JOURNAL OF MATERIALS SCIENCE 26 (1991) 6104–6112

Studies on polybutadiene rubber (PBR)–polystyrene (PS) interpenetrating polymer networks

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Elastomer–plastomer blends based on polybutadiene rubber (PBR) and polystyrene (PS) giving interpenetrating networks (IPNs) were studied. The semi IPNs were formed by allowing the initially formed elastomer (PBR) network to swell in styrene monomer and then completing polymerization of the monomer through the swollen elastomer network. For full interpenetrating network formation selected low doses of divinylbenzene (DVB) was used in the monomer styrene and copolymerization of the styrene–DVB system through the monomer swollen elastomer network was effected subsequently. Dicumyl peroxide (DCP) was used to form the initial PBR network and benzoyl peroxide (Bz_2O_2) was used as the initiator for the polymerization of styrene or styrene–DVB mixture. Effects of variation of DCP dose, DVB dose and PBR–PS blend ratio on the physical–mechanical properties of the blends were examined. The full IPNs exhibited higher tensile strength and modulus while the semi IPNs exhibited greater toughness. A PBR–PS blend ratio of around 50:50 to 40:60 resulted in blends morphologically characterized by spherical domains of PBR encompassed by PS phase appearing fibrillar in nature and a synergism in the toughness property was most prominent in blends of this blend ratio range. For PBR > 50%, the elastomer phase is apparently the continuous phase, while it is just the reverse for PBR < 40 to 50% in general.

1. Introduction

Polystyrene (PS) a relatively low cost thermoplastic material, having some excellent properties, has a prominent limitation in its brittleness. In the past, trials through copolymerization of styrene with butadiene and blending of polystyrene with a diene rubber such as styrene–butadiene rubber (SBR), polybutadiene rubber (PBR) etc. have been made in an effort to improve the impact property of PS. In blends using an elastomer as the toughening agent, PBR produces much desired improvements in view of its relatively favourable chain flexibility, resilience and compatibility in comparison with other diene rubbers. The present work relating to PBR–PS blends was undertaken with the objective of making fresh investigations following somewhat new approaches and techniques involving (a) sequential formation of elastomer–plastomer networks leading to what may be termed as full interpenetrating networks (FIPN) or (b) formation of apparently linear plastomer (PS) through the elastomer (PBR) network to give semi interpenetrating networks (semi IPN), allowing polymerization of the selected vinyl monomer styrene in presence or in absence of small doses of a divinyl compound, namely divinyl benzene (DVB) in the presence of the preformed elastomeric (PBR) networks, respectively.

2. Experimental procedure

2.1. Materials

Polybutadiene rubber (PBR) (96% 1,4 cis structure) of ML-4 at 100 °C 46, specific gravity 0.9, volatile content 0.3%, and ash content 0.2% and styrene monomer were used. The monomer was purified by drying over anhydrous BaO and then by vacuum distillation. The middle fractions were used in polymerization experiments.

Benzoyl peroxide (Bz_2O_2) from BDH, India was purified by repeated crystallization from chloroform and was used as the initiator for polymerization of styrene.

Dicumyl peroxide (DCP) (98% peroxide content) was used as the crosslinker for PBR. Divinylbenzene (DVB) was used as a comonomer along with styrene for achieving crosslinking of polystyrene.

2.2. Synthesis of PBR network

PBR was masticated on a laboratory open mill (cold mill) for 2 to 3 minutes. DCP in different doses (0.05 to 0.5 phr) was mixed with the masticated PBR for a period of 5 to 6 min. DCP mixed PBR in sheet form was then cured in an electrically heated press at a temperature of 170 °C and a pressure of 1 ton/inch^2 (1 ton = 1016 kg, 1 inch = 2.54 cm) for definite time

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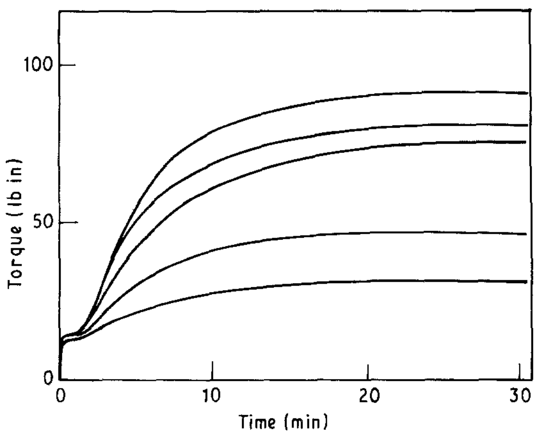

Figure 1 Rheographs showing torque against time plot at 170 °C for PBR cured with different doses of DCP. Data given for each curve is DCP in phr. (1, 0.05, 2, 0.1; 3, 0.2; 4, 0.3; 5, 0.5).

periods much in accordance with the preliminary rheometric data.

2.3. Swelling of PBR network in styrene

Cured PBR of different crosslink densities depending on the DCP dose used, were then allowed to swell with excess styrene monomer for different time periods (1 min to 7 days) and the corresponding percentage styrene intake by different PBR networks for different times of swelling were determined gravimetrically and the respective calibration curves, showing percentage styrene intake plotted against time, were prepared (Fig. 2). Expansion of the cured PBR sheets on swelling in styrene monomer depended on its crosslink density (DCP dose) and time of swelling. A calibration curve for each PBR network, showing percentage increase in length of the swollen strip of specified length plotted against time of swell was also drawn for use as a guideline in subsequent experiments for preparation of IPNs at different PBR–styrene blend ratios (Fig. 3).

Bz_2O_2 (0.5 wt %) and divinyl benzene (0 to 5 wt%) respectively were dissolved or mixed with styrene monomer and five different sets of mixtures containing different doses of the comonomer DVB were prepared. PBR sheets of predetermined sizes of different crosslink densities were then allowed to swell in the monomer (styrene) or monomer mixtures (styrene containing 1 to 5% DVB) for specific time periods so as to obtain the following PBR–styrene ratios (w/w) namely 80:20, 70:30, 60:40, 50:50, 40:60, 20:80 for the swollen mass. In each case, the swollen mass was kept at a temperature of 0 °C for 12 h in a closed chamber for maturation to uniformity with respect to monomer distribution in the PBR network.

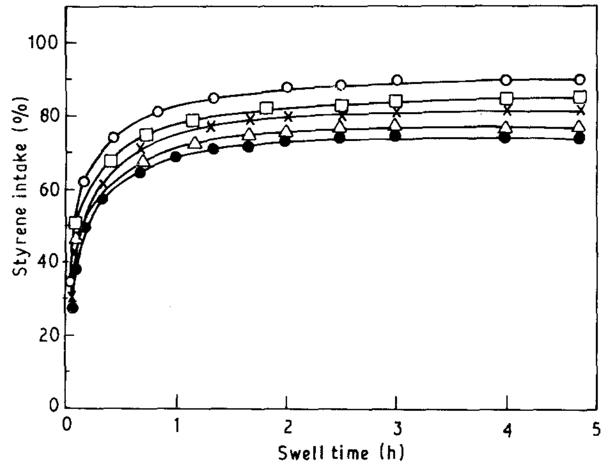

Figure 2 Variation of styrene intake by PBR networks with time at 27 °C. Data given for each curve are DCP in phr. (○ 0.05, □ 0.1, × 0.2, △ 0.3, ● 0.5).

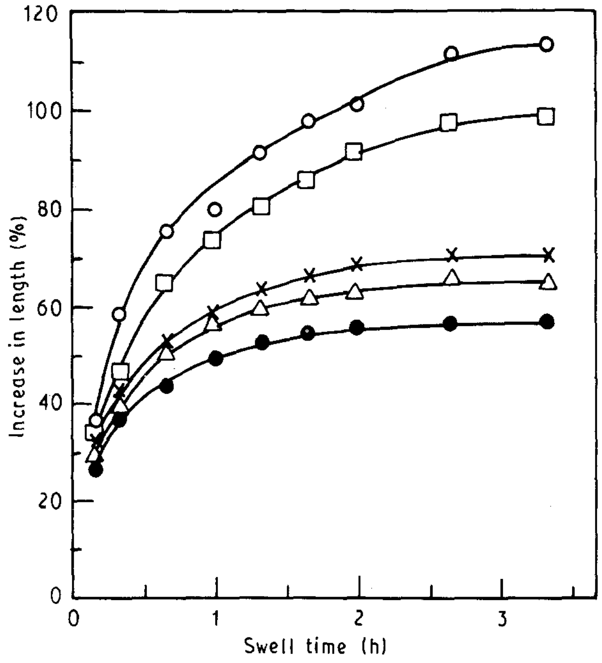

Figure 3 Variation in % increase in length of crosslinked PBR sheet ($20 \times 20 \times 1.5$ mm^3) with time of swelling in styrene monomer. Data given for each curve are DCP in phr. (○ 0.05, □ 0.1, × 0.2, △ 0.3, ● 0.5).

2.4. Formation of PBR–PS IPNs

Each swollen mass was then transferred in a closed mould where the monomer styrene (with or without low doses of DVB) was allowed to polymerize initially at a temperature of 75 °C for 10 h and finally at 100 °C for 2 h into a hardened–stiffened sheet, which was taken out and weighed. Any unreacted monomer, if retained in the polymerized sheet, was finally removed by keeping the sheet in a vacuum chamber for over a week. The weight loss as a consequence to vacuum application was always within 3% of the styrene intake of the initial swollen mass, indicating nearly or more than 97% polymerization of the monomer system in the final phase of polymerization–network formation.

2.5. Characterization of the IPNs

2.5.1. Evaluation of physical–mechanical properties of different PBR–PS full- and semi-IPNs

2.5.1.1. Tensile properties. The major properties measured were tensile strength (TS), percentage elongation at break and modulus at 50% elongation. Measurements were made according to ASTM D-412 and ASTM D-638 for IPN samples having plastomer content less than and greater than 50%, respectively.

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

2.5.1.3. Hardness (Shore A). Hardness of the IPN samples was measured by means of a shore A durometer according to ASTM, D 2240-64T.

2.5.1.4. Density. The density of the samples was measured according to ASTM, D-792.

2.5.1.5. Gel content. Each IPN sample was reduced by crushing or chipping into small granules or flakes and a measured amount was then subjected to Sohxlet extraction using benzene as the solvent for fifteen days and the percentage of insoluble matter was taken as the gel content of the IPN.

2.5.1.6. Molecular weight between crosslinks (M_c). When a cross-linked polymer is placed in a suitable solvent at a given temperature, the polymer imbibes the solvent and undergoes swelling to an extent determined by the nature of the polymer including its crosslink density and nature of the solvent used. At equilibrium the swelling by a good solvent is given by Flory–Rehner equation [1–3] as given below

$$\frac{1}{M_c} = \frac{V_P + \chi V_P^2 + \ln(1 - V_P)}{d_p V_o (V_P^{1/3} - V_{P/2})}$$

where M_c is the Molecular weight between crosslinks, V_P the volume fraction of polymer in swollen mass, V_o the molar volume of the solvent, d_p the density of the polymer and χ the polymer solvent interaction parameter, which was calculated according to the Bistow and Watson equation [4]

For each IPN sample, equilibrium swelling was done using benzene as the solvent at a temperature of 27 °C for seven days.

2.5.1.7. Studies on phase morphology. Selected PBR–PS FIPN and semi IPN specimens in the form of sheets were cut into size and trimmed to a rectangular shape to produce a flat surface. The samples were then subjected to etching [5] in an acid bath containing 100 ml concentrated H_2SO_4, 32.5 ml, H_3PO_4, 31.25 ml, H_2O and 5 g CrO_3 for a period of 2 h at a temperature of 80 °C. The specimens thus etched by the oxyacid system were washed and then dried thoroughly. The dried specimens were duly coated with gold in a sputter coater and examined in a scanning electron microscope.

3. Results and discussion

We tried to develop two different types of network polyblends based on polybutadiene, PBR (elastomer component) and polystyrene, PS (plastomer component). The first network type was one in which the elastomer and plastomer components were sequentially crosslinked, giving what may be called full interpenetrating polymer networks (full IPN) and the other, giving a semi-interpenetrating network (semi IPN), was synthesized by formation of apparently linear plastomers (PS) on the initially formed elastomer (PBR) networks. The variables during network formation were (a) dose of dicumyl peroxide (DCP), effecting variations in the crosslink density of the elastomer (network) component, (b) divinyl benzene (DVB) dose, effecting variations in the crosslink density of the plastomer (network) component and (c) variation of PBR–styrene ratio at the beginning of formation of the plastomer, thereby giving different PBR–PS blend ratios in the finally produced elastomer–plastomer blends. The effects of variations in the crosslink densities of the elastomer and plastomer components and of the variation in the elastomer–plastomer blend ratio were studied and comparatively evaluated and related results are described and discussed below.

Before synthesizing the IPN materials, some preliminary investigations were made on polybutadiene rubber crosslinked with different doses of dicumyl peroxide (DCP), (0.05 to 0.5 phr).

3.1. Curing characteristics of PBR using DCP as the curative

The curing characteristics of DCP-induced crosslinking of PBR are presented in Table I. PBR was mixed with different doses of DCP and the curing of the different compounds was separately studied rheometrically at 170 °C using Monsanto Rheometer 100, and selected rheographs are given in Fig. 1.

Over the DCP range of 0.05 to 0.5 phr, the attainable minimum torque, taken as an index of plasticity of the test compound at the processing temperature, ranges between 13.2 and 15.2 lb in (1 lb = 0.453 kg). The maximum torque in lb in shows an increasing trend, as expected, with increasing dose of the curative (i.e. DCP 0.05 to 0.5 phr). The difference between the maximum and minimum torque consequently shows an increasing trend, beginning from 17.4 lb in corresponding to the use of 0.05 phr DCP to as high a value as 78 lb in corresponding to the use of 0.5 phr DCP (Table I). The scorch safety of the compound decreases as the DCP dose increases. The optimum cure time ranges between 12 to 15 minutes over the range of DCP dose used. The cure rate (lb in $\min^{-1}$) computed from the initial steady part of the torque rise zone of the rheometric curves follows an increasing trend with increasing DCP dose (Table I).

TABLE I Curing characteristics of PBR compounds and physical properties of the vulcanizates: Curing condition temperature 170 °C, pressure 1 ton/inch^{-2}

Properties	DCP (phr)				
	0.05	0.1	0.2	0.3	0.5
Rheometric					
Maximum torque (lb in)	31.6	48.0	76.8	81.6	92.0
Minimum torque (lb in)	13.2	14.0	15.2	14.0	14.0
Torque difference (lb in)	17.4	34.0	61.6	67.6	78.0
Scorch time (min)	3.2	2.0	2.0	2.2	1.4
Optimum cure time (min)	12.5	13.5	15.0	13.7	13.0
Cure rate (lb in min^{-1})	2.2	4.8	6.7	9.9	12.8
Physical					
T.S. (kg cm^{-2})	7.0	13.0	14.0	15.0	10.0
EB (%)	340	410	295	225	100
50% Modulus (kg cm^{-2})	3.0	6.4	7.5	10.2	10.0
Tear strength (kg cm^{-1})	3.3	5.8	4.4	4.3	1.9
Hardness (shore A)	–	36	42	49	51
Density (g cm^{-3})	0.899	0.899	0.901	0.903	0.906
Gel content (%)	83	93	97	98	99
M_c (g mol^{-1})	65837	15552	8431	5402	4229
Toughness (kJ)	0.00018	0.00038	0.00032	0.00025	0.00008

3.2. Swelling behaviour of the crosslinked PBR networks

Five different PBR networks of different crosslink densities corresponding to the use of five different doses of DCP prepared as above were separately allowed to swell with excess styrene monomer for different time periods (1 minute to 7 days) and two different sets of calibration curves, one showing percentage styrene intake plotted against time and the other showing percentage increase in length of the PBR network strip plotted against time were drawn, Figs 2 and 3, respectively. The swelling curves show a levelling off trend beyond about the first 5 to 10 min and after equilibrium swelling under the given condition (allowing greater than 7 days of swelling), the difference in the percentage styrene intake or percentage increase in length by the test strips corresponding to the different DCP doses becomes steady or constant, higher DCP dose showing lower styrene intake and lower linear expansion.

3.3. Physical and Mechanical properties of the PBR networks

Some physical and mechanical properties such as tensile strength (TS), tensile modulus, elongation at break (EB) (%), tear strength, hardness, density, gel content, molecular weight between the crosslinks (M_c) of the PBR networks are also shown in Table I.

The increasing trend in the crosslink density in the PBR networks consequent to the use of increasing dose of DCP in the initial PBR compounds is further reflected in the increasing trend in the gel content and decreasing trend in the M_c values (from a gel content of 83% and M_c value of 65 837 to a gel content 99% and M_c value of 4229 for the use of 0.05 and 0.5 phr DCP respectively (Table I). Considering TS, modulus, EB (%), tear strength data against the gel content and M_c values, it is indicated that a DCP dose of 0.1 phr, produces PBR network giving an overall balance of physical–mechanical properties, and crosslink density. A DCP dose of $\geqslant 0.2$ phr leads to networks of higher TS, modulus and crosslink density (lower M_c value) but the relevant products show much lower elongation and tear strength.

3.4. Properties of PBR–PS IPN systems

The effect of variation of DCP dose and DVB dose on different mechanical and physical properties of PBR–PS semi and full IPNs are shown in Figs 4 and 5. Among the six different blend ratios studied herein (PBR:PS taken as 80:20, 60:40, 50:50, 40:60, 30:70 and 20:80 w/w), data for three of them (80:20, 50:50, and 30:70 blend ratios) showing the effect of variation of DCP dose and DVB dose on the physical and mechanical properties of the final networks (IPNs) are shown in Figs 4 and 5 and those for the other three blend ratios, exhibiting more or less similar property trends, are not shown.

3.4.1. Effect of variation of DCP and DVB dose

3.4.1.1. Tensile strength and tear strength. It is seen from Fig. 4 that as the DCP dose increases, tensile strength (TS) and tear strength follow an initial increasing trend, pass through a maximum and then follow a dropping trend. The maximum corresponds to 0.1 phr dose of DCP for both semi IPN and full IPN systems for all blend ratios (PBR:PS). It is also clear from Fig. 4 that full IPNs are characterized by prominently higher tensile and tear strengths, than the semi IPNs and among the full IPNs the two properties follow an increasing trend with increase in the DVB dose i.e. with development of higher crosslink density of the plastomer phase.

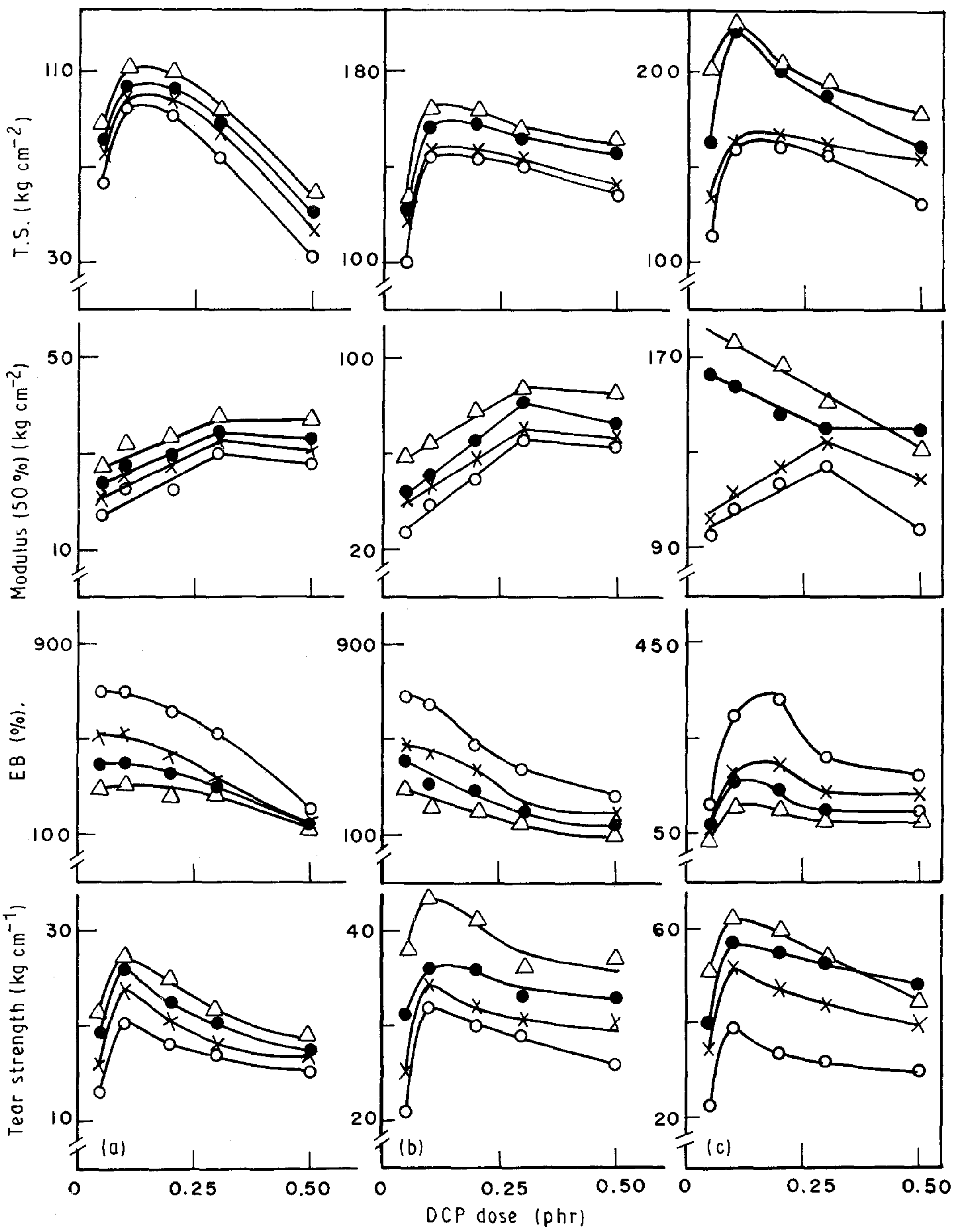

Figure 4 Mechanical properties of PBR–PS FIPNs and semi-IPNs. Effect of DCP dose variation. Sets of curves under A, B and C refer to 80:20, 50:50 and 30:70 PBR–PS blend ratios (W/W) respectively. Data given for each curve are DVB dose (in wt % of styrene monomer): (○ 0, × 1, ● 3, △ 5).

3.4.1.2. Elongation at break, EB (%). EB (%) is usually higher for the semi IPNs than for the full IPNs for all blend ratios and increase in DVB dose progressively lowers the EB (%), as expected.

For 80:20 (and also for 60:40 not shown) PBR:PS blend networks (both semi and full IPNs), the EB (%) values remain close or comparable over the DCP dose range of 0.05 and 0.1 phr, the EB (%) values, however, follow a decreasing trend as the DCP dose further increases, Fig. 4. For 30:70 PBR–PS blend networks (and also for 40:60 and 20:80 blend ratios, not shown), the EB (%) values pass through a distinct maximum over a DCP dose range between 0.1 and 0.2 phr as the DCP dose was varied from 0.05 to 0.5 phr, Fig. 4. For 50:50 PBR–PS blend network systems, EB (%) apparently follows a decreasing trend over the full range of DCP dose studied.

It is interesting to note further from analysis of the full set of data given partly in Fig. 4 that for a higher range of PBR:PS blend ratios (containing ⩾ 50% PBR), the intensity or degree of variation in EB (%) values with variation in the DCP dose tends to taper off or narrow down as the DVB dose in the system increases from 0 to 5% by weight of the styrene monomer. For blends with lower PBR content (PBR < 50 wt %), the difference in EB (%) of different IPNs are narrower at low and high DCP doses but much wider over the DCP dose of 0.1 to 0.2 phr.

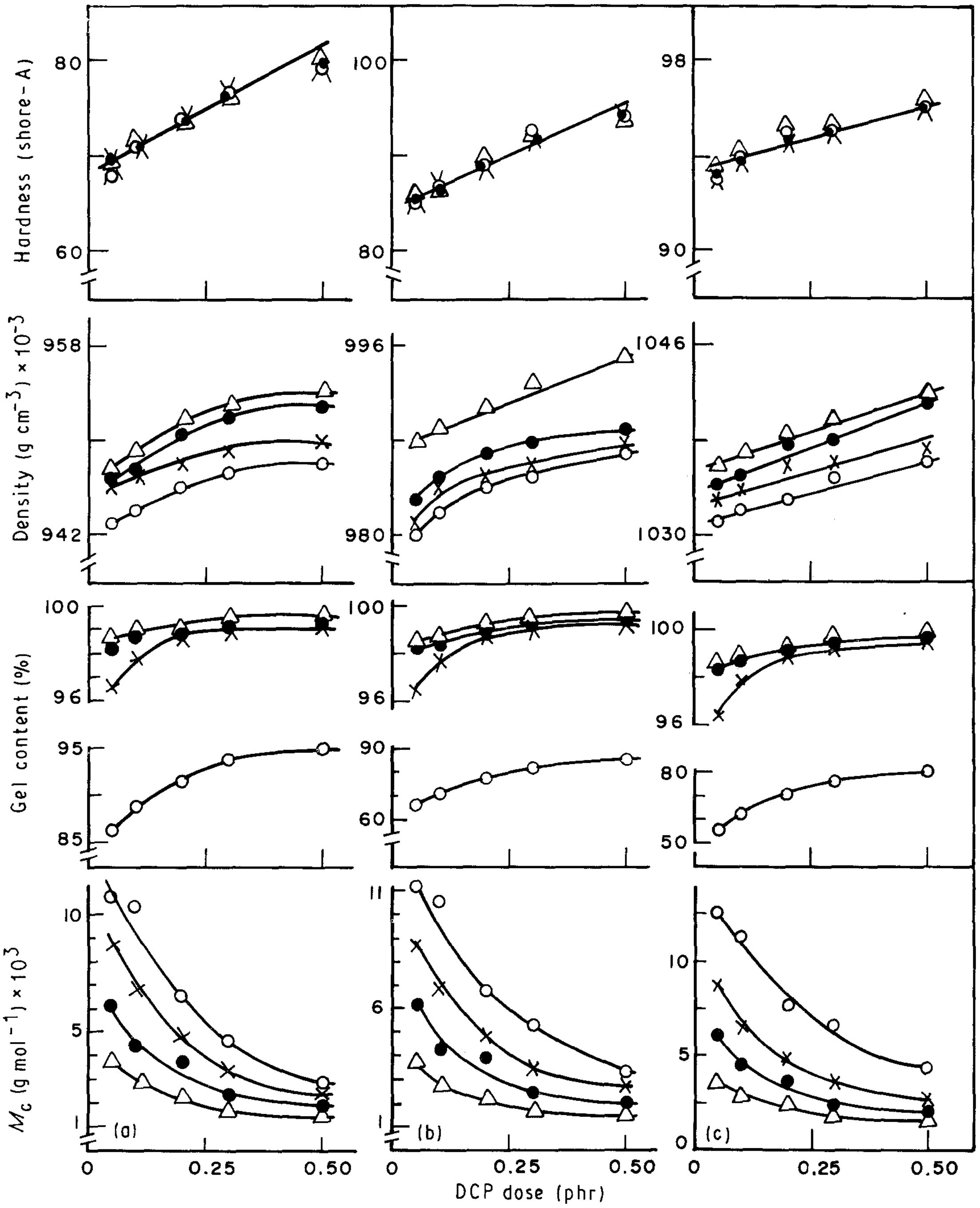

Figure 5 Variation of hardness, density, gel content and M_c of PBR–PS FIPNs and semi-IPNs with variation of DCP dose. Sets of curves under A, B and C refer to 80:20, 50:50 and 30:70 PBR–PS blend ratios (w/w), respectively. Data given for each curve are DVB in wt % of styrene monomer (○ 0, × 1, ● 3, △ 5).

3.4.1.3. Modulus at 50% elongation. Modulus variation with the variations in the doses of DCP and DVB does not apparently follow a uniform pattern. An increasing trend in modulus variation with increase in DCP dose in the initial low range of DCP (upto about 0.3 phr DCP) followed by a levelling off trend is the characteristic feature of blends having high PBR content ($\geqslant$50 wt % PBR).

When polystyrene (PS) becomes the major component in the blend the modulus values tend to show a maximum when plotted against DCP for all semi IPNs and for most full IPNs. For full IPNs with PS content $\geqslant$ 70 wt % the modulus values are also found to follow a decreasing order with increasing DCP dose, more so for full IPNs prepared by using higher doses of DVB, showing at the same time very high modulus values corresponding to blend networks for which the initial elastomer network was prepared using a low DCP dose.

3.4.1.4. Hardness. It is seen from Fig. 5 that for a specific blend ratio of PBR–PS, both the semi IPN and the full IPNs based on different DVB doses exhibit nearly the same or very close hardness values for a given dose of DCP and with increase in the DCP dose, the hardness values of each kind of IPN follow nearly comparable and much the same increasing trend, Fig. 5. For a given blend ratio, the hardness of the IPNs is found to depend on the DCP (elastomer

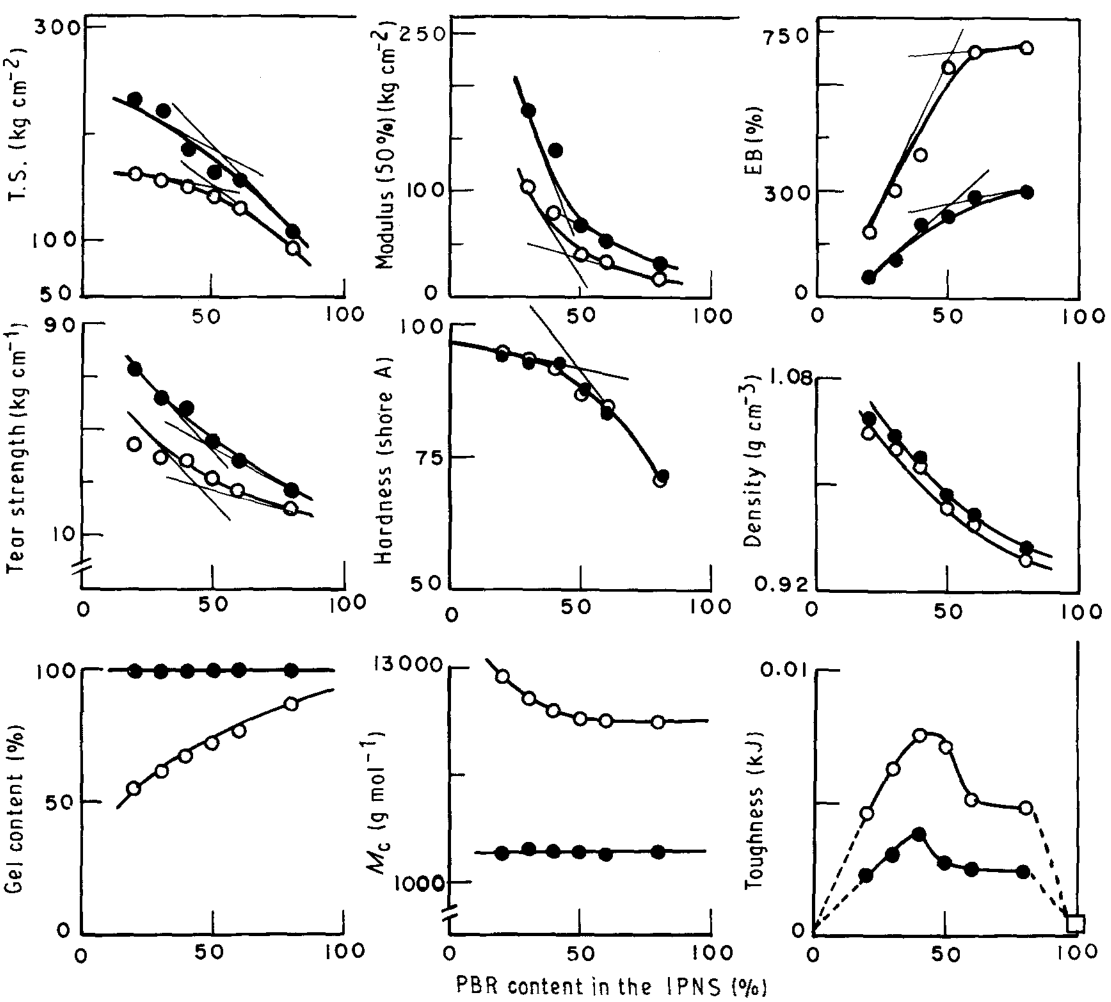

Figure 6 Mechanical and physical properties of PBR–PS FIPNs and semi-IPNs with variation of PBR–PS blend ratio (W/W). Data given for different curves are DCP dose in phr and DVB dose in wt % of styrene monomer (○, 0.1 DCP, 0 DVB, ●, 0.1 DCP, 5 DVB). The symbol □ on the right hand side ordinate represents the toughness of PBR crosslinked with 0.1 phr DCP.

crosslinker) dose only and DVB dose variation (0 to 5 wt % of styrene) produces little change in the hardness value.

3.4.1.5. Density. The PBR–PS blend networks, semi and full IPNs as prepared for the present studies came in the density range of 0.94 to 1.05 g cm^{-3}, Fig. 5. Over the DCP dose range studied (0.05 to 0.5 phr), the densities of both semi and full IPN, show an increasing trend with increasing DCP dose.

For all semi and full IPN systems (having PBR:PS in different weight proportions), the percentage increase in density lies within 0.5 to 0.7% for an increase in DCP dose from 0.05 to 0.5 phr. It is also observed that the densities of the full IPNs are higher than those of the semi IPNs and that for the full IPNs, the density value follows an increasing trend with increase in the DVB dose.

3.4.1.6. Gel content. Full IPNs are characterized by a higher gel content than the corresponding semi IPNs and the differences in gel content between the semi and full IPNs become narrower as the DCP dose increases from 0.05 to 0.5 phr (Fig. 5). The relative increase in gel content with increase in DCP dose was found to be much higher in the semi IPN systems than in the full IPNs.

3.4.1.7. Molecular weight between crosslinks (M_c). The overall M_c values for the IPN systems follow a decreasing trend with an increase in DCP dose. The percent decrease in the M_c value with an increase in the DCP dose was relatively low for the full IPNs than the corresponding semi IPNs (Fig. 5). Full IPNs are characterized by a lower overall M_c value than the semi IPNs and for a specific blend ratio the M_c values for the full IPNs follow a dropping trend with increase in the DVB dose.

3.4.2. Effect of blend ratio variation

From an analysis of Figs 4 and 5 one may frame an idea, though with some difficulty, about the effect of variation of blend ratio on different physical and mechanical properties of PBR–PS blend networks (both semi and full IPNs). For a proper understanding of the effect of blend ratio variation the graphical plots as shown in Fig. 6 will, however, be more helpful.

It is seen from Fig. 6 that with increase in elastomer (PBR) content in the blends the mechanical properties such as tensile strength, modulus, tear strength and hardness follow a dropping trend whereas the elongation at break (%) follows an increasing trend. Regarding TS, modulus and tear strength an important though common observed effect is that the differences in the respective properties, for the different IPNs based on variation of DVB dose (0 to 5 wt% of styrene monomer used) substantially narrow down as the elastomer content of the blend increases. The property differences between the IPNs with respect to EB (%) however, follow a prominent broadening trend with increase in PBR content in the blends. Data given in Fig. 6 are for systems where the DCP dose used to form the initial PBR network was 0.1 phr. IPNs from other DCP doses for initial PBR network formation also produced similar trends of data. As for density of the IPNs formed, a decreasing order is followed with increasing the elastomer content in the blends and the differences in the density values of different IPNs remain practically constant over the whole blend ratio range studied. It is also seen from Fig. 6 that with an increase in the elastomer content, the properties such as gel content and M_c of the network agglomerates for the full IPNs remain almost constant whereas those for semi IPN systems exhibit a good degree of variation; with an increase in the elastomer content, the gel content of semi IPNs increases whereas the M_c values decrease.

Interestingly, the differences in the gel content for the different IPNs narrow down significantly with increase in the elastomer content.

The effect of variation of the blend ratio on the toughness of the semi and full IPN systems needs some special mention and discussion. The toughness of the elastomer–plastomer blend networks (both semi and full IPNs) 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 elongation ($50\,\mathrm{mm\,min^{-1}}$). It is found that the elastomer–plastomer blend networks (both semi and full IPNs) from all blend ratios exhibit toughness values which were substantially higher than that of the pure elastomer (experimentally determined) or of the plastomer (extrapolated value). Semi IPNs are characterized by a much higher toughness value than the full IPNs (Fig. 6). With an increase in the elastomer content in the blends, toughness values of both semi and full IPNs pass through a maximum corresponding to about 40:60 PBR–PS blend ratio. The 40:60 PBR–PS blend ratio, thus, appears to be a critical composition in terms of the structure of the network agglomerates and this is also reflected in many of the properties and physical characteristics of the IPNs. Tangents drawn on the initial and final curved zones of such properties as tensile strength, modulus, elongation, tear strength, hardness and gel content each plotted against PBR content (%), apparently intersect at points that roughly correspond to a blend ratio of nearly 40:60 to 50:50 PBR:PS.

3.5. Phase morphology of PBR–PS IPNs

Selected samples of semi IPN (uncrosslinked PS enmeshed in the PBR network) and full IPN (networks of PS enmeshed and interlocked in the PBR network) were examined under scanning electron microscope (SEM) for elucidation of their phase morphology and to analyse how variations of degree of crosslinking in each type of network and of PBR–PS blend ratio contributed to variation in phase distribution and pattern of phase morphology. The SEM micrographs selected and shown in Fig. 7 are those of (1) 70:30, (2) 50:50 and (3) 20:80 PBR:PS blends. Micrographs of semi IPNs are identified by the code numbers S_1, S_2 and S_3 and those of the full IPNs by the code numbers F_1, F_2 and F_3 corresponding to the above three blend ratios, respectively. DCP dose in each case was 0.05 phr and for the full IPNs, the DVB dose used was 5% on the basis of weight of styrene taken.

It may be seen that for a low PS content ($\leqslant 30\%$) in the blend (as for PBR:PS blend ratio 70:30), the phase contrast is not very prominent, the major phase (PBR given by the shadow or black zone) apparently allows the minor phase (PS given by the white specks or zones) to diffuse in, more so in the semi IPN, indicating little tendency of discrete domain formation or strong encompassment of one phase by the other (S_1 and F_1). The phase distribution was found to be more diffusive and overlap of the elastomer–plastomer phases resulted in still lower degree of phase contrast in the micrographs (not shown) for blends with still higher PBR content (PBR > 70%).

Under otherwise comparable conditions of processing and network build-up, a decreasing order in the PBR:PS blend ratio progressively leads to formation of spherical–round PBR domains and near 50:50 PBR:PS blend ratio, the PBR domains get firmly encompassed on the edges by thin layers of the PS phase, giving what may be called a wire-mesh structure. The domain diameters are usually higher for the semi IPN (S_2) than for the corresponding full IPN (F_2).

The pattern of phase morphology comes in sharp contrast for blend networks of high PS content. The PBR domains progressively fail to hold their spherical–round contour probably due to overgrowth of linear polystyrene or polystyrene networks through *in situ* polymerization of monomer styrene on the monomer swollen PBR network causing a good degree of volume contraction and consequent generation of pressure on the elastomer domains in the process. The PBR domains embedded in the PS matrix take irregular shapes showing relatively wide size distribution, more so in the semi IPN, and the micrograph S_3 shows the phase morphology of a semi IPN having PBR:PS blend ratio of 20:80, while for the corresponding full IPN, the PS matrix encompassing the PBR phase retains the wiremesh type structure, the PS phase appearing as long fine ridges while the PBR domains mostly appear as somewhat elongated (non-spherical domains) troughs between the encompassing ridges of the PS phase, though of wide size distribution (F_3). A micrograph of the IPN corresponding to F_3 but of much higher magnification and coded as F_3' is

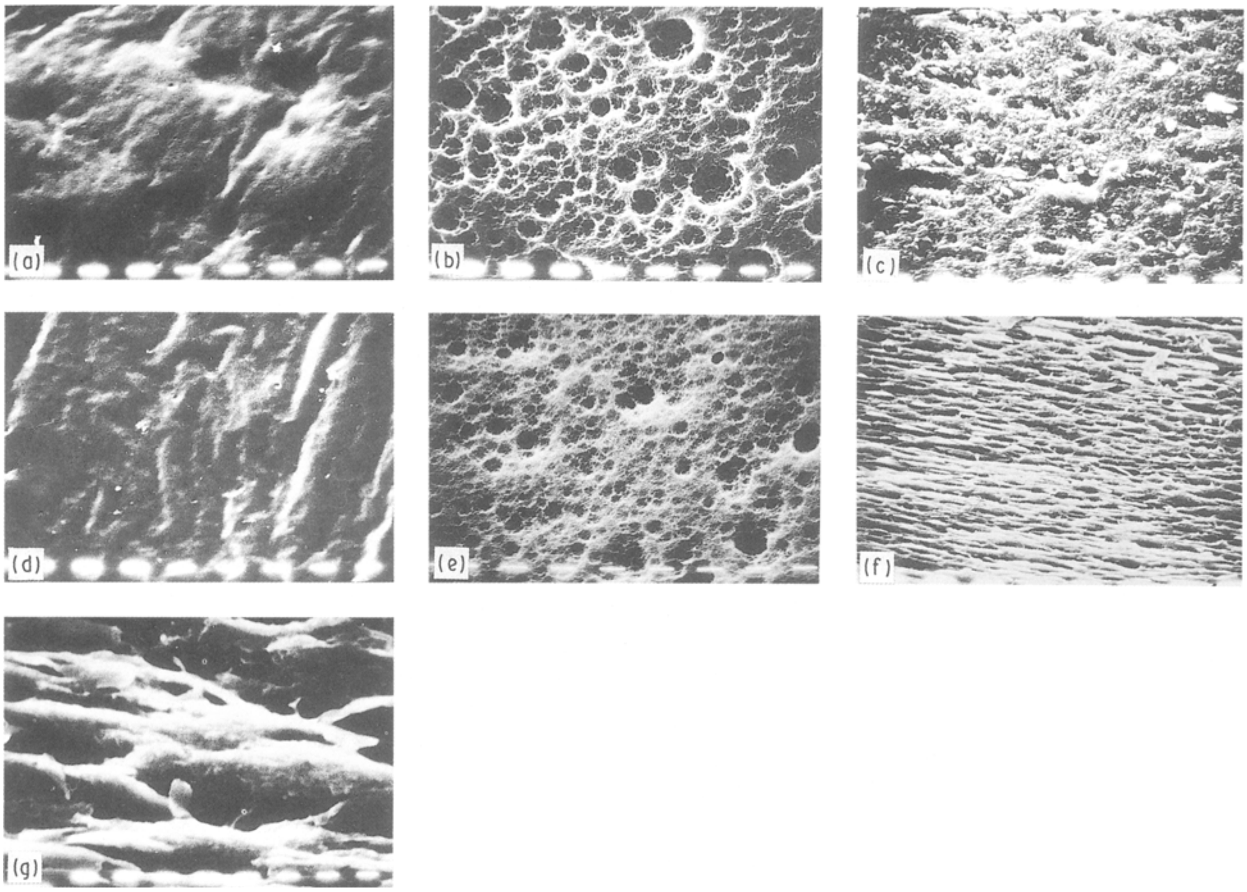

Figure 7 Scanning electron micrographs of PBR–PS FIPNs amd semi-IPNs (800 ×). Description of Micrographs. Semi IPN, DCP 0.05 phr, DVB 0 wt % (a) S_1, (b) S_2, (c) S_3. Full IPNs, DCP 0.05 phr, DVB 5 wt %, (d) F_1, (e) F_2, (f) F_3. Full IPN, DCP 0.05 phr, DVB 5 wt %, (6400 ×) (g) F'_3.

shown side by side for a better appreciation of the phase morphology of the full IPN.

Analysis of the micrographs showing the effect of variation in blend ratio points to a critical range of PBR:PS blend ratio around 50:50 to 40:60. Around this blend ratio, the phase morphological pattern undergoes a notable change akin to phase inversion. The higher mechanical properties of the full IPNs as compared to those of the corresponding semi IPNs are apparently linked to the presence of finer PBR domains in the former. Distribution of the PS phase as continuous long ridge-like or fibrillar structures for full IPNs having high PS content (> 50%) presumably imparts better reinforcing effect and thus contributes to a higher proportionate increase in the tensile strength, modulus, tear strength and hardness values, Fig. 6. Synergism in toughness, most prominent in the 50:50 to 40:60 PBR:PS blend ratio is apparently characteristic of spherical shape of the discrete domains of PBR encompassed by the PS phase.

Acknowledgement

Financial supports in the form of a fellowship Grant (to P. Ray) by the CSIR, India and through a project grant from the Ministry of Human Resources Development, Government of India, Department of Education are sincerely acknowledged.

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Received 30 July 1990
and accepted 12 February 1991