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Effects of chemical composition and structure of unsaturated polyester resins on the miscibility, cured sample morphology and mechanical properties for styrene/unsaturated polyester/low-profile additive ternary systems.
1: Miscibility and cured sample morphology

Yan-Jyi Huang* and Wen-Chinq Jiang
Department of Chemical Engineering, National Taiwan University of Science and Technology†, Taipei, Taiwan 107, ROC

Effects of chemical composition and structure of unsaturated polyester (UP) resins on the miscibility of styrene (ST)/UP/low-profile additive (LPA) ternary systems containing thermoplastic polyurethane (PU), poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) as LPAs, at room temperature and cured sample morphology were investigated. Three series of UP resins were synthesized, which included maleic anhydride (MA)–neopentyl glycol (NPG)–diethylene glycol (DEG) types with varied molar ratio of NPG and DEG; MA–propylene glycol (PG) types with and without modification by a saturated dibasic aromatic anhydride or acid, such as phthalic anhydride (PA) and isophthalic acid (IPA); and MA–PA–PG types modified by a second glycol, such as DEG, 2-methyl-1,3-propanediol (MPDiol), and NPG, to partially replace PG. In addition, based on the MA–PA–PG–DEG type of UP, other UPs with varied degree of unsaturation for C=C bonds and molecular weight, respectively, were synthesized. The dipole moments, μ, for UP and LPA have been calculated on the basis of group contribution methods. Finally, the miscibility data of ST/UP/LPA ternary systems and the characteristics of cured sample morphology have been explained by the calculated polarity difference per unit volume between UP and LPA. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: unsaturated polyester resins; low-profile additives; miscibility)

INTRODUCTION

Adding specific thermoplastic polymers as low-profile additives (LPA) in the unsaturated polyester resins (UP) during the formulation of SMC (sheet moulding compound) and BMC (bulk moulding compound) is a well-known industrial technology. Such thermoset polymer blends, essentially made from UP, styrene monomer and LPA, would lead to a reduction or even elimination of the polymerization shrinkage during the cure process. A Class A smooth surface for the moulded part could then result[1–5].

Lecointe *et al.*[6] and Suspene *et al.*[7] studied the miscibility of styrene (ST)/UP binary systems and ST/UP/LPA ternary systems, respectively, and constructed their cloud point curves (CPC). The former researchers found that for the maleic anhydride (MA)–diethylene glycol (DEG)–neopentyl glycol (NPG) type of UP, the miscibility of UP with styrene increased with increasing NPG content, while the latter investigators reported that for the MA–propylene glycol (PG) type of UP, UP prepolymers with higher polydispersity, higher acid number and lower hydroxyl number would lead to better miscibility for ST/UP binary system and ST/UP/poly(vinyl acetate) (PVAc) ternary system. The cured sample morphologies were demonstrated to be correlated to the ternary system miscibility[7].

Huang and Su[8,9] also pointed out that the static ternary phase characteristics at 25°C for ST/UP/LPA could be employed as a rough guide for accounting for the observed morphology during the reaction at 110°C, where a flake-like or globule microstructure in either the continuous or the dispersed phase would arise. In general, after a phase equilibrium at 25°C for ST/UP/LPA systems, the upper layer (i.e. dispersed phase) was dominated by ST and LPA, while the bottom layer (i.e. continuous phase) was dominated by UP and ST. The molar ratio of styrene to polyester C=C bonds in the upper layer would be greater than that in the original mixture, while the trend would be reversed in the bottom layer. Either high molar ratio of styrene to polyester C=C bonds or high percent of LPA could exert profound segregating effects on microgel particles and would lead to a globule microstructure for the cured sample. In the case of inadequate overall segregating effects on microgel particles, a flake-like microstructure or a coexistence of flake-like and globule microstructures would result. Since the physical and mechanical properties of cured samples would be intimately related to the cured sample morphology, the miscibility studies on ST/UP/LPA systems would be indispensable to compound design in SMC and BMC industries.

The goal of this work is to investigate the effects of chemical composition and structure of UP resins on the miscibility and the cured sample morphology for ST/UP/LPA

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* To whom correspondence should be addressed
† Formerly National Taiwan Institute of Technology before July 31, 1997

ternary systems containing thermoplastic polyurethane (PU), poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) as LPAs. Three series of UP resins including 10 different UPs have been synthesized. Based on the calculated polarity difference per unit volume between UP and LPA, the effects of glycol ratios, saturated dibasic aromatic acid modification, second glycol modification, C=C unsaturation of UP, and molecular weight of UP on the ternary system miscibility at room temperature and cured sample morphology are discussed.

EXPERIMENTAL

Synthesis of UP

Three series of UP resins were synthesized in a five-neck 2 l glass vessel reactor by polycondensation reactions in bulk phase, where a 10% excess hydroxyl equivalents to acid equivalents, a stagewise isothermal temperature program from 70–90 to 210–220°C, and a stagewise nitrogen sparge rate ranging from 30 to 70 ml/min were employed. The reaction was terminated until the acid number was dropped under AN = 25–30, where the reaction time ranged from about 15 to 27 h[10].

The first series of UP was made from maleic anhydride (MA, Janssen Chimica), neopentyl glycol (NPG, Aldrich), and diethylene glycol (DEG, Janssen Chimica) with varied molar ratio of NPG and DEG. Two such UP resins, designated as MA–NPG–DEG65 (or MND65) and MA–NPG–DEG25 (or MND25), containing a molar ratio of NPG to DEG at 45/65 and 85/25, respectively, were made by a two-stage process. For the first stage, MA was reacted with the less-reactive NPG, as compared with DEG, until a diol conversion of 90% was reached at the temperature stage of 195°C. The reactants were then cooled down to 160°C, DEG was added for the second stage of reaction, and the final temperature stage was maintained at 220°C.

The second series of UP was made from MA and 1,2-propylene glycol (PG, Jenssen Chimica) with and without modification by a saturated dibasic aromatic anhydride or acid, such as phthalic anhydride (PA, Janssen Chimica) and isophthalic acid (IPA, Acros). Three UP resins, designated

as MA–PG, MA–PA–PG, and MA–IPA–PG were synthesized by a two-stage method[11], a one-stage method[12], and a full two-stage method[11,13], respectively, where the molar ratio of PA or IPA to MA was chosen to be 1:2. For the two-stage method, one-third of MA was first reacted with all of the PG at 88°C in order to allow PG to form oligomers and thus reduce glycol loss during the synthesis (boiling point of PG ≈ 187°C). The reaction temperature was then raised to 149°C and the remainder of the MA was added. Thereafter, the reaction temperatures were maintained in an increasing stagewise isothermal manner between 160 and 210°C. As to the one-stage method, all the reactants were added at the start of the reaction. By contrast, for the full two-stage method, the less-reactive saturated acid (i.e. IPA), as compared with the unsaturated MA, was first reacted with PG until the conversion of acid was reached above 90%. The reactants were then cooled down to 150°C, MA was added for the second stage of reaction, and the final stage of temperature was maintained at 215°C.

The third series of UP was made from MA, PA, PG, and a second diol, such as DEG, 2-methyl-1,3-propanediol (MPDiol, Aldrich) and NPG. Three UP resins, designated as MA–PA–PG–DEG(1), MA–PA–PG–MPDiol, and MA–PA–PG–NPG, were synthesized by the one-stage method, where the molar ratio of PA to MA and that of PG to another diol were fixed at 1:2 and 45:65, respectively. In addition, based on the MA–PA–PG–DEG type of UP, two other UPs, one with a lower degree of unsaturation for C=C bonds, designated as MA–PA–PG–DEG(2), and the other with a higher molecular weight, designated as MA–PA–PG–DEG(3), were synthesized, where the molar ratio of PA to MA was increased to 1:1 for the former, while a 5% excess hydroxyl equivalents to acid equivalents during the synthesis was employed for the latter.

The raw materials used, the reaction temperature histories in the synthesis of UP, and the properties of UP synthesized are summarized in *Table 1*, *Table 2* and *Table 3*, respectively.

End-group titration

During the synthesis of UP resins, the acid numbers (AN)

Table 1 UP codes and raw materials used in the synthesis

UP code	Feeds	Molar ratio (total wt. in g)	Catalyst (mol)	Inhibitor (ppm)	Stabilizer (mol)	Azeotropic agent (wt.%)
Series I						
MA–NPG–DEG65 (MND65)	MA,NPG,DEG	1:0.45:0.65 (1049.4)	1 N HCl (0.000599)	HQ[a] (200)	(C$_6$H$_5$O)$_3$P[b] (0.000599)	—
MA–NPG–DEG25 (MND25)	MA,NPG,DEG	1:0.85:0.25 (1065.5)	1 N HCl (0.000645)	HQ (200)	(C$_6$H$_5$O)$_3$P (0.000645)	—
Series II						
MA–PG	MA,PG	1:1.10 (908.8)	—	HQ (300)	—	p-Xylene[c] (3)
MA–PA–PG	MA,PA,PG	0.67:0.33:1.1 (992.2)	—	HQ (300)	—	p-Xylene (3)
MA–IPA–PG	MA,IPA,PG	0.67:0.33:1.1(1022.2)	(C$_4$H$_9$O)$_4$Ti (0.2 wt.%)	HQ (300)	—	p-Xylene (3)
Series III						
MA–PA–PG–DEG(1)	MA,PA,PG,DEG	0.67:0.33:0.45:0.65 (1089.7)	—	HQ (300)	—	—
MA–PA–PG–MPDiol	MA,PA,PG, MPDiol	0.67:0.33:0.45:0.65 (1037.7)	—	HQ (300)	—	—
MA–PA–PG–NPG	MA,PA,PG,NPG	0.67:0.33:0.45:0.65 (1083.3)	—	HQ (300)	—	—
MA–PA–PG–DEG(2)	MA,PA,PG,DEG	0.5:0.5:0.45:0.65 (1131.5)	—	HQ (300)	—	—
MA–PA–PG–DEG(3)	MA,PA,PG,DEG	0.67:0.33:0.425:0.625 (1067.0)	—	HQ (300)	—	p-Xylene (3)

[a] Hydroquinone (HQ) added to avoid the homopolymerization of C=C in UP
[b] A stabilizer added to reduce color formation
[c] An azeotropic agent added to facilitate the removal of water

Table 2 Temperature histories and resulting properties in the synthsis of UP

UP code	Temp. history (°C) (duration time in min)	AN[a]	HN[a]	Molar ratio of UP comp.	Odelt rxn (%)	Isomerization (%)
Series I						
MA–NPG–DEG65 (MND65)	25–80(50)–160(60)–175(60)–195(90)– 160(60)–200(120)–220(270)	27.8	72.0	1:0.44:0.68	5.7	96
MA–NPG–DEG25 (MND25)	25–80(50)–160(60)–175(60)–195(180)– 160(60)–200(120)–220(180)	27.0	68.8	1:0.77:0.27	≈ 0	96
Series II						
MA–PG	25–88(250)–149(4)–160(60)–180(60)– 205(240)–210(510)	28.6	31.0	1:1.03	$< 6^{b}$	97
MA–PA–PG	25–80(35)–160(120)–180(120)–205(240)– 210(240)–215(305)	28.3	28.3	0.63:0.37:1.02	$< 6^{b}$	97
MA–IPA–PG	25–120(30)–150(300)–176(360)–181(210)– 150(60)–180(60)–210(240)–215(210)	26.4	28.8	0.65:0.35:1.06	$< 6^{b}$	96
Series III						
MA–PA–PG–DEG(1)	25–80(35)–140(120)–160(120)–180(120)– 200(120)–220(580)	25.4	58.8	0.65:0.35:0.43:0.63	2.8	93
MA–PA–PG–MPDiol	30–70(180)–100(120)–110(120)–120(120)– 140(120)–160(120)–180(120)–200(120)– 220(460)	25.8	69.6	0.68:0.32:0.42:0.58	≈ 0	95
MA–PA–PG–NPG	30–80(35)–140(120)–160(120)–180(120)– 200(120)–220(470)	26.0	74.6	0.67:0.33:0.39:0.61	≈ 0	96
MA–PA–PG–DEG(2)	30–80(35)–140(120)–160(120)–180(120)– 200(120)–220(640)	26.2	64.9	0.47:0.53:0.42:0.66	≈ 0	93
MA–PA–PG–DEG(3)	30–80(35)–140(120)–160(120)–180(120)– 200(120)–220(720)	25.3	26.5	0.64:0.36:0.41:0.71	$< 5^{b}$	96

[a] AN and HN denote acid number and hydroxyl number, respectively
[b] The peak area $\delta = 2.8–3.1$ ppm could not be determined accurately due to the baseline drift

of the samples were measured according to the ASTM D2849. At the end of reaction, the hydroxyl number (HN) of the UP resin was also measured[14]. The number-average molecular weight of the UP resin was then calculated by $\bar{M}_{n} = 2 \times 56\,100/(AN + HN)$.

^{1}H n.m.r.

UP samples were dissolved in CDCl$_3$ solvent first, and were then identified by a 400 MHz ^{1}H n.m.r. for their molar compositions, degree of isomerization from maleate ($\delta = 6.2–6.3$ ppm) to fumarate ($\delta = 6.9–7.1$ ppm) during the synthesis of UP, and the percentage of Ordelt reaction due to the C=C double-bond saturation by glycols ($\delta = 2.8–3.1$ ppm) in the synthesis.

Gel permeation chromatography (g.p.c.)

The molecular weights and molecular weight distribution of UP resins were measured by a gel permeation chromatograph (g.p.c., Polymer Laboratories, with three ultrastyragel columns and mixed-D pore size capable of separating a molecular weight range of 200–400 000 g/mol) equipped with a PL-EMD950 type of evaporative mass detector. Standard samples of narrow-distribution polystyrene were employed in constructing the g.p.c. calibration curves.

Differential scanning calorimetry (d.s.c.)

The glass transition temperatures (T_{g}) of the UP resins were obtained by a differential scanning calorimeter (Du Pont 9000, with a 910 pressurized d.s.c. cell) at atmospheric pressure. Samples were scanned from -60 to $40°C$ at a heating rate of 7.5°C/min.

Preparation of ST/UP/LPA solutions

Three LPAs including thermoplastic polyurethane (PU,

Table 3 Molecular weights, degrees of C=C unsaturation, and glass transition temperatures (T_g) for UP resins

UP code	$\bar{M}_{n}$ (GPC)	$\bar{M}_{w}/\bar{M}_{n}$ (GPC)	$\bar{M}_{n}^{a}$ (abs)	No. of C=C bonds per UP molecule	T_{g} (°C)
Series I					
MA–NPG–DEG65 (MND65)	1749	1.65	1124	5.68	−25.6
MA–NPG–DEG25 (MND25)	1470	2.43	1174	6.22	−19.0
Series II					
MA–PG	2167	2.77	1883	11.89	7.6
MA–PA–PG	1836	2.02	1982	6.88	10.6
MA–IPA–PG	1997	2.61	2033	7.33	11.9
Series III					
MA–PA–PG–DEG(1)	1847	2.39	1333	4.21	−11.8
MA–PA–PG–MPDiol	1884	2.88	1176	4.12	−2.2
MA–PA–PG–NPG	1785	1.92	1115	3.61	8.1
MA–PA–PG–DEG(2)	1814	2.04	1232	2.66	−6.6
MA–PA–PG–DEG(3)	2290	2.56	2166	6.87	−5.6

[a] Calculated by end-group titration methods

LP2030, Olin), poly(vinyl acetate) (PVAc, LP40A, Union Carbide) and poly(methyl methacrylate) (PMMA) were employed, where the number average molecular weights of which were measured to be 6500, 42 000, and 34 000, respectively, by vapor pressure osmometry (VPO). For the sample solution, 10% by weight of LPA was added, and the molar ratio of styrene to polyester C=C bonds was adjusted to be MR = 2/1. The reaction was initiated by 1% by weight of ter-butyl perbenzoate (TBPB). All the materials were employed as received without further purification.

Phase characteristics

To study the compatibility of three different types of LPA (i.e. PU, PVAc and PMMA) with the UP solution in styrene prior to reaction (i.e. the uncured UP resin), sample solutions with a molar ratio of styrene to polyester C=C bonds of MR = 2/1 and an LPA content of 10% by weight were prepared in 60 ml separatory glass cylinders, which were then placed in a constant-temperature water bath at 30°C. The phase separation time was recorded and the mixture of each layer was separated and weighed.

Morphology

The sample solutions were degassed in a vacuum oven at 50°C for 5 min, which were then slowly poured into stainless steel rectangular moulds with inner trough dimensions of $17 \times 1.7 \times 0.42$ cm and sealed with gaskets. The sample solutions were cured at 110°C in a thermostated silicon oil bath for 1 h, followed by a post-cure at 150°C for another 1 h.

In the morphology study, the cured sample in the mould was removed and broken into several pieces. After the usual sample pretreatment[9], a Hitachi S-550 scanning electron microscope (SEM) with accelerating voltage of 20 kV was used to observe the fractured surface of each sample at magnification of 1000× to 5000×.

RESULTS AND DISCUSSION

Synthesis of UP Resins

During the synthesis of the first series of UP (i.e. MA–NPG–DEG type), such primary (1°) glycols as NPG and DEG were intrinsically unfavourable for the elevation of degree of C=C double-bond isomerization from maleate to fumarate, while the isomerization reaction would be more favourable by using a glycol with steric factor caused by bulky substituents near the carbon-bearing –OH, short-chain nature, and close to the structure of a secondary (2°) glycol[15]. Since the reactivity of maleate is much lower than fumarate in the subsequent crosslinking copolymerization of UP and styrene, the degree of isomerization for UP resins should somehow be over 90–95% in order to prevent an inadequate crosslinked density for the polyester network after the cure.

For the first series of UP resins, three approaches were adopted simultaneously to promote the degree of isomerization, namely, employing higher reaction temperature (220°C) at the final stage of synthesis, retaining the water by-product in the reactor for 5 h at the 200–220°C stage of reaction, and adding HCl as a catalyst for the isomerization. Based on the mechanism[16] of acid-catalysed isomerizaton of C=C double-bond shown in *Figure 1*, the first approach to the improvement of isomerization was attempted to provide adequate activation energy for the isomerization (too high temperature should be avoided to reduce colour
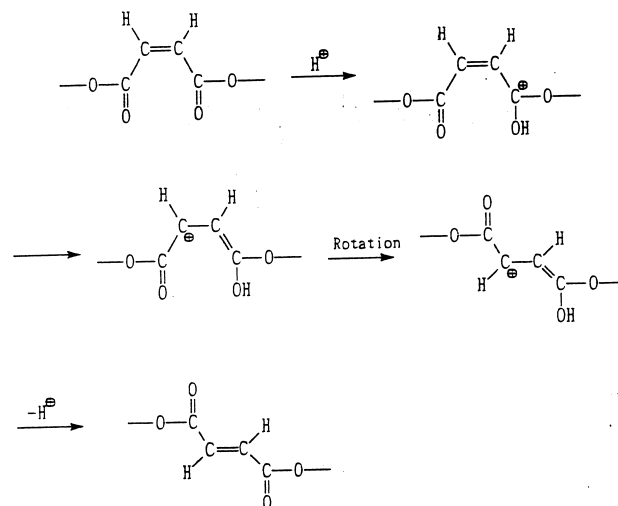
Figure 1 The mechanism of acid-catalysed isomerization of C=C double-bond from maleate to fumarate in the synthesis of UP resins

formation for the UP resin), while the second one was to enhance the C–C single-bond rotation by retarding the reversible polycondensation which could lead to viscosity build-up caused by the increase of UP molecular weight. In contrast, for the third series of UP resins, due to the partial substitution of primary glycols, such as DEG, MPDiol and NPG, for the secondary glycol, PG, the enhancement of degree of isomerization was achieved solely by the first two approaches mentioned earlier (see *Tables 1* and *2*).

In the synthesis of the second series of UP resins, where a higher molecular weight of UP was produced when compared with that of the first series as shown in *Table 3* ($\bar{M}_n$(abs.) = 1850–2050 *versus* 1100–1200), the viscosity of reacting systems at the later stage of reaction would be so high that the addition of an azeotropic agent (*p*-xylene in this work) was required to help remove the water from the reactor and, in turn, facilitate the proceeding of esterification. This was also true of the MA–PA–PG–DEG(3) type of UP system in the third series of syntheses, where a higher molecular weight of UP was produced (*Table 3*). Since the reactivity of IPA was lower than PA in the polycondensation with PG, a catalyst for esterification was also employed (*Table 1*) for the MA–IPA–PG type of UP system.

Characterization of UP resins

The molar composition of the 10 UP resins identified by n.m.r. (*Table 2*) was quite close to the corresponding feed composition (*Table 1*). During the synthesis of UP resins, the degree of isomerization from maleate to fumarate was achieved at a 93–97% level for all of the UP resins, while the Ordelt reaction[17] (the saturation of C=C bond by glycols), which would reduce the degree of C=C unsaturation for UP resins and could lead to a decrease of the crosslinked density for the styrene-crosslinked polyester network, was maintained under a level of 6%. For the first series of UP resin, the Ordelt reaction level was lower for MND25 than for MND65, which would be due to the more steric hindrance encountered by the C=C bonds for the former UP molecule caused by a higher composition of steric NPG (in comparison to DEG) therein. Similar finding was observed for the third series of UP resins, where the modification of UP by more steric molecules, such as MPDiol and NPG, could result in a significant reduction of the Ordelt reaction (see *Table 2*). It was also true of the

MA–PA–PG–DEG(2) type of UP, which contained a higher composition of steric PA (in comparison to MA) than that of MA-PA-PG-DEG(1).

Although the acid numbers (AN) for all of the UP resins fell in the range of 25–30, their hydroxyl numbers were found to be categorized as two groups. A higher HN (HN = 58–75) would generally result when a 10% excess hydroxyl equivalents to acid equivalents was employed in the synthesis of UP (i.e. all UP resins except MA–PA–PG–DEG(3)), while a lower HN (HN = 28–31) would arise when a 5% excess hydroxyl equivalents was used (i.e. MA–PA–PG–DEG(3)). However, when a single glycol instead of two glycols was employed in the synthesis of UP, a lower HN could result (i.e. the second series of UP) even if a 10% excess of hydroxyl equivalents was used.

The number-average molecular weight $\bar{M}_n$ for all the UP resins fell in the range of 1100–2300, while $\bar{M}_n$ was essentially kept constant for a given series of UP. $\bar{M}_n$ obtained by end-group titrations agreed well with that by the g.p.c. method for the second series of UP, while greater deviations were found between the two methods for the first and the third series of UP (except MA–PA–PG–DEG(3)). This discrepancy was also reported in the literature[6] for systems similar to the first series of UP. Yang and Pascault[18] have recently resorted to several side reactions of UP during the synthesis, such as the Ordelt reaction. The polydispersity index $\bar{M}_w/\bar{M}_n$ for all of the UP resins in this work ranged from 1.65 to 2.88.

For the first series of UP, the glass transition temperature was greater for MND25 than for MND65, which would be due to a higher composition of more rigid NPG (in comparison to DEG) in the former UP. For the second series of UP, modification of UP by PA or IPA with aromatic ring structures could lead to an elevation of T_g. It should be noted that modification of UP by IPA would be more effective in elevating T_g than that by PA since IPA, which contributes two neighboring carbon–carbon bonds from the benzene ring as a part of UP backbone, could enhance the chain stiffness of UP better than PA, which provides only one carbon–carbon bond from the benzene ring as a part of UP segment. For the third series of UP, the UP containing NPG residue possessed the highest T_g, followed by that containing MPDiol and DEG residues since the rigidity of glycols would follow the order of NPG > MPDiol > DEG. On the other hand, for the MA–PA–PG–DEG types of UP, a lowering of C=C unsaturation by introducing more PA in the UP molecule (i.e. MA–PA–PG–DEG(2)) could lead to a higher T_g when compared with MA–PA–PG–DEG(1), while an increase in the UP molecular weight (i.e. MA–PA–PG–DEG(3)) could result in an enhancement of T_g when compared with MA–PA–PG–DEG(1). As for the two UPs with similar $\bar{M}_n$,

MA–PA–PG and MA–PA–PG–DEG(3), the latter possessed a lower T_g due to the introduction of more flexible DEG (in comparison to PG) in the UP backbone.

Molecular polarity of UP resin and LPA

The molecular polarity of UP and LPA can be evaluated in terms of dipole moments, μ, which can be calculated by using the Debye's equation[19,20] as follows,

$$P_{LL} - R_{LL} = [(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]M/\rho \quad (1)$$

$$= 4/9 \, \pi N_A \mu^2/kT$$

$$\approx 20.6 \, \mu^2$$

or

$$\mu \approx [(P_{LL} - R_{LL})/20.6]^{1/2} \quad (2)$$

where P_{LL} is molar dielectric polarization, R is molar refraction, ϵ is dielectric constant, n is refractive index, M is molecular weight, ρ is density, N_A is the Avogadro's number, k is the Boltzman's constant, and T is the room temperature at 25°C in Kelvin scale (i.e. 298 K).

Since the molecular polarity of the 10 UP resins and the three LPAs should be compared on the same basis, the dipole moment per unit volume, $\bar{\mu}$, is calculated as below,

$$\bar{\mu} = (\mu^2/V)^{1/2} \approx [(P_{LL} - R_{LL})/(20.6V)]^{1/2} \quad (3)$$

where V is the molar volume.

As an calculation example of μ and $\bar{\mu}$ for the UP resin and LPA, consider the theoretical formula of MND65 type of UP:

$$HO-R-O-(-CO-CH=CH-CO-O-R-O-)_n-H$$
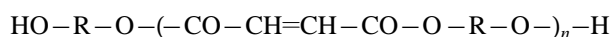
where $-R-$ is $-CH_2-CH_2-O-CH_2-CH_2-$ (DEG residue) or $-CH_2-C(CH_3)_2-CH_2-$ (NPG residue). Since the molar composition of MA, NPG, and DEG for MND65 is 1:0.44:0.68, and $\bar{M}_n = 1124.2$, the average degree of polymerization could be calculated as $n = 5.5$. Based on the group contribution method, the type and number of constitution units for MND65, and their corresponding P_{LL}, R_{LL} and V values[20,21] are displayed in *Table 4*, from which $\Sigma P_{LLi} = 379.03$, $\Sigma R_{LLi} = 261.27$, and $\Sigma V_i = 840.2$. One can then obtain $\mu \approx 2.39$ debye/mol$^{1/2}$ and $\bar{\mu} \approx 0.0825$ debye/cm$^{3/2}$ by using equation (2) and equation (3), respectively. The calculated μ and $\bar{\mu}$ for all of the 10 UP resins and three LPAs are listed in *Table 5*.

For the first series of UP, both μ and $\bar{\mu}$ were lower for MND25 than for MND65, which would be due to a higher composition of highly nonpolar and bulky NPG residue (in comparison to DEG residue) in the former UP. For the second series of UP, modification of UP by PA or IPA with

Table 4 Values for the calculation of dipole moment for the MND65 type of UP as an example

Index units	Constitution	Number	P_{LLi}	R_{LLi}	V_i (cm³/mol)
1	–OH	2	6	2.55	10.0
2	–COO–	2 × 5.5 = 11	15	6.21	18.0
3	–CH=CH–	1 × 5.5 = 5.5	8.9	8.88	27.0
4	–CH$_2$–	(6.5)(0.44/1.12)(2) + (6.5)(0.68/1.12)(4) = 20.89	4.65	4.65	16.1
5	–O–	(6.5)(0.68/1.12) × 1 = 3.95	5.2	1.64	3.8
6	–CH$_3$–	(6.5)(0.44/1.12) × 2 = 5.11	5.64	5.64	33.5
7		(6.5)(0.44/1.12)x1 = 2.55	2.58	2.58	−19.2

Table 5 Calculated values of dipole moments per mole, molar volumes, and dipole moments per unit volume for the UP resins and LPAs

	Dipole moment μ (debye/mol$^{1/2}$)	Molar volume V (cm^3/mol)	Dipole moment per unit volume $\mu/V^{1/2}$ (debye/cm$^{3/2}$)
(a) UP code			
Series I			
MA–NPG–DEG65 (MND65)	2.39	840.2	0.0825
MA–NPG–DEG25 (MND25)	2.37	908.4	0.0786
Series II			
MA–PG	3.20	1360.3	0.0868
MA–PA–PG	3.12[a]	1390.1	0.0837
MA–IPA–PG	3.16[a]	1427.4	0.0836
Series III			
MA–PA–PG–DEG(1)	2.58[a]	935.1	0.0844
MA–PA–PG–MPDiol	2.35[a]	859.7	0.0801
MA–PA–PG–NPG	2.23[a]	837.9	0.0770
MA–PA–PG–DEG(2)	2.43[a]	856.5	0.0830
MA–PA–PG–DEG(3)	3.29[a]	1510.5	0.0847
(b) LPA			
PU[b]	6.28	3426.8	0.107
PVAc	14.44	35260.5[c]	0.0769
PMMA	12.04	29410[d]	0.0702

[a] P_{LLi} value for *o*-phenylene or *m*-phenylene was taken as 25.0, the same as that of *p*-phenylene
[b] Since the chemical structure of the PU used in this work was unknown, a carboxylic acid-terminated PU with $\bar{M}_n = 5043$ g/mol, which was made from 2,4-toluene diisocyanate, diethylene adipate ($\bar{M}_n = 1886$ g/mol) synthesized in our laboratory, and maleic anhydride, was employed for the calculation
[c] An experimental value of 72.2 cm^3/mol for PVAc repeating unit was employed
[d] An experimental value of 86.5 cm^3/mol for PMMA repeating unit was employed

aromatic ring structures could lead to a decrease of μ and $\bar{\mu}$. For the third series of UP, the UP containing NPG residues possessed the lowest μ and $\bar{\mu}$, followed by that containing MPDiol and DEG residues since the polarity of glycols would follow the order of NPG < MPDiol < DEG. On the other hand, for the MA–PA–PG–DEG types of UP, a lowering of C=C unsaturation by introducing more PA in the UP molecule (i.e. MA–PA–PG–DEG(2)) could cause lower μ and $\bar{\mu}$ values when compared with MA–PA–PG–DEG(1), while an increase in the UP molecular weight (i.e. MA–PA–PG–DEG(3)) could lead to an increase in μ and $\bar{\mu}$ when compared with MA–PA–PG–DEG(1). As for the two UPs with similar $\bar{M}_n$, namely, MA–PA–PG and MA–PA–PG–DEG(3), the latter possessed higher μ and $\bar{\mu}$ values due to the introduction of more molar DEG residue (in comparison to PG residue) in the UP backbone.

As shown in *Table 5*, the decreasing order of molecular polarity in terms of the dipole moment per unit volume, $\bar{\mu}$, among the 10 UPs and three LPAs would be PU ($\bar{\mu} = 0.107$) > UP ($\bar{\mu} = 0.077$–0.087) > PVAc ($\bar{\mu} = 0.0769$) > PMMA ($\bar{\mu} = 0.0702$). This is because the urethane linkage, –NH–COO–, in the backbone of PU would be the most effective in the enhancement of molecular polarity, followed by the ester linkage, –COO–, in the backbone of UP, the side group, –COO–, linking to the backbone of PVAc via –O–, and the side group, –COO–, linking to the backbone of PMMA via –C–.

Table 6 Effects of chemical structures of UP on the miscibility of ST/UP/PVAc and ST/UP/PMMA unreacted ternary systems at 30°C

| UP code	Phase separation time (min)		Upper layer (wt.%)		Bottom layer (wt.%)	
	10% PVAc	10% PMMA	10% PVAc	10% PMMA	10% PVAc	10% PMMA
Series I						
MA–NPG–DEG65 (MND65)	one-phase	140	—	13.6	—	86.4
MA–NPG–DEG25 (MND25)	one-phase	one-phase	—	—	—	—
Series II						
MA–PG	230	190	94.8	17.1	5.2	82.9
MA–PA–PG	one-phase	40	—	29.0	—	71.0
MA–IPA–PG	one-phase	240	—	11.5	—	88.5
Series III						
MA–PA–PG–DEG(1)	33	22	18.3	15.5	81.7	84.5
MA–PA–PG–MPDiol	one-phase	516	—	35.7	—	64.3
MA–PA–PG–NPG	one-phase	one-phase	—	—	—	—
MA–PA–PG–DEG(2)	one-phase	25	—	13.8	—	86.2
MA–PA–PG–DEG(3)	480	1515	21.7	32.8	78.3	67.2
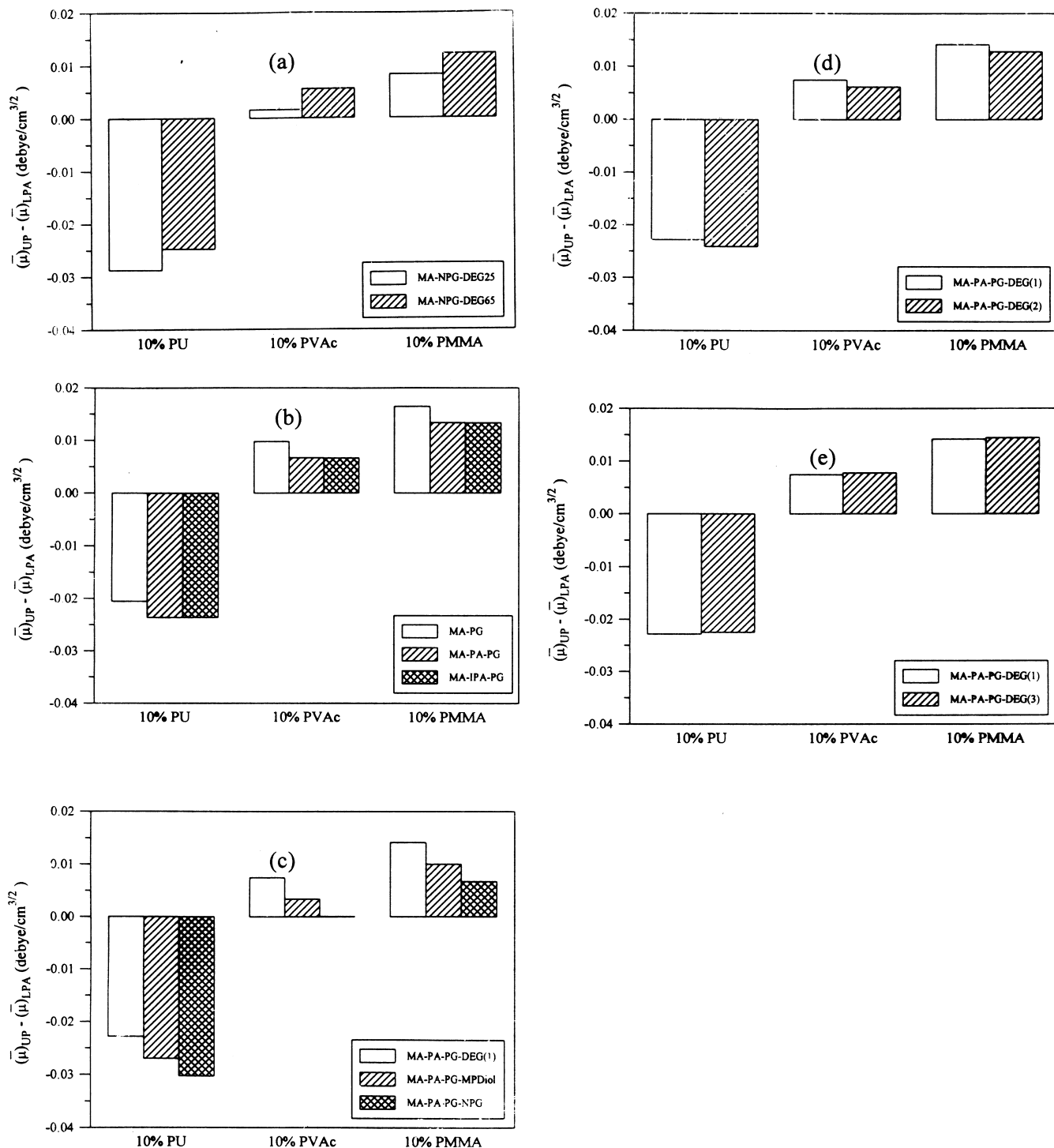
Figure 2 The effects of UP chemical composition and structure on the polarity difference per unit volume between UP and LPA. (a) variation of glycol ratio for MA–NPG–DEG type of UP, (b) modification by PA or IPA for MA–PG type of UP, (c) modification by a second diol for MA–PA–PG–Diol type of UP, (d) variation of C=C unsaturation for MA–PA–PG–DEG type of UP, and (e) variation of UP molecular weight for MA–PA–PG–DEG type of UP

Relationship between polarity difference of UP and LPA per unit volume and compatibility of styrene/UP/LPA systems

Figure 2 shows the effects of UP chemical composition and structure on the polarity difference of UP and LPA per unit volume. Although the polarity difference (the absolute value) between UP and PU-based LPA per unit volume was the greatest among the UP/LPA pairs, the styrene/UP/PU system still formed a homogeneous solution after a phase equilibrium at 30°C. This is because of both the strong polar interaction between the urethane linkage, –NHCOO–, in the PU and the ester linkage, –COO–, in the UP, and the

chemical reaction between –NCO– or –OH end groups in the PU and –COOH or –OH end groups in the UP, which could enhance the miscibility for the ST/UP/LPA system characterized by an upper critical solution temperature (UCST). (On heating from 30 to 110°C, each of the ST/UP/LPA ternary system in this work would appear as a single homogeneous phase prior to reaction, and no global phase separation could be observed.)

In contrast, the static phase characteristics of styrene/UP/PVAc and styrene/UP/PMMA systems at 30°C would be greatly affected by UP resin structures as shown in *Table 6*.
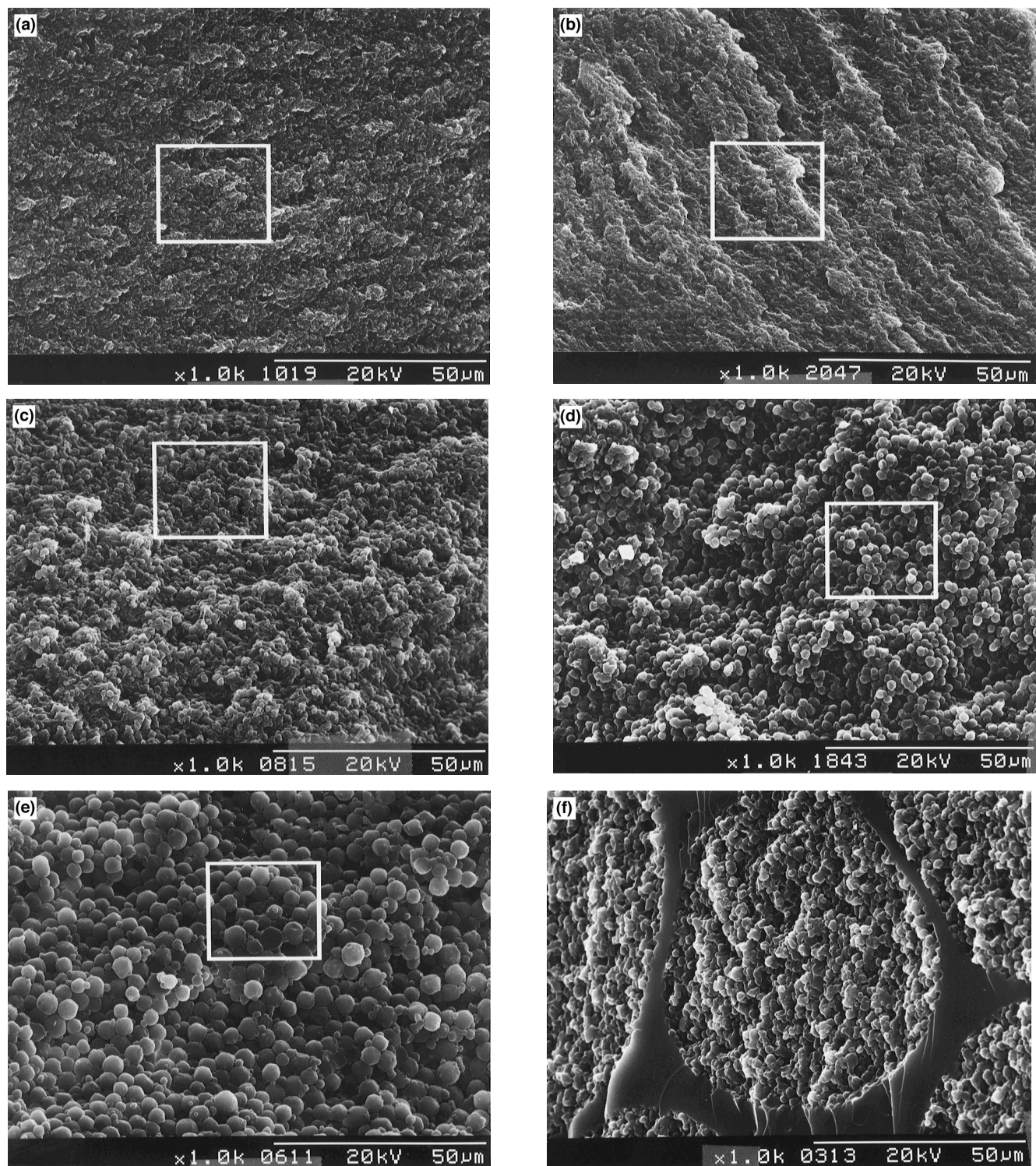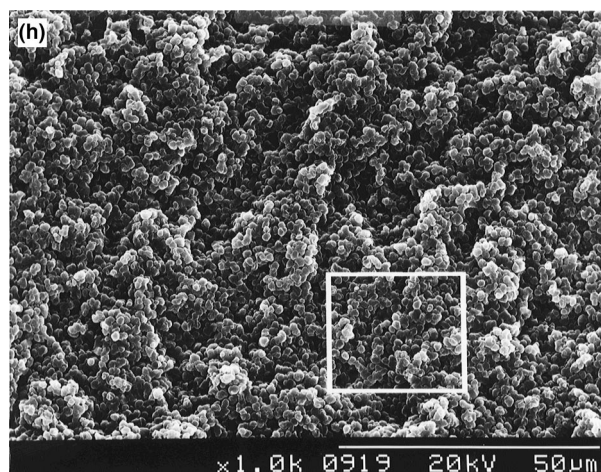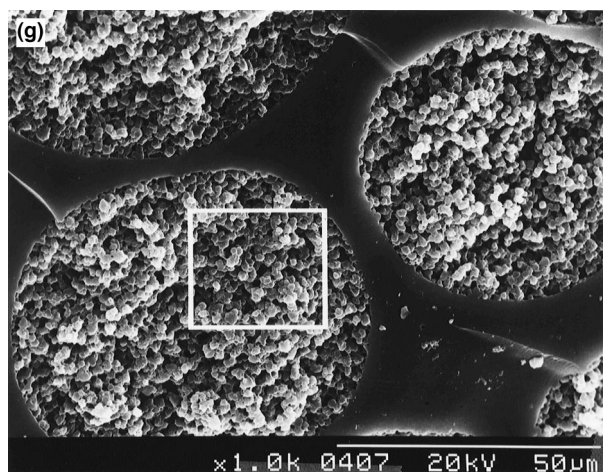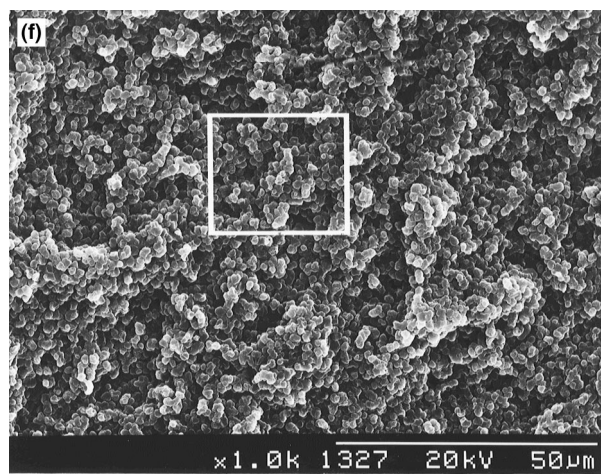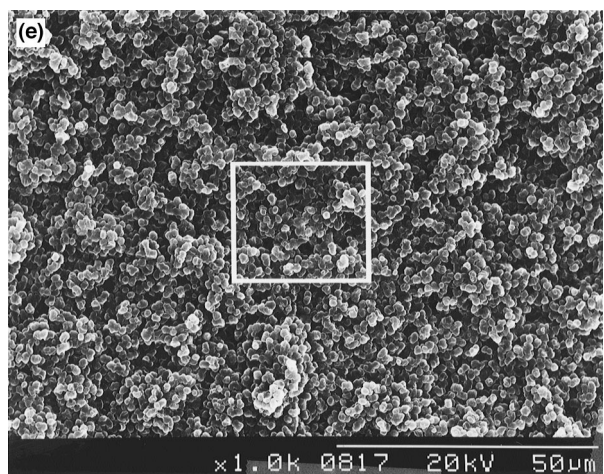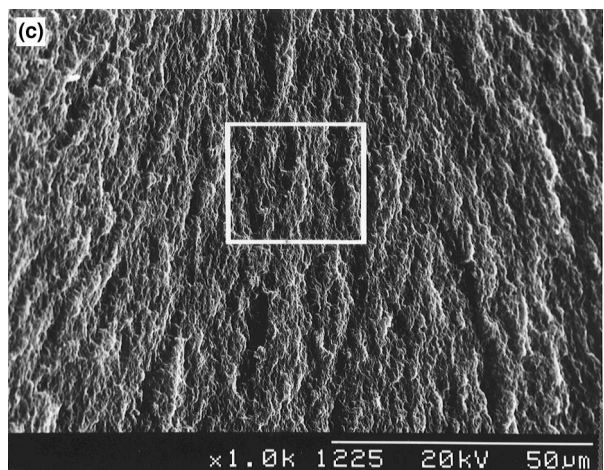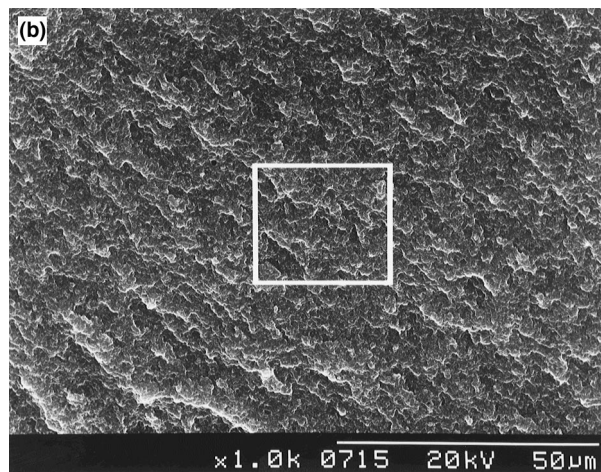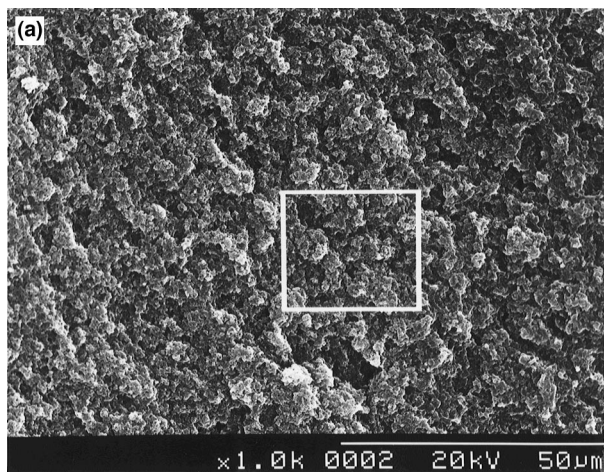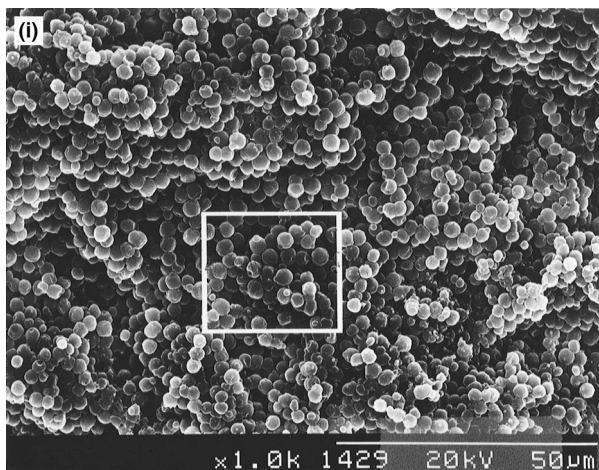
Figure 3 SEM micrographs of fractured surface for MA–NPG–DEG (MND) type of UP resins containing 10% PU, 10% PVAc and 10% PMMA. (a) MND25 + PU, (b) MND65 + PU, (c) MND25 + PVAc, (d) MND65 + PVAc, (e) MND25 + PMMA, and (f) MND65 + PMMA; micrographs obtained at 1000×

For the first series of UP resins, the styrene/MND65/PMMA system exhibited phase separation phenomena, while the other three systems showed single-phase characteristics. This could be explained by the polarity difference per unit volume between UP and LPA. As shown in *Figure 2a*, the polarity difference per unit volume between MND65 and PMMA was higher than those of the other three pairs, such as MND25/PMMA, MND65/PVAc and MND25/PVAc, leading to the less compatibility for the styrene/MND65/PMMA system at 30°C.

Similarly, for the second and third series of UP resins, as the polarity difference per unit volume between UP and LPA was reduced, the styrene/UP/LPA system at 30°C generally would either remain a single homogeneous phase or exhibit a slower rate of global phase separation (compare *Figure 2* and *Table 6*). However, the phase separation rate was slower for the styrene/MA–PA–PG–DEG(3)/LPA than the styrene/MA–PA–PG–DEG(1)/LPA despite the greater polarity difference per unit volume between MA–PA–PG–DEG(3) and LPA (*Figure 2e*), which would be due to the
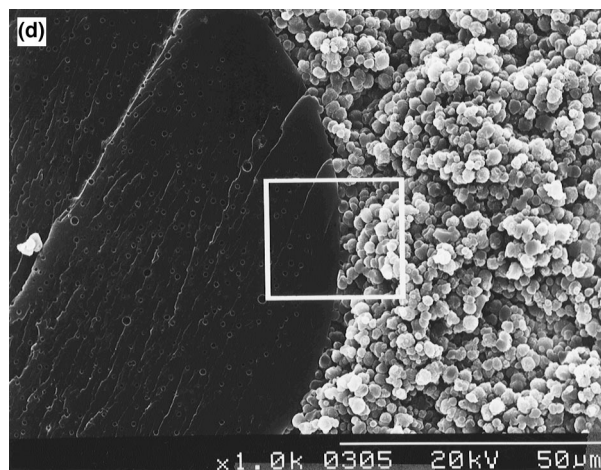
Figure 4 SEM micrographs of fractured surface for MA–PG type of UP resins containing 10% PU, 10% PVAc and 10% PMMA. (a) MA–PG + PU, (b) MA–PA–PG + PU, (c) MA–IPA–PG + PU, (d) MA–PG + PVAc, (e) MA–PA–PG + PVAc, (f) MA–IPA–PG + PVAc, (g) MA–PG + PMMA, (h) MA–PA–PG + PMMA, and (i) MA–IPA–PGL + PMMA; micrographs obtained at 1000×

higher viscosity for the MA–PA–PG–DEG(3) system resulting in a reduction in the phase separation rate.

Effects of polarity difference per unit volume between UP and LPA on morphology

Figure 3 shows the effects of UP chemical composition and structure on the cured sample morphology for the first series of UP resins. For the neat UP resin system, a flake-like microstructure was observed (not shown). Adding PU or PVAc in the neat UP resins, a co-continuous globule microstructure, consisting of a crosslinked UP phase (i.e. globules or microgel particles) and LPA phase, would result after the cure (*Figure 3a–d*). The LPA phase would surround the microgel particles but had been washed off in the extraction procedure. For the PU system, the microdomain of crosslinked UP phase appeared much smaller than that of PVAc system (0.2–0.4 *versus* 1–2 μm) due to the better compatibility between PU and UP resin (caused by the strong polar interaction and the chemical reaction between UP and PU as mentioned earlier) than between PVAc and UP resin. For the PU system, the microgel particles would be more closely overlapped and be less independent for MND25 than for MND65, while for the PVAc system, the size of microgel particles would be smaller for MND25 than for MND65. In contrast, for PMMA as an LPA, either a globule microstructure (MND25 system in *Figure 3e*), with a relatively large microgel particles (3–5 μm) compared with PU and PVAc systems, or a two-phase microstructure (MND65 system in *Figure 3f*), containing a flake-like continuous phase and a globule LPA-dispersed phase, would generally arise.

All of these generally imply that the closer the polarity difference per unit volume between UP and LPA, the more compatible the ST/UP/LPA system, leading to a globule microstructure characterized by smaller size of microgel particles and less overlapping between microgel particles after the cure (compare *Figure 2a* and *Figure 3*). For a large polarity difference per unit volume between UP and LPA, a two-phase microstructure of the cured sample could even arise.

Similar observations were found from the SEM micrographs of the second (*Figure 4*) and third (not shown) series of UP resins containing PU, PVAc and PMMA. For a large polarity difference per unit volume between UP and LPA, such as ST/MA–PG/PVAc and ST/MA–PG/PMMA systems for the second series of UP (*Figure 2b*) and ST/MA–PA–PG–DEG(1)/PVAc, ST/MA–PA–PG–DEG(3)/PVAc,

ST/MA–PA–PG–DEG(1)/PMMA, ST/MA–PA–PG–DEG(2)/PMMA and ST/MA–PA–PG–DEG(3)/PMMA systems for the third series of UP (*Figure 2c–e*), a two-phase microstructure of the cured sample would result (*Figure 4d,g*).

CONCLUSIONS

The decreasing order of molecular polarity in terms of the calculated dipole moment per unit volume, $\bar{\mu}$, among the 10 UPs and three LPAs in this work would be generally PU > UP > PVAc > PMMA. Pertinent introduction of benzene ring structure, such as PA and IPA, and rigid component, such as MPDiol and NPG, into the UP backbone could decrease the molecular polarity of UP, so could the successive reduction in the degree of C=C unsaturation by introducing more PA content in the UP, from 2/3 to 1/2 for instance. A smaller polarity difference for UP/PVAc and UP/PMMA pairs but a larger polarity difference for UP/PU pair would then result. In contrast, increasing the UP molecular weight could increase the molecular polarity of UP, resulting in a larger polarity difference for UP/PVAc and UP/PMMA pairs but a smaller polarity difference for UP/PU pair.

The calculated polarity difference per unit volume between UP and LPA could be employed as an index parameter for the miscibility of ST/UP/LPA systems and the characteristics of cured sample morphology. As the polarity difference per unit volume between UP and LPA decreases, the styrene/UP/LPA system at 30°C generally would either remain a single homogeneous phase or exhibit a slower rate of global phase separation. Also, the closer the polarity difference per unit volume between UP and LPA, the more compatible the ST/UP/LPA system, leading to a globule microstructure characterized by smaller size of microgel particles and less overlapping between microgel particles after the cure. For a large polarity difference per unit volume between UP and LPA, a two-phase microstructure of the cured sample could even arise.

Although the polarity difference between UP and PU-based LPA per unit volume is the greatest among the UP/LPA pairs, the styrene/UP/PU system still forms a homogeneous solution after a phase equilibrium at 30°C. This is because of both the strong polar interaction and the chemical reaction between PU and UP resin. As a result, a co-continuous globule microstructure, consisting of a crosslinked UP phase (i.e. globules or microgel particles)

and LPA phase, would arise after the cure, where the microdomain of crosslinked UP phase appears much smaller when compared with that of ST/UP/PVAc system.

Increasing the UP molecular weight could lead to a decrease in the phase separation rate for the ST/UP/PVAc and ST/UP/PMMA systems due to the viscosity increase despite the concomitant increase in the polarity difference per unit volume between UP and LPA.

ACKNOWLEDGEMENTS

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