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ORIGINAL CONTRIBUTION

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Modification of aqueous polyurethanes by forming latex interpenetrating polymer networks with polystyrene

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Abstract A series of latex particles with interpenetrating polymer network structure have been synthesized from waterborne polyurethane (PU) and polystyrene (PS). The effect of PU/PS composition, cross-linking density in the PS domain as well as in PU have been studied in terms of dispersion size, transmission electron microscopy morphology, mechanical and dynamic mechanical properties in addition to swellability in water and toluene of the dispersion cast film. It was found that inverted core (PS)–shell (PU) morphology was well defined and that the domain size as well as the film properties were well controlled by the latex composition and cross-linking density of both phases.

Key words Latex interpenetrating polymer network · Polyurethane · Polystyrene

Introduction

Waterborne polyurethanes (PUs) can be formulated into coatings, adhesives, and finishings for a number of surfaces with little or no solvent and form films at ambient temperature. These are great advantages over the conventional solvent-borne type, and a wide variety of applications have been developed from PU chemistry [1–3].

The unique method of dispersing PUs is with built-in hydrophilic groups, either of ionic or nonionic type. An industrially important class of waterborne PUs is the ionic type, among which the anionic type is dominant [4, 5]. These ionic groups contribute positively to the mechanical strength and the elastomeric character of the materials. However, the hydrophilic nature of the ionic groups provides the materials with poor water and solvent resistance and slow evaporation of water during drying. Basically these properties can be improved by incorporating a minimum ionic content as far as the dispersion is stable and higher cross-linking density as far as the drying temperature does not matter.

Cationic as well as anionic PUs containing polypropylene glycol in their backbone have been modified by grafting acrylate monomers onto the main chains [5]. Recently interpenetrating polymer networks (IPNs) have also been synthesized in aqueous media, and hydrogen bonds of core–shell [6] and damping characteristics [7, 8] of these materials have been reported. A latex IPN has a great advantage in processing over the bulk IPN, where cross-linkings pose a difficulty in melt processing.

We consider the modification of waterborne PUs by forming latex IPNs and semi-IPNs with polystyrene (PS) in a broad range of composition, and the dispersion size, the transmission electron microscope (TEM) morphology, the mechanical and dynamic mechanical properties, and the swellability in water and toluene of the cast film are reported.

Experimental

Materials

1,4-Butanediol (1,4-BG) and poly(propylene glycol) (PPG, $M_n = 2000$ g/mol), which were chain extenders and soft segments in PUs, were dried for 5 h at room temperature and 2 h at 100 °C under vacuum before use. Anionic internal emulsifier (dimethylol propionic acid, DMPA, Aldrich) was purified and dried at 100 °C for 2 h in a vacuum oven. Extra-pure grades of dimethylformamide (DMF) and triethylamine (TEA) were dried over 3-Å molecular sieves before use. 2-Hydroxyethyl acrylate (HEA), styrene, and divinylbenzene (DVB) were purified and dried by fractional distillation under vacuum and stored under an inert atmosphere. Extra-pure grade isophorone diisocyanate (IPDI), dibutyltin dilaulate (DBTDL), and potassium persulfate (KPS) were used as received. Cycloaliphatic diisocyanates are most often used owing to their low reactivity with water.

Synthesis

The basic formulation of PU and latex IPNs and semi-IPNs are given in Tables 1 and 2. The procedures to obtain PU dispersions are available in our earlier works [9, 10] and are shown schematically in Scheme 1. A 500-ml four-necked round-bottomed separable flask equipped with a mechanical stirrer, thermometer, condenser with a drying tube, and N_2 inlet was used as the reactor. The reaction was carried out in a constant-temperature oil bath. IPDI, 1,4-BG, DMPA, PPG, and DBTDL (0.03 wt% based on base PU) were first mixed and reacted at 80 °C to obtain NCO-terminated prepolymer. The stability of the NCO terminated prepolymer against water is essential in a PU dispersion. So, aliphatic or cycloaliphatic diisocyanate (IPDI) is exclusively used in the prepolymer process. Soft segments as well as hard segments of PUs obtained from those materials do not crystallize. In addition, the pendant methyl groups effectively protect carboxylic groups from reactions with diisocyanates. The change in the NCO value during the reaction was determined using a standard dibutylamine back titration method. Then, the NCO-terminated prepolymer was cooled to 60 °C, and TEA and HEA dissolved in DMF (5 wt% based on PU) were added and reacted for 1 h to obtain hydrophilic vinyl terminated prepolymer (HVTP). Since the water addition rate is a critical parameter to obtain a stable dispersion, a tubing pump was used and water was added for 10 min at a constant flow rate. The phenomenon of phase inversion, the viscosity and the conductivity change during the dispersion process are well documented Dieterich [11]. To obtain the latex IPNs or semi-IPNs, HVTPs were first polymerized in the presence of KPS (0.5 wt% based on HVTP), followed by the polymerization of styrene monomers in the cross-linked PUs [12]. The resulting product was a stable dispersion with a solid content of about 25%.

Tests

The swelling of the film in water and solvent was measured by immersing a film in a water and solvent bath at room temperature until the film was in equilibrium with the water and the solvent. The degree of swelling was calculated by

$$\text{Degree of swelling} = 1 + (W_0 - W_\mathrm{b})/d_\mathrm{s}/(W_\mathrm{b}/d_\mathrm{p}) \ , \tag{1}$$

where W_0, W, W_b, d_p, and d_s are the weight of the swelled sample, the initial weight of the sample, the weight of the dried sample after swelling, the density of the sample, and the density of solvent, respectively. To determine the amount of linear PS, films were extracted in toluene and the sol fraction was calculated according to the equation

$$\text{Sol fraction} = \frac{W - W_\mathrm{b}}{W} \ .$$

The particle size of the dispersion was measured using an Autosizer (Malvern IIC). Approximately 0.15 ml emulsion was taken and diluted with deionized water to an appropriate concentration for the measurements, followed by setting the pin hole to 200 μm. The z-average diameters were measured at 25 °C.

The films were prepared by casting the dispersion on a Teflon plate, followed by drying at 80 °C for 5 h. The resulting films were

Table 1 Recipe of polyurethane (*PU*) acrylate anionomer (PU, total solid = 100 g, in moles)

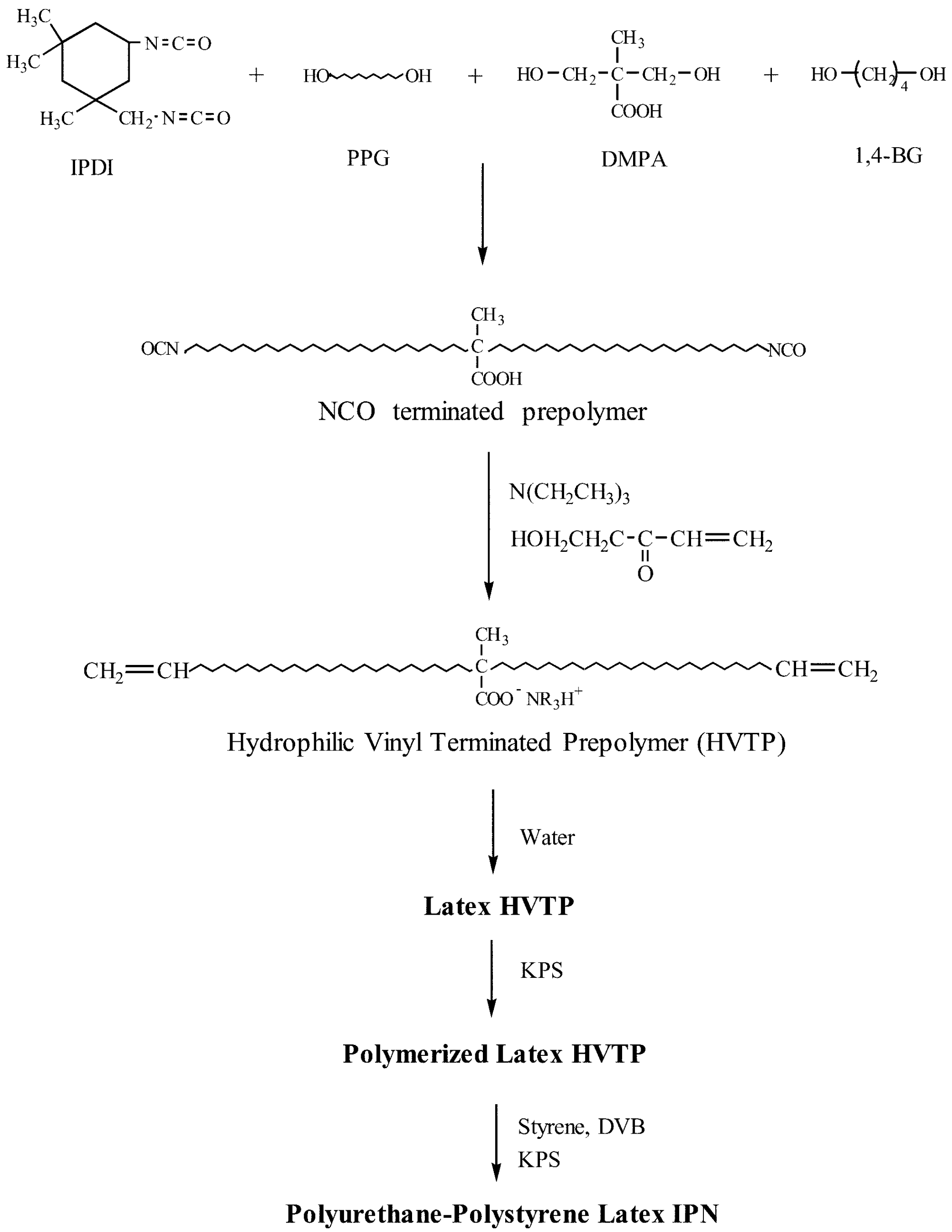
	Poly (propylene glycol) (2000 g/mol)	Dimethylol propionic acid	1,4-Butanediol	Isophorone diisocyanate	Triethylamine	2-Hydroxyethyl acrylate	M_n of hydrophilic vinyl terminated prepolymer[a]
PU-1	3.3	3.0	0	9.3	3.0	6.0	3,000
PU-2	3.3	3.0	1.1	9.6	3.0	4.4	4,000
PU-3	3.3	3.0	1.7	9.8	3.0	3.6	5,000

[a] Determined from $(1 + r)/(1 - r)$, where r is the molar ratio of [dimethylol propionic acid + 1,4-butanediol + poly(propylene glycol)]/isophorone diisocyanate

Table 2 Recipe of PU/polystyrene (*PS*) latex interpenetrating polymer network (*IPN*) and semi-IPN (by weight ratio)

Variable	Sample Code	PU-1 (3000 M_n)	PU-2 (4000 M_n)	PU-3 (5000 M_n)	PS/divinylbenzene
Latex composition	A_1	100			0/0
	A_2	90			10/0
	A_3	80			20/0
	A_4	70			30/0
	A_5	60			40/0
Divinylbenzene content	B_1	70			27/3
	B_2	70			24/6
M_n of hydrophilic vinyl terminated prepolymer	C_1		70		30/0
	C_2			70	30/0

Scheme 1 The synthesis process of polyurethane-polystyrene latex interpenetrating polymer network



then heated overnight in an oven at 60 °C under 2–3 mmHg. Microtensile test specimens were prepared according to ASTM D-1822.

The tensile behavior of the dispersion cast films was measured using a Tinius Olsen tensile tester at a cross-head speed of 500 mm/min, and the average of at least five measurements was taken.

Dynamic mechanical tests for cast films were performed with a Rheovibron (Orientec, DV-01FP) from −100 to 100 °C at 11 Hz, with a sample size of 0.03 × 0.2 × 3 cm. The morphologies of the latex IPN cast film were measured using a TEM (Jeol, JSM-1200 EX IIC). The samples were cut to 100 nm in thickness using a microtome (Reichert-Jung SuperNova), and stained with OsO_4 for over 3 days.

Results and discussion

Latex particle size

The average particle size of the dispersion as a function of PS content is shown in Fig. 1. As the PS content increases from 0 to 40%, the average particle size of the dispersion increases from below 80 to over 120 nm. The increase is primary due to the inclusion of PS in the PU particles to form inverted core–shell morphology. However, the rapid increase with high PS

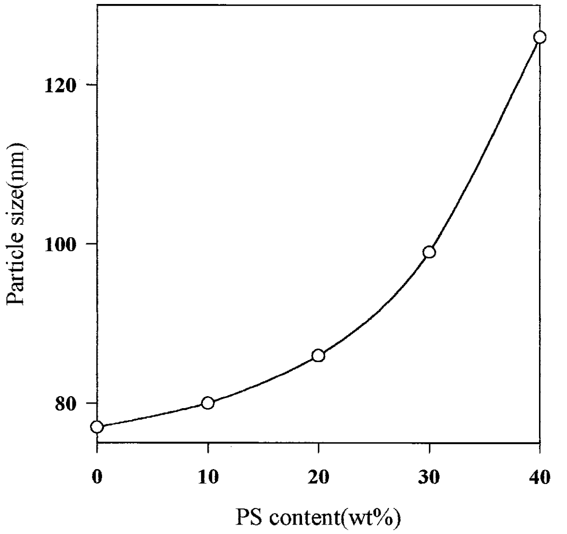


Fig. 1 Particle size versus polystyrene (*PS*) content of latex cast film (A_1-A_5)

contents may imply the instability of a swelled particle with insufficient ionic group content on the surface, leading to particle coalescence.

Film morphology

TEM morphologies of the PU/PS latex cast films are given in Fig. 2. In these micrographs, the bright isolated domains are PS and the dark continuous phase is PU, which is stained with OsO_4. The inverted core (PS)–shell (PU) morphology is obvious, confirming that styrene monomers are polymerized in the core of the latex particles. The average domain size of the cast film is certainly smaller than the latex particles (Fig. 1) when compared for the same condition. This is simply due to the fact that the latex particles include both PU and PS, whereas the domains in the film are only PS. It is seen that the domain size increases with increasing amount of PS and with increasing M_n of HVTP and significantly decreases upon introducing cross-linkings in the PS domains. HVTP is a tetrafunctional prepolymer since it contains a vinyl group (HEA) at both ends, which are subject to a chain extension reaction via a radical mechanism. So, M_n of HVTP corresponds to the molecular weight between cross-linking (M_c) in the PU phases. Therefore, the increase in the domain size with increasing M_n of HVTP is expected owing to the decreased cross-linking density in the PU phase, leading to the decreased number of physical interlockings between PU and PS chains. The decrease in the domain size with increasing number of cross-linkings in the PS domains implies that PU–PS phase separation is physically suppressed owing to the intensive interlockings between PU and PS chains. It seems that control of the cross-linking density in both phases is an effective way to controls the domain size and hence the extent of phase separation.

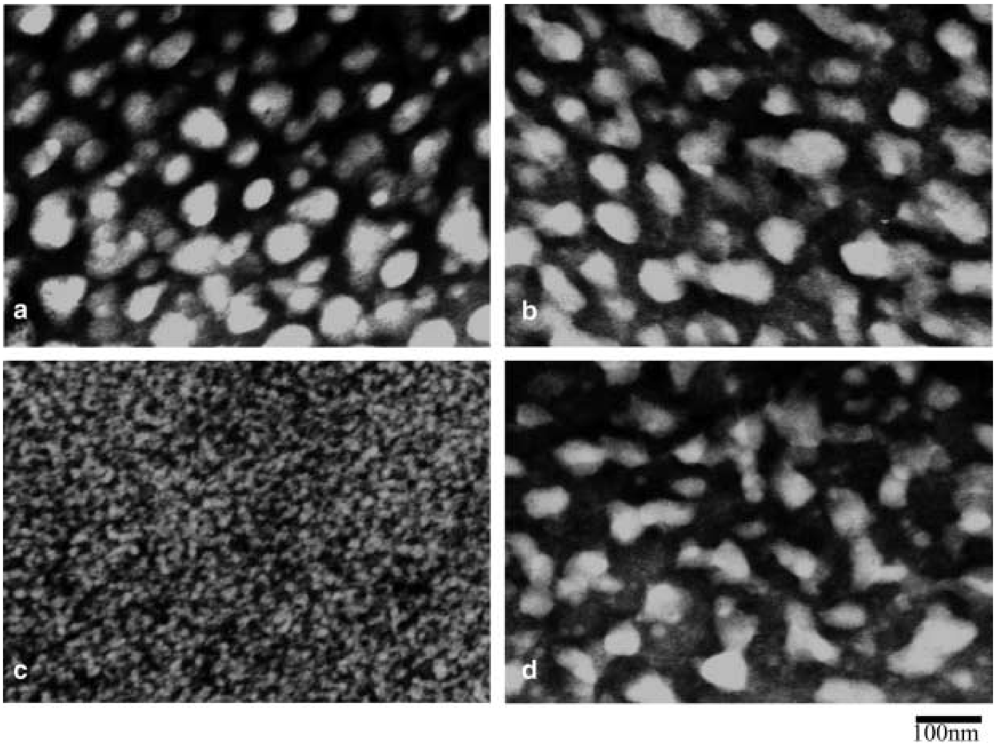


Fig. 2 Transmission electron microscope micrographs of polyurethane (*PU*)/PS latex cast film: **a** A_4, **b** A_5, **c** B_1, **d** C_2

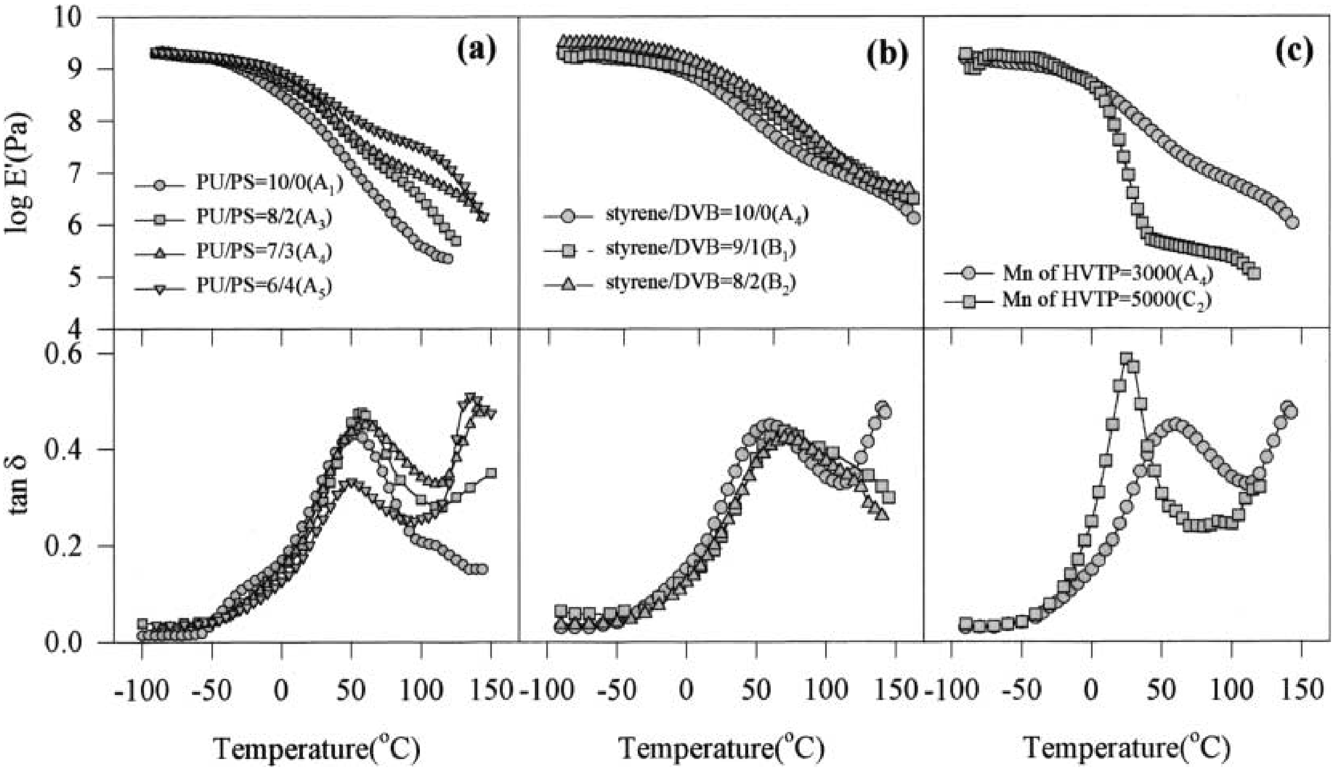


Fig. 3 Storage modulus (E') and tan δ of PU/PS latex cast film: **a** effect of composition (A_1,A_3-A_5), **b** effect of divinylbenzene (*DVB*) content (A_4,B_1,B_2), **c** effect of M_n of hydrophilic vinyl terminated prepolymer (*HVTP*) (A_4,C_2)

Dynamic mechanical properties

The dynamic mechanical properties of PU/PS latex cast films are shown in Fig. 3. The storage modulus (E') increases with the increase in the PS content (Fig. 3a) and the cross-linking density of PS (Fig. 3b) as well as PU (Fig. 3c) phases. Notably, with $M_n = 3{,}000$, the glass–rubber transition occurs over a broad range of temperature. However, with $M_n = 5000$ a sharp drop in the storage modulus at about 30 °C is seen. tan δ of the PU/PS latex cast film generally shows two peaks: one at about 50 °C corresponding to the glass-transition temperature (T_g) of PU and the other at 130 °C corresponding to the T_g of PS. The low-temperature peak moves toward lower temperatures with increasing PS content and increasing M_n of HVTP, probably owing to the increased PU–PS phase separation, and toward high temperatures with increasing DVB content, indicative of suppressed phase separation [13, 14]. However, the variation of low T_g (PU) is much more pronounced with the cross-linking density of PU (M_n of HVTP) than with that of PS. It seems that the T_g of the PU phase is mainly governed by the cross-linking density of the PU phase, although the physical interlockings with PS restrict its segmental motion to some extent.

Mechanical properties

The mechanical properties of the PU/PS latex cast films are shown in Figs. 4 and 5. With the addition of increasing amounts of PS, the tensile modulus and strength of the cast films increase monotonically. Elongation at break also increases from about 150 (PU) to

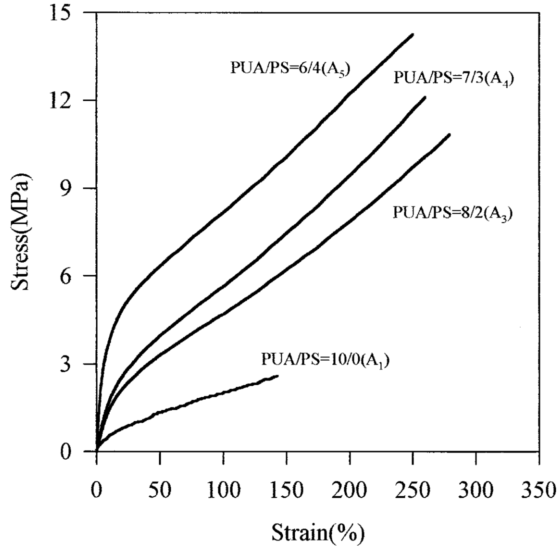


Fig. 4 Stress–strain curve of PU/PS latex cast film versus PS content (A_1,A_3-A_5)

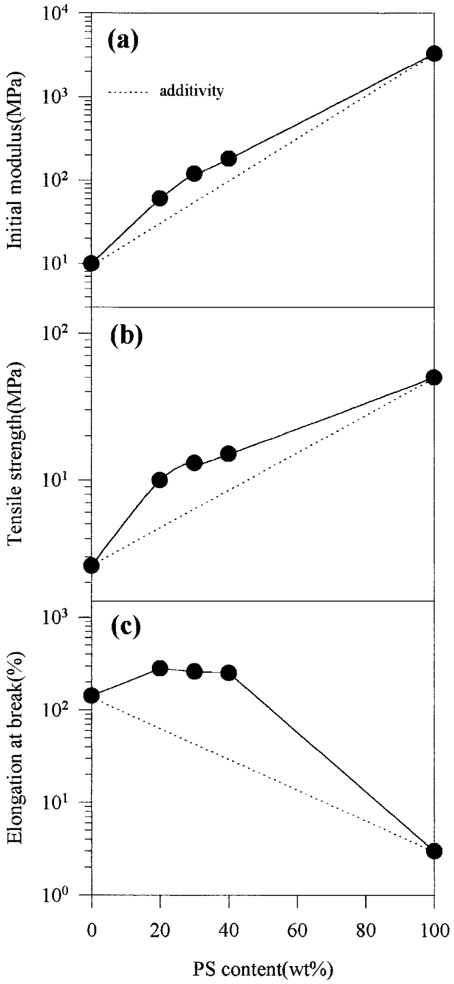


Fig. 5 Additivity of mechanical properties for PU/PS latex cast film (A_1,A_3-A_5,PS); **a** initial modulus, **b** tensile strength, **c** elongation at break

about 250% for PU/PS (8/2), but remains almost constant with further addition of PS.

The PU/PS latex cast films gave a positive deviation in the modulus (Fig. 5a), the strength (Fig. 5b), and the elongation at break (Fig. 5c) from the simple additivity (dotted lines in the figures). The positive deviations in the mechanical properties are caused by the intimate physical interlockings, a typical characteristic of the interpenetrating structure and the extent of phase mixing seemingly governs the extent of the deviations [15, 16].

The effect of DVB content on the tensile behavior of the latex cast film is shown in Fig. 6. As expected, the modulus increases and the elongation at break decreases with increasing DVB content, while the strength remains almost constant. As expected, the modulus and the strength decrease and the elongation at break increases with increasing M_n of HVTP (Fig. 7).

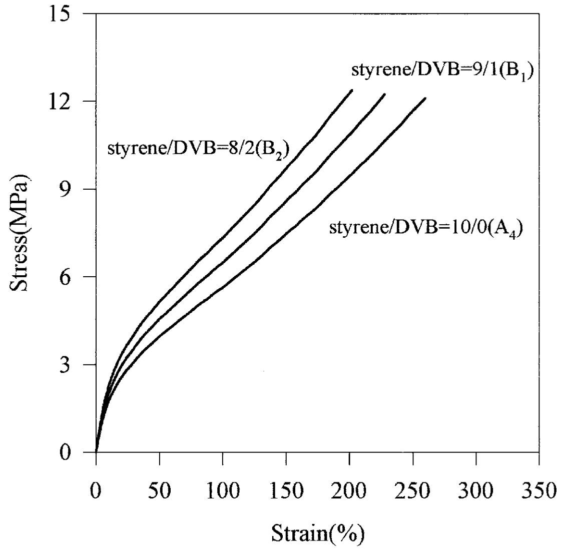


Fig. 6 Stress–strain curve of PU/PS (7/3) latex cast film versus DVB content (A_4,B_1,B_2)

Swelling and extraction

The swelling in water and toluene and the sol fraction in toluene of the latex cast films are shown in Table 3. As expected, the swelling in water generally decreases with increasing PS and DVB content and increases with increasing the M_n of HVTP. The increase in the swelling in water with initial addition of PS to PU is probably due to the interruption of the otherwise homogeneous PU structure with PS. The swelling in toluene, a good solvent for PS, increases with the PS

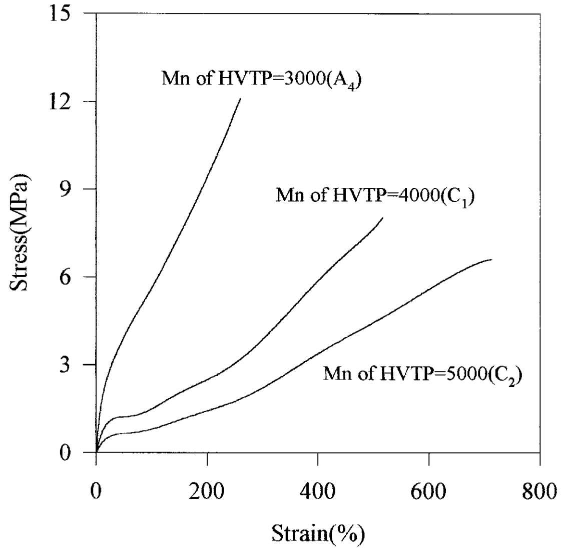


Fig. 7 Stress–strain curve of PU/PS (7/3) latex cast film versus M_n of HVTP (A_4,C_1,C_2)

Table 3 Amounts of swelling and sol fraction of cast films

Variables	Sample code	Swelling in water (%)	Swelling in toluene	Sol fraction in toluene (%)	Remarks
Latex composition	A_1	17.2	2.3	3.8	M_n = 3,000 divinylbenzene = 0
	A_2	22.5	2.4	8.0	
	A_3	24.4	2.9	9.8	
	A_4	19.4	3.1	20.0	
	A_5	13.9	3.7	30.1	
Divinylbenzene content	B_1	14.1	2.3	9.0	PU/PS (7/3) M_n = 3,000
	B_2	13.5	2.0	6.7	
M_n of hydrophilic vinyl terminated prepolymer	C_1	50.3	5.0	29.4	PU/PS (7/3) divinylbenzene = 0
	C_2	62.0	6.3	39.0	

content and the M_n of HVTP and decreases with increasing DVB content. The weight decrease of the films upon extraction in toluene is proportional to the amount of linear PS formed in the IPNs. So, the sol fraction increases with the PS content and the M_n of HVTP and decreases with increasing DVB content.

Conclusions

1. PU/PS latex particles formed well defined core (PS)–shell (PU) morphology, which was effectively controlled by the cross-linking density of the PS phase.
2. PU/PS hybrid latex cast films generally showed two tanδ peaks, each corresponding to the T_g of PU and PS domains, respectively. PU–PS phase separation decreased with increasing cross-linking density of both phases, implying that the phase separation is suppressed by physical interlockings between PU and PS phases.
3. Positive deviations of the mechanical properties showed that the PU/PS hybrids films form intensive interlocking structures between the two components.

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