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The Effect of Unsaturated Polyester Resin from Recycled PET as Compatibilizer for Styrene-Butadiene (SBR)/Acrylonitrile-Butadiene (NBR) Rubber Blend

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Abstract. Unsaturated polyester resin (UPR) from recycled PET flakes was prepared by depolymerization with propylene glycol and polyesterified with adipic acid. The effect of addition of 5, 10 and 15 phr of unsaturated polyester resin (UPR) on the compatibility and physicomechanical properties of styrene-butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR) blends were studied. DSC, TGA, MDR, FTIR and chemical methods were used to determine the degree of compatibility. The mechanical and physical properties of the blends were found to improve with addition of 10 phr UPR for SBR/NBR blend.

Keywords: polyester resin, PET flakes recycled, Styrene-butadiene rubber, acrylonitrile-butadiene rubber, depolymerization, unsaturated polyester resin, rubber blends

Introduction

Polymeric blending became an increasingly important area of research work because it offers less expensive alternative for developing totally new polymeric materials. Polymer blends are prepared to serve high performance in varied environmental conditions being cost effective, recyclable and time saving. Rubber industry needs a variety of elastomers with new characteristics in order to increase the resistance to chemical, mechanical and thermal properties in rubber components. Majority of the elastomer polymers are immiscible with each other; their blends undergo phase separation with poor adhesion and yield a material with poor mechanical and physical properties. In the case of elastomer blends, compatibilization may be necessary to aid uniform distribution of fillers, curatives and plasticizers to obtain morphologically and mechanically sound product (Markham, 1988). Immiscible blends can be improved by mixing of compatibilizer, which may be a copolymer of thermoplastics resin, copolymer of acrylates or polar components.

Addition of a copolymer reduces the interfacial energy between two phases, permits a finer dispersion during mixing and provides a measure of stability against gross segregation resulting in improved interfacial adhesion (Roland, 2001; Teyssie *et al.*, 1981; Utracki, 1998; Heikens and Barentsen, 1977). Compatiblization may be carried out in non-reactive and reactive mode. Non-reactive compatibilization can be achieved by adding an external compatibilizer such as block or graft or random copolymers (Roland, 2001; Teyssie *et al.*, 1987; Coran *et al.*, 1985; Kohler *et al.*, 1968a; 1968b; Reiss *et al.*, 1967; Molau, 1970). Whereas, reactive compatibilization can be carried out by functionalizing one of the blend components of two phases of EPDM and nylon with MA-g-EPDM as demonstrated by Epstein *et al*. (1987), or by reacting with functional chemicals during blending (Coran and Patel, 1983). Compatibilization may also be carried out by rubber filler interaction by surface activation to improve mechanical properties (Bandopadhyay *et al.*, 1996). High level of compatibility achieved by self crosslinking involves thickening of the interphase by two opposite charges of rubber blend during processing (Antony *et al*., 1999).

Effects of the polyester resins on the properties of many kinds of rubber have been extensively studied before (Fagerburg, 1987; Von Harpe *et al*., 1980; 1979; Coran and Patel, 1978). Styrene-butadiene rubber (SBR) is a general purpose synthetic rubber with good mechanical properties but poor in oil and ageing resistance. Acrylonitrite-butadine rubber (NBR) is a polar elastomer having good oil resistance but less in mechanical properties. The blend of SBR/NBR due to difference in polarity is immiscible (Callan *et al.*, 1971). The improvement of SBR/NBR blend could be possible so as to impart properties of individual components to a single blended material. Aim of the present work is to study the effect of unsaturated polyester resin from recycled PET flakes on the mechanical and physical properties of styrene-butadiene rubber (SBR) and acrylonitrile butadiene rubber (NBR) blends with reference to the component miscibility.

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Materials and Methods

Materials: (i) Styrene butadiene 1502 with specific gravity 0.94 of Ulsan Korea. (ii) Acrylonitrile butadiene rubber (NBR; acrylonitrile content ~ 28%) with specific gravity 0.96 was obtained from market. (iii) The rubber chemicals used such as sulphur, dicumyl peroxide, zinc oxide, stearic acid and mercaptobenzothiazol disulphide (MBTS) were of commercial grade obtained from Bayer Ltd. (iv) Unsaturated polyester (UPE) used in this study was based on glycolysed product of commercially available PET flakes esterified with adipic acid. The prepared UPR had viscosity of 2300-2400 cps at 25 °C.

Blend preparation and rheometric study. Mixing of rubber was carried out in Brabender plasticoder PL 2´00 at 145 °C with cam-type rotors, an optimum batch size of 55 g and a rotor speed 12 rpm for 5 min. Five different ratios of rubber blends SBR/NBR 100/0, 70/30, 50/50, 30/70, 0/100 were run. The rubber blends were then mixed with and without 5, 10, 15 phr of prepared unsaturated polyester resin (UPR) along with dicumyl peroxide and other additives on laboratory two roll mill size (160 x 320 mm) according to ASTM design D 3184-80 (Table 1). After completing the mixing of rubber ingredients, the rheometric characteristic of the blends were studied by determining the minimum torque(M_L), maximum torque (M_H), scortch time (T_{S1}) and optimum cure time by using rheocheck profile model MDR 2000 (moving die rheometer), Gibitre Italy according to ASTM D 6204. The vulcanizates were obtained in heated plate laboratory press, under pressure of 100 bars and temperature 160 °C for 15 min. Densities of the prepared blends were determined with the help of density meter-balance check (Gibitre).

Table 1. Formulation of blend

Ingredients	Phr
Rubber polymers	100
Zinc oxide	4
Stearic acid	2
MBTS	1.5
Sulphur	1.5
DCP	4
Resin	5, 10, 15

Testing techniques. The infrared spectra were recorded on Thermo Nicolet Avatar in the range of 4000-400 cm^{-1}. For the determination of glass transition temperature (Tg), differential scanning calorimeter measurements were carried out with DSC 822^e Mettler Toledo, under an atmosphere of nitrogen (flow rate 50 ml/min). Each sample was weighed 9-10 mg and sealed in aluminum crucible (40 ml). The thermograms were collected from -50 to 300 °C at heating rate of 10 °C/min. Empty aluminum pan was used as standard. TG and DTG were carried out using TGA/SDTA 851^e Mettler Toledo; samples were scanned from 30-700 °C with heating rate of 10 °C/min under nitrogen.

Mechanical properties were measured at room temperature using material testing machine, Instron Model 4301 according to ASTM D412. Rebound resilience property was measured using Rebound Check Model REB 2002010. Compression set and solvent behaviour were determined as per ASTM D395-B and D471.

Oil effect was observed by taking specimens from vulcanized blend sheets of 3.5 mm thickness in ASTM oil #3. The specimens were cut out in dumbell shaped for study of tensile properties and in rectangular pieces of 1x2" for observing change in volume. All these specimens were aged at 50 °C for 96 h.

Results and Discussion

To study the effects of resin (UPR) compatibility on the properties of SBR/NBR blends, different techniques were carried out. SBR, NBR, resin and blends with 0 and 10 phr of resin were first analysed through FTIR. The SBR spectra in Fig.1a. show characteristic peak of benzene in the region of 1650-1550 cm^{-1} and 700-720 cm^{-1} for out of plane deformation of aromatic C-H. Fig.1b shows the characteristic peak for nitrile group of NBR at 2236 cm^{-1}. The spectra of resin (Fig.1c) show carbonyl peak at 1718 cm^{-1} and C-O stretch in the region of 1000-1251 cm^{-1}. Peaks in the region of 1550- 1600 cm^{-1} represent double bond of phenyl ring and 720 cm^{-1} corresponds to methylene group. Fig. 2 shows two IR spectra for blends with different phr of resin. Fig. 2a shows the spectra of blend with zero phr of resin which has no peak for carbonyl group while the spectra (Fig. 2b) in which the blend is mixed with 10 phr of resin show peak at 1736 cm^{-1}. This characteristic peak of carbonyl group appeared due to introduction of resin in the blend.

Thermal analysis is one of the known techniques used for determining the compositional changes in the system mixed with two or three components. DSC thermograms collected for various blends are shown in Fig. 3. Table 2 shows the glass transition temperature (Tg), crystallinity peak temperature (Tc) and enthalpy of crystallinity (DHc). Glass transition temperatures (mid point) observed for NBR and resin are 28 °C, and -14 °C, respectively. It is noted that on introduction of resin in blend and then gradually increasing the concentration of resin, the glass transition temperature (Tg) shifts to the lower side. The glass transition temperature for 30/70 blend

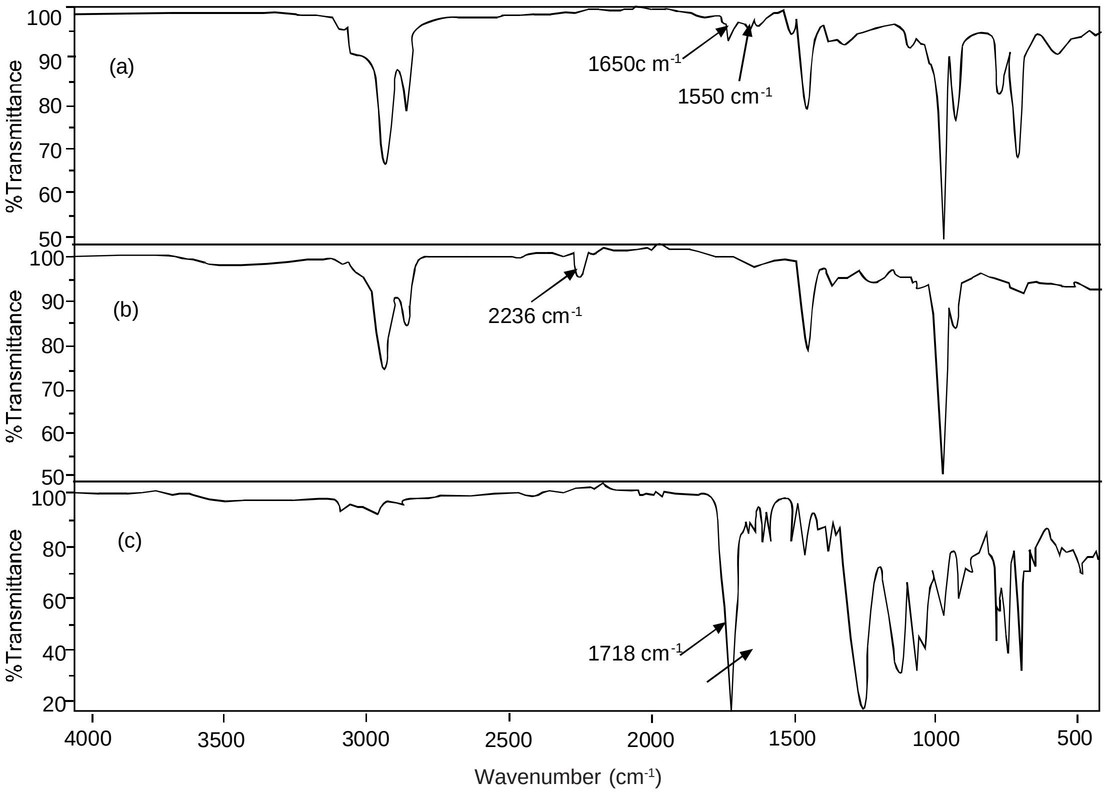

Fig. 1. FTIR spectra (a) SBR; (b) NBR; (c) Resin.

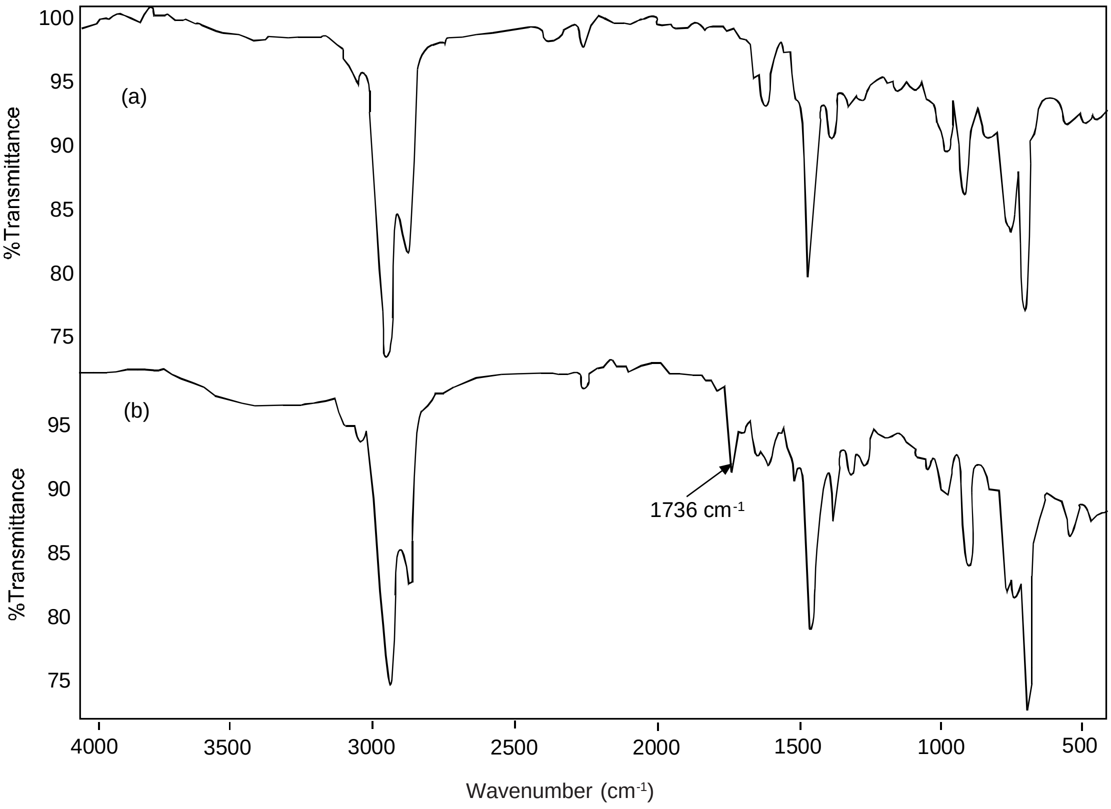

Fig. 2. FTIR spectra of blend of SBR/NBR 30/70 compatibilized with resin a) 0 phr; b) 10 phr.

Table 2. DSC data of SBR/NBR 30/70 blend, resin and rubber polymer

DSC Data	Glass transition temperature, Tg (°C)	Enthalpy of crystallization, DH_C, (J/g)	Crystalinity peak temp., T_C , (°C)
NBR	-28.2	117.1	180.1
Blend with 0% resin	-26.2	121.0	183.0
Blend with 5% resin	-27.3	128.8	182.8
Blend with 10% resin	-28.1	151.2	183.4
Blend with 15% resin	-30.8	138.2	182.4
Resin	-14.0	-	-

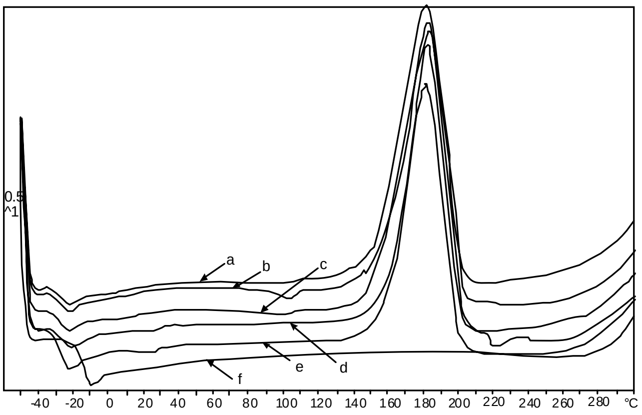

Fig. 3. DSC thermograms of a) Blend of SBR/NBR 30/70 compatibilized with a) 0%; b) 5%; c) 10%; d) 15% resin; e) NBR; f) resin.

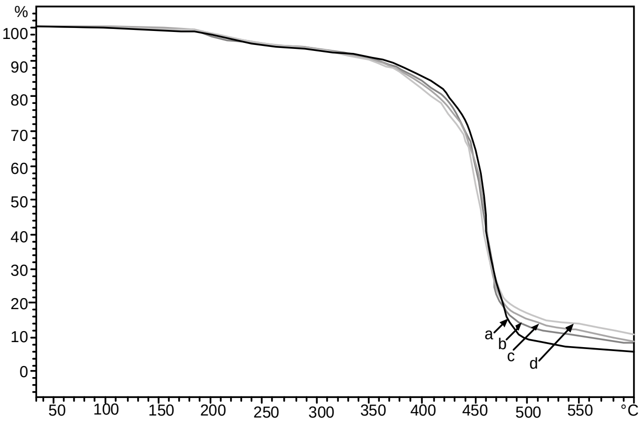

Fig. 4. TGA curves of blend of SBR/NBR 30/70 compatibilized with resin a) 0%; b) 5%; c) 10%; d) 15%.

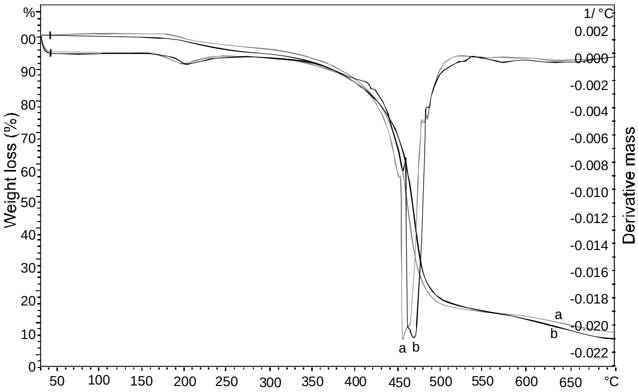

Fig. 5. TGA and derivative curves of a) SBR/NBR 50/50 blend compatibilized with 10 phr resin; b) SBR/NBR 30/70 blend compatibilized with 10 phr resin.

of SBR/NBR with 15 phr of resin was found to be -30.8 °C which is the lowest among all the blends. This lowering of temperature might be due to the plasticizing effect of resin. For the enthalpy of crystallization (DHc), it is noted that with the increase in resin concentration in blend, enthalpy increases. The value of DHc was maximum for blend with 10 phr of resin which is found to be 151.2 J/g at 183.4 °C peak temperature.

The blends were then subjected to TGA to get the decomposition pattern of blends, for which the thermogravimetric curves are presented in Fig. 4 and Fig. 5. The first and the second step mass loss percentage and thermal degradation temperatures of blends with different resin concentrations are given in Table 3. A two step degradation pattern is observed for all blends. It was noted that on the increase of resin concentration, the mass loss percentage decreased showing the presence of crosslinked system. For 30/70 blend with 15 phr of resin the second mass loss is 80.7%, which is the least among all the 30/70 and 50/50 blends of SBR/NBR. This mass loss is in the region of 250-550 °C. It can be seen that the mass loss percentages are lower for the compatibilized system as compared to the uncompatibilized one. This indicates the improvement in the thermal stability of the system upon compatibilization. It is observed that the blends with 10 phr of resin shows good thermal stability as thermal degradation temperature (Td) in 30/70 blend was 460.3 °C and in 50/50 blend, was 450.1 °C (Fig. 5). Thus the addition of resin in blend was good enough with 10 phr of resin as on further increase in the concentration, the thermal degradation temperature again slightly decreased.

Cure characteristic of five blend ratios at various temperatures were studied on MDR rheometer. The rheological data of 30/70 and 50/50 SBR/NBR blends, carried out at 160 °C for 10 min, are presented in Table 4. Gradual increase of resin concentration in blends decreased the scortch time. It was observed that for 30/70 blend, the scortch time decreased upto the addition of 10 phr of resin and then again increased. This shows that crosslinks in between the resin and the two elastomers increases upto10 phr and as this concentration reaches 15 phr, plasticizing effect increases the scortch time. Minimum torque, M_L, was found to be 1.19 dN.m for 30/70 blend with 10 phr of UPR. This is the maximum value among all the blends. This trend shows that with the increase in the cross linking of resin with blend, the viscosity also increases, but with 15 phr of resin, the viscosity of 30/70 blend decreases due to plasticizing effect. Maximum torque which tells about the cross linking density, shows a similar pattern as it is maximum for 30/70 blend with 10 phr resin. The t_{90} value is the least for 30/70 blend; when added with 10 phr of resin, the least time is required for curing.

Mechanical properties and solvent effect. Variation in mechanical properties with varying content of UPR on SBR/NBR blends is presented in Table 5. The data shows that by the addition of resin from 5 to 15 phr the tensile strength, elongation and tear strength gradually increased and reached at maximum with 10 phr of UPR while these values were lowered by the addition of 15 phr of UPR being more prominent in elongation. This trend might be due to the plasticizing effect of UPR on the blend system. Aging of SBR/NBR blends in the presence and absence of UPR was carried out in ASTM oil # 3 at 50 °C for 96 h. The results are presented in Table 6. The blend of SBR/NBR showed good oil resistance in 30/70 blend ratio. It was further improved by the addition of various amounts of UPR as compatibilized in blend. The change in the volume with oil absorption of blend system of 30/70 in ASTM oil # 3 gave a very encouraging value in all ratios of the added UPR. This shows that the addition of unsaturated polyester resin

Table 3. TGA data of SBR/NBR blend 30/70 and 50/50 with varying concentration of UP resin

Resin (phr)	0%		5%		10%		15%	
NBR/SBR	30/70	50/50	30/70	50/50	30/70	50/50	30/70	50/50
1^{st} Step mass loss (%)	5.6	4.4	4.8	3.7	5.0	3.6	4.1	5.2
2^{nd} Step mass loss (%)	86.1	86.5	83.2	83.5	81.7	82.8	80.7	86.0
Td 1 (^{o}C)	185.8	189.3	189.4	187.4	186.1	186.6	184.6	188.0
Td 2 (^{o}C)	446.5	448.7	446.1	448.0	460.3	450.1	445.8	447.6
Residue (%)	8.4	9.4	12.2	13.4	13.6	14.4	15.5	8.2

Table 4. Rheometric characteristic of SBR/NBR blend with varying concentration of UP resin

	30/70 SBR/NBR				50/50 SBR/NBR			
UPR	0%	5%	10%	15%	0%	5%	10%	15%
M_L (dN.m)	0.77	1.10	1.19	1.09	0.76	1.04	1.14	1.16
T_{S1} (min)	2.37	2.01	1.87	2.01	2.52	2.04	1.97	1.80
M_H (dN.m)	7.47	8.10	8.80	8.30	6.93	8.24	8.45	7.25
t_{90} (min)	7.44	6.75	5.83	6.17	7.11	6.33	6.08	5.72

Table 5. Physicomechanical properties of SBR/NBR blend vulcanized at optimum cure time with various ratios of UP resin

Properties	30/70 SBR/NBR				50/50 SBR/NBR				70/30 SBR/NBR			
	0	5	10	15	0	5	10	15	0	5	10	15
Tensile strength (MPa)	21.50	22.0	23.50	23.0	19.50	19.85	20.0	18.0	18.5	18.90	19.0	16.00
Elongation at break (%)	350	351	353	250	330	332	330	290	300	301	305	270
Tear strength (Kg/cm)	47	32	34	32.5	45	30	32	29	42	31	30	28.7
Hardness shore-A (%)	80	82	87	81	80	80.1	80.5	79	78	79	79.1	72
Rebound resistance (%)	26.0	26.5	27.8	25.0	27	27.8	28.0	26.0	26.5	26.6	26.7	26.9
Compression set (%) at 70^{o}C x 22hr	14.0	12.9	12.0	13.0	29	14	14.5	15	27	26.5	26.0	26.9

enhances crosslink density between the two elastomer chains. This interaction in the blend system creates steric hindrance and suppresses the absorption of oil which helps in oil resistance property of blend.

Table 6. Aging characteristic of SBR/NBR blend in ASTM oil # 3.

Blend SBR/NBR	Unsaturated polyester resin (phr)	Volume change %	Change in tensile strength %	Change in elongation %
30/70	0	+33	-20	-60
	5	+20	-18	-55
	10	+14	-16	-53
	15	+22	-22	-62

Conclusion

Mechanical and oil resistance data show that the addition of unsaturated polyester resin obtained from depolymerization and polycondensation of recycled PET flakes produces improvement in rubber characteristics. The attachment of the polyester molecule to the butadiene molecules in blends of SBR/NBR increases crosslink density which improves the oil swelling and mechanical properties. The increase of NBR content in 30/70 blend of SBR/NBR becomes more enhanced by the addition of unsaturated polyester resin upto 10 phr. The unsaturated polyester resin obtained from recycled PET flakes can be used upto 10 phr in SBR/NBR blends for upgrading of oil resistance characteristics along with mechanical properties.

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