Semiinterpenetrating Polymer Network Latexes via Concentrated Emulsion Polymerization

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SYNOPSIS

Latexes of semiinterpenetrating polymer networks (SIPN) of polyurethane (PU) and poly(methyl methacrylate) (PMMA) were prepared via the concentrated emulsion polymerization. In this procedure, a partially cross-linked PU was first prepared in a low polarity solvent from the appropriate precursors. Subsequently, MMA and an initiator were introduced into the solution, and the solution was used as the dispersed phase of a concentrated emulsion in water. Finally, SIPN latexes were obtained via the polymerization of the concentrated emulsion. For comparison purposes, SIPN materials have been also prepared via bulk polymerization. The studies with differential scanning calorimetry and transmission electronic microscopy showed that partial interpenetration was achieved in the SIPN latexes. The tensile behavior and particle morphology of the SIPN materials were investigated by changing the proportion of PU, the molar ratio of NCO/OH, the theoretical cross-link density, and the concentration of the initiator. The SIPN latexes prepared possess a high toughness. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) constitute a special type of polymer blends that combine two networks. If only one of the two components is in the form of a network while the other one is in the form of a linear polymer, the composite is called a semi-IPN or SIPN. Sperling[1,2] and Frisch[3] and their coworkers demonstrated that in many cases the interpenetration of the two phases yields materials with new or enhanced properties. A number of methods have been developed to produce IPNs, such as latex blending,[4,5] sequential polymerization,[6,7] and simultaneous polymerization.[8,9] A large number of useful IPN materials have been produced by coupling various polymers. Among the coupled polymers, IPNs or SIPNs based on polyurethane (PU) and poly(methyl methacrylate) (PMMA) have received a lot of attention because they can find ap-

plications as structural,[10] energy damping,[11,12] and biomaterials.[13] Allen[14-18] and Meyer[10,11,19-21] and their coworkers have thoroughly investigated the PU/PMMA IPNs and shown that they exhibit improved impact and shear resistance. However, the PU/PMMA IPN materials were exclusively prepared by the bulk polymerization method, which produces bulk materials difficult to process. It is clear that if IPN materials could be prepared in the form of latexes, which are more easily processable,[4,22] their usefulness will be increased. However, the conventional pathway to IPN latexes, namely the seed latex method, is not suitable for the PU/PMMA system because the isocyanate, which is a necessary precursor in the formation of PU, reacts rapidly with water. Hence water cannot be used as a reaction medium. Furthermore, the polymerizations of PU and PMMA occur via different mechanisms, namely by step addition and free radical polymerization, respectively, and consequently the seed method cannot be employed.

In this study, a recently developed procedure, based on concentrated emulsions,[23,24] was employed to prepare PU/PMMA SIPN latexes. A concentrated emulsion differs from the conventional emul-

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Table I Chemicals Used

Chemicals	Description	Code
Diols	Poly(propylene glycol) diol MW	
	725	PPG725 II
	1000	PPG1000 II
	2000	PPG2000 II
	Polybutadiene diol MW = 4900	
Triols	Poly(propylene glycol) triol MW	
	725	PPG725 III
	1500	PPG1500 III
	3000	PPG3000 III
Isocyanate	Toluene-2,4-diisocyanate, 80% remainder 2,6 isomer	TDI
Catalyst	Dibutyltin dilaurate, 95%	DBTL
Monomer	Methyl methacrylate, 99%	MMA
Initiator	Azobisisobutyronitrile	AIBN
Surfactant	Dodecyl sulfate sodium salt, 70%	SDS
Solvents	Chloroform, 99%	
	Toluene, 99%	

Purchased from Aldrich.

sion in that the volume fraction of the dispersed phase is larger than 0.74, which represents the most compact arrangement of spheres of equal size, and can be as large as 0.99. At high volume fractions, the dispersed phase is in the form of polyhedral droplets separated by a network of thin films of the continuous phase. PU/PMMA SIPN materials were also prepared via simultaneous bulk polymerization for comparative purposes.

In the proposed procedure a partially cross-linked PU polymer was first prepared in a solvent (chloroform). Then, the MMA monomers as well as an initiator were introduced and the system thus obtained was used as the dispersed phase of a concentrated emulsion in water. SIPN latexes were prepared via the polymerization of the concentrated emulsion. It is important in the first step, when the PU is prepared, that the cross-linking of the PU is moderate. In this manner only, the viscosity of the system also remains moderate, and the dispersion in water, to generate a concentrated emulsion, is possible.

EXPERIMENTAL

Materials

The chemicals employed are listed in Table I. MMA was distilled before use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. The other compounds were used as received. Water was deionized and distilled.

Preparation Procedure

Concentrated Emulsion Polymerization

The preparation was carried out in two steps. The PU precursors [poly(propylene glycol) (PPG) diol and triol, and [toluene-2,4-diisocyanate (TDI)] were mixed with a solvent (usually chloroform) in a test tube at room temperature. In order to increase the hydrophobicity of the system and provide contrast in the transmission electron microscopy (TEM) study, 2 g polybutadiene diol/100 g of the PPGs was incorporated. After the catalyst dibutyltin dilaurate (DBTL) (1 g/100 g of PU precursors) was added to the system, the tube was introduced into a water bath at 60°C to allow the PU formation, and kept for a time shorter by half an hour than the time needed for gelation to occur. This ensures that enough cross-linking has taken place, without being too advanced for the viscosity of the system to become exceedingly high. After the PU solution was cooled to room temperature, the MMA monomer as well as the initiator (AIBN) were introduced in various amounts, and the solution was kept at room temperature for more than 12 h. While its viscosity greatly increased, it remained in a range suitable to be dispersed as the dispersed phase of a concentrated emulsion. The concentrated emulsion was prepared as follows. An aqueous solution of sodium dodecyl sulfate (SDS) (10 wt %) was placed in a single neck 100 mL flask provided with a mechanical stirrer. The above solution was added dropwise with a syringe into the flask with vigorous stirring in the lat-

ter. The volume fraction of the SDS aqueous solution was 0.15 of the whole system. The whole addition process lasted about 15 min, and took place at room temperature. The gel-like concentrated emulsion thus formed was additionally stirred under a flow of nitrogen for 15 min and finally transferred to a tube of 30 mL capacity. The tube was sealed with a rubber septum and shaken under nitrogen flow for 10 min. The tube was finally introduced into a water bath at 60°C to carry out the polymerization of MMA, which lasted 48 h. The product thus obtained was then washed with methyl alcohol in an extractor for 24 h and dried in a vacuum oven for another 24 h.

Simultaneous Bulk Polymerization

The reactants (PU precursors, MMA, and initiator, free of DBTL and solvent) were mixed in a tube, which was introduced into a Cole Parmer ultrasonic mixer, at 60°C, for 3 h. After 3 h the viscosity of the system became so high that further mixing was no longer possible. Consequently, the tube was transferred into a water bath of 60°C where it was kept for 48 h.

Thermal Transition Temperatures

The thermal transitions of the samples were measured by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC instrument. Each sample was heated from −70 to 210°C, with a heating rate of 10°C/min.

Tensile Testing

Powders of the products of the concentrated emulsion polymerization, or bulk material for the products of bulk polymerization, were hot pressed in a Laboratory Press (Fred S. Carver, Inc.) at 180°C for 3–5 min, and then cooled to room temperature. The sheets thus obtained were cut to the size required

by the ASTM D.638-58T. The tensile testing was conducted at room temperature, with an Instron Universal Testing Instrument (model 1000). The elongation speed of the instrument was 20 mm/min.

TEM

The phase morphology was examined by TEM (Philips T-400). The samples were first thermopressed in the same way as for tensile testing, then sectioned with an ultramicrotome, and stained with OsO_4.

Scanning Electron Microscopy (SEM)

The particle morphology was examined by SEM (Hitachi S-800).

RESULTS AND DISCUSSION

Gelation Time of PU

As already noted, the polymerization of PU must be halted below gelation, otherwise the system acquires such a high viscosity that it cannot be dispersed to generate a concentrated emulsion. The effects of the concentrations of the PU precursors as well as the temperature on the gelation time is summarized in Table II. Gelation occurred when the solution lost its flowability. As expected, the time of gelation increases with an increasing amount of solvent. The gelation time should be long enough to allow for the preparation of the concentrated emulsion. On the basis of the gelation experiments we selected a volume of the solvent that was twice as large as the volume of the precursors, and 60°C as the reaction temperature. Under these conditions the system exhibits a suitable viscosity, which is not too high to impede the generation of a concentrated emulsion.

Table II   Gelation Time (min) for Various PU Polymerization Systems

| Vol. Ratio of Solvent/PU Precursors	Chloroform ($R = 0.9$)		Chloroform ($R = 1.0$)		Toluene ($R = 1.0$)	
	Room Temp.	60°C	Room Temp.	60°C	Room Temp.	60°C
1.0	630	58	550	55	540	54
1.5	1050	97	960	94	910	90
2.0	2580	270	2340	252	2280	245
3.0	NG	1500	NG	1350	NG	1300

PU precursors: PPG725II/PPG3000III weight ratio = 6/4. R = molar ratio of isocyanate/hydroxyl groups. NG, no gelation.

Table III   Thermal Transition for PU/PMMA SIPNs

PU/PPMMA Wt Ratio	NCO/OH Molar Ratio	PPG Composition 725II/3000III Wt Ratio	M_c	Transition Range (°C)
1/3	1.0	6/4	5000	75–110
1/3	1.0	4/6	3333	70–105
1/3	1.1	6/4	5000	80–110
1/3	1.1	4/6	3333	85–115
1/2	1.0	6/4	5000	50–75
1/2	1.0	4/6	3333	50–90
1/2	1.1	6/4	5000	55–90
1/2	1.1	4/6	3333	55–95

DSC Measurements

Instead of the sharp transitions of the individual polymer species, a diffuse transition region was observed on each of the DSC diagrams. This is typical for the interpenetration or semiinterpenetration structures. Because of the interpenetration, the segments of different polymers are entangled and move together. Consequently, a transition range between the glass-transition temperatures (T_gs) of the two polymers will be generated. Indeed, the T_g of PPG[10] is −60°C and that of PMMA[25] is 115°C and the transition ranges, listed in Table III, are located between 50 and 115°C. Although these transitions cannot be ascribed to a particular phase structure, the temperature shift indicates some interpenetration. The effect of some of the parameters should be noted. The PU/PMMA weight ratio has a major effect on the transition temperature. The starting temperature of the transition for samples with a PU/PMMA weight ratio of 1/3 is by about 25°C higher than that with a ratio of 1/2. Because the PMMA segments are much stiffer than those of PPG, the greater the number of PMMA segments included, the higher the transition-starting temperature. The NCO/OH molar ratio has a minor effect. The samples with NCO/OH = 1.0 have a somewhat lower transition-starting temperature than those with NCO/OH = 1.1. From the investigation of the mechanical properties, we concluded that the samples with a ratio NCO/OH = 1.0 provide the highest toughness, hence probably the best interpenetration. Consequently, a lower starting transition temperature is associated with a better interpenetration. The presence of a transition range was also reported by Klempner and Frisch[26] who attributed it also to the physical interpenetration of the two polymer chains.
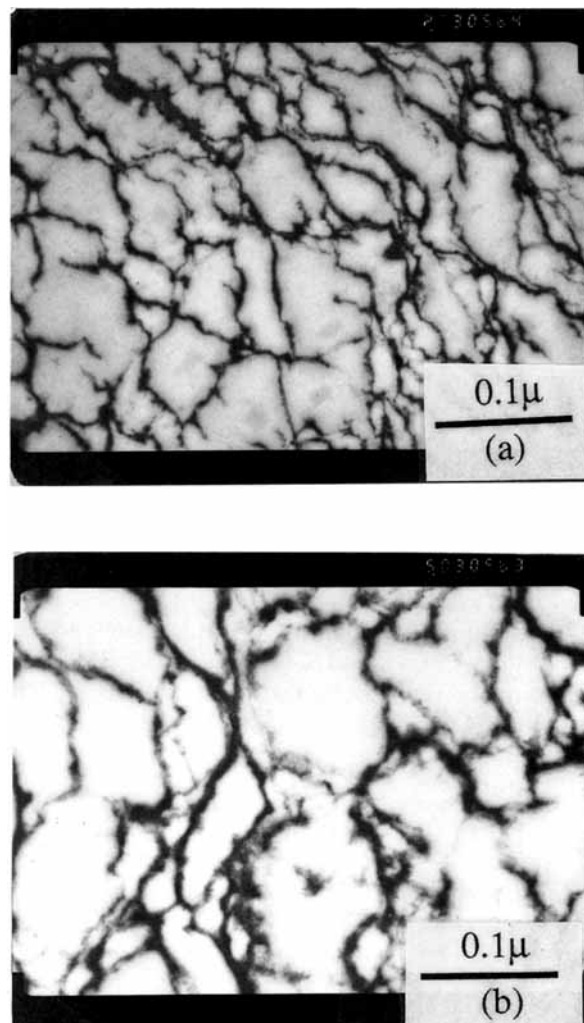
Figure 1   Phase morphology of PU/PMMA SIPN latexes, NCO/OH molar ratio: (a) 1.0 and (b) 0.8. PU composition: PPG725II/PPG3000III weight ratio = 6/4, PU/PMMA weight ratio = 1/2 [AIBN] = 1 g/100 g MMA.

The theoretical cross-linking density, expressed in terms of the average molecular weight, M_c, between two successive cross-linked points, seems not to play a major role regarding the transition temperature. The data in the lower part of Table III show a somewhat broader transition range for a lower M_c.

Phase Morphology

The TEM micrographs of the SIPN latexes are presented in Figure 1, where the black regions represent the polybutadiene which was included in PU, because in the present systems only the polybutadiene can be stained by OsO_4. Considering that the white regions are largely occupied by PMMA, the size of the PMMA domains for a sample with NCO/OH = 1.0 [Fig. 1(a)] is 50–100 nm, but is somewhat larger for NCO/OH = 0.8 [Fig. 1(b)]. As previously reported,[27] in such a range of domain sizes, a pronounced toughening is expected to occur.

Stress–Strain Curves

The stress–strain behavior was examined for PU/ PMMA SIPN with various PU/PMMA weight ra-
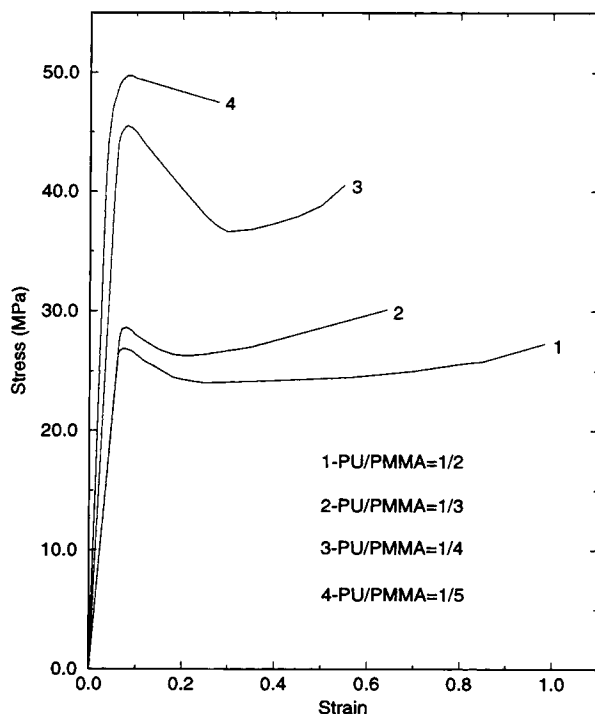
Figure 2 Stress–strain curves of PU/PMMA SIPN latexes for different PU/PMMA weight ratios: (1) PU/ PMMA = 1/2; (2) PU/PMMA = 1/3; (3) PU/PMMA = 1/ 4; (4) PU/PMMA = 1/5. PU composition: PPG725II/ PPG3000III weight ratio = 6/4, NCO/OH molar ratio = 1.0, [AIBN] = 1 g/100 g MMA.
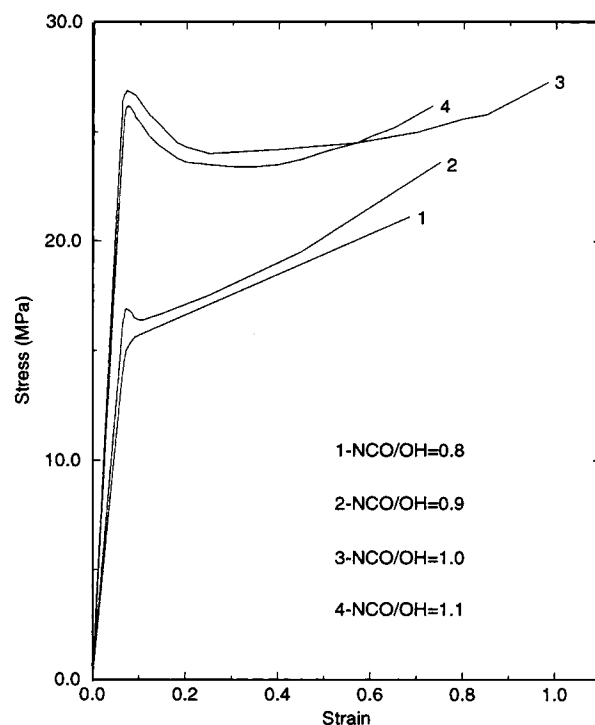
Figure 3 Stress–strain curves of PU/PMMA SIPN latexes for different NCO/OH molar ratios: (1) NCO/OH = 0.8; (2) NCO/OH = 0.9; (3) NCO/OH = 1.0; (4) NCO/ OH = 1.1. PU composition: PPG725II/PPG3000III weight ratio = 6/4, PU/PMMA weight ratio = 1/2, [AIBN] = 1 g/100 g MMA.

tios (Fig. 2), and also for SIPNs with a constant PU/PMMA weight ratio, but various molar ratios (R) of isocyanate to hydroxyl groups (NCO/OH) (Fig. 3). The curves of Figure 2 show that with increasing elastomer (PU) content, SIPN changes from a rather brittle material to a ductile one. The samples with a PU/PMMA weight ratio between 1/4 and 1/2 behave like leather. Whatever the PU content, all the specimens break without necking. Very light stress whitening was observed that suggests that the physical entanglement of the two phases prevents the interfacial decohesion and that the interpenetration is satisfactory. Figure 3 shows that for values of R between 0.9 and 1.1, the tensile curves exhibit a yield point. For lower values of R, the yield point disappears.

Effect of R of Isocyanate to Hydroxyl Group

Table IV shows that the optimum values of R for concentrated emulsion and bulk polymerizations are different. For the bulk polymerization, the highest toughness (measured as the area under the stress–strain curve) and the highest elongation are for R

Table IV Tensile Properties of PU/PMMA SIPN for Various NCO/OH Molar Ratios

NCO/OH Molar Ratio	Concentrated Emulsion Polymerization						Simultaneous Bulk Polymerization					
	Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)		Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)	
	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE
0.8	23.1	0.8	68.3	5.3	13.6	1.4	18.6	1.2	120.3	5.0	18.8	1.7
0.9	23.6	1.2	75.0	7.1	15.2	1.4	20.7	0.9	125.7	6.5	21.9	2.0
1.0	27.3	2.4	98.4	7.7	20.8	2.1	20.4	0.6	75.2	1.7	16.2	0.7
1.1	26.2	1.9	73.4	5.5	16.9	1.1	20.6	0.8	51.2	5.8	10.4	0.9

PU composition: PPG725II/PPG3000III wt ratio = 6/4, PU/PMMA wt ratio = 1/2, [AIBN] = 1 g/100 g MMA. SE, standard error.

= 0.9; for the concentrated emulsion polymerization they are for R = 1.0. For bulk polymerization, the increase of R above 0.9 does not change the tensile strength, but the elongation at break point and the toughness decrease sharply. For the samples prepared via the concentrated emulsion method, the change in R moderately changes the tensile strength and somewhat more strongly the elongation and toughness. Consequently, the effect of R in the concentrated emulsion method is less strong than in bulk polymerization. Because part of the isocyanate groups are consumed in side reactions with water, the optimum value of R is a little higher for the concentrated emulsion method.

It was reported[11,14] that, for bulk polymerization, a ratio NCO/OH of 1.1–1.2 constitutes the optimum value, while the value determined by us was R = 0.9.

Some differences in the PU precursors are probably responsible for the different results.

Effect of Concentration of Initiator (AIBN)

The variation of tensile strength, elongation at break, and toughness for a set of SIPN prepared with various amounts of AIBN is presented in Table V. The tensile strength remained substantially constant, over the range investigated, for both kinds of polymerization, the elongation at break of the materials based on the concentrated emulsion method remaining also constant but passing through a maximum for those based on bulk polymerization.

A full interpretation of the above results is difficult, because, even for the simpler linear blends, the contribution of each phase to the mechanical

Table V Tensile Properties of PU/PMMA SIPN for Various AIBN Concentrations

[AIBN] (g/100 g MMA)	Concentrated Emulsion Polymerization (R = 1.0)						Simultaneous Bulk Polymerization (R = 0.9)					
	Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)		Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)	
	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE
0.6	32.7	3.1	68.3	5.0	17.9	2.4	26.6	2.5	71.8	3.7	16.0	3.0
0.8	34.6	2.9	72.5	6.6	20.8	1.8	26.9	3.4	98.3	4.8	21.8	4.8
1.0	33.7	1.7	74.2	4.9	20.7	2.7	22.7	1.6	110.8	6.1	22.2	2.6
1.2	35.0	3.3	73.8	4.4	20.7	3.1	23.1	0.9	88.0	7.5	19.3	1.9

PU composition: PPG1000II/PPG3000III wt ratio = 2/1, PU/PMMA wt ratio = 1/3. SE, standard error.

Table VI Tensile Properties of PU/PMMA SIPN for Various Values of M_c

PU Composition Wt Ratio of PPG725II/ PPG3000III	M_c	Concentrated Emulsion Polymerization (R = 1.0)						Simultaneous Bulk Polymerization (R = 0.9)					
		Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)		Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)	
		Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE
3/7	2850	24.7	2.1	35.6	2.7	7.5	1.3	20.5	1.8	43.5	3.2	8.7	1.8
4/6	3333	25.2	1.2	50.7	4.4	10.6	1.9	20.9	1.4	58.1	5.4	11.4	2.5
5/5	4000	24.0	1.5	97.2	7.0	19.7	2.6	17.8	0.9	85.7	6.9	14.3	3.1
6/4	5000	23.6	1.2	98.4	7.7	20.8	2.1	20.7	1.0	125.7	6.5	21.9	2.0
7/3	6666	24.5	1.2	30.5	2.4	6.0	1.1	21.6	1.2	31.7	1.7	6.2	1.3

PU/PMMA wt ratio = 1/2, [AIBN] = 1 g/100 g MMA. SE, standard error.

properties is not easy to evaluate. Theoretically, higher content of AIBN may result in higher polymerization rates and lower molecular weights. However, the polymerization of MMA is complicated by the autoacceleration (gel) effect[28] in which the viscosity of the medium plays a role. This effect is additionally enhanced in concentrated emulsions. The maximum that appears in the elongation of the samples prepared via bulk polymerization is probably due to the fact that the proper concentration of AIBN provides the proper initial polymerization rate of MMA which matches the rate of PU formation, thus leading to a system with smaller PMMA domains more uniformly distributed. Because in a simultaneous bulk polymerization the formation of polymers is accompanied by phase sep-

aration,[1] only when the rate of MMA polymerization and PU formation are comparable can one avoid the formation of PMMA domains that are too large.

Effect of Theoretical Cross-link Density (M_c)

The effect of the variation of the M_c of the PU on the tensile strength, elongation, and toughness is presented in Table VI. Both the elongation and the toughness are strongly dependent on M_c, but the tensile strength is almost independent. When the PU network is highly cross-linked (low M_c), the SIPNs have a low elongation and low toughness, and the materials are rather brittle. For lightly cross-linked networks (high M_c), both the elongation and the toughness are again low. However, for moderate

Table VII Tensile Properties of PU/PMMA SIPN for Various PU/PMMA WT Ratios

PU/PMMA Wt Ratio	Concentrated Emulsion Polymerization (R = 1.0)						Simultaneous Bulk Polymerization (R = 0.9)					
	Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)		Tensile Strength (MPa)		Elongation (%)		Toughness (kJ/m^3)	
	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE	Ave. Value	SE
1/2	23.6	1.2	98.4	7.7	20.8	2.1	20.7	0.9	125.7	6.5	21.9	2.0
1/3	30.1	1.4	64.2	4.0	16.4	1.7	25.5	2.3	76.4	3.8	17.8	2.3
1/4	40.5	0.9	52.0	4.2	16.8	2.1	33.0	2.2	63.8	3.9	16.8	2.5
1/5	48.8	1.9	27.8	2.6	10.8	1.5	42.2	1.5	32.1	2.6	11.6	1.6

PU composition: PPG725II/PPG3000III wt ratio = 6/4, [AIBN] = 1 g/100 g MMA. SE, standard error.
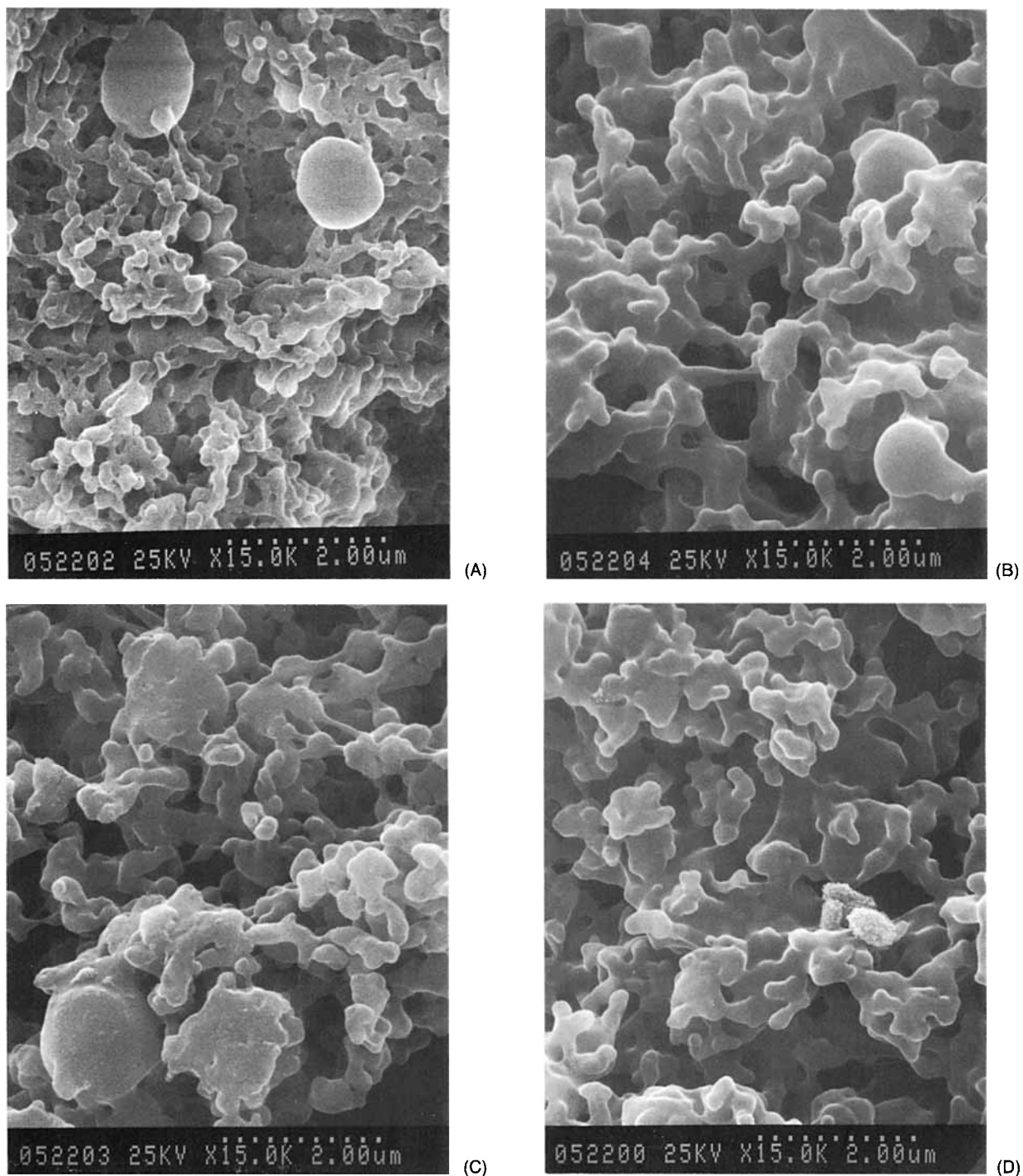
Figure 4   Particles morphologies of SIPN latexes prepared with various solvents: (a) volume ratio of chloroform to PU precursors = 2; (b) volume ratio of toluene to PU precursors = 2; (c) volume ratio of 50/50 v/v chloroform/toluene mixture to PU precursors = 2; (d) volume ratio of chloroform to PU precursors = 3. PU composition: PPG725II/PPG3000III weight ratio = 6/4, PU/PMMA weight ratio = 1/2, [AIBN] = 1 g/100 g MMA, NCO/OH molar ratio = 1.0.

cross-linking, there are maxima in elongation and toughness. The samples prepared by different procedures have somewhat different optimum values for M_c. The samples based on simultaneous bulk polymerization exhibit maxima near $M_c = 5,000$, whereas those based on concentrated emulsion polymerization have maxima between 4,000–5,000. One may note that for $M_c > 5,000$, both the elongation and the toughness show a sharp fall in both cases. This is probably due to the increase in the density of hydrogen bonds, which make the PU chains stiffer.

Effect of PU/PMMA Ratio

The effect of the PU/PMMA ratio upon the tensile strength, elongation at break, and toughness of the SIPNs is presented in Table VII. The tensile strength exhibits a sharp decrease from the value 70 MPa[27] of the unmodified PMMA. The elongation at break increases from its value for PMMA (1–2%) rapidly. Comparing these mechanical properties of the samples prepared via the concentrated emulsion polymerization with those prepared via bulk polymerization, one can note that the former has a higher tensile strength, but a lower elongation at break, the toughness being roughly the same for both. The somewhat different behaviors in mechanical properties can be explained as follows. Because of the presence of water in the concentrated emulsion, a fraction of NCO groups will react with water, and some OH groups at the free ends of the PU molecules will remain unreacted, thus generating defects in the PU network. Because of these defects additional physical entanglements between the PMMA molecules occur and, as a result, the elongation becomes somewhat lower and the tensile strength larger. In addition, in the concentrated emulsion polymerization, because of the gel effect, the average molecular weight of PMMA is higher than in the bulk polymerization, resulting in a higher physical entanglement. Consequently the tensile strength is somewhat higher and the elongation somewhat smaller. The differences in the tensile properties in the polymers obtained by the two procedures are however small because: the polymerizations of the precursors that lead to PU and PMMA are independent processes; and the polymerization of the concentrated emulsion occurs in solution, the PU formed is swollen in the solvent, and MMA penetrates inside and polymerizes there. Thus an SIPN is formed in a manner similar to that generated in simultaneous bulk polymerization.

Morphology of Particles

The micromorphologies of the samples are presented in the SEMs of Figure 4. All samples appear to be composed of microparticles bound together. In a concentrated emulsion, the volume fraction of the dispersed phase, ϕ, is large (in the present case $\phi = 0.85$). The cells of the dispersed phase are therefore tightly compacted together, and the intercell binding and reaction are inevitable. Perhaps the OH end groups of PU in adjacent cells are bridged by the diisocyanate molecules. Several chemical parameters have an influence on the morphology. The effect of different solvents can be seen from Figure 4(a–c), which represent samples prepared with chloroform, toluene, and a 50/50 v/v mixture of chloroform and toluene, respectively. One can see that the particles in (a) are finer than in (b). Chloroform is a good solvent for both PU and PMMA, toluene is a good solvent for PU and MMA monomer, but a less good solvent for PMMA. For this reason, in toluene more PU segments tend to bind together than in chloroform, resulting in a coarser morphology. The sample based on the 50/50 v/v mixture of chloroform and toluene has an intermediary morphology between (a) and (b). A comparison of (a) and (d) shows the effect of the amount of solvent used. In a more diluted system, the size of the particles is larger than in a less diluted one.

CONCLUSION

SIPN latexes of PU/PMMA were prepared via the concentrated emulsion polymerization method. DSC and TEM investigations revealed that semiinterpenetration was achieved in the obtained material. As the relative proportion of PU/PMMA increases, the elongation at the break point and the toughness increase, but the tensile strength falls. The molar ratio of isocyanate to hydroxyl groups (R) affects the elongation at the break point and the toughness of the SIPN. There is an optimum value of R, 1.0 for concentrated emulsion polymerization and 0.9 for simultaneous bulk polymerization, for which the elongation at the break point and the toughness are maxima. There is also an optimum theoretical crosslink density (M_c) for optimum toughness.

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