

Physical, Mechanical, and Morphological Behavior of Sequential Polybutadiene–Poly(methyl methacrylate) Interpenetrating Polymer Networks

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SYNOPSIS

Both full and semi-interpenetrating polymer networks (IPNs) of polybutadiene and poly(methyl methacrylate) were synthesized by sequential polymerization. The effect of compositional variation and the cross-linking agent of both elastomer and plastomer on the physical, mechanical, and morphological properties were investigated. Full-IPNs exhibited improved tensile strength, modulus, tear strength, gel content, and density, whereas the corresponding semi-IPNs exhibited better toughness and elongation at break. Phase morphology of full-IPNs were characterized by compact, tight network structures compared to those of semi-IPNs. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are defined as a mixture of two or more cross-linked polymer networks with partial or total physical interlocking. IPNs can be synthesized by latex blending, sequential polymerization, and simultaneous polymerization techniques.¹

Like other multipolymer systems, IPNs exhibit limited phase separation, arising from the mutual incompatibility inherent in most polymer-blend systems. Interpenetration plays a significant role in enhancing the intermixing of the polymer components through physical interlocking, which prohibits further phase separation when the polymerization proceeds after the gel point is reached.²

Improvement in polymer properties may be achieved by the formation of heterogeneous systems in which one polymer exists above its glass transition temperature, T_g , whereas the other exists below its T_g at room temperature.^{3–9} By varying the relative amounts of each polymer in the IPN, the properties may be altered, but these are dependent mainly upon which of the two materials forms the continuous phase. Thus, the product may range from a reinforced rubber to a high-impact plastic. The main

objective is to gain insight into the factors determining the properties of IPNs so that materials with properties attuned to the particular application requirements may be produced.

In this article, we examine the morphological behavior as well as the physical and mechanical properties of full- and semi-IPNs based on polybutadiene and poly(methyl methacrylate).

EXPERIMENTAL

Materials

Polybutadiene Rubber (PBR)

PBR from IPCL, Baroda, India, having the following characteristics was used:

<i>cis</i> ,1,4 content	> 96%
ML ₄ at 100°C	46
Volatile percent	0.3
Ash percent	0.2
Specific gravity (g/cc)	0.9

Methyl Methacrylate (MMA)

MMA monomer from E. Merck, India, was used. Before use, the monomer was freed from the inhib-

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itor by washing first with aqueous sodium hydroxide, then with distilled water, followed by drying over anhydrous calcium chloride and, finally, distilling under vacuum.

Benzoyl Peroxide (Bz_2O_2)

Bz_2O_2 obtained from BDH, India, was purified by repeated crystallization from chloroform and was used as an initiator for polymerization of the MMA monomer.

Dicumyl Peroxide (DCP)

DCP (98% peroxide content) supplied by E. Merck, Germany, was used as supplied as the cross-linker for PBR.

Divinyl benzene (DVB)

DVB (Fluka) was used as supplied, as a comonomer along with MMA for cross-linking PMMA.

IPN Synthesis

PBR was masticated in a two-roll mill at room temperature. DCP in different doses (ranging from 0.05 to 0.5 phr) was mixed with the masticated PBR. The optimum cure times (OCT) of each PBR stock containing different DCP doses were determined by rheometry at 170°C. The rubber stock was then cured in an electrically heated hydraulic press at 170°C under a pressure of 100 kg/cm² for a predetermined time. In this way, cross-linked PBR sheets of different cross-link densities were obtained.

Cured PBR sheets having different cross-link densities were then swelled in distilled MMA monomer containing benzoyl peroxide and DVB (0–6% by weight based on the MMA monomer). The swelled rubber networks were then kept in a closed container at a temperature of 0°C for a few hours to achieve an equilibrium distribution of MMA in the cross-linked rubber matrix.

Swollen and matured PBR networks were taken in a closed mold and the monomer MMA was allowed to polymerize inside the rubber matrix. Initially, the temperature was kept constant at 70°C for 8 h and finally postcured at 100°C for 2 h for complete polymerization of the monomers. The hardened sheets were then taken out from the mold and kept in vacuum for 2–3 days until constant weight was obtained. A wide range of semi- and full-IPN samples differing in blend ratios and cross-link densities of both PBR and PMMA were thus prepared.

A wide range of product properties may be obtained by varying the following three variables:

1. The extent of cross-linking of PBR by using different DCP doses.
2. The extent of cross-linking of the plastomer component by incorporating different proportions of DVB.
3. The relative proportion of elastomer and plastomer components.

Measurements

Tensile Properties

The major properties like tensile strength (TS), percent elongation at break (EB %), and modulus at 50% elongation were measured using an Instron universal tensile testing machine (Model 4301). Measurements were made according to ASTM D-412 and ASTM D-638 for IPN samples having a plastomer content less than and greater than 50%, respectively.

Tear Strength

ASTM D-624 was followed for measuring the tear strength of IPNs having elastomer as the major component (> 50%), whereas ASTM D-1004 was followed for IPN samples having plastomer as the major component (> 50%).

Hardness

The hardness of the IPN samples was measured using Shore A durometer according to ASTM D-2240-64T.

Density

The density of the samples was measured at room temperature using a hydrostatic technique according to ASTM D-792.

Gel Content

The gel content of the IPN samples was measured by Soxhlet extraction using benzene as the solvent.

Molecular Weight Between Cross-links (M_c)

The Flory–Rehner equation^{10–12} was used to determine M_c by the equilibrium swelling technique.

Electron Micrographs

The phase morphology of IPN samples, fractured cryogenically, was examined in a Philips PSEM-500

Table I Physical and Mechanical Properties of 65 : 35 PBR-PMMA IPNs and Semi-IPNs

DCP Dose (Phr)	DVB Dose (Wt %)	Density (gm/cc)	Gel Content (%)	MC (g/mol)	Tensile Strength (TS) (MPa)	Elongation at Break (%)	Modulus at 50% (MPa)	Tear Strength (N/mm)	Toughness (MPa)
0.05	0	1.056	78.0	7800	6.6	425	0.82	10.2	0.8927
	2	1.060	94.1	6100	6.8	330	0.84	10.8	0.8721
	4	1.065	95.2	4250	7.0	310	0.87	11.4	0.8620
	6	1.069	97.0	2981	7.3	295	0.90	11.6	0.8510
0.1	0	1.059	81.0	7630	6.8	410	0.85	10.5	0.9820
	2	1.062	95.3	5850	7.1	325	0.86	11.2	0.9610
	4	1.067	96.9	4120	7.4	295	0.89	11.8	0.9525
	6	1.071	98.2	2540	7.6	282	0.93	12.0	0.9420
0.3	0	1.062	83.0	7210	7.1	401	0.86	10.9	0.8720
	2	1.064	95.9	4825	7.3	318	0.89	11.3	0.8520
	4	1.069	97.2	3250	7.6	289	0.91	11.9	0.8410
	6	1.073	98.9	2130	7.9	278	0.96	12.2	0.8325
0.5	0	1.066	86.0	6840	7.5	396	0.88	11.2	0.8450
	2	1.068	98.6	4210	7.8	304	0.92	11.7	0.8120
	4	1.071	99.1	2910	8.0	280	0.94	12.1	0.8020
	6	1.075	99.3	1720	8.2	270	0.98	12.3	0.7924

scanning electron microscope after etching the sample surface with benzene.

RESULTS AND DISCUSSION

Each measurement was carried out by taking five samples and their average value has been reported.

The range of error for the studies has been found to be $\pm 2-5\%$ and the points are drawn after taking into account this percentage of error. The present studies based on semi-IPN (where only PBR was cross-linked with DCP) and full-IPN (where both PBR and PMMA were cross-linked) were carried out to evaluate the effect of variation of the PBR: PMMA blend ratio, elastomer cross-linker (DCP)

Table II Physical and Mechanical Properties of 55 : 45 PBR-PMMA IPNs and Semi-IPNs

DCP Dose (Phr)	DVB Dose (Wt %)	Density (gm/cc)	Gel Content (%)	MC (g/mol)	Tensile Strength (TS) (MPa)	Elongation at Break (%)	Modulus at 50% (MPa)	Tear Strength (N/mm)	Toughness (MPa)
0.05	0	1.060	71.2	8471	8.7	350	1.98	11.5	1.987
	2	1.062	94.5	6250	9.1	280	2.01	11.9	1.920
	4	1.066	95.6	4420	9.3	260	2.19	12.5	1.901
	6	1.071	97.2	3010	9.6	248	2.26	12.8	1.892
0.1	0	1.062	74.1	8120	9.0	335	2.10	12.01	2.467
	2	1.064	95.5	5720	9.3	267	2.20	12.8	2.206
	4	1.069	97.1	3930	9.5	248	2.28	13.2	2.179
	6	1.073	98.6	2730	9.9	230	2.40	13.8	2.069
0.3	0	1.063	76.5	7735	9.5	328	2.20	12.5	1.856
	2	1.065	96.1	5420	9.7	260	2.35	13.0	1.810
	4	1.070	97.6	3380	10.0	239	2.40	13.4	1.809
	6	1.075	98.9	2420	10.3	210	2.48	14.0	1.708
0.5	0	1.067	79.1	7480	9.7	319	2.41	13.1	1.620
	2	1.069	98.6	5129	9.9	249	2.48	13.6	1.420
	4	1.072	99.2	2930	10.1	231	2.58	13.9	1.350
	6	1.079	99.4	2021	10.5	200	2.70	14.5	1.310

Table III Physical and Mechanical Properties of 50 : 50 PBR-PMMA IPNs and Semi-IPNs

DCP Dose (Phr)	DVB Dose (Wt %)	Density (gm/cc)	Gel Content (%)	MC (g/mol)	Tensile Strength (TS) (MPa)	Elongation at Break (%)	Modulus at 50% (MPa)	Tear Strength (N/mm)	Toughness (MPa)
0.05	0	1.065	65.0	8920	11.5	310	3.5	16.0	2.584
	2	1.066	94.6	6920	11.8	250	3.7	16.4	2.108
	4	1.070	95.7	5160	12.1	242	3.8	16.7	1.980
	6	1.073	97.2	3520	12.3	230	4.1	17.1	1.965
0.1	0	1.066	67.2	8630	11.8	296	3.8	17.0	3.805
	2	1.069	95.3	6120	12.1	238	4.1	17.3	3.625
	4	1.072	97.5	4645	12.5	228	4.2	17.7	3.515
	6	1.074	98.5	3125	12.8	215	4.5	18.1	3.205
0.3	0	1.068	68.9	8380	12.0	289	4.1	18.2	2.303
	2	1.072	96.3	5820	12.4	229	4.5	18.7	2.103
	4	1.075	97.8	3928	12.6	216	4.7	19.2	1.986
	6	1.078	99.0	2830	13.0	198	5.0	19.7	1.965
0.5	0	1.070	72.3	7923	12.3	270	4.3	19.2	1.986
	2	1.073	98.5	5520	12.6	219	4.7	19.8	1.967
	4	1.077	99.3	3518	12.7	201	4.8	20.1	1.958
	6	1.081	99.5	2328	13.1	185	5.1	20.7	1.940

dose, and plastomer cross-linker dose (DVB) on the properties of IPN samples. Different blend ratios of PBR:PMMA (i.e., 65 : 35, 55 : 45, 50 : 50, and 35 : 65) were obtained by incorporating different proportions of MMA monomer to the cross-linked PBR. Elastomer cross-link densities and plastomer cross-link densities were varied by using different

doses of DCP (viz., 0.05, 0.1, 0.3, and 0.5 phr) and DVB (viz., 0, 2, 4, and 6 wt %), respectively.

Influence of Variation of Elastomer and Plastomer Cross-linker Content

Tables I-IV illustrate the effect of variation of elastomer (PBR) and plastomer (PMMA) cross-linker

Table IV Physical and Mechanical Properties of 35 : 65 PBR-PMMA IPNs and Semi-IPNs

DCP Dose (Phr)	DVB Dose (Wt %)	Density (gm/cc)	Gel Content (%)	MC (g/mol)	Tensile Strength (TS) (MPa)	Elongation at Break (%)	Modulus at 50% (MPa)	Tear Strength (N/mm)	Toughness (MPa)
0.05	0	1.075	58.1	9330	14.0	210	11.97	22.8	1.605
	2	1.079	94.5	7100	14.2	140	12.50	23.4	1.485
	4	1.084	95.8	5350	14.4	128	12.90	23.9	1.353
	6	1.089	97.7	4020	14.6	120	13.10	24.4	1.310
0.1	0	1.080	62.5	9090	14.2	192	12.21	23.0	1.925
	2	1.083	95.4	6930	14.5	129	12.60	23.8	1.715
	4	1.086	97.6	5006	14.7	115	13.10	24.5	1.605
	6	1.091	98.4	3723	15.0	105	13.30	25.2	1.523
0.3	0	1.084	67.7	8823	14.5	180	12.50	23.6	1.582
	2	1.088	96.3	6528	14.7	115	12.80	24.1	1.513
	4	1.091	97.8	4729	14.9	103	13.20	24.6	1.490
	6	1.095	99.1	3527	15.3	90	13.60	25.4	1.430
0.5	0	1.090	72.2	8688	14.8	168	12.8	24.0	1.318
	2	1.094	98.6	6207	15.1	108	13.5	24.5	1.208
	4	1.099	99.4	4530	15.3	95	14.1	25.3	1.118
	6	1.103	99.6	3210	15.7	72	14.5	26.1	1.080

doses on tensile strength (TS) and percent elongation at break (EB %) of different IPNs. As the DCP and DVB doses were increased, an increase in TS and decrease in EB (%) values were observed. Again, semi-IPNs were characterized by lower TS but higher EB (%) values than those of the corresponding full IPNs.

The change of tear strength and modulus of the IPNs with the change in elastomer and plastomer cross-linker doses can be observed from the tables. An increase in DCP and DVB doses resulted in an enhancement of both tear strength and modulus of the network blends and all the IPNs exhibited similar behavior in this respect. The overall rate of increase of tear strength and modulus was found to be almost comparable for semi- and full-IPNs. However, semi-IPNs were characterized by lower tear strength and modulus values than those of the

corresponding full-IPNs. On average, about 20% gain in tear strength could be obtained for both semi- and full-IPNs by increasing the DCP dose from 0.05 to 0.5 phr. Again, for a change from semi- to full-IPNs (e.g., for a change in DVB dose from 0 to 6 wt %), the percent gain in tear strength and modulus was 7 and 17%, respectively (for 50 : 50 PBR:PMMA having the elastomer component cross-linked with 0.6 phr DCP).

The toughness of the elastomer-plastomer blend network was calculated from the stress-strain graph: It is the energy absorbed before breaking during tensile stress application at a constant rate of strain development. In all blend ratios, the toughness values of both semi- and full-IPNs exhibited a maximum corresponding to a DCP dose of 0.1 phr (Tables I-IV) for variation of the DCP dose from 0.05 to 0.5 phr. Semi-IPNs were characterized by higher

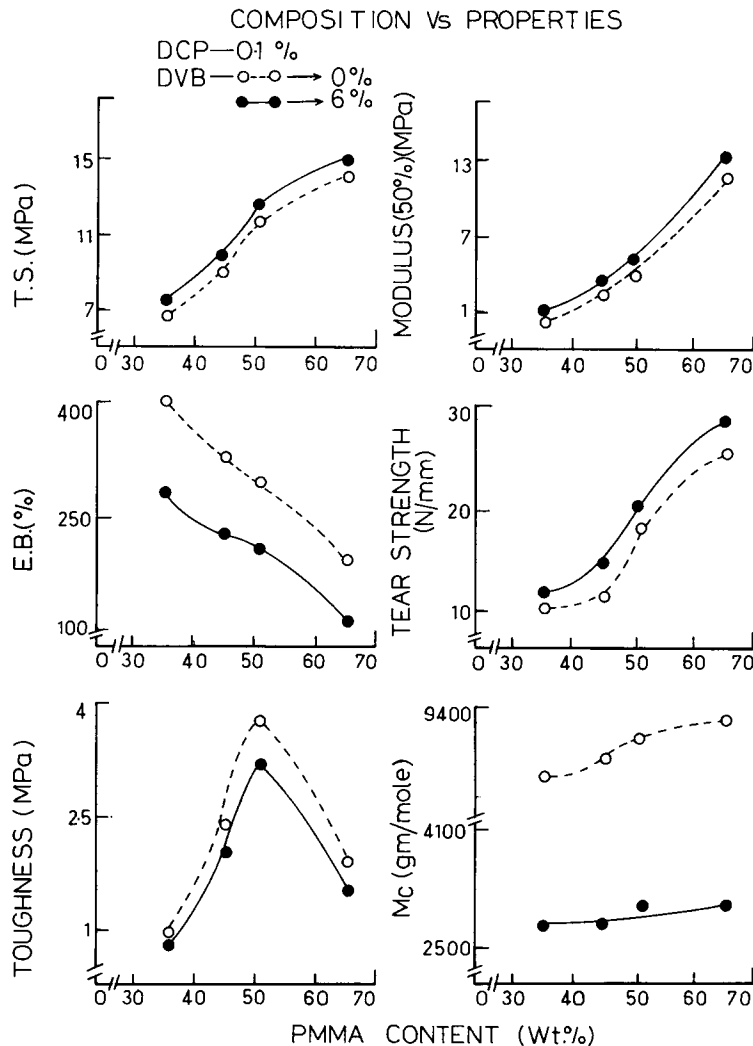


Figure 1 Composition vs. properties of PBR:PMMA sequential IPNs.

toughness values than those of the corresponding full IPNs.

The overall M_c values for the IPN system followed a decreasing trend with an increase in DCP dose. The percent decrease in the M_c values with increase in the DCP dose was relatively lower for the full-IPNs than that of the corresponding semi-IPNs (Tables I-IV). Full-IPNs were characterized by a lower overall M_c value than that of the semi-IPNs, and for a specific blend ratio, the M_c values for the full-IPNs tended to decrease with increase in the DVB dose.

Densities of both semi- and full-IPNs increased with increasing DCP dose (Tables I-IV). It was also observed that the densities of the full-IPNs were higher than those of the semi-IPNs, and that for

the full-IPNs, the density values followed an increasing trend with increase in the DVB dose.

Full-IPNs were characterized by a higher gel content than that of the corresponding semi-IPNs and the difference in gel content between the semi- and full-IPNs became narrower as the DCP dose increased from 0.05 to 0.5 phr. The relative increase in gel content with increase in DCP dose was found to be much higher in semi-IPNs compared to the full-IPNs.

Influence of the Blend Ratio

From an analysis of data represented graphically, one may form an idea about the effect of variation of the blend ratio on different physical and me-

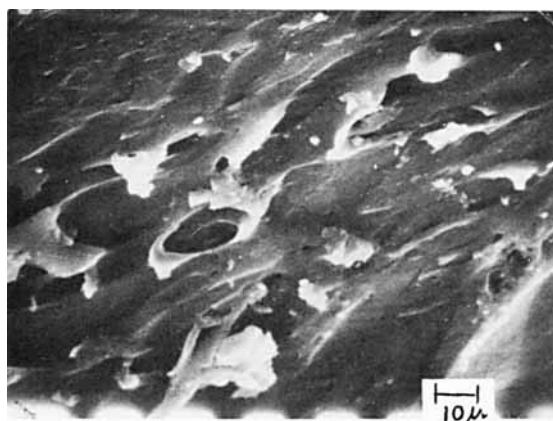
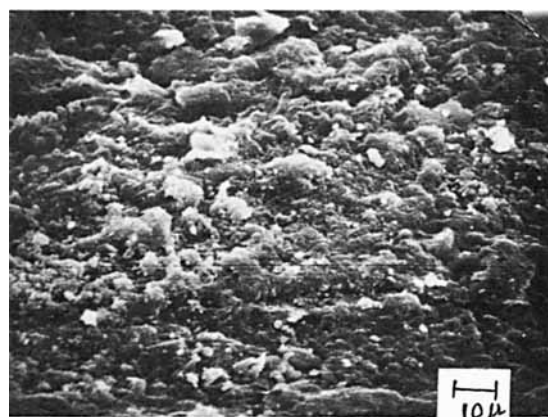
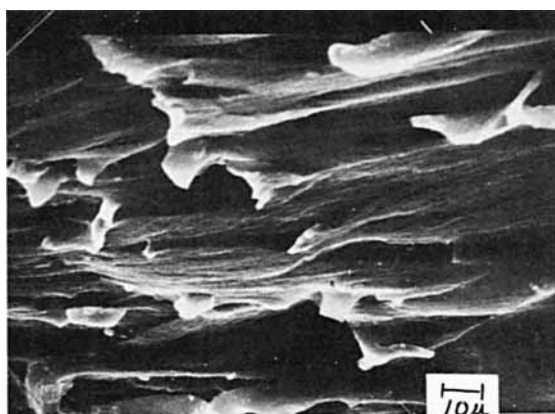
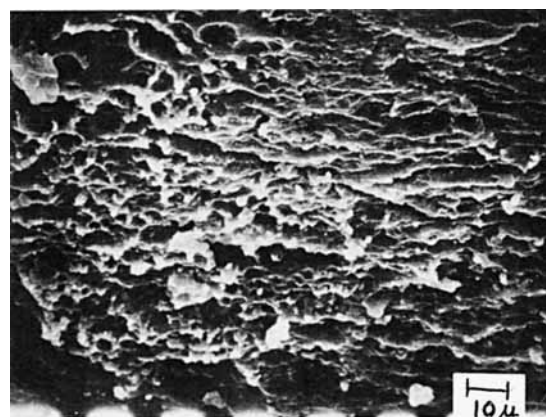
A₁C₁A₂C₂

Figure 2 Scanning electron micrographs (SEMs) of PBR:PMMA sequential IPNs (800 \times). Sets of micrographs A₁/A₂ and C₁/C₂ refer to 65 : 35 and 50 : 50 PBR:PMMA blend ratios (w/w), respectively, each containing 1.0 phr of DCP. A₁/C₁ refers to semi-IPNs (0 wt % DVB) and A₂/C₂ refers to full-IPNs (6 wt % DVB).

chanical properties of PBR:PMMA blend networks (both semi- and full-IPNs). It is seen from Figure 1 that with increase in the PMMA content in the blends the properties such as TS, modulus, tear strength, and M_c values followed an increasing trend, whereas the EB % decreased gradually.

The modulus of the IPNs increased at relatively slower rates for an increase in PMMA content from 35 to 50%. An increase in PMMA content beyond 50% resulted in a rapid increase in the modulus. The tear strengths of both semi- and full-IPNs increased with increase in the plastomer content. This is due to the combined effect of increased modulus and TS.⁷ The increase in TS, modulus, and tear strength of the IPNs with increase in the PMMA content is a clear indication of the reinforcement of the base material (PBR). A sharp fall in EB (%) values with increase in the PMMA content was observed due to the negligible elongation of PMMA.

It is also seen from the graph (Fig. 1) that with an increase in the plastomer content the properties like M_c of the networks for full IPNs remained almost constant, whereas those for the semi-IPN systems exhibited just the opposite trend. With an increase in the plastomer content, the gel content decreased, whereas the M_c value increased.

Toughness values of both semi- and full-IPNs passed through a maximum corresponding to about a 50 : 50 PBR:PMMA blend ratio. Toughness is generally dependent upon two factors: viz., TS and EB (%) of the particular compound. Network blends having plastomer as the major component exhibited high TS but very low EB (%) values. But blends having intermediate compositions were characterized by reasonably high TS and, at the same time, quite substantial EB (%) values, i.e., in this case, a unique balance between the two is obtained.

Phase Morphology of PBR:PMMA IPNs

Analysis of micrographs given in Figure 2 shows that full-IPNs (A_2C_2) were characterized by a more ordered, compact, and uniform phase distribution compared to that of the corresponding semi-IPNs (A_1C_1). The higher TS, modulus, and tear strength of full-IPNs over semi-IPNs might be due to these distinct differences in morphological features. The comparatively loosely bound morphology of semi-

IPNs was probably responsible for the higher EB (%) values compared to the corresponding full IPNs.

CONCLUSION

On the basis of these observations, we can conclude that higher PMMA content in the blend increases the tensile strength, modulus, and tear strength and decreases the elongation at break (%) values. The properties of full-IPNs over semi-IPNs follow the same trend. The toughness value shows a maximum at a certain composition, then decreases, and this is true for both semi- and full-IPNs. Phase morphological behavior of the semi- and full-IPN samples also confirmed the above physical and mechanical properties.

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