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Polybutadiene/polystyrene network composites prepared via concentrated emulsion polymerization

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A series of polybutadiene/polystyrene (PB/PS) network composites in the form of latexes were prepared via the concentrated emulsion polymerization method. The polymerization rate and the relative content of the crosslinked species were determined and compared at various polymerization temperatures, concentrations of initiator, and with vinyl-terminated PBs of different molecular weights. The mechanical properties of the composites were studied by tensile testing. The effects of the reactant composition and conversion on the mechanical properties were investigated.

(Keywords: polybutadiene; polystyrene; network composites)

INTRODUCTION

Polybutadiene (PB) has long been employed as a toughener in styrene-based materials. Chains of PB and polystyrene (PS) can be combined in several ways. Dissolving PB in styrene monomers and subsequently polymerizing the solution results in high-impact PS[1,2], in which some of the styrene (St) monomers are grafted onto the PB chains. By connecting PB and PS chains in a head–tail manner[3,4], block copolymers can be generated. Many diblock, triblock and multiblock copolymers are now commercially available. In more complicated cases, styrene, usually together with another monomer, is introduced into a seed emulsion of pre-polymerized PB. The system thus obtained is subjected to further polymerization and a graft copolymer with a core–shell structure is obtained, such as acrylonitrile/butadiene/styrene (ABS) copolymer[5] or methyl methacrylate/butadiene/styrene (MBS) copolymer[6,7], etc. In the present work, PB and PS chains were combined in a different way, i.e. in an AB crosslinked composite[8–11]. The crosslinking can improve the anti-solvent, anti-degradation properties of the materials. However, if the composite is prepared by bulk polymerization, the processability will be poor and its application limited. In order to make the network composite material easily processable, the concentrated emulsion polymerization method was employed to prepare latexes of network composites. Since the crosslinking is limited to each latex, the resultant material possesses flowability.

The concentrated emulsion polymerization method[12,13] was recently developed by this group. A concentrated emulsion has the appearance of a paste, and differs from the conventional emulsion in that the volume fraction ϕ of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangement of spheres of the same size), and may be as high as 0.99. In the present work, a volume fraction $\phi = 0.85$ was employed. This is in contrast with conventional emulsions employed for polymerization[14] for which ϕ is below 0.57. The higher volume fraction of the dispersed phase means a higher yield per unit volume. In a previous publication[15], network latexes from polycaprolactone and poly(methyl methacrylate) were prepared via the concentrated emulsion polymerization method and impact-improved materials were obtained. In the present system (PB/PS), the same method seems to be the proper one to follow. In this system, vinyl-terminated polybutadiene (VTPB) and styrene are employed as precursors of the composite. In the polymerization, three reactions are expected to take place simultaneously: the copolymerization of VTPB and St, the homopolymerization of St and the grafting of St onto the PB chains. The effects of the polymerization conditions on each of the reactions and on the mechanical properties were investigated.

EXPERIMENTAL

Materials

The chemicals employed are listed in *Table 1*. Styrene (St) was distilled before use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Vinyl-terminated polybutadiene (VTPB) and ethyl-terminated polybutadiene (ETPB) were prepared from hydroxy-terminated polybutadiene (PB diol). The other compounds were used as received. Water was deionized and distilled.

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Table 1 Chemicals used (purchased from Aldrich)

Chemical	Description	Code
Diol	PB diol, *MW* = 1200	PB1200
	PB diol, *MW* = 2800	PB2800
	PB diol, *MW* = 4900	PB4900
Triethylamine	99%	TEA
Acryloyl chloride	96%	AC
Propionyl chloride	97%	PC
Monomer	Styrene, 99%	St
Initiator	Azobisisobutyronitrile	AIBN
Surfactant	Sodium dodecyl sulfate, 70%	SDS
Solvent	Toluene, 99%	

Preparation procedures

Preparation of vinyl-terminated PB (VTPB). A solution of PB diol (molecular weight (*MW*) of 4900, 2800 or 1200) in toluene (20 g per 100 ml) was placed in a single-necked flask equipped with a magnetic stirring bar. Triethylamine (TEA) (one mole for each mole of OH groups in the dissolved PB diol) was added to the solution. The flask was sealed with a rubber septum, and the solution subjected to magnetic stirring. Acryloyl chloride (AC) (one mole for each mole of OH groups) was introduced dropwise with a syringe through the rubber septum at room temperature. The OH group reacts with AC to form a vinyl group

$$\mathrm{HO{-}PB{-}OH + 2ClC(O)CH{=}CH_2}$$
$$\longrightarrow \mathrm{2CH_2{=}CHC(O)O{-}PB{-}O(O)CCH{=}CH_2 + 2HCl}$$

The HCl molecules produced in the above reaction react with TEA

$$\mathrm{HCl + NEt_3 \longrightarrow NEt_3HCl}$$

and the formed quaternary ammonium salt remains suspended in the system as a white powder. By removing the white powder through filtration, a toluene solution of VTPB was obtained.

When propionyl chloride was employed instead of AC, the hydrogens of the OH groups were replaced by ethyl groups and ethyl-terminated PB (ETPB) with no terminal functional groups was obtained, which was used for comparison purposes.

Concentrated emulsion polymerization. In the VTPB toluene solutions (0.2 g ml^{-1} toluene), styrene monomers in various proportions and a suitable initiator (AIBN) in various amounts were introduced. The solution thus prepared was used as the dispersed phase of a concentrated emulsion. An aqueous solution of sodium dodecyl sulfate (SDS) (0.05 g g^{-1} water) was first placed in a single-necked flask provided with a mechanical stirrer. Then, the solution containing the VTPB and styrene was added dropwise with vigorous stirring into the flask with a syringe until the volume fraction of the SDS aqueous solution became 0.15. The whole addition process lasted about 15 minutes and took place at room temperature. The paste-like concentrated emulsion thus formed was additionally stirred for 30 minutes under a flow of nitrogen, and finally transferred to a test tube. The tube was sealed with a rubber septum and introduced into a water bath at 60°C (or 50°C) to carry out the copolymerization of styrene and VTPB. After a certain polymerization time, the reactant system was moved out from the test tube and washed three times with methyl alcohol in a beaker and dried in a vacuum oven for 24 hours. The product of concentrated emulsion polymerization was obtained as a white powder. The ratio of the weight of the powder to the original weight of the reactants (styrene and VTPB) was considered as the conversion.

Tensile testing

The powders from the concentrated emulsion polymerization method were thermo-pressed in a Carver laboratory press at 180°C for three to five minutes, and then cooled to room temperature. The sheets thus obtained were cut to the size required by ASTM D.638-58T. The tensile testing was conducted at room temperature with an Instron 1000 universal testing instrument. The elongation speed of the instrument was 20 mm min^{-1}.

Gel content determination

A pre-weighed composite sheet prepared as for tensile testing was immersed in toluene in a test tube for 60 hours. Subsequently, the swollen sheet was retrieved and redried in a vacuum oven for 48 hours to remove the solvent. The ratio of the weight of the remaining sheet to that of the original sheet was taken as the gel content (the crosslinked part of the composite, as a percentage).

RESULTS AND DISCUSSION

Polymerization rate

The polymerization rates of various systems are presented as conversion–time curves in *Figures 1–3*. Several factors affect the polymerization rate.

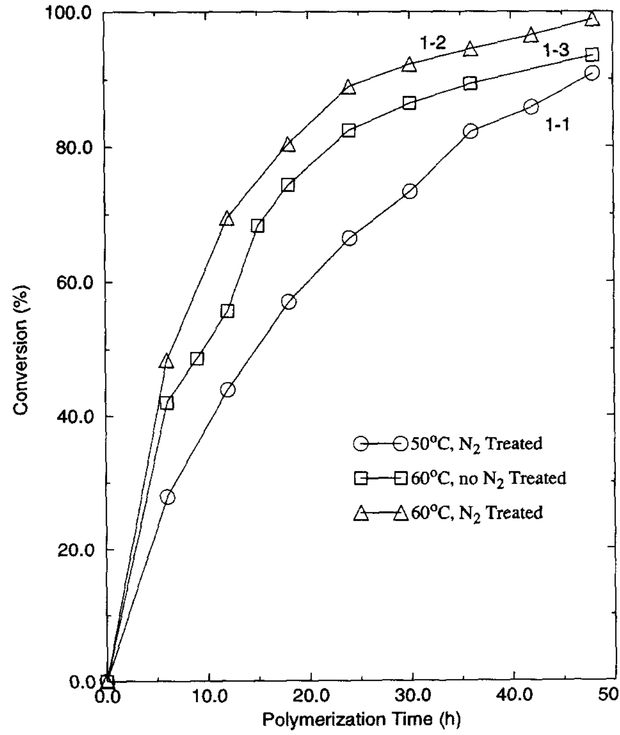

Figure 1 Conversion–time curves for different temperatures (*MW* of VTPB = 2800, [AIBN] = 0.7 g per 100 g St, VTPB/St weight ratio = 2/8): (1-1) 50°C, N_2 treated; (1-2) 60°C, N_2 treated; (1-3) 60°C, not N_2 treated

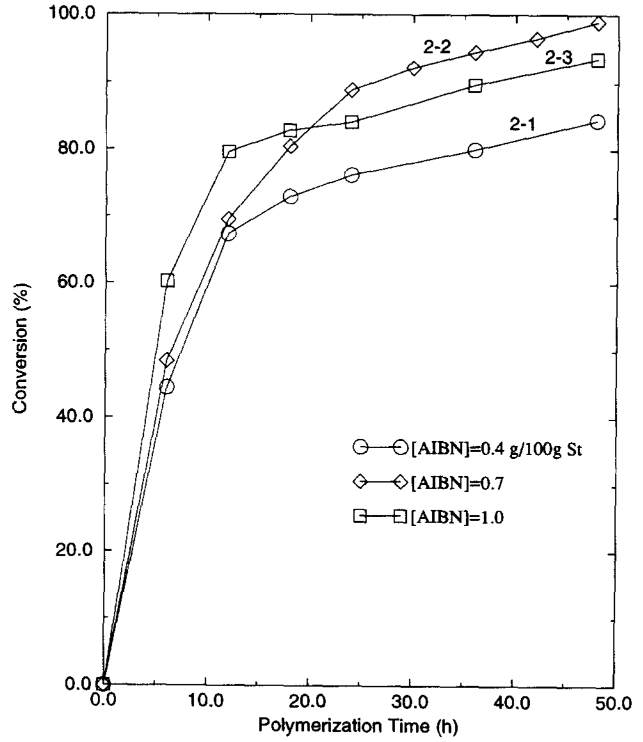

Figure 2 Conversion–time curves for different [AIBN] (*MW* of VTPB = 2800, polymerization temperature = 60°C, VTPB/St weight ratio = 2/8): (2-1) 0.4 g per 100 g St; (2-2) 0.7 g per 100 g St; (2-3) 1.0 g per 100 g St

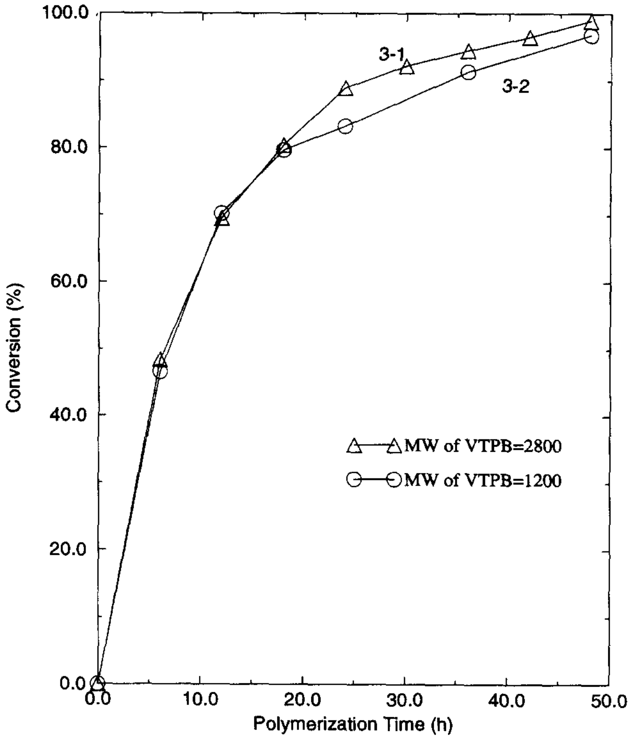

Figure 3 Conversion–time curves for different *MW*s of VTPB ([AIBN] = 0.7 g per 100 g St, VTPB/St weight ratio = 2/8, polymerization temperature = 60°C): (3-1) 2800; (3-2) 1200

Effect of polymerization temperature. The curves 1-1 and 1-2 of *Figure 1* are conversion–time plots for the temperatures of 50°C and 60°C, respectively. It is obvious that the initial polymerization rate at 60°C is twice as high as that at 50°C. In a mixture of styrene and toluene, the decomposition rate of AIBN increases from $3 \times 10^{-6}\,s^{-1}$ at 50°C to $10 \times 10^{-6}\,s^{-1}$ at 60°C[16]. In addition, the viscosity of the system is lower at higher temperatures and the monomers acquire a higher mobility. Both the above factors suggest a higher initial polymerization rate at a higher temperature. However, for temperatures higher than 65°C, the concentrated emulsion is no longer stable and phase separation occurs. For this reason, most polymerizations conducted in this work were kept at or below 60°C.

Effect of oxygen in air. After the concentrated emulsion had been generated, it was usually kept further under both stirring and a nitrogen flow for 30 minutes to remove the air, which retards the polymerization, from it. In order to evaluate the effect of air on the polymerization rate, a conversion–time curve (curve 1-3 in *Figure 1*) is presented for the polymerization of a concentrated emulsion which was not treated with a nitrogen flow. One can see that at 60°C the initial polymerization rate of the concentrated emulsion without nitrogen flow is somewhat lower than that with the flow, but higher than that for polymerization at 50°C with nitrogen flow. This indicates that the effect of the presence of air in the concentrated emulsion is not as important as the change in temperature.

Effect of the concentration of initiator. In *Figure 2* three conversion–time curves of polymerizations with different concentrations of initiator ([AIBN]) are presented. One can see that the higher the [AIBN], the higher the initial polymerization rate. However, after 80% conversion there is an optimum [AIBN] (0.7 g per 100 g St) (curve 2-2). The system with [AIBN] = 1.0 g per 100 g St (curve 2-3) possesses the highest concentration of active centres, and hence the highest initial polymerization rate. However, after a certain conversion is attained (80%), the concentration of monomer becomes low and termination by the coupling of two growing chains becomes important. As a result, the polymerization is slowed down.

Effect of the molecular weight of VTPB. VTPBs of various molecular weights (*MW*s) were employed in this work. VTPB that was prepared from a PB diol with $MW = x$ is denoted as VTPB*x*. From *Figure 3* and *Tables 2* and *7*, one can see that the initial polymerization rate of the concentrated emulsion based on VTPB1200 is roughly the same as that based on VTPB2800. However, around a conversion of about 80%, the former seems to be somewhat slower. Since for the same initial weight fraction of VTPB, VTPB1200 possesses a higher molar fraction than VTPB2800, it will generate a higher degree of crosslinking. As a result, the viscosity of the system will be higher and the diffusion of St monomers slower. Consequently, the polymerization will be slowed down.

Gel content

In this paper, the gel content is defined as the weight percentage of toluene insoluble species. From *Table 8*, one can see that the higher the initial weight fraction of VTPB in the reactant system, or the lower the *MW* of the VTPB at the same weight fraction, the higher the gel content in the product sample. This is as expected, since a

Table 2 Conversion and solubility data of PB/PS composites[a]

Sample number	Time of polymerization (h)	Conversion (%)	Gel content (wt%)	St included in network (wt%)	St included in PS homopolymer (wt%)
A1-1	6	48.4	75.5	20.7	14.8
A1-2	12	69.5	58.3	25.6	36.2
A1-3	18	80.4	52.3	27.6	47.9
A1-4	24	88.9	47.7	28.0	58.1
A1-5	30	92.2	49.3	31.8	58.4
A1-6	36	94.5	48.9	32.7	60.4
A1-7	42	96.5	48.5	33.5	62.1
A1-8	48	98.9	47.7	34.0	64.7

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 60°C

higher fraction of VTPB or a lower *MW* of VTPB results in a higher degree of crosslinking, and hence in a higher gel content. However, the change in the gel content with conversion seems to be counterintuitive, since, as shown by *Figure 4*, the higher the conversion, the lower the gel content. A possible explanation of this behaviour is as follows. As mentioned earlier, three types of reaction take place: the copolymerization of VTPB and St to form a network, the homopolymerization of St and the grafting of St onto PB chains. The data in *Tables 2–7* show that more than 80% of the whole gel content is formed before a conversion of 50%. It is reasonable to suppose that the reactivity of VTPB is higher than that of St. For this reason, at the early stages of polymerization the major reaction should be the copolymerization of VTPB and St to form an AB network, which constitutes the insoluble gel content. After a conversion of 50%, the VTPB is almost used up, and the remaining reactions are those of St, which forms PS homopolymer, reacts with the reactive centres of the network or is grafted onto the PB chains. The homopolymerization of St is, of course, the dominant process. According to this supposed mechanism, the previously formed PB/PS network is wrapped up by the PS chains, and a core–shell structure is formed. Since the PS homopolymer is soluble in toluene, the gel content decreases as the conversion increases.

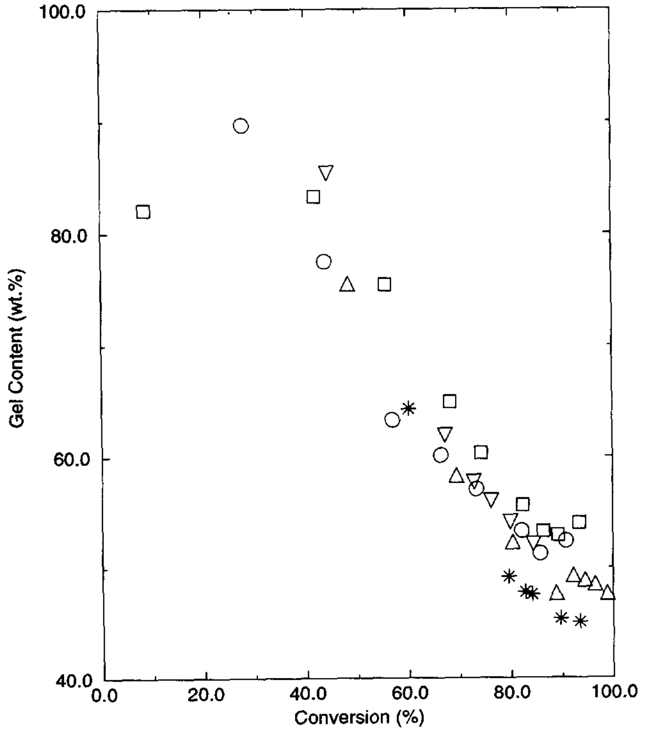

Figure 4 Effect of conversion on gel content (for all points, *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8): (○) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 50°C; (□) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C, not N_2 treated; (△) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C; (▽) [AIBN] = 0.4 g per 100 g St, polymerization temperature = 60°C; (*) [AIBN] = 1.0 g per 100 g St, polymerization temperature = 60°C

In order to examine more closely the change in composition with conversion, we calculated the distributions of St in the network and in the homopolymer at each stage of polymerization, based on the supposition that the VTPB was used up in the first six hours of polymerization. The calculated data are listed in the last two columns on the right-hand side of *Tables 2–7*.

It should be emphasized that the process in which a PB/PS AB network is formed first and is gradually wrapped up by PS chains is very significant for PS toughening. It is well known that PS can be toughened with rubber particles of 0.1–0.5 μm in diameter dispersed in the bulk phase. In the conventional preparation[1,2] of high-impact PS, the rubber/St system must be vigorously stirred during polymerization to achieve the phase inversion, i.e. to disperse the rubber as small particles. In the present work, the rubber phase was formed as the dispersed phase without stirring. This is an advantage of the concentrated emulsion polymerization method.

Besides the terminal vinyl groups, a VTPB chain also contains many double bonds in the main chain and some vinyl side groups. In order to evaluate the effect of these double bonds on the crosslinking, an ETPB sample (*MW* = 2800) was prepared and polymerized with St and AIBN via the concentrated emulsion polymerization technique. The gel content of the ETPB/PS composite was, however, only 3–5%. This indicates that crosslinking through the double bonds of the main chain and the vinyl side groups is not important compared with that through the terminal vinyl groups.

Table 3 Conversion and solubility data of PB/PS composites[a]

Sample number	Time of polymerization (h)	Conversion (%)	Gel content (wt%)	St included in network (wt%)	St included in PS homopolymer (wt%)
A2-1	6	44.4	85.4	22.4	8.1
A2-2	12	67.3	61.9	27.1	32.1
A2-3	18	72.9	57.7	27.6	38.5
A2-4	24	76.2	56.0	28.3	41.9
A2-5	36	80.0	54.1	29.1	45.9
A2-6	48	84.4	52.1	30.0	50.5

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.4 g per 100 g St, temperature of polymerization = 60°C

Table 4 Conversion and solubility data of PB/PS composites[a]

Sample number	Time of polymerization (h)	Conversion (%)	Gel content (wt%)	St included in network (wt%)	St included in PS homopolymer (wt%)
A3-1	6	60.2	64.3	23.4	26.9
A3-2	12	79.6	49.2	24.0	50.5
A3-3	18	82.8	47.8	24.4	54.0
A3-4	24	84.1	47.6	25.0	55.1
A3-5	36	89.7	45.4	25.9	61.2
A3-6	48	93.5	45.1	27.7	64.2

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 1.0 g per 100 g St, temperature of polymerization = 60°C

Table 5 Conversion and solubility data of PB/PS composites[a]

Sample number	Time of polymerization (h)	Conversion (%)	Gel content (wt%)	St included in network (wt%)	St included in PS homopolymer (wt%)
A4-1	6	42.0	83.3	18.7	8.7
A4-2	9	48.6	82.1	24.8	10.9
A4-3	12	55.7	75.4	27.4	17.1
A4-4	15	68.3	64.9	30.4	30.8
A4-5	18	74.3	60.3	31.0	36.9
A4-6	24	82.4	55.6	32.3	45.7
A4-7	30	86.4	53.3	32.6	50.4
A4-8	36	89.3	52.9	34.0	52.6
A4-9	48	93.5	54.0	38.1	53.7

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 60°C. The concentrated emulsion was not treated with nitrogen before polymerization

Table 6 Conversion and solubility data of PB/PS composites[a]

Sample number	Time of polymerization (h)	Conversion (%)	Gel content (wt%)	St included in network (wt%)	St included in PS homopolymer (wt%)
A5-1	6	27.9	89.7	6.3	3.6
A5-2	12	43.9	77.5	17.5	12.3
A5-3	18	57.0	63.3	20.1	26.1
A5-4	24	66.4	60.1	24.9	33.1
A5-5	30	73.3	57.1	27.3	39.3
A5-6	36	82.3	53.3	29.8	48.0
A5-7	42	85.8	51.3	30.0	52.2
A5-8	48	90.8	52.4	34.5	54.0

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 50°C

Table 7 Conversion and solubility data of PB/PS composites[a]

Sample number	Time of polymerization (h)	Conversion (%)	Gel content (wt%)	St included in network (wt%)	St included in PS homopolymer (wt%)
B1-1	6	46.6	95.8	30.8	2.4
B1-2	12	70.2	86.8	51.2	11.6
B1-3	18	79.7	76.7	51.5	23.1
B1-4	24	83.2	73.9	51.7	27.2
B1-5	36	91.3	68.8	53.5	35.6
B1-6	48	96.8	65.7	54.5	41.5

[a] *MW* of VTPB = 1200, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 60°C

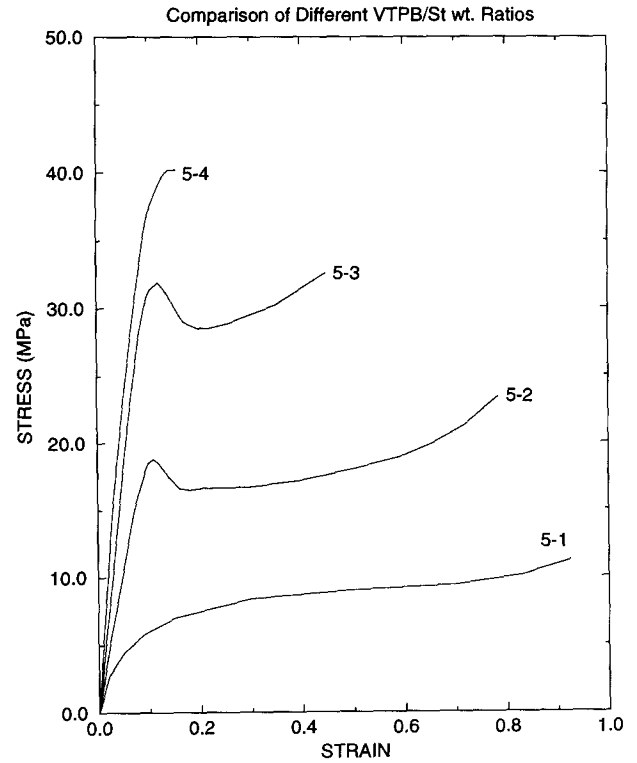

Figure 5 Stress–strain curves of PB/PS composites for different VTPB/St weight ratios (*MW* of VTPB = 2800, [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C): (5-1) 4/6; (5-2) 3/7; (5-3) 2/8; (5-4) 1/9

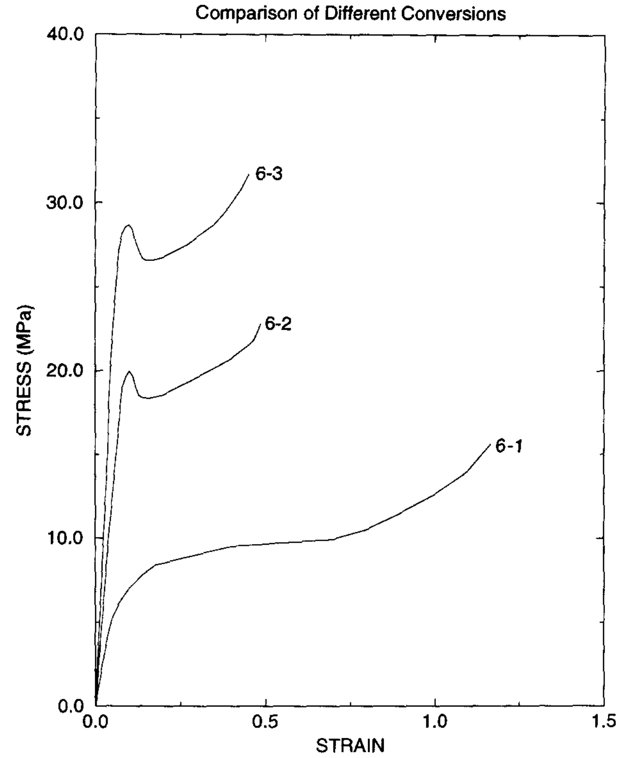

Figure 6 Stress–strain curves of PB/PS composites for different conversions (*MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C): (6-1) 42%; (6-2) 75%; (6-3) 95%

Tensile properties

Stress–strain curves. Figure 5 presents the stress–strain curves of the PS/PB composites prepared from different initial VTPB/St weight ratios. One can see that the materials change from brittle plastics to tough plastics, and to elastomers, as the content of the initial VTPB increases. For the brittle material (curve 5-1), the sample breaks before yielding. The tough plastics (curves 5-2 and 5-3) exhibit a yield point and subsequently a large strain. For the elastomer (curve 5-4), the large content of rubber chains makes the material very flexible and a large strain is developed without a yield point. In *Figure 6*, the stress–strain curves of the samples based on the same initial VTPB/St weight ratio but at different conversions are presented. One can see that the change in the curves as conversion increases is somewhat like that for decreasing VTPB contents. The sample at low conversion (<50%, curve 6-1) is an elastomer, while samples at higher conversions (curves 6-2 and 6-3) possess the features of tough plastics. As was noted in the previous sections, even though the initial composition of the reactants is the same, different proportions of constituents are generated for different conversions. As a result, various tensile behaviours should indeed be observed.

Effect of the initial VTPB/St weight ratio. As one can see from the stress–strain curves of *Figures 5* and *6* and *Table 8*, the initial weight ratio of VTPB to St plays an important role in the tensile strength and elongation at break. PB is a flexible component with a T_g as low as 75°C[16]. If PB is introduced into PS and is well combined with it, higher flexibility (larger elongation at break) and lower tensile strength can be produced. This has long been a common practice in both industry and

Table 8 Effect of composition on tensile properties of PB/PS composites[a]

Sample number	*MW* of VTPB	VTPB/St weight ratio	Gel content (wt%)	Tensile strength (MPa)		Elongation (%)	
				Average	Standard error	Average	Standard error
A0-1	2800	4/6	93.1	11.2	1.0	92.5	4.6
A0-2		3/7	72.0	23.4	1.9	78.5	4.5
A0-3		2/8	51.2	32.6	2.4	44.8	3.7
A0-4		1/9	47.7	40.2	2.1	15.5	2.5
B0-1	1200	4/6	93.3	14.6	0.9	78.7	5.3
B0-2		3/7	75.4	28.7	1.7	52.3	4.4
B0-3		2/8	65.4	37.2	2.7	28.4	1.9
B0-4		1/9	55.2	44.3	2.0	9.6	0.8

[a] [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 60°C

Table 9 Effect of conversion on tensile properties of PB/PS composites[a]

Sample number	Conversion (%)	Tensile strength (MPa)		Elongation (%)	
		Average	Standard error	Average	Standard error
A1-1	48.4	21.8	1.7	88.5	6.6
A1-2	69.5	23.0	1.9	74.7	4.9
A1-3	80.4	26.3	2.3	70.3	5.3
A1-4	88.9	29.6	2.5	53.2	3.7
A1-5	92.2	30.9	1.9	47.8	3.5
A1-6	94.5	32.2	2.4	47.7	4.0
A1-7	96.5	31.6	2.8	45.6	1.9
A1-8	98.9	33.5	1.2	42.4	3.3

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 60°C

Table 10 Effect of conversion on tensile properties of PB/PS composites[a]

Sample number	Conversion (%)	Tensile strength (MPa)		Elongation (%)	
		Average	Standard error	Average	Standard error
A2-1	44.4	15.4	1.3	80.1	7.1
A2-2	67.3	17.7	1.0	74.4	4.3
A2-3	72.9	19.6	1.3	72.3	5.1
A2-4	76.2	24.3	2.0	58.8	4.2
A2-5	80.0	25.2	1.8	42.1	3.6
A2-6	84.4	29.7	2.2	38.6	2.2

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.4 g per 100 g St, temperature of polymerization = 60°C

Table 11 Effect of conversion on tensile properties of PB/PS composites[a]

Sample number	Conversion (%)	Tensile strength (MPa)		Elongation (%)	
		Average	Standard error	Average	Standard error
A3-1	60.2	21.3	1.8	76.1	6.7
A3-2	79.6	25.5	2.0	66.8	4.8
A3-3	82.8	26.7	1.1	47.2	3.5
A3-4	84.1	28.3	0.9	44.0	3.3
A3-5	89.7	29.7	2.2	43.1	2.6
A3-6	93.5	32.9	1.5	39.9	2.0

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 1.0 g per 100 g St, temperature of polymerization = 60°C

Table 12 Effect of conversion on tensile properties of PB/PS composites[a]

Sample number	Conversion (%)	Tensile strength (MPa)		Elongation (%)	
		Average	Standard error	Average	Standard error
A4-1	42.0	15.6	0.7	116.5	5.2
A4-2	48.6	16.8	0.9	97.3	4.7
A4-3	55.7	19.1	1.4	77.5	5.0
A4-4	68.3	22.5	1.5	50.1	3.3
A4-5	74.3	22.8	1.9	48.8	3.8
A4-6	82.4	24.9	2.0	46.2	2.7
A4-7	86.4	27.7	1.7	45.3	2.4
A4-8	89.3	28.3	2.2	46.0	3.0
A4-9	93.5	31.7	2.9	45.1	3.5

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 60°C. The concentrated emulsion was not treated with nitrogen before polymerization

Table 13 Effect of conversion on tensile properties of PB/PS composites[a]

Sample number	Conversion (%)	Tensile strength (MPa)		Elongation (%)	
		Average	Standard error	Average	Standard error
A5-1	27.9	11.3	0.9	88.6	5.3
A5-2	43.9	14.7	1.4	73.2	6.1
A5-3	57.0	18.9	1.7	68.6	5.2
A5-4	66.4	23.3	2.0	47.4	3.5
A5-5	73.3	25.0	1.8	43.3	3.3
A5-6	82.3	25.5	0.8	44.2	2.4
A5-7	85.8	25.4	2.1	43.0	4.0
A5-8	90.8	29.5	1.9	41.1	2.6

[a] *MW* of VTPB = 2800, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 50°C

Table 14 Effect of conversion on tensile properties of PB/PS composites[a]

Sample number	Conversion (%)	Tensile strength (MPa)		Elongation (%)	
		Average	Standard error	Average	Standard error
B1-1	46.6	23.2	1.1	64.3	4.8
B1-2	70.2	28.8	2.3	52.0	4.0
B1-3	79.7	30.7	0.6	43.7	3.6
B1-4	83.2	35.2	1.4	37.6	3.2
B1-5	91.3	37.4	2.6	31.9	2.7
B1-6	96.8	38.6	2.5	27.5	2.4

[a] *MW* of VTPB = 1200, VTPB/St weight ratio = 2/8, [AIBN] = 0.7 g per 100 g St, temperature of polymerization = 60°C

laboratories. In the present system, the PB and PS segments are combined not only by crosslinking but also by the grafting of St onto PB chains. The combination of the PB and PS segments provides excellent mechanical properties when the chain of PB is not too long. In such cases, most of the samples are, as expected, either elastomers or tough plastics. The toughness of PS is greatly improved. The higher the PB content, the higher the elongation at break and the lower the tensile strength.

Effect of the MW *of VTPB.* For the same VTPB/St weight ratio, the *MW* of VTPB affects the gel content. *Table 8* shows that a composite based on VTPB1200 has generally a higher gel content than one based on VTPB2800 at the same weight fraction. This is because the number of moles of VTPB2800 is smaller, and hence the amount of polystyrene which is crosslinked and the gel content are also smaller. However, if the *MW* of PB is too high, the crosslinked constituent will involve too small an amount of PS. As a result, the crosslinked constituent of the material will become incompatible with PS and phase separation should be expected. We prepared a series of PB/PS composites based on VTPB4900. The product obtained turned out to contain incompatible constituents, and possessed not only very low tensile strength but also a very low elongation at break.

Tensile properties and conversion. As found in the studies of conversion and gel content, the PB/PS

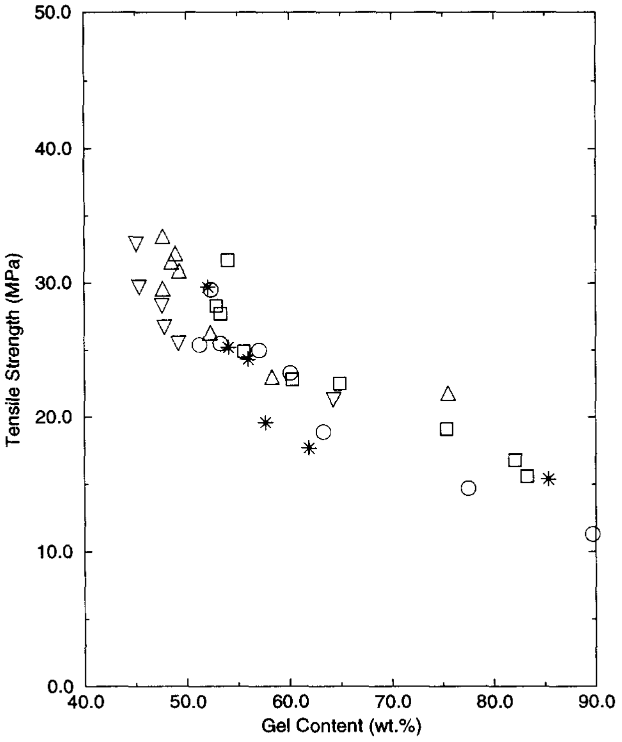

Figure 7 Effect of gel content on the tensile strength: (○) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 50°C; (□) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C, not N_2 treated; (△) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C; (▽) [AIBN] = 0.4 g per 100 g St, polymerization temperature = 60°C; (*) [AIBN] = 1.0 g per 100 g St, polymerization temperature = 60°C. For all points, *MW* of VTPB = 2800 and VTPB/St weight ratio = 2/8

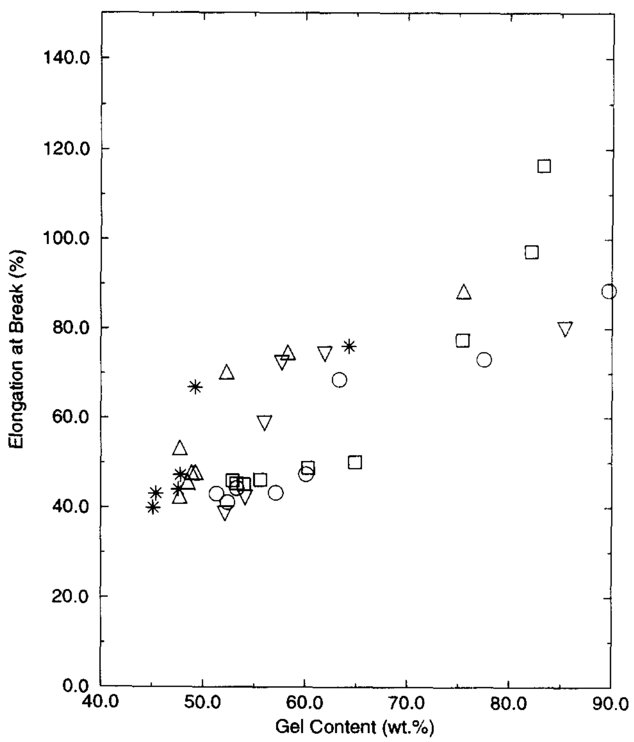

Figure 8 Effect of gel content on the elongation at break: (○) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 50°C; (□) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C, not N_2 treated; (△) [AIBN] = 0.7 g per 100 g St, polymerization temperature = 60°C; (▽) [AIBN] = 0.4 g per 100 g St, polymerization temperature = 60°C; (*) [AIBN] = 1.0 g per 100 g St, polymerization temperature = 60°C. For all points, *MW* of VTPB = 2800 and VTPB/St weight ratio = 2/8

composites prepared by us do not consist of a network alone; they are a blend of a PB/PS network and PS homopolymer. The products at different conversions possess different gel contents. The higher the conversion, the lower the gel content and the higher the proportion of PS homopolymer. For an initial VTPB/St weight ratio of 2/8, the proportion of PS homopolymer at high conversion is usually higher than 50%. In such a blend, the PB/PS network constitutes the flexible component, which contributes to higher elongation at break and lower tensile strength; the PS homopolymer constitutes the rigid component, and contributes to a lower elongation at break and higher tensile strength. As a result (see *Tables 9–14*), the higher the conversion, the higher the tensile strength and the lower the elongation at break.

Other polymerization conditions, such as the temperature and the concentration of the initiator, affect the mechanical properties of the composites through the changes in the gel content (and conversion). These effects are summarized in *Figures 7* and *8*, in which the tensile strength and the elongation at break are plotted against the gel content, respectively.

CONCLUSION

Latexes of PB/PS network composites were prepared via the concentrated emulsion polymerization method. The material obtained was a blend of a PB/PS AB network with PS homopolymer. The PB/PS network was mainly formed in the early stages of polymerization. The higher the conversion, the higher was the PS homopolymer content. The presence of the PB/PS network played an important role in the mechanical properties of the composites. As the relative proportion of PB in the initial reactants or the relative proportion of PB/PS network in the composite increased, the elongation at break increased and the tensile strength decreased. The polymerization temperature and the concentration of the initiator affected the polymerization rate significantly.

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