optical properties such as total transmittance, total diffuse, and haze were measured using a Suga test haze meter (model 206) as per ASTM D1003.

X-ray powder pattern recording and analysis

Microcrystalline parameters of the IPNs have been calculated using wide angle X-ray data. X-ray diffraction patterns of the IPNs were recorded using a STOE powder X-ray diffractometer with germanium monochromated Cu Kα (λ = 1.5406A°) radiation in the 2θ range 5–50° at intervals of 0.03° using a curved position sensitive detector (CPSD) in the transmission mode. The intensity was corrected for Lorentz-polarization factors and also for broadening using the Stokes method.[18]

We have computed crystal imperfection parameters like crystal size (N) and lattice distortion (g in %) by matching the simulated intensity profile with the experimental using Hosemann's one-dimensional linear paracrystalline model,[19] and the detailed procedure for the simulation of the X-ray profile has been given in our earlier references.[15,16,19] The following equations were employed for this purpose.

The scattered intensity is:

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

where

$$I_N(s) = 2\mathrm{Re}[(1 - I^{N+1})/(1 - I) \times \{I\nu/d(1 - I)^2\}\{I^N(N(1 - I) + 1) - 1\}]^{-1} \quad (2)$$

Where

$$v = 2ia^2s + d,\ I = I_1(s) = \exp(-a^2s^2 + ids),\ a^2 = \omega^2/2. \quad (3)$$

I_n^1 (s), the modified intensity for the probability peak centered at D is given by

$$I_N(s) = \frac{(2a_N)}{D(\pi)^{1/2}} \exp(iDs) \times [1 - a_N S\{2D(a_N S) + I(\pi)^{1/2} \exp(-a_N^2 S^2)\}] \quad (4)$$

where $a_N^2 = N\omega^2/2$; ω is the standard deviation of the nearest neighbor probability function associated with the distortion of the lattice and it is related to the strain

TABLE II
Effect of PU/Polyacrylate Composition on the Physico-Mechanical Properties of IPNs

Sample code	Density (g/cc) Exptl	Density (g/cc) Theo	Tensile strength (MPa) ± 2%	% elongation at break ± 2%	Tear strength (MPa) ± 2%	Surface hardness (Shore A) ± 2%
IPN1	1.090	1.094	4.48	64	7.04	82
IPN2	1.119	1.117	7.81	43	8.49	85
IPN3	1.142	1.129	9.28	38	10.41	89
IPN4	1.159	1.141	11.39	33	11.16	90
IPN5	1.170	1.806	13.56	30	14.35	94
IPN6	1.072	1.092	3.64	32	6.74	81
IPN7	1.118	1.114	3.86	29	7.76	83
IPN8	1.136	1.125	6.55	26	8.19	88
IPN9	1.160	1.136	7.32	24	8.87	90
IPN10	1.172	1.158	10.20	20	10.45	95
IPN11	1.099	1.088	3.10	80	6.07	80
IPN12	1.109	1.100	3.25	52	7.45	82
IPN13	1.133	1.115	6.22	45	8.27	84
IPN14	1.151	1.124	7.22	40	8.67	88
IPN15	1.158	1.142	8.92	37	9.49	91

by g = (ω/d); $D(a_N s)$ is the Dawson's integral or the error function with complex argument and can be computed; N 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 the real part of the expression; "s" is $\sin\theta/\lambda$; λ is the wavelength of X-rays used; s_o is the scattering vector; "a" is related to the standard deviation "ω" of the lattice distribution function; and D is the crystal size (= N d_{hkl}); $I'_N(s)$ is the modified intensity for the probability peak centered at D. SIMPLEX, a multidimensional algorithm, has been used to minimize the difference between the experimental and simulated profiles.[19]

RESULTS AND DISCUSSION

Physico-mechanical properties

The calculated physico-mechanical properties, such as density, tensile strength, percentage elongation at break, tear strength, and surface hardness values, are given in Table II. The densities of PU/polyacrylate IPNs are heavier than water because they are crosslinked. The density values of IPNs lie in the range 1.072–1.172 g/cc. The calculated densities were obtained by the volume additive principle, which states that $d = w_1d_1 + w_2d_2$, where d is the density of the IPN sample, w_1 and w_2 are the weight fraction of the constituents, and d_1 and d_2 are the corresponding densities, respectively. From Table II it is observed that the density of the IPNs lies between the corresponding homopolymers. As the proportion of the polyacrylate content increased in the IPN, the density value increased from 1.090 to 1.170, from 1.072 to 1.172, and from 1.099 to 1.158 g/cc for PU/PMMA, PU/PMA, and PU/PEA, correspondingly. This is due to increase in the high dense polyacrylate phase in IPNs. Disagreement of the actual and theoretical density is due to the interaction between the -NH group of PU and the carbonyl group of acrylate.[20–22] From Table II, it is also observed that there is a higher density value for PU/PMMA than for PU/PEA systems. This is due to the bulky side group present in PEA.

From Table II it is found that tensile strength and tear strength increases with increase in acrylate content for all three series of IPNs. This can be attributed to increase in the plastic phase (polyacrylate) in the flexible PU system and also due to formation of a hydrogen bond between PU and the polyacrylate polymer networks.[22] The PU/PEA system possesses low tensile strength compared to PU/PMMA and

TABLE III
Optical Properties of PU/Polyacrylate IPNs

Sample code	Total transmittance (%)	Total diffuse (%)	Percent parallel	Haze (%)
IPN1	72	38	31	34
IPN2	74	42	29	36
IPN3	69	28	15	23
IPN4	70	33	35	25
IPN5	87	38	48	24
IPN6	75	53	22	28
IPN7	78	56	22	31
IPN8	69	55	4	28
IPN9	84	76	8	39
IPN10	85	75	10	40
IPN11	80	23	56	19
IPN12	71	37	27	37
IPN13	68	39	17	25
IPN14	70	45	18	26
IPN15	75	58	15	30

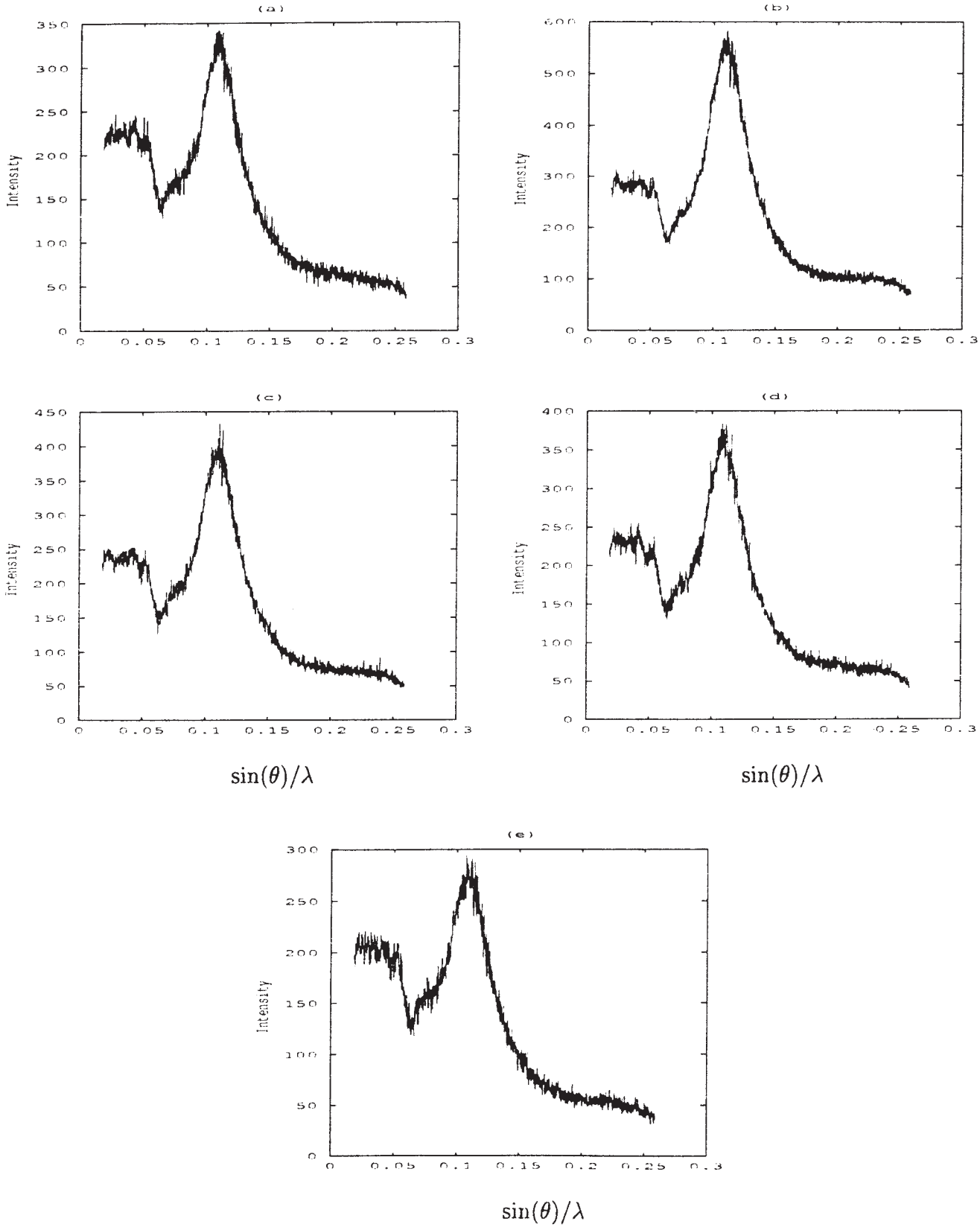

Figure 1 X-ray diffractograms for PU/PMMA IPNs.

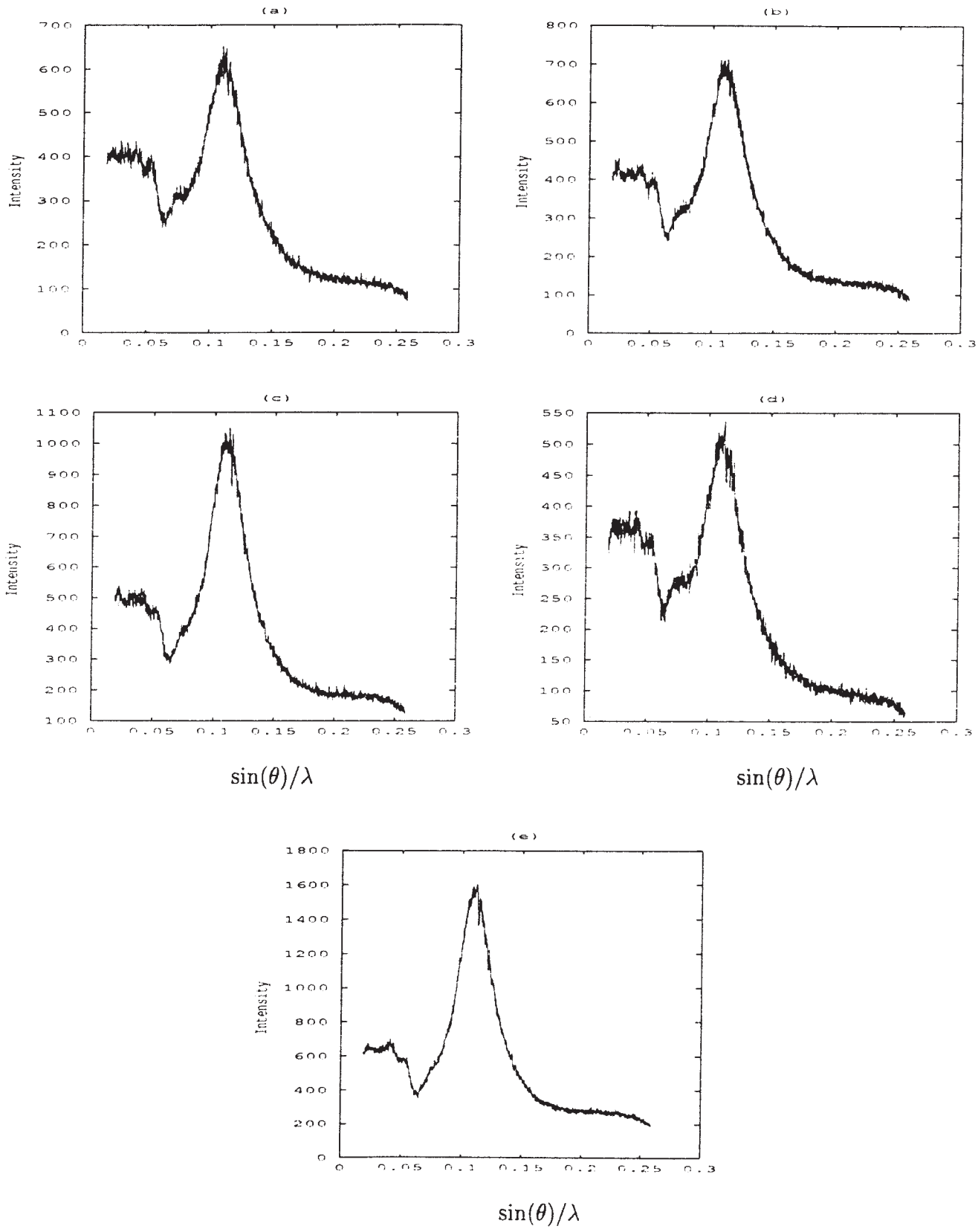

Figure 2 X-ray diffractograms for PU/PMA IPNs.

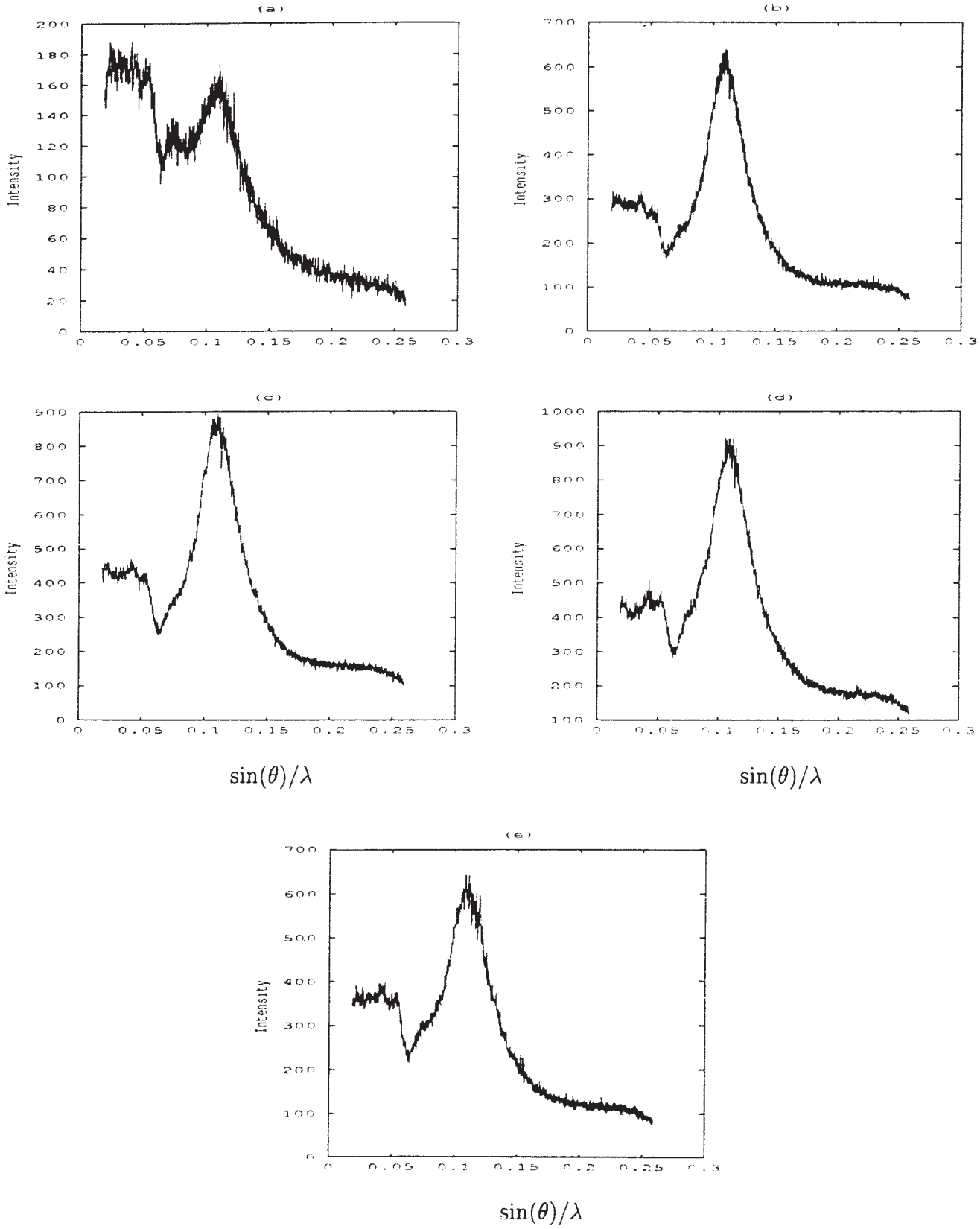

Figure 3 X-ray diffractograms for PU/PEA IPNs.

TABLE IV
Microstructural Parameters of PU/Polyacrylates IPNs

Sample code	N	g (%)	δ (%)	d_{hkl} (A^0)	α*	D (=N d_{hkl}) (A^0)
IPN1	11.80	5.3	4.96	4.56	0.23	53.81
IPN2	4.64	2.7	4.97	4.56	0.06	21.15
IPN3	6.74	1.1	4.40	4.56	0.03	30.73
IPN4	7.36	7.9	5.11	4.56	0.22	33.56
IPN5	4.42	5.1	3.22	4.56	0.11	20.15
IPN6	6.67	5.4	4.06	4.52	0.14	30.16
IPN7	4.45	5.3	1.93	4.52	0.11	20.12
IPN8	5.42	7.3	1.80	4.52	0.17	24.51
IPN9	5.34	4.9	2.73	4.52	0.12	24.15
IPN10	4.33	3.5	1.76	4.52	0.07	19.58
IPN11	6.64	3.3	4.95	4.57	0.08	30.34
IPN12	4.45	4.2	2.20	4.50	0.08	20.05
IPN13	5.28	5.5	3.13	4.50	0.13	23.79
IPN14	5.61	6.7	2.11	4.57	0.16	25.67
IPN15	5.47	7.5	2.39	4.54	0.18	24.84

PU/PMA IPNs because PEA has more soft segment than PMA and PMMA. Percentage elongation at break decreases with increase in acrylate content in all three series. This is due to the increase in the thermoplastic (acrylate) phase. Surface hardness values reflect the dimensional stability of the IPNs. Surface hardness values in all three series increase with increase in acrylate content. This value lies in the range 82–94, 81–95, and 80–91 Shore A for PU/PMMA, PU/PMA, and PU/PEA, respectively. This is due to the increase in the thermoplastic component in the soft PU system and also due to entanglement and hydrogen bond formation between PU and polyacrylate.

Optical properties

The effect of composition on percentage transmittance of IPNs was measured, and the results are summarized in Table III. From Table III, it was noticed that the percentage transmittance value decreases with increase in acrylate content from 20 to 50%. With a further increase in acrylic content from 50 to 80%, percent transmittance increases. That means 50/50 PU/polyacrylate shows a lower percentage transmittance compared to 20/80 and 80/20 PU/polyacrylate systems. This result reveals that (1) both homopolymers have high transmittance compared to their IPNs, and (2) phase separation or increase in domain size of the second phase in the (50/50) IPN matrix occurs. The percentage transmittance of PU based IPNs also depends upon the NCO/OH or soft/hard segment ratio. Haze values of IPNs lies in the range of 19–40%. But there was no systematic variation in haze values with acrylate composition, because of the complicated chemical structure and morphology of IPNs.

X-ray profile analysis

Wide angle X-ray scattering (WAXS) study of all three series of PU/polyacrylate IPNs have been carried out in the 2θ range 5–60°. X-ray diffractograms for all three series of IPNs are shown in Figures 1–3 for IPNs of PU with PMMA, PMA, and PEA, respectively. All the diffractograms show one intense broad peak in the 2θ range 15–33°. We have estimated both crystal size and lattice strain using a more general Hosemann's paracrystalline model,[19] which takes into account the presence of disorder of the second kind. In fact, broadening of reflections arises mainly due to two main factors. According to Warren,[23] broadening in any polymer sample arises due to (1) crystal size (N) and (2) lattice disorder (g in %) present in the material. Table IV lists the computed values of various microcrystalline parameters, such as crystal size (N), lattice strain (g), spacing of the (hkl) planes (d_{hkl}), enthalpy (α*), and surface weighted crystal size (D_s = N d_{hkl}).

For the sake of completeness, we have reproduced in Figures 4 (a)-(c), the simulated and experimental profiles for selected PU/polyacrylate IPNs. In fact, the goodness of the fit was less than 2% in all the samples. From Table IV, it was observed that the values of N, g, and D_s decrease drastically with increase in acrylate content above 20%. These changes do not have a linear relation with the concentration of acrylate, since the process of formation of the polymer network in the IPN becomes more complex in nature. A graphical representation for the variation of crystal size with acrylate composition of the IPNs given in Figure 5 shows that the values of N decrease with increase in concentration. The physico-mechanical properties, like tensile strength and tear strength, show a marked improvement when N, g, and D_{surf} values are minimum. The variation of crystalline size with tensile

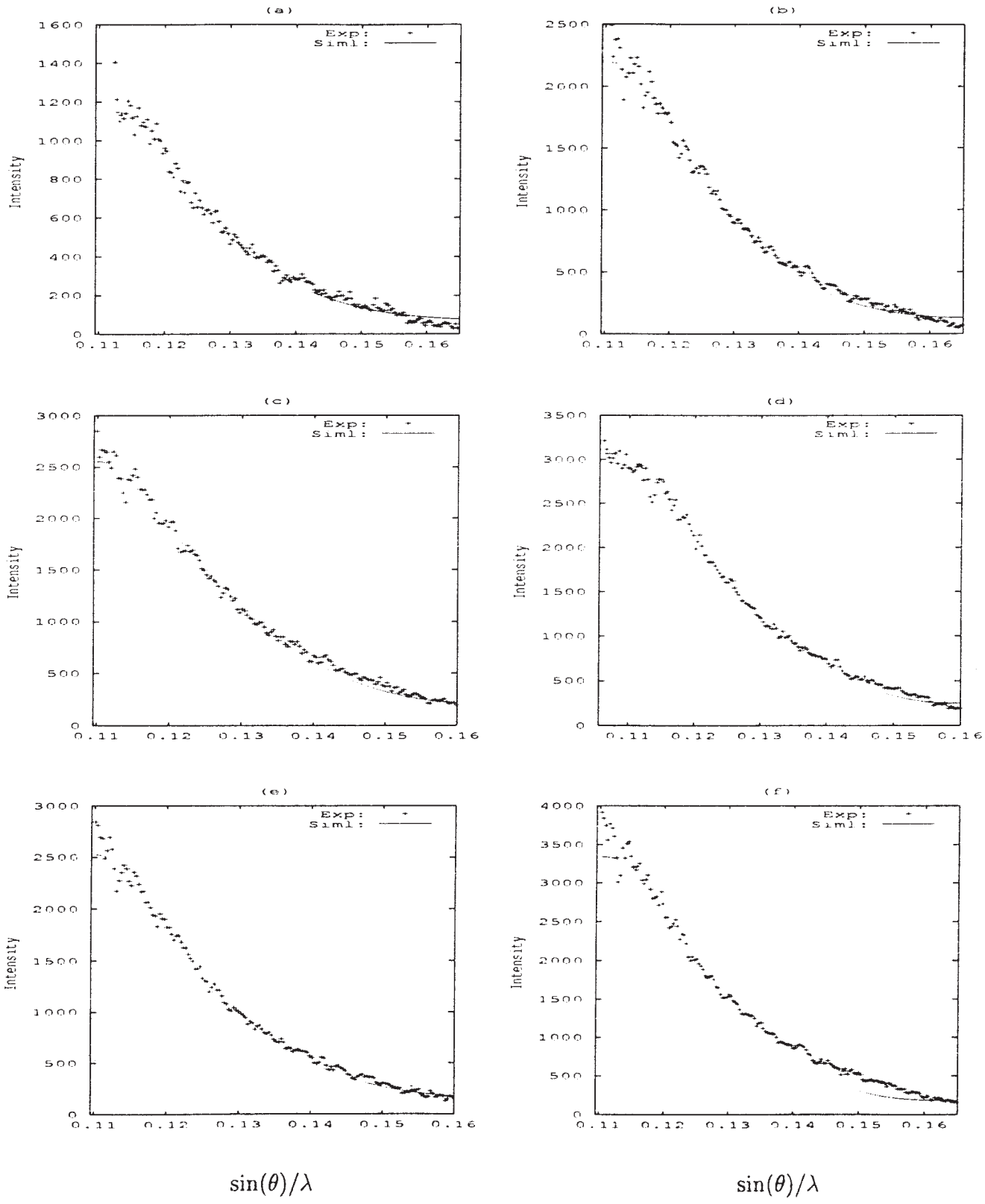

Figure 4 Experimental and simulated intensity profiles of (a) PU/PEA (80/20), (b) PU/PEA (60/40), (c) PU/PMA (80/20), (d) PU/PMA (60/40), (e) PU/PMMA (60/40), and (f) PU/PMMA (50/50).

strength and transmittance are shown in Figure 6. The order of magnitude of the surface weighted (D_{surf}) crystal size clearly indicates the extent of crystallinity present in the surface. From these parameters we can also estimate the minimum enthalpy that defines the equilibrium state of microparacrystals in PU/polyacrylate IPNs at different composition using relation[24]

$$\alpha^* = N_g^{1/2} \quad (5)$$

This enthalpy (α^*) value implies physically that the growth of paracrystals in a particular material is appreciably controlled by the level g in the net plane structure. The estimated value of enthalpy (α^*) is also given in Table IV, and this value lies between 0.03–0.23 for all three series of IPNs, which is in broad agreement with the values obtained for other types of polymers. It is also noticed that the incorporation of acrylate into PU reduces the α^* value, but there is no systematic variation in the α^* value.

CONCLUSIONS

The physico-mechanical properties, like tensile strength, tear strength, and surface hardness, of PU/polyacrylate IPNs increases with increase in acrylate content. This is due to increase in the plastic phase (acrylate phase) and hydrogen bond formation between the -COONH group of PU and the carbonyl group of acrylate. The increase in the order of mechanical properties with acrylate content is PU/PMMA>PU/PMA>PU/PEA. Variation in percentage transmittance is due to the presence of crystal lattice disorder. All PU/polyacrylate IPNs behave as semicrystalline polymers because IPNs are made up of both soft and hard segments as confirmed from the WAXS studies. The phase stabilization occurs for all compositions of IPNs. This conclusion has been arrived at on the basis of the minimum value of α^*. It is also observed that in these systems the crystal size decreases with increase in the mechanical property, which is due to the complex nature of the rearrangement of the polymer network in the presence of acrylates.

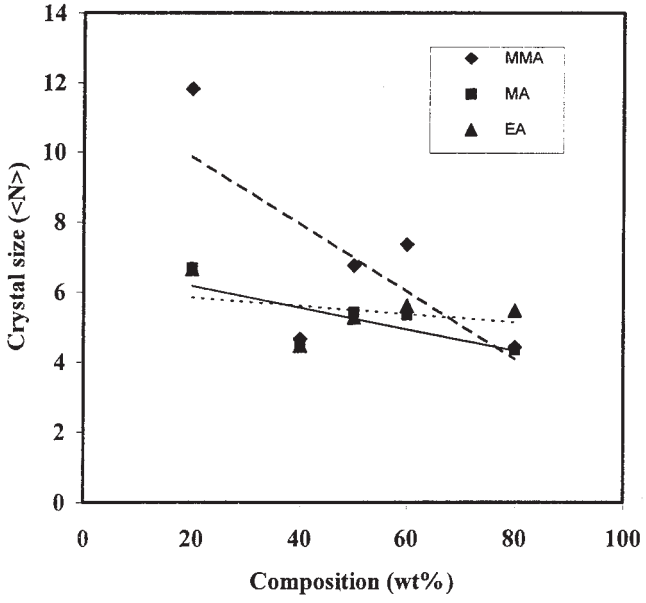

Figure 5 Effect of composition of acrylate on crystal size.

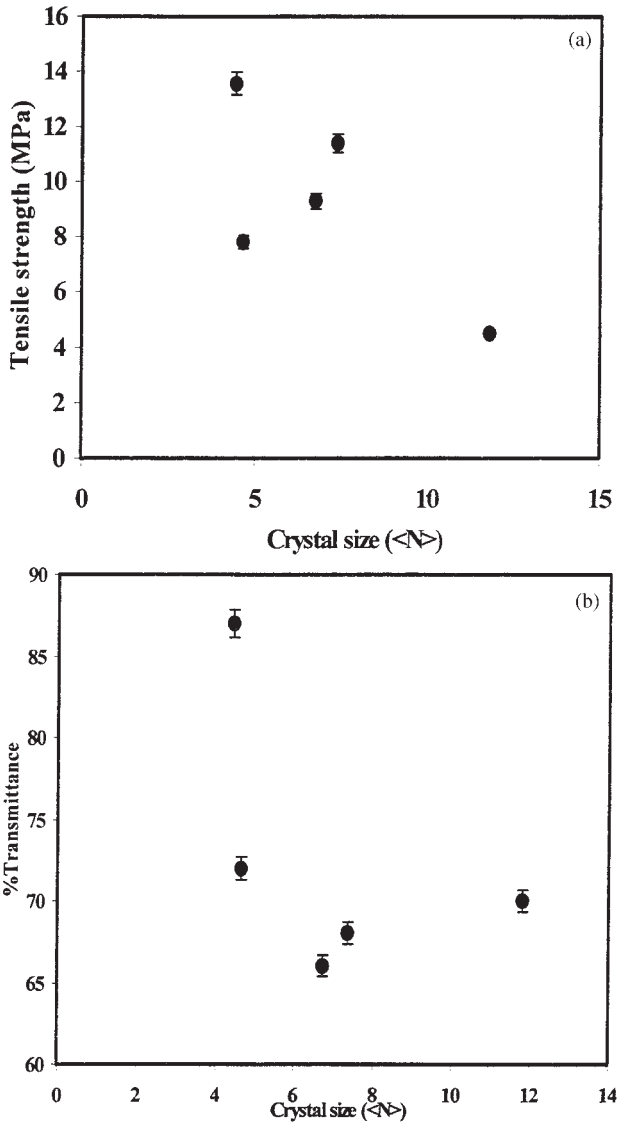

Figure 6 Variation of crystal size with (a) tensile strength and (b) percentage transmittance.

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