Polymer International *Polym Int* 50:1298–1308 (2001)
DOI: 10.1002/pi.775

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Compatibilization of SBR/NBR blends using chemically modified styrene-*co*-butadiene rubber
Part 2. Effect of compatibilizer loading

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Abstract: The present work focuses on the compatibization of styrene-*co*-butadiene rubber (SBR)/ acrylonitrile-*co*-butadiene rubber (NBR) blends with dichlorocarbene modified styrene-co-butadiene rubber (DCSBR) as a function of concentration of compatibilizer and composition of the blend. FTIR studies, differential scanning calorimetry and dynamic mechanical analysis reveal molecular level miscibility in the blends in the presence of compatibilizer. The formation of interfacial bonding is assessed by analysis of swelling behaviour, cure characteristics, stress–strain data and mechanical properties. These studies show that the compatibilizing action of DCSBR becomes more prominent as the proportion of NBR in the blend increases. The resistance of the vulcanizate towards thermal and oil ageing improved with compatibilization. The change in technological properties is correlated with the crosslink density of the blends assessed from swelling and stress–strain data.

Keywords: compatibilizer; dichlorocarbene modified styrene butadiene rubber; SBR/NBR blend; crosslink density

INTRODUCTION

Blending of two incompatible polymers yields a material with poor mechanical properties. The mechanical properties of such blends can be significantly improved by the addition of a suitable compatibilizer[1–4] during the processing stage. The compatibilizers can be block, graft or random copolymers[5–9] and the segments of these copolymers can be chemically identical with those in the respective phases.[10–12] These compounds reduce the macroscopic inhomogeneities and improve the morphological stability, by decreasing the interfacial tension and subsequently reducing the dispersed phase size[13–15] as expected from Taylor's theory.[16,17]

The selection of a copolymer as a compatibilizer for a polymer blend is important to ensure better compatibility. According to Paul and Barlow,[18] the compatibilizer must fulfil certain requirements. It is essential to know whether the copolymer is able to, (a) ensure fine dispersion during mixing, (b) be preferentially located at the interface between phases, (c) provide a stabilization effect against gross separation during processing, and (d) improve adhesion between blend components. Suitably selected copolymer may form an interphase between the immiscible blend components, so that imposed stresses can be transferred between the phases *via* the covalent bonds along the copolymer backbone.[19–21]

A thorough understanding of blend morphology is important because the properties of polymer blends are strongly dependent upon it.[22–26] It has also been observed that the procedure used to prepare compatibilized blends has a significant effect on their morphology and ultimate mechanical properties.[27,28]

Chlorinated polyethylene acts as a compatibilizer in chloroprene (CR)/ethylene-*co*-propylene diene monomer rubber (EPDM) and acrylonitrile-*co*-butadiene (NBR)/EPDM blends.[29] Poly(methyl methacrylate) (PMMA) acts as a compatibilizer in blends of natural rubber NR/NBR[30] and CR is also a compatibilizer in NR/NBR blends.[30] NBR is a good compatibilizer for PVC/styrene-*co*-butadiene rubber (SBR) blends.[31] Karger-Kocsis *et al*[32] and Thomas and co-workers[33] studied the relationship between morphology and impact behaviour of various polymer blends. Recently, the reactive compatibilization technique has been used for compatibilizing polystyrene having oxazoline reactive groups (OPS) and polyethylene with carboxylic acid groups (CPE).[34] Modifications of 70/30 PVC/NBR blends using NR and SBR have been attempted by George *et al.*[35] Their studies show that replacement of NBR by NR up to 15% (by weight) improves mechanical properties and decreases the cost of the blend.

It is possible to use a blend of high acrylonitrile NBR with styrene-*co*-butadiene rubber to obtain a degree of

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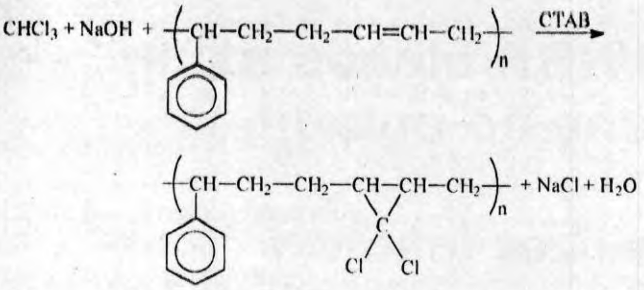
(Received 8 August 2000; revised version received 19 May 2001; accepted 29 June 2001)



Scheme 1. Structural changes of SBR during dichlorocarbene modification.

oil resistance equal to that given by a low acrylonitrile NBR with an overall reduction in cost. Products made from high acrylonitrile NBR have a tendency to shrink in contact with hot lubricating oils, and replacement of part of it by SBR overcomes this defect. Besides oil resistance, oil seals and gaskets sometimes require lower compression set at higher temperatures, and these can be improved by blending with SBR; blending also improves the processing properties. Blends of SBR and NBR are found to be immiscible[36] and can possibly be made miscible by using compatibilizers that can interact with both SBR and NBR. In this paper the effect of dichlorocarbene modified SBR (DCSBR) as a compatibilizer in SBR/NBR blends is evaluated and the amount of DCSBR required for compatibilization is studied in detail with reference to component miscibility, cure characteristics, swelling behaviour, mechanical properties, oil resistance and air ageing behaviour.

EXPERIMENTAL

The basic materials used in the study and their sources are as follows. Styrene-*co*-butadiene rubber (Synaprene 1502) having 25 wt% bound styrene was obtained from Synthetics and Chemicals Ltd, Bareilly, UP, India. Acrylonitrile-*co*-butadiene rubber (Aparene N553 NS) having 34% bound acrylonitrile content was supplied by Gujarat Apar Polymers Ltd, Mumbai, India. Dichlorocarbene modified styrene-*co*-butadiene rubber (DCSBR) containing 25% chlorine was used as the compatibilizer; it was prepared by alkaline hydrolysis of chloroform using cetyltrimethyl ammonium bromide as a phase transfer agent as described in a previous paper.[37] The structural change taking place during chemical modification is shown in Scheme 1. The number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$) and z average or sedimentation average molecular weight ($\overline{M}_z$), together with the polydispersities of the materials are given in Table 1. Rubber additives were reagent grade obtained from local rubber chemical suppliers.

Table 1. Molecular characteristics of SBR, NBR and DCSBR

Material	M_n (*g mol*$^{-1}$)	M_w (*g mol*$^{-1}$)	M_z (*g mol*$^{-1}$)	*Polydispersity*
SBR	125550	359500	996000	2.86
NBR	103120	268910	801410	2.61
DCSBR	164980	525780	1241100	3.19

Table 2. Formulation of 70/30 SBR/NBR blends

	Concentration of DCSBR (phr)				
Chemical	*0*	*1*	*3*	*5*	*10*
SBR	70	70	70	70	70
NBR	30	30	30	30	30
Zinc oxide	5	5	5	5	5
Stearic acid	1.2	1.2	1.2	1.2	1.2
CBS[a]	0.7	0.7	0.7	0.7	0.7
TMTD[b]	0.3	0.3	0.3	0.3	0.3
TDQ[c]	1.0	1.0	1.0	1.0	1.0
Sulphur	1.69	1.69	1.69	1.69	1.69

[a] CBS is *N*-cyclohexyl 1,2-benzothiazol sulphenamide.
[b] TMTD is tetramethyl thiuram disulphide.
[c] TDQ is 2,2,4-trimethyl 1,2-dihydroquinoline.

Table 3. Formulation of 50/50 SBR/NBR blends

	Concentration of DCSBR (phr)				
Chemical	*0*	*1*	*3*	*5*	*10*
SBR	50	50	50	50	50
NBR	50	50	50	50	50
Zinc oxide	5	5	5	5	5
Stearic acid	1.0	1.0	1.0	1.0	1.0
CBS[a]	0.5	0.5	0.5	0.5	0.5
TMTD[b]	1	1	1	1	1
TDQ[c]	1.0	1.0	1.0	1.0	1.0
Sulphur	1.35	1.35	1.35	1.35	1.35

[a–c] See footnotes in Table 2.

Master batches of SBR and NBR were prepared separately with all compounding ingredients without accelerator and sulphur. The master batches were blended at 70/30, 50/50 and 30/70 compositions. The compatibilized blends were prepared by adding DCSBR at various dosages of 1–10 parts per hundred resin (phr). The required quantities of curatives were then added and mixed properly with the preblended mixes as per formulation given in Tables 2–4. The mixing was done on a laboratory size two-roll mixing

Table 4. Formulation of 30/70 SBR/NBR blends

	Concentration of DCSBR (phr)				
Chemical	*0*	*1*	*3*	*5*	*10*
SBR	30	30	30	30	30
NBR	70	70	70	70	70
Zinc oxide	5	5	5	5	5
Stearic acid	0.8	0.8	0.8	0.8	0.8
CBS[a]	0.3	0.3	0.3	0.3	0.3
TMTD[b]	0.7	0.7	0.7	0.7	0.7
TDQ[c]	1.0	1.0	1.0	1.0	1.0
Sulphur	1.01	1.01	1.01	1.01	1.01

[a–c] See footnotes to Table 2.

mill (15 cm × 30 cm) at a friction ratio of 1:1.25 as per ASTM D-15-627.

Cure characteristics were studied using a Monsanto (USA) Rheometer R-100 at 150 °C according to ASTM D2705. The samples were vulcanized to their respective optimum cure time in a hydraulic press at 150 °C and pressure of 45 kg cm^{-2} on the mould. The tensile strength and tear resistance of samples were tested with a Zwick (Germany) Universal Testing Machine (Model 1474) at a temperature of 25 ± 2 °C and a crosshead speed of 500 mm min^{-1} according to ASTM D412-80 and ASTM D624-81, respectively. All other physical properties were determined according to the relevant ASTM standards.

The efficiency of compatibilizer was assessed by determination of T_g using a Perkin Elmer (USA) differential scanning calorimeter, operated at a heating rate of 15 °C min^{-1} within the temperature range −80 to +20 °C. IR spectra of the blends were recorded with a Shimadzu-8101 (Singapore) M Fourier transform infrared spectrometer using a pyrolysate of the sample. The dynamic mechanical analyses of blends were carried out using a dynamic mechanical analyser (DMTA MK-II) at 4% dynamic strain and at a frequency of 0.1 Hz.

RESULTS AND DISCUSSION

Differential scanning calorimetry

The DSC traces of pure SBR, NBR and 50/50 SBR/NBR blend in the presence and absence of compatibilizer are presented in Fig 1. Pure SBR shows a T_g at −56 °C[38] and pure NBR (containing 34% AN) shows two transitions[39] at −38 °C and −28 °C. For uncompatibilized 50/50 blend, there appear to be two transitions in the temperature range −68 to −28 °C which shows the presence of microlevel inhomogeneity. The transitions at −56 °C and −28 °C for the blend correspond to the transition of pure SBR and pure NBR, respectively. However, the 50/50 blend with 3 phr DCSBR (Fig 1(e)) exhibits two transitions which become closer than in uncompatibilized blends, indicating that 3 phr DCSBR is insufficient to bring about enhanced interaction between the SBR and NBR phases. However, the blend with 5 phr compatibilizer shows a single transition at −44 °C in the temperature range −68 to −29 °C; the single transition implies that one phase is present, showing that DCSBR acts a compatibilizer in the blends of SBR/NBR.

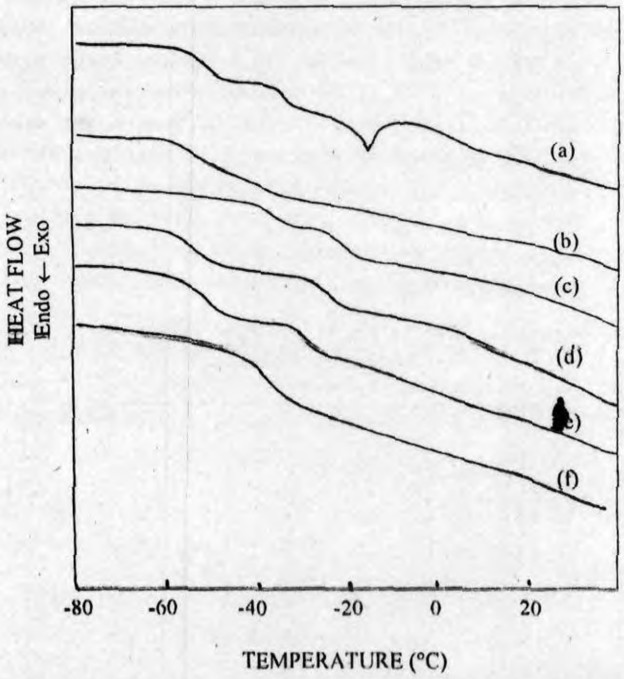


Figure 1. DSC thermograms of (a) DCSBR, (b) SBR, (c) NBR, (d) 50/50 SBR/NBR blend, (e) 50/50 SBR/NBR with 3 phr compatibilizer, and (f) 50/50 SBR/NBR with 5 phr compatibilizer.

FTIR analysis

IR spectra of the pyrolysates of SBR, NBR, DCSBR, 50/50 SBR/NBR and 50/50 SBR/NBR containing 3 and 5 phr of DCSBR containing 25% chlorine are shown in Fig 2, and the IR absorption data are given in Table 5.

It is assumed that there would be polar–polar interactions between the chlorine of DCSBR and the cyanide group of acrylonitrile repeat units present in NBR which leads to miscibility in these blends. It was shown earlier[30] that methyl methacrylate grafted

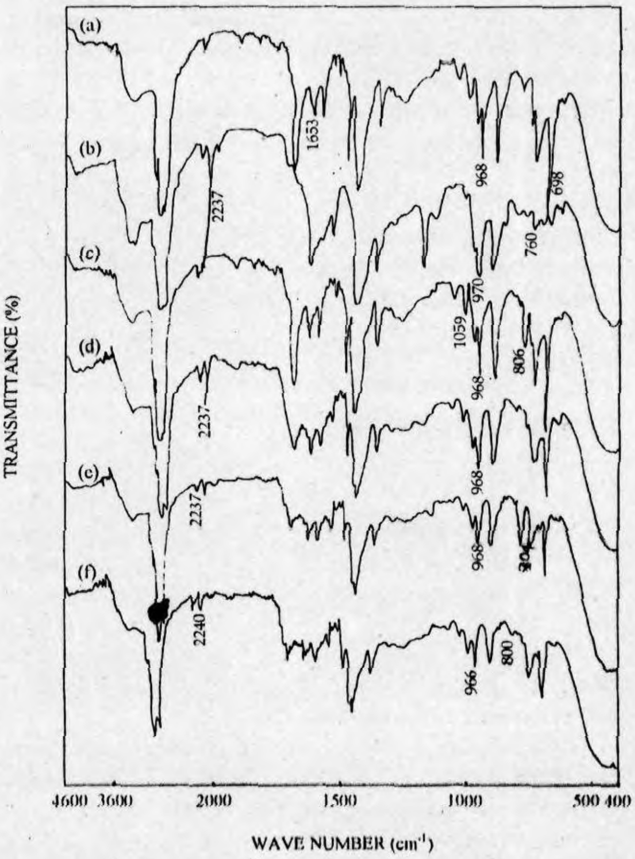


Figure 2. FTIR spectra of pyrolysates of (a) SBR, (b) NBR, (c) DCSBR, (d) 50/50 SBR/NBR, (e) 50/50 SBR/NBR containing 3 phr DCSBR and (f) 50/50 SBR/NBR containing 5 phr DCSBR.

Table 5. IR absorption peaks of SBR, NBR, DCSBR, 50/50 SBR/NBR, 50/50 blend containing 3 phr DCSBR, and 50/50 blend containing 5 phr DCSBR

Material	*Wavenumber (cm^{-1})*	*Assignment*
SBR	968	*Trans*-CH=CH—
	698	Aromatic substitution
	1653	*Cis*-CH=
NBR	2237	—C≡N
	970	*Trans*-CH=CH—
	760	Aromatic substitution
DCSBR	968	*Trans*-CH=CH—
	806	C—Cl
	1059	Cyclopropane
50/50 SBR/NBR	2237	—C≡N
	968	*Trans*-CH=CH—
	756	Aromatic substitution
50/50 SBR/NBR with 3 phr DCSBR	2237	—C≡N
	804	C—Cl
	968	*Trans*-CH=CH—
	756	Aromatic substitution
50/50 SBR/NBR with 5 phr DCSBR	2240	—C≡N
	966	*Trans*-CH=CH—
	800	C—Cl
	758	Aromatic substitution

natural rubber and CR act as compatibiliser in blends of NR/NBR because of the possible interactions between the compatibilized NBR units. The polar–polar interactions affect IR absorption peaks of the groups concerned.[40–42] As seen from the IR spectrograph and IR absorption data, with an optimum concentration of DCSBR there is sufficient polar interaction between DCSBR and NBR. Pure NBR and 50/50 blends of NBR and SBR show an IR absorption at 2337 cm^{-1} due to CN stretching, whereas NBR/SBR blends containing 5 phr DCSBR show a shift in absorption to 2240 cm^{-1}. There is no shift in the IR absorption for SBR/NBR blends containing 3 phr DCSBR because the amount of DCSBR is not sufficient to affect the interaction in the IR region.

Dynamic mechanical analysis

Figure 3 is the plot of storage modulus *versus* temperature for SBR and NBR from which it is clear that there is a transition in the storage modulus of SBR for a temperature range −35 to −14 °C. In the case of NBR, the transition in the storage modulus occurs in the temperature range −49 to −36 °C; there is also another weak transition in the temperature range −20 to −3 °C. It can be seen that SBR shows a slightly higher storage modulus than NBR.

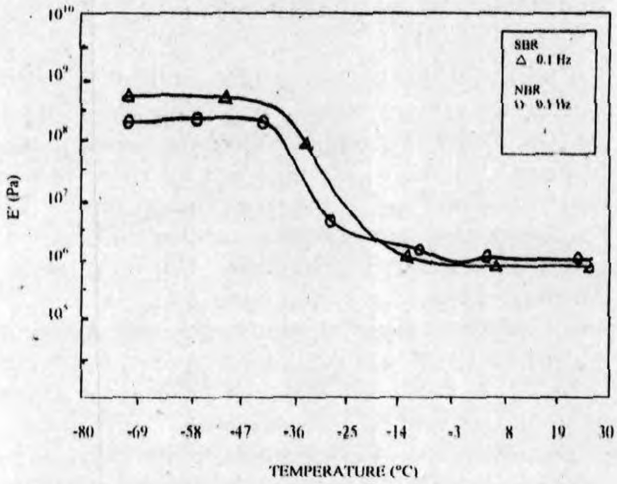


Figure 3. Variation of storage modulus *E'* at 0.1 Hz with temperature for SBR (△) and NBR (○).

The variation of storage modulus with temperature for uncompatibilized and compatibilized 50/50 SBR/NBR blends is shown in Fig 4. It is clear that uncompatibilized and compatibilized samples show higher storage moduli than their individual components. The uncompatibilized 50/50 blend shows a drop in storage modulus at around −36 and −14 °C revealing its incompatibility. After the addition of 3 phr DCSBR, the drop in storage modulus is again a two-step process, but when the concentration of DCSBR increases to 5 phr there is only a single transition in storage modulus at around −25 °C, thus revealing that DCSBR acts as a compatibilizer in SBR/NBR blends.

The above behaviour could be seen very clearly in the plots of loss modulus and tan δ. The variation of loss modulus with respect to temperature is presented in Fig 5. The loss modulus reaches a peak value for the SBR sample at around −30 °C while in the case of NBR there are two maxima at −17 and −9 °C. The presence of two T_g values for NBR has been reported.[39]

Blends have a lower loss modulus than pure SBR and NBR (Fig 6). In the case of 50/50 SBR/NBR blend there are two maxima in the viscous modulus at −34.67 °C and −12.7 °C. However, with the addition of 5 phr of DCSBR containing 25% chlorine, two peaks are no longer visible and instead a single peak appears at −25 °C. When the concentration of DCSBR is 3 phr, there are again two peaks with

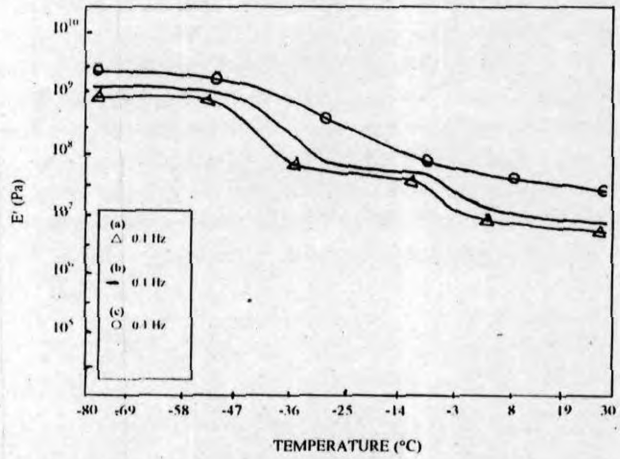


Figure 4. Variation of storage modulus *E'* at 0.1 Hz with temperature for 50/50 SBR/NBR blends (△), blend with 3 phr DCSBR (—), and blend with 5 phr DCSBR (○).

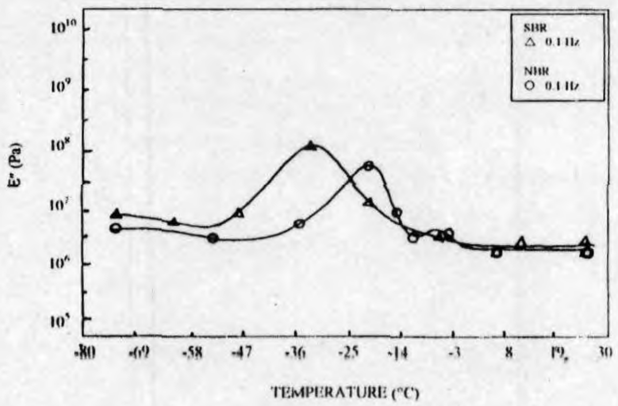


Figure 5. Variation of loss modulus E'' at 0.1 Hz with temperature for SBR (△) and NBR (○).

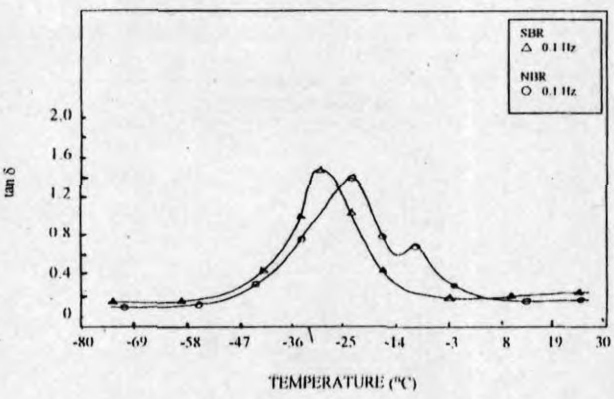


Figure 7. Variation of tan δ at 0.1 Hz with temperature for SBR (△) and NBR (○).

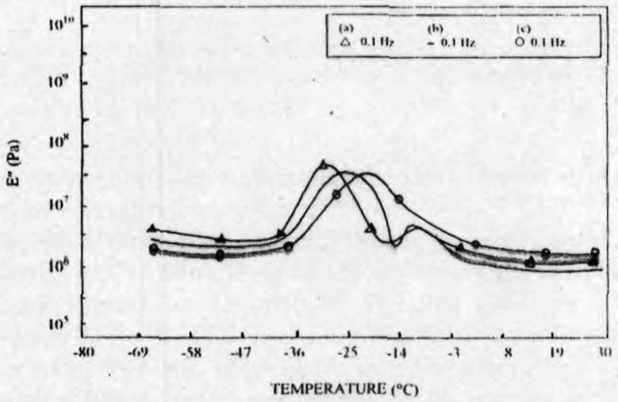


Figure 6. Variation of loss modulus E'' at 0.1 Hz with temperature for 50/50 SBR/NBR blend (△), blend with 3 phr DCSBR (—), and blend with 5 phr DCSBR (○).

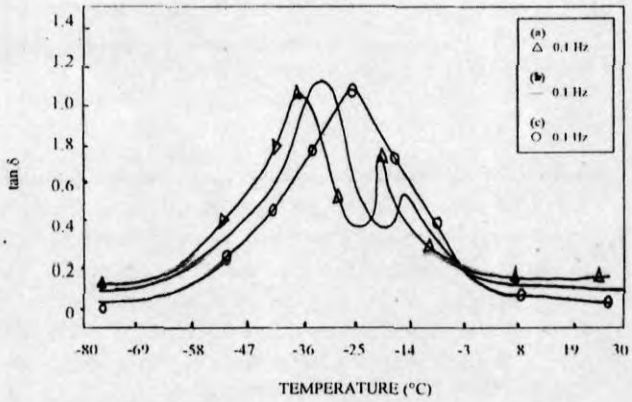


Figure 8. Variation of tan δ at 0.1 Hz with temperature for 50/50 SBR/NBR (△), (b) blend with 3 phr DCSBR (—), and blend with 5 phr DCSBR (○).

maxima at −32 °C and −13 °C showing that compatibilizer with a concentration of 3 phr is not sufficient to saturate the interface.

The tan δ plots for the similar compositions are given in Figs 7 and 8. The T_g obtained from the temperature corresponding to a maximum in tan δ is shown in Table 6. SBR presents a slightly higher tan δ value (damping) compared to NBR. SBR shows a T_g at −27.5 °C while that of NBR shows two T_g values, one at −22 °C and another at −8 °C. The blends have lower damping values than their individual components. The 50/50 SBR/NBR blend shows two T_g values (at −36 and −18 °C) due to the presence of two immiscible SBR and NBR phases. In the 50/50 blend containing 5 phr DCSBR, there is only one T_g at −25 °C which indicates the formation of a miscible SBR/NBR blend.

Effect of concentration of DCSBR on processing characteristics

Figures 9–11 show the rheographs of SBR/NBR blends containing various concentrations of DCSBR in different blend ratios. Table 7 gives the optimum cure time for SBR/NBR blends in the presence and absence of compatibilizer. The optimum cure time increases, whereas the scorch time and induction time decrease, as the NBR content of the blend increases. During vulcanization, interface crosslinking occurs *via*

Table 6. T_g determined from maxima in viscous modulus and damping for SBR, NBR, 50/50 SBR/NBR, 50/50 blend containing 3 phr DCSBR, and 50/50 blend containing 5 phr DCSBR at a frequency of 0.1 Hz

Sample	*Viscous modulus (°C)*	*Tan δ (°C)*
SBR	−29.5	
NBR	−17, −9	−22.5, −7
50/50 SBR/NBR	−34.67, −12.7	−36, −18
50/50 SBR/NBR with 3 phr DCSBR	−32.4, −12.1	−34, −14
50/50 SBR/NBR with 5 phr DCSBR	−25.8	−26.5

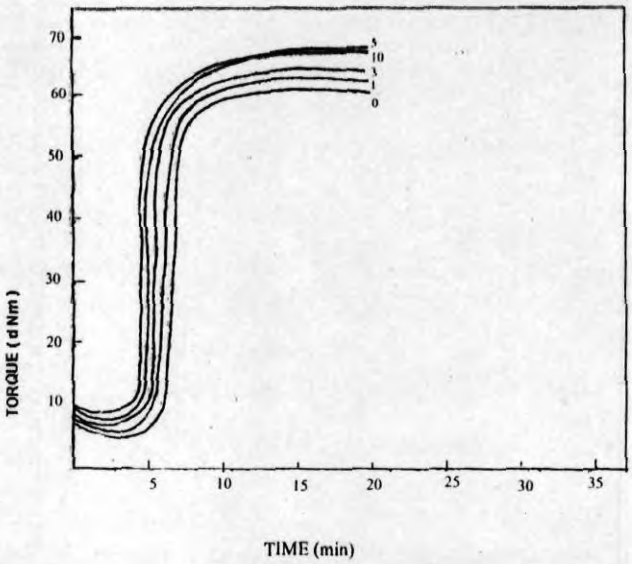


Figure 9. Rheographs of 70/30 SBR/NBR blends at 150°C with various concentrations (0, 1, 3, 5 and 10 phr) of DCSBR.

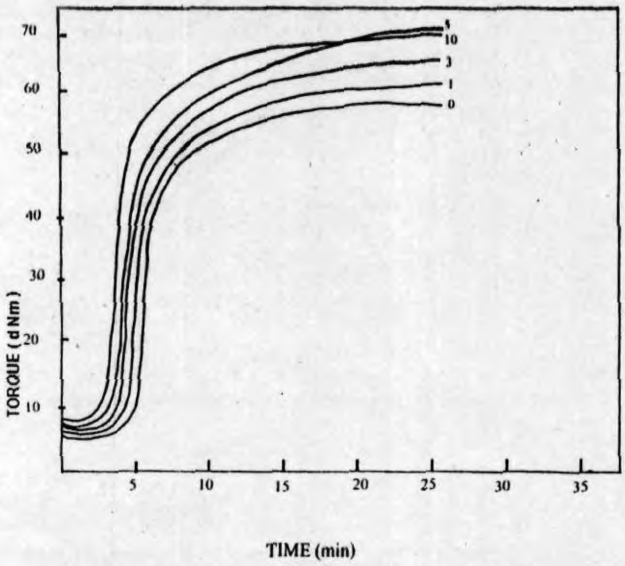


Figure 11. Rheographs of 30/70 SBR/NBR blends at 150°C with various concentrations (0, 1, 3, 5 and 10 phr) of DCSBR.

attractive interactions between chlorine units of DCSBR and cyanide groups of nitrile rubber; this leads to an increased cure time. Studies on the effect of loading of compatibilizer on the different blend compositions make it clear that the maximum cure time is achieved at a loading of 5 phr of DCSBR. When the compatibilizer concentration increases above 5 phr, the compatibilizer efficiency decreases. This reduces the interfacial area and thereby causes a decrease in optimum cure time. The minimum time needed to start vulcanization (t_1) is lower for compatibilized blends, showing that the components are dispersed with better interfacial adhesion.

The increase in torque due to the crosslinking process (Mh − Mn) of compatibilized and uncompatibilized SBR/NBR blends is shown in Table 7. As the loading of compatibilizer increases, the difference in torque value increases and then decreases in all blend compositions. At lower concentration of compatibilizer the torque variation with blend composition is negligible, but as the concentration of compatibilizer increases from 5 to 10 phr, the torque attained increases with concentration of NBR. Of all the blend compositions, that with 5 phr DCSBR shows the maximum difference in torque; hence at this concentration, the compatibilizer enhances the formation of interdiffused chains with higher crosslinking that lead to development of a higher torque.

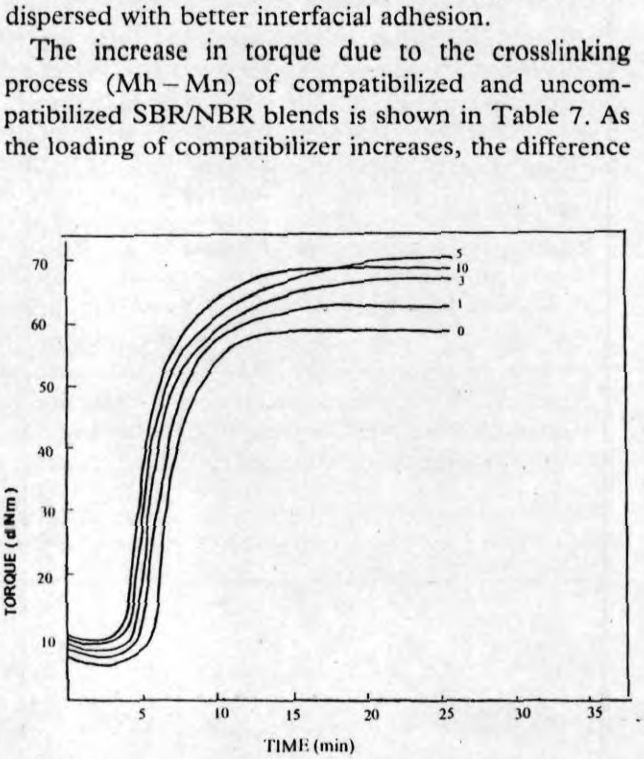


Figure 10. Rheographs of 50/50 SBR/NBR blends at 150°C with various concentrations (0, 1, 3, 5 and 10 phr) of DCSBR.

Effect of loading of compatibilizer on swelling behaviour

According to the equation of Lorentz and Parks[43,44]

$$Q_c/Q_u = ae^{-z} + b \qquad (1)$$

where Q is defined as grams of solvent per gram of hydrocarbon and is calculated by

$$Q = \frac{\text{swollen weight} - \text{dried weight}}{\left(\frac{\text{original weight} \times 100}{\text{formula weight}}\right)} \qquad (2)$$

The subscripts c and u of eqn (1) refer to compatibilized and uncompatibilized vulcanisates, respectively; z is the ratio by weight of compatibilizer to rubber hydrocarbon in the vulcanizate, and a and b are constants. The higher the Q_c/Q_u values, the lower the extent of interaction between the compatibilizer and rubber blends, ie between the polar (DCSBR) and non-polar solvent. Parks[45] also showed that the value of $1/Q$ can be used to study the effect of interaction between two polymers. Table 8 shows the Q_c/Q_u and $1/Q$ values for SBR/NBR blends as a function of concentration of compatibilizer after swelling in n-heptane. The lowest value of Q_u/Q_c is obtained for 5 phr compatibilizer loading on all the blend ratios, which confirms that 5 phr DCSBR brings about

Table 7. Cure characteristics of SBR/NBR blends compatibilized by DCSBR

Blend composition	*Dosage of DCSBR (phr)*	*Optimum cure time at 150°C (t_{90}) (min)*	*Scorch time at 150°C (t_2) (min)*	*Induction time at 150°C (t_1) (min)*	*Mh – Mn (dNm)*
SBR/NBR 70/30	0	7.5	5.5	5	56
	1	8	5	4.5	57
	3	8.5	4.5	4	58
	5	8.5	4	3.5	60
	10	8	3.5	3	57
SBR/NBR 50/50	0	9	4.5	4	53
	1	9.5	4	3.5	56
	3	10.5	3.75	3.25	59
	5	11.5	3.5	3	62
	10	10	2.5	2	59
SBR/NBR 30/70	0	10	4.25	3.75	54
	1	10.5	3.75	3.25	56
	3	11.5	3.5	3	58.5
	5	13.5	3.25	2.75	64
	10	11.5	2.75	2.25	61

sufficient adhesion between the phases from polar interactions among the blend constituents.[46] As the loading of compatibilizer increases above 5 phr, the interaction between the two phases becomes negligible which leads to slightly higher swelling values. The result from $1/Q$ values also supports this observation. Plots of volume uptake of solvent (*n*-heptane) *versus* blend composition are given in Fig 12. As seen from the figure the volume of solvent absorbed is below the additive average with increase in concentration of compatibilizer up to 5 phr. If interfacial bonds are formed during covulcanization, the lightly swollen phase will restrict swelling of the highly swollen phase below the additive average.[47] This confirms that interfacial bonds are formed in blends of SBR and NBR in the presence of DCSBR.

The volume fraction of rubber in the solvent swollen sample is calculated by the method of Ellis and Welding.[48]

$$V_r = \frac{(d - fw)\rho_r^{-1}}{(d - fw)\rho_r^{-1} + A_0\rho_s^{-1}} \tag{3}$$

where d is the weight after drying out the sample, and w is the weight of the swollen sample. A_0 is the weight of the absorbed solvent, f is the fraction of insoluble components, and ρ_r and ρ_s are the densities of the rubber and solvent, respectively. The Kraus[49] and Tinker[50] theory can be applied to blends of SBR and NBR:

$$\frac{V_{r_0}}{V_{r_c}} = 1 - M\left(\frac{\phi}{1 - \phi}\right) \tag{4}$$

where V_{r_0} is the volume fraction of elastomer in the swollen gel when no dispersed phase is present V_{r_0} is the volume fraction of the continuous phase elastomer when a lightly swollen dispersed phase. V_{r_c} is the volume fraction of dispersed phase in the unswollen covulcanizate and M is a parameter depending on V_{r_0} and the extent of swelling restriction. A plot of V_{r_0}/V_r as a function of the volume fraction of SBR in blends in the presence and absence of compatibilizer is given in Fig 13. Because V_{r_0}/V_r deviates from unity with addition of compatibilizer in all blend ratios there is formation of interfacial bonds,[47,50] but interfacial

Table 8. Swelling characteristics, crosslink density parameters *C*1, *C*2, and crosslink density values for SBR/NBR blends with and without compatibilizer

	Loading of compatibilizer (phr)														
	70/30 SBR/NBR					*50/50 SBR/NBR*					*30/70 SBR/NBR*				
Property	*0*	*1*	*3*	*5*	*10*	*0*	*1*	*3*	*5*	*10*	*0*	*1*	*3*	*5*	*10*
$1/Q$	1.3103	1.8132	1.8872	1.9272	1.5693	1.6286	2.4182	2.5437	2.5674	1.5697	3.8865	4.1179	4.1921	4.2019	2.9091
Q_c/Q_u	–	0.7289	0.7001	0.6799	0.6887	–	0.6734	0.6402	0.6269	1.0375	–	0.9559	0.9438	0.9249	1.3358
V_{r_0}/V_{r_c}	–	0.9381	0.9265	0.9115	0.9229	–	0.9045	0.8939	0.6269	1.0082	–	0.9926	0.9895	0.9881	1.0459
Crosslink density Flory–Rehner $\times 10^{-3}$ (g mmol cm^{-3})	1.39	3.21	3.40	3.51	3.31	2.36	3.40	4.16	5.11	4.63	4.12	4.67	5.85	6.97	5.24
$2C_2$ (N mm^{-2})	0.64	1.04	1.20	1.28	1.20	1.04	1.20	1.52	2.08	1.64	1.52	1.76	1.96	2.48	1.98
$2C_1$ (N mm^{-2})	0.72	0.95	1.04	1.1	1.08	0.88	0.96	1.17	1.48	1.29	1.1	1.3	1.37	1.78	1.49
Crosslink density Mooney–Rivlin (10^{-3} g mmol cm^{-3})	1.04	1.16	1.2	1.28	1.26	1.25	1.53	1.79	2.1	1.99	1.41	1.61	1.98	2.62	2.31

bond formation increases only as the concentration of SBR in the blend increases from 0 to 50 phr, and at higher concentration the interfacial bond formation is not very effective because the Kraus plots deviate from linearity. Thus the compatibilizing action is higher when the concentration of SBR in the blend is 50 phr or lower. This is clear from the mechanical properties discussed later.

Calculation of crosslink density

The crosslink density values were calculated from both the swelling data using Flory–Rehner[51] equations and stress–strain data using the Mooney–Rivlin[52] equation (a) from swelling studies.

The molecular weight between the crosslinks is calculated using the following equation:

$$M_c = \left[\frac{-\rho_p V_s (V_r)^{1/3}}{\ln(1-V_r) + V_r + \chi V_r^2}\right] \qquad (5)$$

where ρ_p is the density of polymer, V_s the molar volume of solvent, V_r the volume fraction of polymer in the fully swollen state, which is determined by the method of Ellis and Welding[48] and χ is the interaction parameter given by Hildebrand[53] equations as

$$\chi = \beta + \frac{V_s}{RT}(\delta_s - \delta_p)^2 \qquad (6)$$

where V_s and δ_s are the molar volume and solubility parameter, respectively, of the solvents; β is the lattice constant, whose value is normally taken as 0.34; R is the universal gas constant; and T is the absolute temperature. From the crosslink densities shown in Table 8, it is found that crosslink density increases with the content of compatibilizer in all blend compositions up to a concentration of 5 phr compatibilizer and then decreases. These effects are noted to be maximal for 30/70 and minimal for 70/30 SBR/NBR compositions because of the restriction on swelling which causes an increase in V_r and in turn increases the crosslink density values.

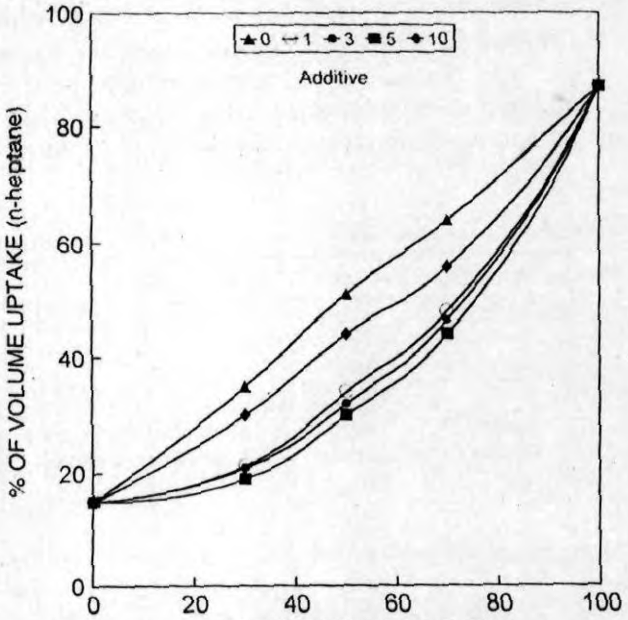


Figure 12. Interfacial bonding in SBR/NBR blends in the presence of DCSBR compatibilizer at concentrations of 0, 1, 3, 5 and 10 phr.

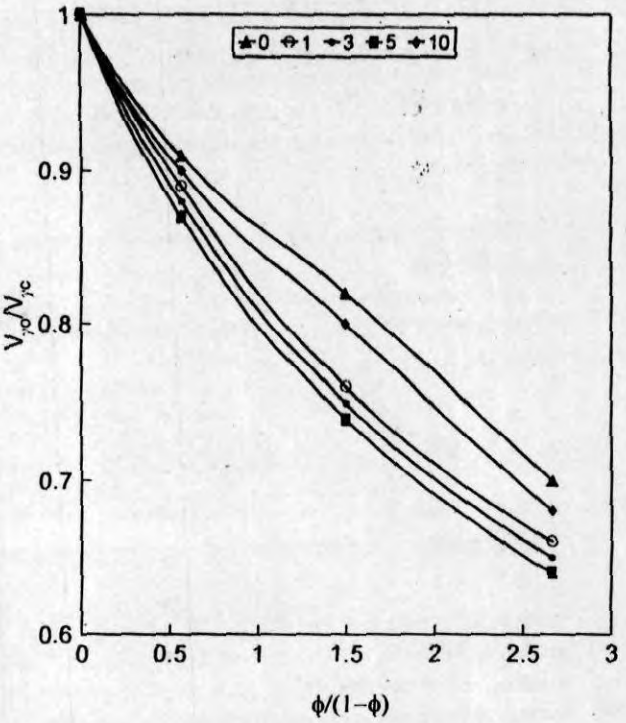


Figure 13. Kraus plots for SBR and blends of SBR with NBR in the presence of DCSBR compatibilizer at concentrations of 0 (▲), 1 (○), 3 (●), 5 (■) and 10 phr (◆).

Stress–strain data

The physical effects of crosslinks in an elastomer can be understood from the Mooney–Rivlin equation[52]

$$F = 2A_0(\lambda - \lambda^{-2})(C_1 + \lambda^{-1}C_2) \qquad (7)$$

where F is the extension force required to stretch a piece of rubber vulcanizate of cross-sectional area A_0 to an extension ratio λ. From the plot of $F/2A_0$ $(\lambda - \lambda^{-2})$ and λ^{-1}, the constants C_1 and C_2 can be determined, ie the intercept curve on the $F/2A_0$ $(\lambda - \lambda^{-2})$ axis corresponds to the value of C_1 and its slope corresponds to the value of C_2. The physically effective crosslink density (ν_{phys}) is given by the equation

$$C_1 = \rho\, RT\, \nu_{\text{phys}} \qquad (8)$$

The plot of the stress–strain data is shown in Fig 14, and the values of crosslink density are presented in Table 8. It can be seen that the crosslink density increases as the concentration of DCSBR increases up to 5 phr and then decreases, in good agreement with the rheometric torque. C_2, a term which serves as a measure of departure of the observed stress–strain behaviour from the form suggested by statistical theories,[54] is given in Table 8. The $2C_2$ value increases with the loading of DCSBR up to 5 phr and then decreases. The higher C_2 value obtained for the 30/70 SBR/NBR blends shows the presence of higher chain entanglements.[55] Because the elastomeric matrix is composed of two components, higher entanglements show better mixing at the molecular level.

Effect of loading of compatibilizer on physical properties

The variation of mechanical properties with varying content of DCSBR on SBR/NBR blends is presented in Table 9. The data reveal that compatibilization substantially increases the tensile strength. In compatibilized blends tensile strength increases as concentration of NBR in the blend increases. The tensile strength value slowly increases with the compatibilizer concentration and peaks at a dosage of 5 phr; with further increase in the concentration of compatibilizer, the tensile strength drops because of the poor interaction between the interface of blend constituents and the compatibilizer.

As in the case of tensile strength, tear resistance improves with the addition of DCSBR, becoming

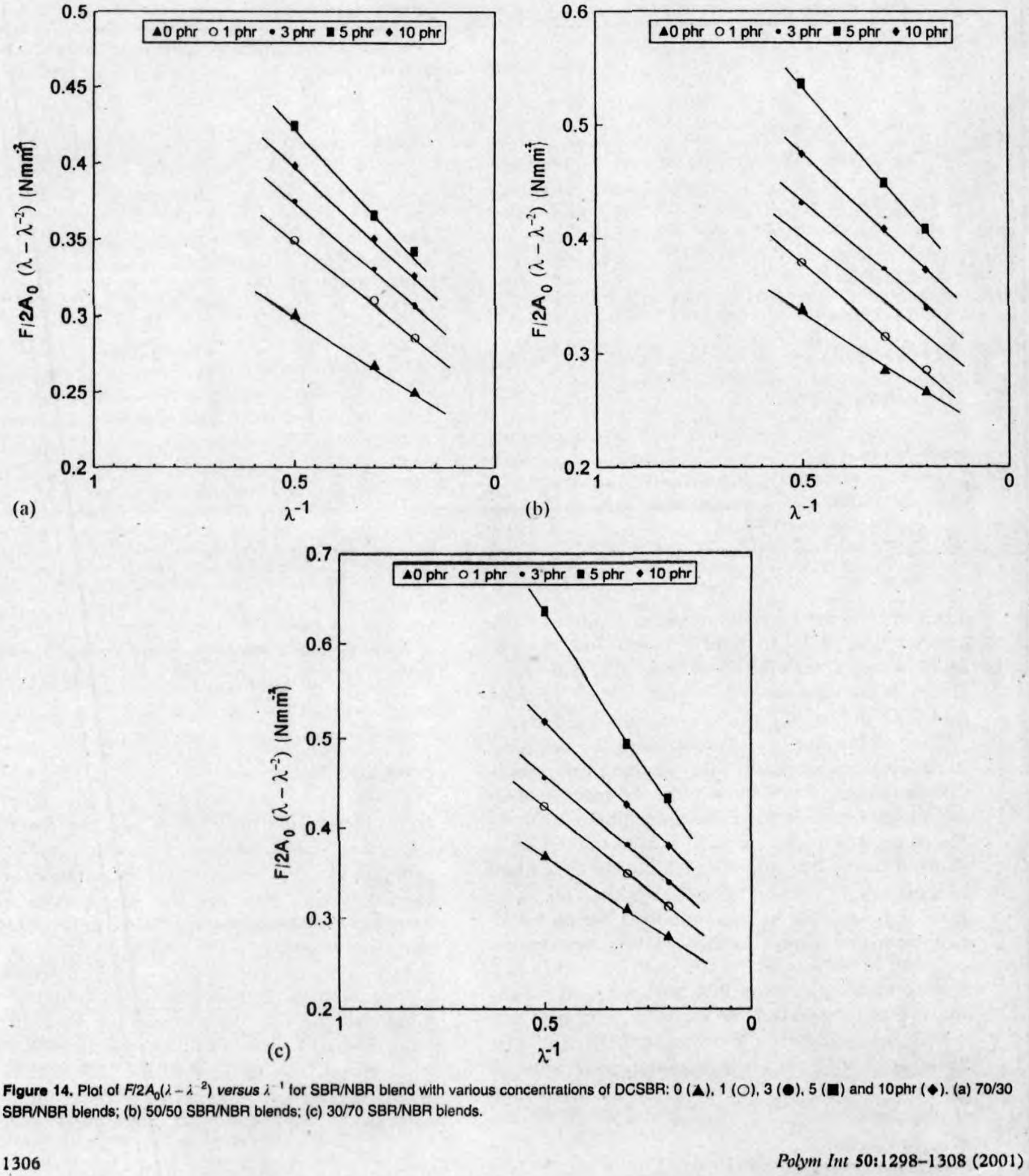


Figure 14. Plot of $F/2A_0(\lambda - \lambda^{-2})$ *versus* λ^{-1} for SBR/NBR blend with various concentrations of DCSBR: 0 (▲), 1 (○), 3 (●), 5 (■) and 10 phr (♦). (a) 70/30 SBR/NBR blends; (b) 50/50 SBR/NBR blends; (c) 30/70 SBR/NBR blends.

Table 9. Variation of physical properties of SBR/NBR blends compatibilized with DCSBR with dosage (phr) of compatibilizer

	70/30 SBR/NBR					*50/50 SBR/NBR*					*30/70 SBR/NBR*				
Property	*0*	*1*	*3*	*5*	*10*	*0*	*1*	*3*	*5*	*10*	*0*	*1*	*3*	*5*	*10*
Modulus, 300% (MPa)	1.98	2.46	2.82	3.47	3.01	2.51	2.73	2.91	3.18	3.01	1.99	2.11	2.49	2.7	2.64
Tensile strength (MPa)	2.9	3.4	4.7	5.2	5.0	3.5	4.1	5.3	6.2	6.0	3.0	4.0	5.6	6.8	6.0
Elongation at break (%)	310	350	440	555	510	325	390	470	515	495	360	300	425	450	430
Tear strength (kNm^{-1})	15.7	16.9	19.0	22.8	21.6	16.1	18.9	22.8	24.2	24.0	18.8	20.9	23.7	26.4	25.8
Hardness (Shore A)	40	41	42	44	45	41	42	43	44	46	42	43	44	46	48
Resilience (%) (Dunlop tripsometer)	68	68	69	71	69	62	63	65	67	64	58	59	60	62	63
Compression set (%) after 22h at 70°C	17.5	17.0	16.7	15.6	16.1	18.0	16.5	15.3	14.2	14.9	18.3	17.0	16.1	15.6	16.8

Table 10. Air ageing (96h at 70°C) and oil resistance (5 days at 25°C) of SBR/NBR blends

		Swell in ASTM Decrease in % (w/w)			*Change in tensile properties after ageing at 70°C for 96h*	
Blend composition	*Dosage of DCSBR (phr)*	*ASTM oil no 1*	*ASTM oil no 2*	*ASTM oil no 3*	*Decrease in tensile strength (%)*	*Decrease in EB[a] (%)*
SBR/NBR 70/30	0	6.68	11.31	37.15	39	20
	1	6.63	11.28	37.3	36	18
	3	6.60	11.24	37	35	17
	5	6.58	11.2	36.1	34	16
	10	6.55	11.11	35.8	36	15
SBR/NBR 50/50	0	4.81	8.32	26.73	42	24
	1	4.77	8.3	26.13	40	22
	3	4.69	8.11	25.92	36	20
	5	4.41	7.9	25.23	49	20
	10	4.56	7.3	24.81	34	19
SBR/NBR 30/70	0	3.02	5.14	16.31	45	26
	1	2.98	5.02	15.8	43	25
	3	2.89	4.80	15	41	23
	5	2.8	4.46	13.95	40	21
	10	2.73	4.01	13.36	42	23

[a] EB is elongation at break.

maximal at 5 phr of compatibilizer. Uniformly distributed finer domains tend to form and elongate under higher strain, effectively preventing tear propagation. With increasing the concentration of compatibilizer above 5 phr, the tear strength decreases.

The compression set decreases and the resilience increases with increase in SBR content of the blend. Compatibilized blends show a lower compression set and a higher resilience than uncompatibilized blends. The compression set is minimal at 5 phr of DCSBR in all blend ratios. Uncompatibilized blends show lower hardness than compatibilized samples. Increased interfacial adhesion in compatibilized blends eliminates air spaces therein and hence hardness increases.

Ageing of SBR/NBR blends in the presence and absence of compatibilizer was carried out in ASTM oils at room temperature for 5 days at 25 °C and in air at 70 °C for 96 h; the results are presented in Table 10. Blending of NBR with SBR imparts considerable oil resistance to SBR and this is improved by the addition of compatibilizer. The ageing resistance of the uncompatibilized blend is improved by the addition of compatibilizer because of the enhanced crosslink density obtained, as revealed from swelling studies.

CONCLUSIONS

Dichlorocarbene modified SBR acts as a compatibilizer in blends of SBR/NBR as revealed from DSC, DMA and FTIR studies. The efficiency of compatibilization depends on the concentration of compatibilizer and also on the blend ratio of the components. The addition of even 1 phr of DCSBR considerably enhances the interfacial adhesion in the blends. The compatibilizing action increases with concentration of compatibilizer up to 5 phr in all blend compositions. The effectiveness of DCSBR as a compatibilizer increases with increase in NBR content in the blend. The addition of DCSBR enhances the overall mechanical properties including air and oil resistance. The change in mechanical properties correlates well with change in crosslink density measured by both swelling and stress–strain data.

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