

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

2. Mechanical properties

Yan-Jyi Huang* and Lih-Der Chen

Department of Chemical Engineering, National Taiwan University of Science and Technology†, Taipei, Taiwan 107, Republic of China

(Received 13 October 1997; revised 26 January 1998; accepted 12 February 1998)

The effects of three series of unsaturated polyester (UP) resins with different chemical composition or structure on the mechanical properties of three low-shrink UP resins containing thermoplastic polyurethane, poly(vinyl acetate) and poly(methyl methacrylate) respectively have been investigated by an integrated approach of static phase characteristics–cured sample morphology–reaction conversion–property measurements. The three series of UP resins synthesized include: maleic anhydride (MA)–neopentyl glycol (NPG)–diethylene glycol (DEG) types, with various molar ratios of NPG and DEG; MA–1,2-propylene glycol (PG) types with and without modification by a saturated dibasic aromatic anhydride or acid, such as phthalic anhydride (PA) or isophthalic acid; and MA–PA–PG types modified by a second glycol, such as DEG, 2-methyl-1,3-propanediol or NPG, to partially replace PG. Based on the Takayanagi mechanical models, 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 mechanical properties will be discussed. © 1998 Elsevier Science Ltd. All rights reserved.

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

INTRODUCTION

Adding specific thermoplastic polymers such as low-profile additives (LPAs) to unsaturated polyester (UP) resins could lead to a reduction or even elimination of the polymerization shrinkage during the curing process^{1,2}. In part 1 of this paper³, the chemical composition and structure of UP resins were demonstrated to be intimately connected with the miscibility and cured sample morphology for styrene/UP/LPA systems. Due to a drift in styrene/polyester composition^{4–6} as a result of phase separation during curing of the styrene/UP/LPA system, it is of interest to further study how the mechanical properties of ultimately cured samples would be affected by the UP chemical composition and structure.

Several researchers^{7–9} have studied the effects of LPAs on the mechanical properties of styrene-cross-linked polyester matrices with a given chemical composition and structure of UP. Their experimental results were essentially explained by cured sample morphology and microvoid formation^{10,11}, while other factors, such as the cross-linking densities of the ultimately cured samples in both the continuous and dispersed phases, were disregarded.

The objective of this work is to investigate the effects of chemical composition and structure of UP resins on the mechanical properties of three low-shrink UP resins

containing thermoplastic polyurethane (PU), poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) respectively. Using an integrated approach of static ternary phase characteristics of styrene/UP/LPA at 30°C, morphology, reaction conversion and property measurements, in depth elucidation of the experimental results is given.

EXPERIMENTAL

Materials

The UP resins employed were synthesized by polycondensation reactions in the bulk phase^{3,12}. The first series of UP was made from maleic anhydride (MA), neopentyl glycol (NPG) and diethylene glycol (DEG), with various molar ratios of NPG and DEG. Two such UP resins, designated as MA–NPG–DEG65 (or MND65) and MA–NPG–DEG25 (or MND25), containing molar ratios of NPG to DEG of 45:65 and 85:25 respectively, were made.

The second series of UP was made from MA and 1,2-propylene glycol (PG), with and without modification by a saturated dibasic aromatic anhydride or acid, such as phthalic anhydride (PA) and isophthalic acid (IPA). Three UP resins, designated as MA–PG, MA–PA–PG and MA–IPA–PG, were synthesized, where the molar ratio of PA or IPA to MA was chosen to be 1:2.

The third series of UP was made from MA, PA, PG and a second diol, such as DEG, 2-methyl-1,3-propanediol (MPDiol) or NPG. Three UP resins, designated as

* To whom correspondence should be addressed

† Formerly National Taiwan Institute of Technology (before 31 July 1997)

MA-PA-PG-DEG(1), MA-PA-PG-MPDiol and MA-PA-PG-NPG, were synthesized, 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 of hydroxyl equivalents to acid equivalents during the synthesis was employed for the latter. (A 10% excess of glycols was used for the other nine UP resins in the synthesis.) The molecular characteristics of the 10 UP resins are summarized in *Table 1*.

Three LPAs, containing thermoplastic PU (LP2030, Olin), PVAc (LP40A, Union Carbide) and PMMA, were employed, the number-average molecular weights of which were measured to be 6500, 42 000 and 34 000 respectively by vapour 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 2:1. The reaction was initiated by 1% by weight of tert-butyl perbenzoate (TBPB). All the materials were employed as received without further purification.

Instrumentation and procedure

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

For the cure conversion study, 6–10 mg sample solution was placed in a hermetic aluminium sample pan. The isothermal reaction rate profile at 110°C was measured by a DuPont 9000 differential scanning calorimeter and the final conversion of total C=C bonds at 110°C was calculated¹³.

In the morphological study, the cured sample in the mould was removed and broken into several pieces. After the usual sample pretreatment⁵, 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 magnifications of × 1000 to × 5000.

For the mechanical tests, dumb-bell-shaped specimens based on ASTM D638-82a, type V were used to determine the tensile properties of polyester matrices on the Micro 500 universal testing machine (Testometric Co.) at a constant crosshead speed of 1.0 mm min⁻¹. The Izod impact test was also carried out based on ASTM D-256-81, method A by using an impact tester (Frank Pendulum Impact Tester, 53568 type).

RESULTS AND DISCUSSION

Molecular polarity and chain flexibility of UP

For each series of UP resins, the chain flexibility could be inferred from the glass transition temperature, as shown in *Table 1*, while the molecular polarity could be evaluated in terms of the calculated dipole moment per unit volume³, $\mu/V^{1/2}$, as summarized in *Table 2*.

For the first series of UPs, both the molecular polarity and the chain flexibility were better for MND65 than for MND25, due to the greater rigidity of NPG than DEG.

For the second series of UPs, both the degree of C=C unsaturation and the molecular polarity were lower for

Table 1 Molecular characteristics of UP resins

(a)	Series I		Series II		
	MND65	MND25	MA-PG	MA-PG-PA	MA-PG-IPA
Molar ratio of UP comp. ^a	1:0.44:0.68	1:0.77:0.27	1:1.03	0.63:0.37:1.02	0.65:0.35:1.06
AN ^b	27.8	27.0	28.6	28.3	26.4
HN ^b	72.0	68.8	31.0	28.3	28.8
M_n (abs.) ^c	1124	1174	1883	1982	2033
M_n (GPC)	1749	1470	2167	1836	1997
M_w/M_n (GPC)	1.65	2.43	2.77	2.02	2.61
T_g (°C) ^d	-25.6	-19.0	7.6	10.6	11.9
No. of C=C bonds per UP5.68		6.22	11.89	7.13	7.39
(b)	Series III				
	MA-PA-PG-DEG(1)	MA-PA-PG-MPDiol	MA-PA-PG-NPG	MA-PA-PG-DEG(2)	MA-PA-PG-DEG(3)
Molar ratio of UP comp. ^a	0.65:0.35:0.43:0.63	0.68:0.32:0.42:0.58	0.67:0.33:0.39:0.61	0.47:0.53:0.42:0.66	0.64:0.36:0.41:0.71
AN ^b	25.4	25.8	26.0	26.2	26.4
HN ^b	58.8	69.6	74.6	64.9	26.5
M_n (abs.) ^c	1333	1176	1115	1232	2166
M_n (GPC)	1847	1884	1785	1814	2290
M_w/M_n (GPC)	2.39	2.88	1.92	2.04	2.56
T_g (°C) ^d	-11.8	-2.2	8.1	-6.6	-5.6
No. of C=C bonds per UP4.39		4.47	3.94	2.80	6.78

^aMeasured by ¹H n.m.r.

^bAN and HN denote acid number and hydroxyl number respectively

^cCalculated by end-group titration methods

^dMeasured by differential scanning calorimetry

Table 2 Calculated dipole moment per unit volume, $\mu/V^{1/2}$, for the 10 UP resins and three LPAs, and the dipole moment difference between the UPs and LPAs used in this work

UP code or LPA	μ^a	V^b	$\mu/V^{1/2}{}^c$	$(\mu/V^{1/2})_{UP} - (\mu/V^{1/2})_{LPA}{}^d$		
				PU	PVAc	PMMA
Series I						
MND65	2.39	840.2	0.0825	-0.0245	0.0056	0.0123
MND25	2.37	908.4	0.0786	-0.0284	0.0017	0.0084
Series II						
MA-PG	3.20	1360.3	0.0868	-0.0202	0.0099	0.0166
MA-PA-PG	3.12 ^e	1390.1	0.0837	-0.0233	0.0068	0.0135
MA-IPA-PG	3.16 ^e	1427.4	0.0836	-0.0234	0.0067	0.0134
Series III						
MA-PA-PG-DEG(1)	2.58 ^e	935.09	0.0844	-0.0226	0.0075	0.0142
MA-PA-PG-MPDiol	2.35 ^e	859.72	0.0801	-0.0269	0.0032	0.0099
MA-PA-PG-NPG	2.23 ^e	837.94	0.0770	-0.030	0.00010	0.0068
MA-PA-PG-DEG(2)	2.43 ^e	856.47	0.0830	-0.024	0.0061	0.0128
MA-PA-PG-DEG(3)	3.29 ^e	1510.46	0.0847	-0.0223	0.0078	0.0145
LPA						
PU ^f	6.28	3426.8	0.107			
PVAc	14.44	35260.5 ^g	0.0769			
PMMA	12.04	29410 ^g	0.0702			

^aDipole moment (debye mole^{-1/2})^bMolar volume (cm³ mol⁻¹)^cDipole moment per unit volume (debye cm^{-3/2})^dDifference in dipole moment per unit volume between UP and LPA (debye cm^{-3/2})^e P_{LLi} value for *o*-phenylene or *m*-phenylene was taken as 25.0, the same as that of *p*-phenylene³^fSince the chemical structure of the PU used in this work was unknown, a carboxylic acid-terminated PU with $M_n = 5043$ g mol⁻¹, which was made from 2,4-toluene diisocyanate, diethylene adipate ($M_n = 1886$ g mol⁻¹) synthesized in our laboratory and maleic anhydride, was employed for the calculation^gExperimental values of 72.2 and 86.5 cm³ mol⁻¹ for the molar volumes of PVAc and PMMA repeating units respectively were employed

MA-PA-PG and MA-IPA-PG than for MA-PG, while the chain stiffness was higher for the former two resins due to the introduction of the benzene ring structure in the main chain. It should be noted that both the molecular polarity and the chain flexibility were better for MA-PA-PG than for MA-IPA-PG, since IPA, which contributes two neighbouring carbon-carbon bonds from the benzene ring as part of the UP backbone, could enhance the chain stiffness of UP better than PA, which provides only one carbon-carbon bond from the benzene ring as part of the UP segment.

For the third series of UPs, the decreasing order of both molecular polarity and chain flexibility was MA-PA-PG-DEG (1) > MA-PA-PG-MPDiol > MA-PA-PG-NPG, due to the decreasing order of rigidity, NPG > MPDIol > DEG. On the other hand, an increase in PA content to reduce the C=C unsaturations in the UP resin could lead to a decrease in the molecular polarity of UP, hence the molecular polarity would be smaller for MA-PA-PG-DEG(2) than MA-PA-PG-DEG(1). In contrast, an increase in UP molecular weight could cause an enhancement of UP molecular polarity, hence the molecular polarity would be greater for MA-PA-PG-DEG(3) than MA-PA-PG-DEG(1).

Drift in styrene/polyester composition during curing

As pointed out in part 1 of this paper³, for a styrene/UP/LPA system with molar ratio = 2:1 and 10% by weight of LPA, the styrene/UP/PU system formed a homogeneous solution after a phase equilibrium at 30°C, while the static

phase characteristics of the styrene/UP/PVAc and styrene/UP/PMMA systems at 30°C would rely on the polarity difference of UP and LPA. (The decreasing order of molecular polarity among the 10 UPs and three LPAs used in this work would generally be PU > UP > PVAc > PMMA, as shown in Table 2.)

After a phase equilibrium at 30°C for styrene/UP/LPA systems, the upper layer (i.e. dispersed phase) would be dominated by styrene and LPA, while the bottom layer (i.e. continuous phase) would be dominated by UP and styrene^{5,6}. Hence, 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.

On heating from 30 to 110°C, each of the styrene/UP/LPA ternary systems which exhibited phase separation phenomena at 30°C in part 1 of this paper³ would appear as a single homogeneous phase prior to reaction, and no global phase separation could be observed. As the cure reaction at 110°C proceeded, the increase in molecular weights of the reacting species via cross-linking reactions could enhance the phase separation (due to the decrease in entropy of mixing), the onset of which would generally occur at very low reaction conversion⁵ ($\alpha < 1\%$). Near the gelation point ($\alpha \approx 10\%$)¹⁴, the mass transfer into or out of the continuous phase or the dispersed phase would essentially cease. To a first approximation, the compositions in either phase for the ultimately cured sample could then be represented, in an average sense, by those based on the static phase characteristics at 25°C^{5,6}. In reality, the true compositions

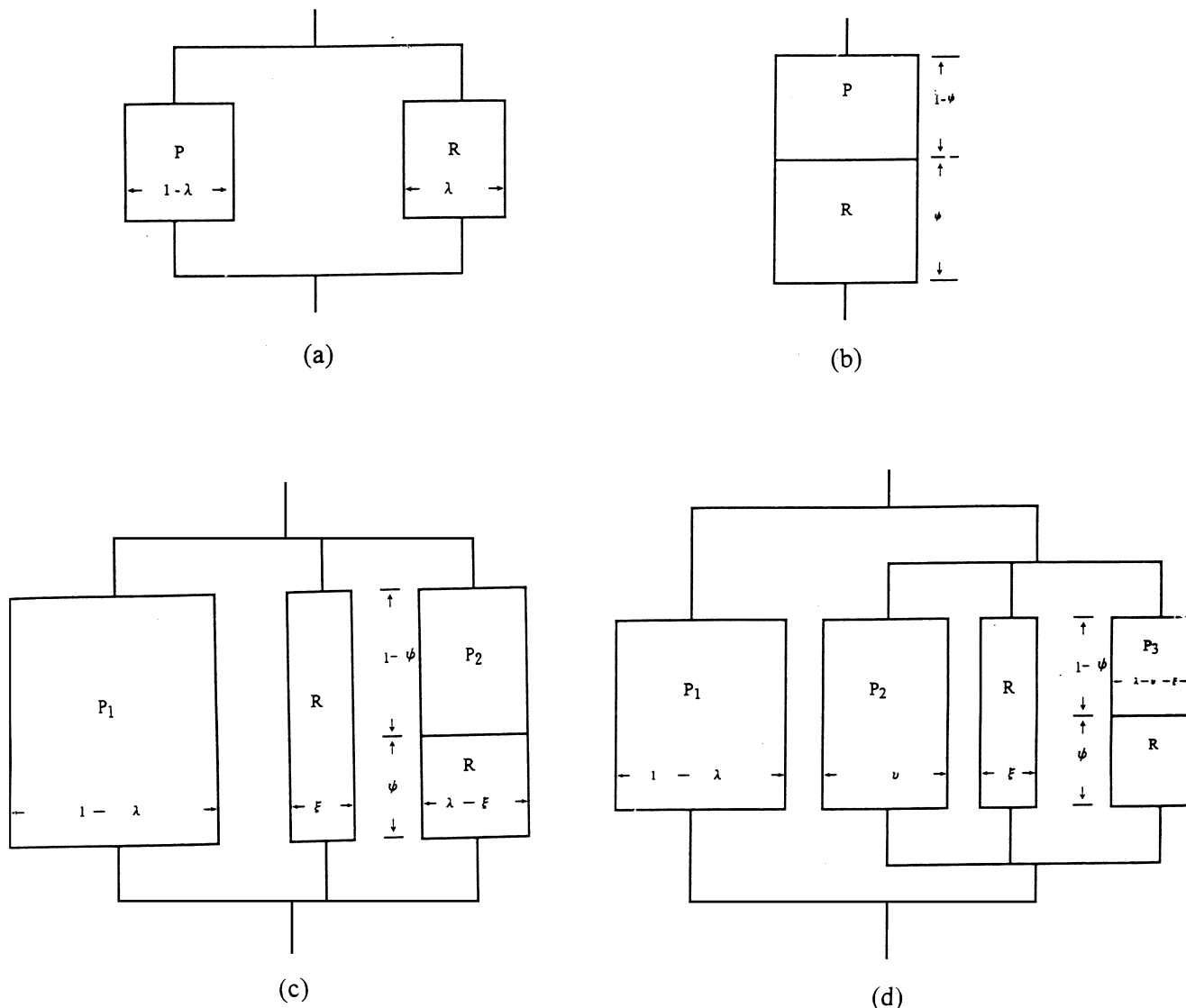


Figure 1 Takayanagi models for the mechanical behaviour of cured LPA-containing UP resin systems. (a) parallel (P) model. (b) Series (S) model. (c) Parallel-parallel-series (P-P-S) model. (d) Parallel-parallel-parallel-series (P-(P-P-S)) model. The area of each diagram is proportional to the volume fraction of the phase

of the two phases for the cured sample may depend on dynamic phase characteristics, which would be connected with the reaction kinetics and the rate of ongoing phase separation.

Relationship between morphologies and mechanical properties—the Takayanagi models

For the cured LPA-containing UP resin systems with morphologies as shown in Figures 2–4, their mechanical behaviour can be approximately represented by the Takayanagi models^{15–17}, where arrays of weak LPA (R) and stiff styrene-cross-linked polyester (P) phases are indicated (see Figure 1). The subscripts 1, 2 and 3 for P phases are employed due to distinguish between styrene and UP compositions as a result of phase separation during curing, and the quantities λ , φ , ξ and ν or their indicated multiplications indicate volume fractions of each phase. Four combinations, parallel (P), series (S), parallel-parallel-series (P-P-S) and parallel-parallel-parallel-series (P-(P-P-S)) models, are shown in Figure 1. For the parallel element, an iso-strain condition exists when the element is subjected to a longitudinal stress, while for the series element, an iso-stress condition results.

Figure 1a apparently represents the case where the phase P and the phase R form a co-continuous phase morphology. It may also denote the upper bound behaviour of a relatively stiff material consisting of a stiff continuous phase P and a weak dispersed phase R. On the other hand, Figure 1b denotes the lower bound behaviour of a relatively weak material consisting of a weak continuous phase R and a stiff discontinuous phase P. For the systems shown in Figure 2a–c, e, f, h, i, Figure 3a, b and Figure 4a, the microgel particles (phase P₁) would be surrounded by a layer of LPA (phase R). Between the LPA-covered microgel particles, there would be some other microgel particles (phase P₂), with different compositions of styrene and UP from those in phase P₁, dispersed in the LPA phase (phase R). Hence, the characteristic globule microstructure may be represented by the P-P-S model as shown in Figure 1c, which is a parallel combination of the three elements, i.e. P₁, R and P₂-R in series. In contrast, for the system shown in Figure 3c and Figure 4b, c, the microstructure consists of a flake-like stiff continuous phase of styrene-cross-linked polyester (phase P₁) and a weak globule LPA-dispersed phase, whose globule morphology can also be represented by a P-P-S model. Hence, the upper bound of mechanical

behaviour for the overall morphology can be represented by a P-(P-P-S) model as shown in *Figure 1d*, which is simply a parallel combination of the continuous phase P₁ and the dispersed phase denoted by a P-P-S model.

The mechanical properties of cured samples change not only with morphology, but also the cross-linking density of styrene-cross-linked polyester in the P₁, P₂ and P₃ phases, with the major continuous phase P₁ being dominant. The latter information is not easily obtained, but can be inferred from the static phase characteristics of styrene/UP/LPA systems at 25°C before curing^{5,6}.

Effects of polarity difference between UP and LPA on morphology

Figures 2–4 show the effects of UP chemical composition and structure on the cured sample morphology for the third series of UP resins, while the scanning electron micrographs of the first and second series of UP resins containing PU, PVAc and PMMA have been shown elsewhere³. The polarity of UP and LPA would generally follow the order PU > MA-PA-PG-DEG(1) > MA-PA-PG-MPDiol > MA-PA-PG-NPG > PVAc > PMMA (*Table 2*). The closer the polarity difference between UP and LPA, the more compatible the styrene/UP/LPA system, leading to a globule microstructure characterized by smaller microgel particles and less overlap between microgel particles (*Figure 2a–c, e, f, h, i*). For a large polarity difference between UP and LPA, a two-phase microstructure of the cured sample could even arise (*Figure 2d, g*). Although the polarity difference (absolute value) between UP and the PU-based LPA was the largest among the UP/LPA pairs (*Table 2*), the strong polar interaction and chemical reaction between UP and PU would prevent global phase separation for the styrene/UP/LPA system during curing, leading to a globule microstructure (*Figure 2a–c*). However, as the polarity difference between UP and PU-based LPA became larger, more styrene would diffuse from the major continuous phase of styrene-cross-linked polyester (i.e. microgel particles) to the minor LPA-dispersed phase, leading to less swollen microgel particles after the cure (*Figure 2b, c*).

Reduction of C=C unsaturation by the introduction of more PA in the UP backbone would cause a larger polarity difference between UP and LPA for the styrene/UP/PU system, while the trend would be reversed for the styrene/UP/PVAc and styrene/UP/PMMA systems. (The polarity would follow the order PU > MA-PA-PG-DEG(1) > MA-PA-PG-DEG(2) > PVAc > PMMA.) When compared with the MA-PA-PG-DEG(1) and MA-PA-PG-DEG(2) systems, the observed sample morphologies reveal a less compatible styrene/UP/PU system, with more compatible styrene/UP/PVAc and styrene/UP/PMMA systems for the MA-PA-PG-DEG(2) system. The former could be evidenced by the less independent microgel particles associated with the MA-PA-PG-DEG(2) system (compare *Figure 2a* and *Figure 3a*), while the latter was confirmed by either a globule microstructure for the PVAc system (compare *Figure 2d* and *Figure 3b*) or a smaller volume fraction for the LPA-dispersed phase for the PMMA system (compare *Figure 2g* and *Figure 3c*) associated with the MA-PA-PG-DEG(2) system.

Increasing the UP molecular weight would lead to a decrease in the phase separation rate during curing, and, in turn, less deviation (negative deviation) from the molar ratio 2:1, and a higher volume fraction in both the major

continuous phases. Indeed, scanning electron micrographs reveal that, for the PU system, the microgel particles were much more swollen by styrene for the MA-PA-PG-DEG(3) system in the major continuous phase (compare *Figure 2a* and *Figure 4a*), while for the PVAc and PMMA systems, the volume fraction in the major continuous phase was larger and the microgel particles were much less swollen by styrene in the LPA-dispersed phase for both the MA-PA-PG-DEG(3) systems (compare *Figure 2d* and *Figure 4b*; *Figure 2g* and *Figure 4c*).

Effects of microgel structure on cure conversion

For the first series of UP resins, the final conversion was found to be higher for the MND25 system than for the MND65 system by about 3% (*Table 3a*). This is because the MND65 type UP would be much more coiled due to its higher content of flexible DEG chains, and hence more C=C bonds in the long-chain UP molecules would be buried in the compact microgel structure¹³ during curing, resulting in a lower final conversion.

For the second series of UP resins, modification of UP resin by a saturated aromatic dibasic acid could lead to an increase of the final conversion by about 2–10%. This is ascribed to the fact that UP resins modified by PA or IPA would not only be less flexible, but also have lower degrees of C=C unsaturation than their unmodified counterparts, which could considerably reduce the amount of C=C bonds in the UP molecules buried in the microgel structure during curing, and thus greatly elevate the final conversion.

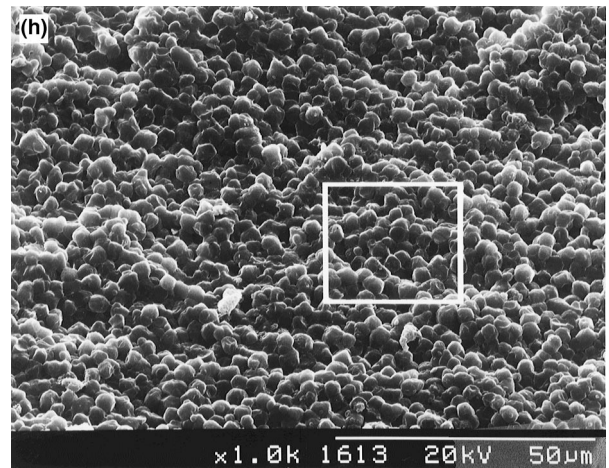
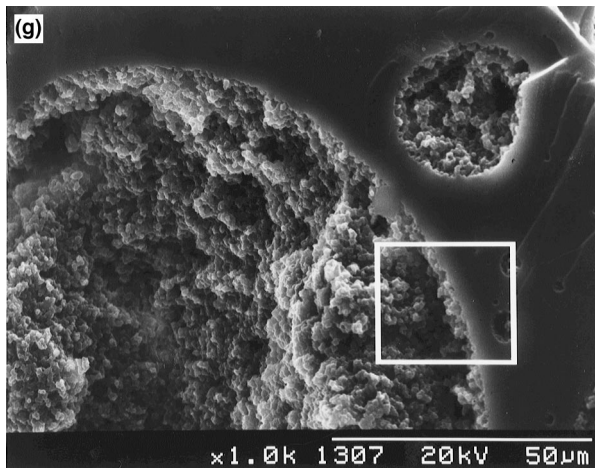
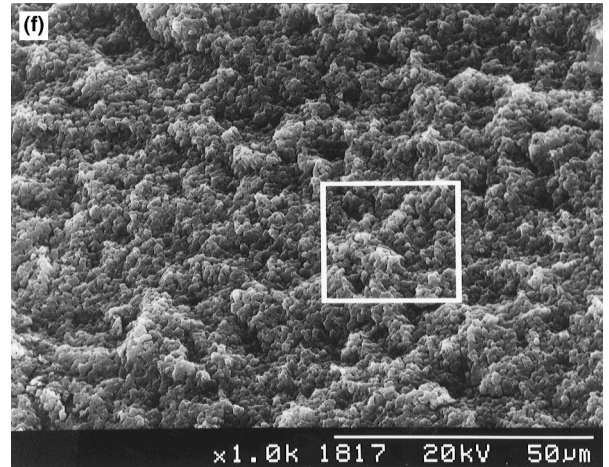
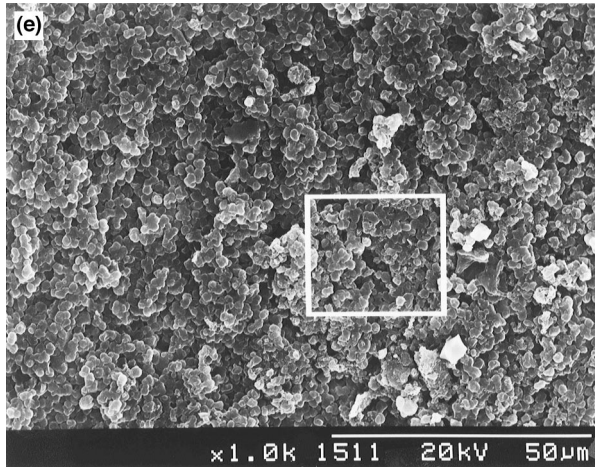
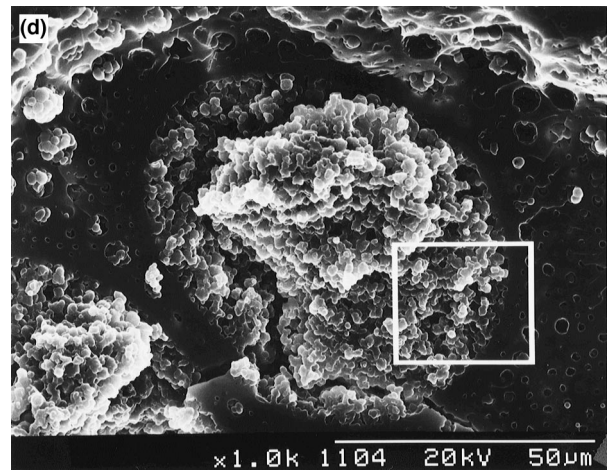
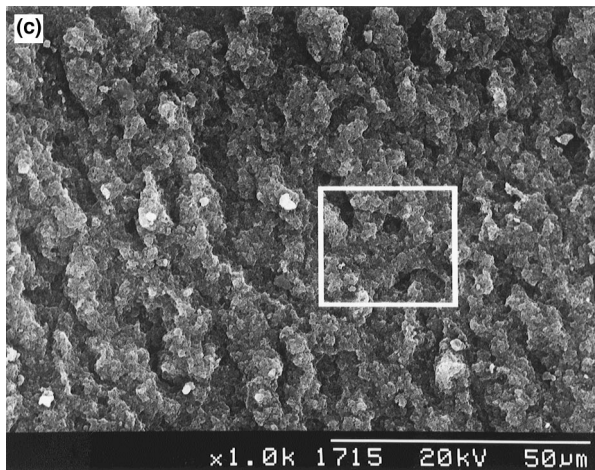
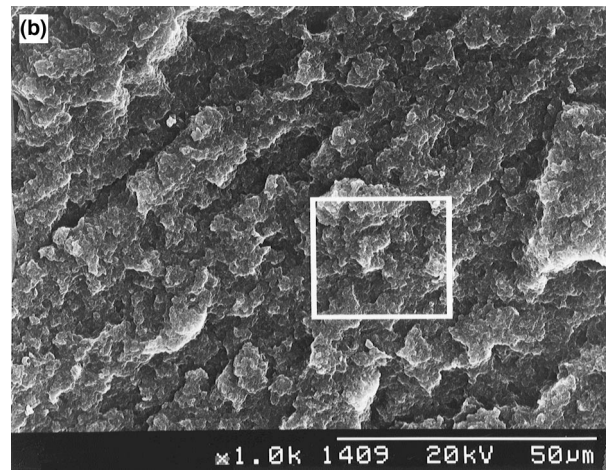
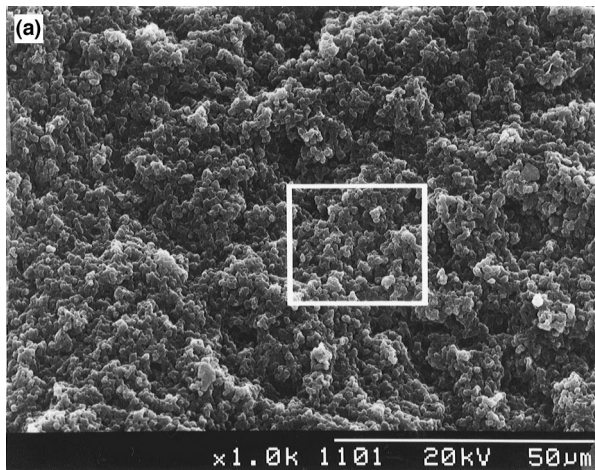
As for the third series of UP resins (*Table 3b*), introduction of a more rigid glycol in the UP backbone could result in a higher cure conversion (i.e. MA-PA-PG-NPG > MA-PA-PG-MPDiol > MA-PA-PG-DEG(1)), as could the reduction of C=C unsaturation by introduction of more PA in the UP backbone (i.e. MA-PA-PG-DEG(2) > MA-PA-PG-DEG(1)), the reasons for which would be similar to those explained above for the first and second series of UP resin systems respectively.

Increasing the UP molecular weight could lead to an enhancement of cure conversion (i.e. MA-PA-PG-DEG(3) > MA-PA-PG-DEG(1)). This would be due to the molar ratio of styrene consumed to polyester C=C bonds reacted deviating less from (less than) 2:1 in the major continuous phase during curing for the MA-PA-PG-DEG(3) system (caused by a slower phase separation rate), leading to a less compact microgel structure in that phase and, in turn, a higher overall cure conversion. (The higher the molar ratio, the higher the final conversion¹³.)

Effects of elastic active chain length and interfacial adhesion on impact strength

Table 4 shows the effects of UP chemical composition and structure on the impact strength of cured samples containing LPAs (PU, PVAc or PMMA). For the MA-NPG-DEG systems (series I), the impact strength was the largest for the sample containing PU, followed by the PVAc- and the PMMA-containing samples. In general, better interfacial adhesion between the cross-linked polyester phase and the LPA phase, as revealed by a globule microstructure with smaller and more independent microgel particles (*Figures 2–4*), as well as a lower *T_g* for the LPA (*T_g* values for PU, PVAc and PMMA are –45, 27 and 105°C respectively), would be favourable for the increase of impact strength.

For a given LPA, the impact strength was better for MND65 than for MND25 for PU-containing samples, while



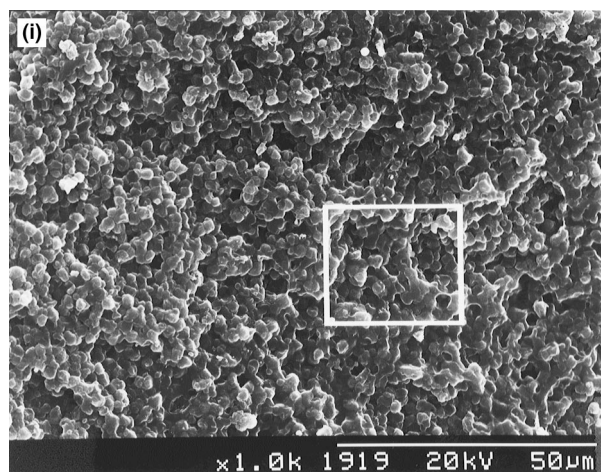


Figure 2 Scanning electron micrographs of the fractured surface for MA-PA-PG-Diol type UP resins containing 10% PU, 10% PVAc and 10% PMMA. (a) MA-PA-PG-DEG(1) + PU. (b) MA-PA-PG-MPDiol + PU. (c) MA-PA-PG-NPG + PU. (d) MA-PA-PG-DEG(1) + PVAc. (e) MA-PA-PG-MPDiol + PVAc. (f) MA-PA-PG-NPG + PVAc. (g) MA-PA-PG-DEG(1) + PMMA. (h) MA-PA-PG-MPDiol + PMMA. (i) MA-PA-PG-NPG + PMMA. Micrographs obtained at $\times 1000$

the trend was reversed for PVAc- and PMMA-containing samples. In light of the polarity order, $PU > MND65 > MND25 > PVAc > PMMA$ (Table 2), this is because, the smaller polarity difference between UP and LPA, the better the interfacial adhesion between the cross-linked polyester phase and the LPA phase, leading to a higher impact strength.

For MA-PG type systems (series II), all of the three LPA-containing samples exhibited a higher impact strength, by 10–50%, when the UP resin was modified by PA or IPA. The introduction of a saturated aromatic dibasic acid or anhydride in the UP backbone decreased the degree of C=C unsaturation (Table 1), and, in turn, diminished the cross-linking density of the cured sample. The resulting increase in the average length of polyester chain segment between cross-link points (i.e. elastic active chain length of the polyester) in the polyester network would raise the crack initiation energy during the impact test. Moreover, the introduction of a benzene ring structure in the UP backbone would help elevate the crack propagation energy. A higher impact strength could then result.

On the other hand, the interfacial adhesion would also affect the impact strength. The impact strength of the MA-PG-PA system was higher than that of MA-PG-IPA for the PU-containing sample, while the trend was reversed for the PVAc- and PMMA-containing samples. This could be explained by the variation of interfacial adhesion due to the change of polarity difference between UP and LPA, as mentioned earlier. (The polarity would follow the order $PU > MA-PG > MA-PG-PA > MA-PG-IPA > PVAc > PMMA$ in this case.)

As for the third series of UP resins, introduction of a more rigid glycol in the UP backbone could result in a higher impact strength for the PVAc and PMMA systems (i.e. MA-PA-PG-NPG $>$ MA-PA-PG-MPDiol $>$ MA-PA-PG-DEG(1)), while the trend was reversed for the PU system, which exhibited the same trend as that of the first series of UP resins.

Reduction of C=C unsaturation by introduction of more PA in the UP backbone could only slightly increase the impact strength of the PVAc and PMMA systems (i.e. MA-PA-PG-DEG(2) $>$ MA-PA-PG-DEG(1)), which is unlike those of the second series UP resins, where it has a more pronounced effect. On the other hand, for the PU system, the impact strength was curtailed insignificantly for

the MA-PA-PG-DEG(2) system. This is because, with a lower molecular polarity for MA-PA-PG-DEG(2), the polarity difference between UP and PU-based LPA would be larger, leading to a lower impact strength caused by the decrease in interfacial adhesion.

Increasing the UP molecular weight could lead to a noticeable enhancement of impact strength (i.e. MA-PA-PG-DEG(3) $>$ MA-PA-PG-DEG(1)). This would be due to the molar ratio of styrene consumed to polyester C=C bonds reacted deviating less from (smaller than) a molar ratio of 2:1 in the major continuous phase (phase P₁ in Figure 1c, d) during curing for the MA-PA-PG-DEG(3) system, as mentioned earlier, leading to a higher impact strength for that phase. (The impact strength would reach a maximum at a molar ratio of 2:1 for the neat UP resins according to our previous research.)

Effects of UP chain stiffness and cross-linking density on tensile strength

Based on the iso-strain model in Figure 1c and d, tensile strength of the sample would be dominated by $(1 - \lambda)\sigma_{P_1}$ provided that the major continuous phase is less brittle than the minor co-continuous or dispersed phase, and there is sufficient phase P₁ to carry the tensile load even after phases R, P₂ and P₃ have failed, where $(1 - \lambda)$ and σ_{P_1} are the volume fraction and the tensile strength for the stiff P₁ phase respectively.

Table 4 also shows the effects of UP chemical composition and structure on the tensile strength of cured samples. For a fixed UP resin, the tensile strength was highest for PU-containing samples, followed by PVAc- and PMMA-containing samples. This is because the degree of phase separation after curing will be the most pronounced for the PMMA-containing samples, followed by the PVAc- and PU-containing samples. Therefore, the molar ratio of styrene consumed to polyester C=C bonds reacted in the continuous phase of cross-linked polyester for the PMMA-containing samples would exhibit the greatest negative deviation from 2:1, leading to the lowest cross-linking density in that phase (i.e. phase P₁ in Figure 1c, d), and, in turn, the greatest reduction in tensile strength for the whole sample. (As reported in the literature¹⁸, the cross-linking density of a cured sample would reach a maximum at a molar ratio of 2:1 for the styrene/UP reaction system.)

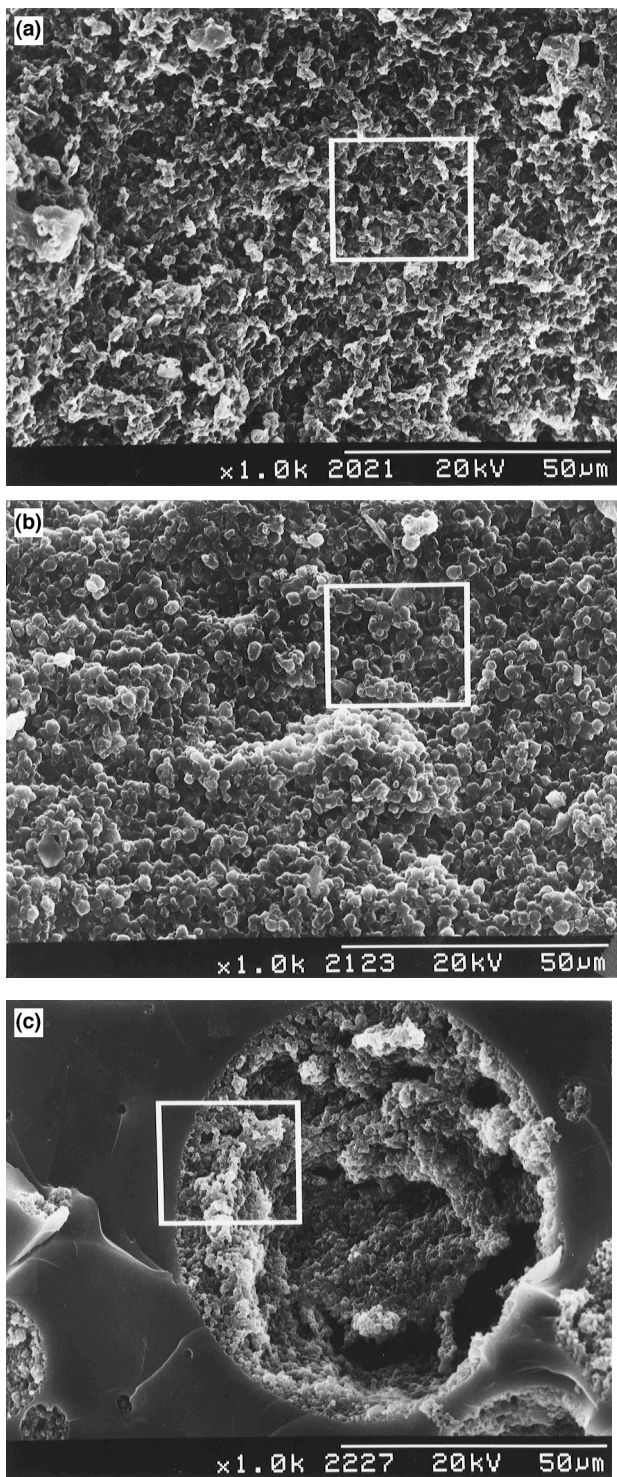


Figure 3 Effects of C=C unsaturation of UP resins on the scanning electron micrographs of the fractured surface for MA-PA-PG-DEG type UP resins containing 10% PU, 10% PVAc and 10% PMMA. (a) MA-PA-PG-DEG(2) + PU. (b) MA-PA-PG-DEG(2) + PVAc. (c) MA-PA-PG-DEG(2) + PMMA. Micrographs obtained at $\times 1000$

For the MA-NPG-DEG systems (series I), the tensile strength was higher for the MND25 system than for the MND65 system. This could be due to the higher cure conversion of the former (Table 3), leading to a higher cross-linking density. For the MA-PG type systems (series II), modification of UP by PA or IPA would result in an increase in the tensile strength due to the enhancement of UP chain stiffness caused by the benzene ring structure. The better tensile strength could also be attributed to the higher cure

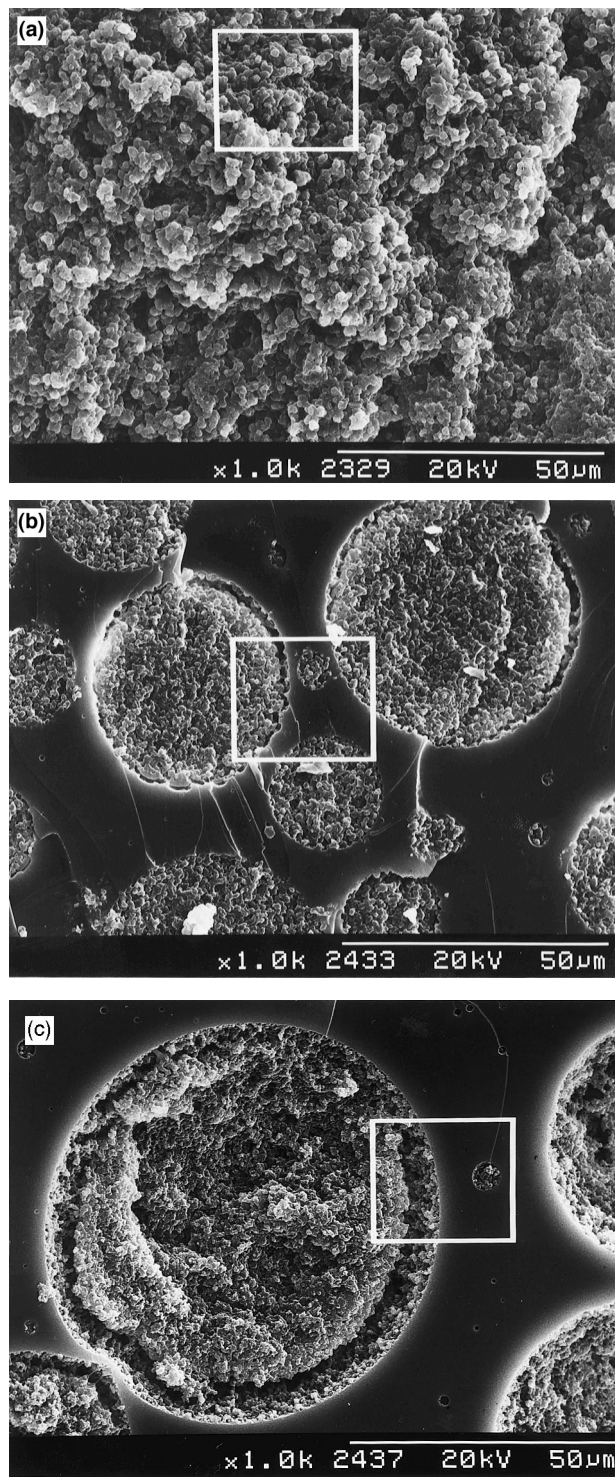


Figure 4 Effects of UP molecular weight on the scanning electron micrographs of the fractured surface for MA-PA-PG-DEG type UP resins containing 10% PU, 10% PVAc and 10% PMMA. (a) MA-PA-PG-DEG(3) + PU. (b) MA-PA-PG-DEG(3) + PVAc. (c) MA-PA-PG-DEG(3) + PMMA. Micrographs obtained at $\times 1000$

conversion (Table 3). It should be noted that modification of UP by IPA would be more effective in elevating the tensile strength than that by PA, since IPA could enhance the chain stiffness of UP better than PA, as mentioned earlier.

As for the third series of UP resins, introduction of a more rigid glycol in the UP backbone could result in a higher tensile strength (i.e. MA-PA-PG-NPG > MA-PA-PG-MPDiol > MA-PA-PG-DEG(1)), which exhibited the same trend as that of the first series of UP resins.

Table 3 Final conversion of total C=C bonds (%) measured by differential scanning calorimetry^a for isothermal reactions at 110°C

(a)	Series I		Series II		
	MND65	MND25	MA-PG	MA-PG-PA	MA-PG-IPA
Neat resin	83.0	85.5	82.5	89.3	84.1
10% PU	78.5	81.1	80.7	84.0	86.7
10% PVAc	80.8	81.2	78.1	88.5	84.3
10% PMMA	81.8	83.1	79.3	86.7	88.1
(b)	Series III				
	MA-PA-PG-DEG(1)	MA-PA-PG-MPDiol	MA-PA-PG-NPG	MA-PA-PG-DEG(2)	MA-PA-PG-DEG(3)
Neat resin	—	—	—	—	—
10% PU	82.0	84.6	86.5	89.1	84.2
10% PVAc	81.7	83.5	86.9	88.6	83.9
10% PMMA	82.1	83.5	86.6	87.9	84.0

^aThe errors of final conversion measured by differential scanning calorimetry would be within 1%

Table 4 Impact and tensile properties of 10 cured UP resins containing 10% PU, 10% PVAc and 10% PMMA respectively

UP system	Impact strength ^a (J m ⁻¹)			Tensile strength ^b (MPa)			Young's modulus ^b (MPa)		
	PU	PVAc	PMMA	PU	PVAc	PMMA	PU	PVAc	PMMA
Series I									
MND65	15.2 (0.4) ^c	8.8 (0.7)	8.0 (0.5)	21.5 (2.0)	13.7 (1.1)	4.1 (0.2)	549 (30)	634 (39)	699 (47)
MND25	14.7 (0.7)	10.5 (0.6)	9.6 (0.6)	33.2 (2.6)	14.7 (1.0)	5.4 (0.4)	469 (33)	552 (50)	578 (45)
Series II									
MA-PG	13.0 (0.6)	11.6 (0.4)	10.7 (0.5)	21.6 (1.1)	18.2 (1.0)	13.8 (1.4)	356 (22)	453 (39)	530 (29)
MA-PA-PG	19.3 (0.5)	12.4 (0.3)	12.1 (0.4)	31.2 (1.7)	26.4 (1.6)	18.5 (1.3)	393 (29)	488 (33)	551 (32)
MA-IPA-PG	16.3 (0.4)	13.6 (0.2)	12.9 (0.7)	36.5 (2.2)	36.1 (2.0)	22.8 (0.9)	478 (27)	510 (42)	568 (41)
Series III									
MA-PA-PG-DEG(1)	16.5 (0.3)	13.6 (0.3)	13.2 (0.1)	22.7 (0.9)	21.9 (1.1)	17.7 (1.2)	385 (27)	401 (29)	525 (40)
MA-PA-PG-MPDiol	15.2 (0.3)	13.7 (0.4)	13.5 (0.3)	32.8 (0.8)	24.0 (1.2)	20.5 (0.8)	422 (34)	457 (32)	575 (45)
MA-PA-PG-NPG	15.0 (0.2)	14.0 (0.4)	13.6 (0.4)	35.8 (1.2)	31.9 (0.7)	24.4 (0.8)	434 (22)	444 (30)	561 (47)
MA-PA-PG-DEG(2)	16.4 (0.4)	14.0 (0.4)	13.3 (0.4)	17.6 (0.8)	16.4 (1.0)	14.3 (0.5)	340 (—)	357 (—)	473 (—)
MA-PA-PG-DEG(3)	19.5 (0.5)	17.7 (0.4)	16.6 (0.3)	25.7 (1.2)	24.1 (1.1)	18.6 (1.0)	366 (—)	417 (—)	543 (—)

^aThe sample mean of five measurements was reported. For each measurement, a composite of 10 specimens was used, and the measured value was divided by 10

^bThe sample mean of 10 measurements was reported

^cThe values in parentheses are the maximum deviation from the sample means

Reduction in the degree of C=C unsaturation by introduction of more PA in the UP backbone (from 2:3 to 1:2) could decrease the tensile strength (i.e. MA-PA-PG-DEG(2) < MA-PA-PG-DEG(1)), which shows the reverse trend to that seen in the second series of UP resins. The tensile strength of cured samples would be increased with increasing cross-linking density, which is a product of the cross-linkable density prior to curing, as contributed by the C=C bonds in the UP molecule, and the

degree of cross-linking after curing. The decrease of tensile strength for the MA-PA-PG-DEG(2) system simply implies that the increase of the degree of cross-linking, as inferred from the cure conversion in *Table 3*, could not make up for the decrease of cross-linkable density in comparison to the MA-PA-PG-DEG(1) system, leading to a lower cross-linking density after curing for the former system.

Increasing the UP molecular weight could lead to an increase of tensile strength (i.e. MA-PA-PG-DEG(3) >

MA-PA-PG-DEG(1)). This would be due to the molar ratio of styrene consumed to polyester C=C bonds reacted deviating less from (less than) 2:1 in the major continuous phase (phase P₁ in Figure 1c, d) during curing for the MA-PA-PG-DEG(3) system, leading to a higher tensile strength for that phase. (The tensile strength would also reach a maximum at a molar ratio of 2:1 for the neat UP resins according to our previous research.)

Effects of UP chain stiffness and network compactness on Young's modulus

Based on the iso-strain model in Figure 1c and d, Young's modulus of the sample would be dominated by $(1-\lambda)E_{P_1}$, since the moduli of phases R, P₂ and P₃ multiplied by their corresponding volume fractions would generally be much smaller than that of phase P₁ multiplied by its volume fraction (i.e. $(1-\lambda)E_{P_1}$), where E_{P_1} is Young's modulus of the major continuous phase.

Table 4 also shows the effects of UP chemical composition and structure on Young's modulus for cured samples. For a fixed UP resin, Young's modulus would be highest for the PMMA-containing sample, followed by PVAc- and PU-containing samples, which reveals that a less compatible styrene/UP/LPA system could result in a higher Young's modulus after curing. Since Young's modulus represents the extent of resistance to deformation for a sample in the initial stage of tensile testing, during which the sample would be unbroken, it would be connected with the degree of tightness of the network rather than the degree of cross-linking of the sample. For styrene/UP/LPA systems, a higher degree of phase separation during curing would lead to a lower styrene content in the continuous phase of cross-linked polyester (phase P₁ in Figure 1c, d). A lower average cross-link length of styrene and a more compact network in that phase would result after curing, which, in turn, could lead to a higher Young's modulus for the whole sample. Furthermore, increasing T_g of the LPA could also enhance Young's modulus of cured samples (T_g (PMMA) > T_g (PVAc) > T_g (PU)), due to the contribution of ξE_R (Figure 1c, d).

For the MA-NPG-DEG systems (series I), Young's modulus was higher for MND65 than for MND25, which exhibited a reversed trend to that of the tensile strength. This is because MND65 would be much more coiled than MND25 during curing, due to a higher content of flexible DEG in the backbone of the former, leading to a higher concentration of polyester C=C bonds in the reacting systems and a more compact network after curing, and, in turn, a higher Young's modulus.

In contrast, Young's modulus showed the same trend as the tensile strength for the MA-PG type systems (series II); modification of UP by PA or IPA could increase the chain stiffness of UP and hence increase Young's modulus.

As for the third series of UP resins, introduction of a more rigid glycol in the UP backbone could result in a higher Young's modulus (i.e. MA-PA-PG-NPG > MA-PA-PG-MPDiol > MA-PA-PG-DEG(1)), which would be due to the increase of UP chain stiffness. Modification of UP by NPG was more effective than that by MPDiol for the PU system, while the trend was reversed for the PVAc and PMMA systems. This is because the larger the polarity difference between UP and LPA, the lower the compatibility of the styrene/UP/LPA system, leading to a higher Young's modulus, as mentioned earlier. (The decreasing order of molecular polarity would be PU > MA-PA-PG-DEG(1) > MA-PA-PG-MPDiol > MA-PA-PG-NPG > PVAc > PMMA.)

Reduction of C=C unsaturation by introduction of more

PA in the UP backbone would decrease Young's modulus (i.e. MA-PA-PG-DEG(2) < MA-PA-PG-DEG(1)), which shows the reverse trend to those of the second series UP resins. This is due to the decrease of cross-linkable density for the MA-PA-PG-DEG(2) system, resulting in a looser network structure after curing, and, in turn, a reduction in Young's modulus.

Increasing the UP molecular weight could lead to a decrease of Young's modulus for the PU system (i.e. MA-PA-PG-DEG(3) < MA-PA-PG-DEG(1)), while the trend was reversed for the PVAc and PMMA systems. Increasing the UP molecular weight would lead to a decrease in the phase separation rate during curing and, in turn, less deviation from a molar ratio of 2:1, and a higher volume fraction in the major continuous phase, as mentioned earlier. Experimental results of Young's modulus imply that, for the PU system, the former effect, leading to a less compact network therein (i.e. a lower E_{P_1} for the MA-PA-PG-DEG(3) system), would be more significant than the latter one, while for the PVAc and PMMA systems, the latter effect (i.e. a higher $(1-\lambda)$ for the MA-PA-PG-DEG(3) system), as evidenced by the scanning electron micrographs (compare Figure 2d and Figure 4b; Figure 2g and Figure 4c), would be more pronounced.

CONCLUSIONS

The effects of UP chemical composition and structure on the mechanical properties of styrene-cross-linked low-shrink polyester matrices containing PU, PVAc and PMMA have been investigated by an integrated approach of static styrene/UP/LPA ternary phase characteristics-cured sample morphology-cure conversion-property measurements. The mechanical properties generally depend not only upon the chain characteristics of UP, such as chain stiffness and cross-linkable density of C=C bonds, but also the polarity difference between UP and LPA, which would affect the cured sample morphology, and the molar ratio of styrene consumed to polyester C=C bonds reacted in the major continuous phase of styrene-cross-linked polyester as a result of phase separation during curing.

Pertinent introduction of a benzene ring structure, such as PA and IPA, and a rigid component, such as MPDiol and NPG, into the UP backbone could enhance the chain stiffness of the polyester skeleton in the styrene-cross-linked polyester network, leading to favourable effects on the tensile strength and Young's modulus. On the other hand, successive reduction in the degree of C=C unsaturation by introducing more PA in the UP, from 2:3 to 1:2 for instance, could lower the cross-linkable density, leading to adverse effects on tensile strength, yet could increase the elastic active chain length of the polyester, leading to favourable effects on impact strength.

For styrene/UP/LPA systems, as the UP chemical composition and structure varies, a concomitant variation in the polarity difference between the UP and LPA would result. In general, the smaller the polarity difference, the more compatible the styrene/UP/LPA system, resulting in better interfacial adhesion between the cross-linked polyester phase and the LPA phase, and a less negative deviation of the molar ratio of styrene consumed to polyester C=C bonds reacted from a molar ratio of 2:1 in the major continuous phase. The former effect would be favourable for impact strength, while the latter, based on Takayanagi's mechanical models, would be favourable for tensile strength due to a higher cross-linking density in that phase, but could

be detrimental to Young's modulus due to an inadequate tightness of the polyester network therein.

Increasing the UP molecular weight would lead to a decrease in the phase separation rate during curing and, in turn, a less negative deviation from a molar ratio of 2:1 and a higher volume fraction in the major continuous phase. The former effect would lead to better interfacial adhesion and higher cross-linking density (both favourable for impact strength and tensile strength), but a less compact network (unfavorable for Young's modulus), while the latter effect would be favourable for all of the three mechanical properties mentioned above.

ACKNOWLEDGEMENTS

This work was sponsored by the National Science Council of the Republic of China (NSC 85-2216-E-011-009). Material donation from the Union Carbide Corporation, USA is also greatly appreciated.

REFERENCES

1. Bartkus, E. J. and Kroekel, C. H., *Appl. Polym. Symp.*, 1970, **15**, 113.
2. Atkin, K. E., in *Sheet Molding Compounds: Science and Technology*, Ch. 4, ed. H. G. Kia. Hanser, New York, 1993.
3. Huang, Y. J. and Jiang, W. C., *Polymer*, 1998, **39**, 6631.
4. Hsu, C. P., Kinkelaar, M., Hu, P. and Lee, L. J., *Polym. Eng. Sci.*, 1991, **31**, 1450.
5. Huang, Y. J. and Su, C. C., *J. Appl. Polym. Sci.*, 1995, **55**, 323.
6. Huang, Y. J. and Liang, C. M., *Polymer*, 1996, **37**, 401.
7. Lam, P. W. K., *Polym. Eng. Sci.*, 1989, **29**, 690.
8. Bucknall, C. B., Partridge, I. K. and Phillips, M. J., *Polymer*, 1991, **32**, 786.
9. Park, M. B. C. and McGarry, F. J., *48th Ann. Conf. Compo. Inst.*, Vol. 10B. SPI, 1993.
10. Pattison, V. A., Hindersinn, R. R. and Schwartz, W. T., *J. Appl. Polym. Sci.*, 1974, **18**, 2763.
11. Pattison, V. A., Hindersinn, R. R. and Schwartz, W. T., *J. Appl. Polym. Sci.*, 1975, **19**, 3045.
12. Jiang, W. C., M.S. thesis, National Taiwan Institute of Technology, 1996.
13. Huang, Y. J. and Su, C. C., *J. Appl. Polym. Sci.*, 1995, **55**, 305.
14. Huang, Y. J. and Su, C. C., *Polymer*, 1994, **35**, 2397.
15. Takayanagi, M., Imada, K. and Kajiyama, T., *J. Polym. Sci., Part C*, 1966, **15**, 263.
16. Ward, I. M. and Hadley, D. W., *An Introduction to the Mechanical Properties of Solid Polymers*, Ch. 8. Wiley, New York, 1993, p. 154.
17. Sperling, L. H., *Introduction to Physical Polymer Science*, 2nd edn, Ch. 10. Wiley, New York, 1992, p. 464.
18. Cook, W. D. and Delatycki, O. J., *J. Polym. Sci., Polym. Phys. Edn*, 1974, **12**, 2111.