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Self-cross-linkable plastic–rubber blend system based on poly(vinyl chloride) and epoxidized natural rubber

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Melt-mixed blends of poly(vinyl chloride) and epoxidized natural rubber become cross-linked during moulding at elevated temperatures in the absence of any cross-linking agent. Such a system of self-cross-linkable plastic–rubber blend is immiscible, as is evident from differential scanning calorimetric studies and dynamic mechanical analysis. Such blends were found to have good oil resistance, high abrasion resistance, high modulus but low resilience with moderate tensile and tear strength.

1. Introduction

While studying the blend of polyvinyl chloride (PVC) and epoxidized natural rubber (ENR), we observed that the PVC–ENR blend becomes cross-linked during moulding at temperatures above 140 °C, even in the absence of any curing agent. Because no cross-linking agent was used, such a system was designated a "self-cross-linkable plastic–rubber blend". In this paper, we report the results of our preliminary studies on self-cross-linkable PVC–ENR blend. Recently, De and co-workers [1–3] developed novel self-vulcanizable rubber–rubber blend systems based on elastomers containing reactive groups which form cross-links between themselves during moulding. Examples of such blends include chlorosulphonated polyethylene–epoxidized natural rubber [4] and polychloroprene–epoxidized natural rubber systems [5].

2. Experimental procedure

Details of the materials used are given in Table I and formulation of the blends is shown in Table II.

Mixing was carried out in a Brabender Plasticorder (model PLE-330) using a cam-type mixer at a rotor speed of 60 r.p.m. and temperature of 180 °C. First, PVC resin was allowed to melt for 2 min and ENR was then added. In all cases, the total mixing time of ENR with molten PVC was 6 min. The molten mix was then quickly removed from the mixing chamber and sheeted out in the tight nip of a laboratory two-roll mill.

Rheographs of the blends were taken at 140, 150, 160, 170 and 180 °C using a Monsanto Rheometer R-100. The minimum Mooney viscosity and scorch time were determined using a Mooney shearing disc viscometer, model MK-III according to ASTM D 1646-1963. The blends were vulcanized for 60 min in the case of PE-25 and for 32 min in the case of PE-50, which correspond to 75% of the maximum torque at 180 °C for the respective blends.

The following physical properties of the vulcanizates were determined according to standard test methods. Stress–strain (ASTM D-412-87), tear (ASTM D 624-86), hardness (Shore D, ASTM 2240-86), resilience (BS 903 Part A8 1963 Method A), compression set (ASTM D 395-85 Method B), heat build-up (ASTM D 623-78), and abrasion resistance (BS 903 Part A9 Method C). Volume fraction of the rubber (V_r) in the solvent (tetrahydrofuran) swollen vulcanizate was determined by swelling studies as reported by Ellis and Welding [6]. In order to study oil resistance, the vulcanizates were swollen in ASTM oil no. 3 for 48 h at room temperature and the per cent increase in weight was noted.

Dynamic mechanical properties were measured at a strain amplitude of 0.0025 cm and frequency of 3.5 Hz. The procedure was to cool the sample to -100 °C and record the measurements during warm up. The temperature rise was 1 °C min^{-1}.

Differential scanning calorimeter (DSC) studies were done in a nitrogen atmosphere. Glass transition temperatures (T_g) were taken as the mid-point of the step in the scan, run at a heating rate of 20 °C min^{-1}.

3. Results and discussion

Processing behaviour of the blends are shown in Table III. Both PE-25 and PE-50 contains plastic and rubber components in the ratio 1:1 by weight. The minimum Mooney viscosity of PE-50 blend is higher than PE-25 presumably due to higher segment–segment interaction between PVC and ENR-50 as compared to PVC and ENR-25 [7]. The Mooney scorch times of both blends are extremely long, showing extraordinarily high processing safety of the blend. PE-50 blend shows a scorch time of 153 min and PE-25 blend registers a scorch time higher than 300 min.

Rheographs of the two blends at different temperatures (140, 150, 160, 170 and 180 °C) are shown in

TABLE I Details of materials used

Materials	Description	Source
Poly(vinyl chloride), PVC	Suspension-polymerized PVC (NOCIL PVC Polymer S67-311) K-value 66–69.	NOCIL, Bombay
Epoxidized natural rubber (ENR-50)	50 mol % epoxidized natural rubber, specific gravity = 1.03 g cm^{-3}	The Malaysian Rubber Producers' Research Association, UK
Epoxidized natural rubber (ENR-25)	25 mol % epoxidized natural rubber, specific gravity = 0.97 g cm^{-3}	The Malaysian Rubber Producers' Research Association, UK
Tribasic lead sulphate (TBLS)	Lead-based stabilizer for PVC, specific gravity = 6.5 g cm^{-3}	Waldies Ltd, Calcutta

TABLE II Composition of the blends (in parts by weight)

Components	Blend designation	
	PE-25	PE-50
PVC	100	100
ENR-25	100	–
ENR-50	–	100

TABLE III Processing characteristics of PVC–ENR blends

	Blend	
	PE-25	PE-50
Minimum Mooney viscosity at 120 °C	31	73
Mooney scorch time at 120 °C (min)	> 300	153
Rheometer torque minimum (dN m):		
140 °C	11.5	25.0
150 °C	11.0	24.5
160 °C	10.0	20.5
170 °C	9.0	14.5
180 °C	8.0	14.5
Rheometer scorch time (min):		
140 °C	85	40
150 °C	40	19
160 °C	30	12
170 °C	18	8
180 °C	12	7

Figs 1 and 2. It is evident that at 140 °C the rate of increase in torque with curing time is very slow in the case of PE-50 and there was almost no increase in the case of PE-25 even after 120 min. At higher temperatures the rate of increase in torque with curing time increases. But the increase in torque in the case of PE-25 is less than that of PE-50 at all temperatures. At prolonged curing at 180 °C, both PE-25 and PE-50 show signs of reversion. From the rheometer studies it is apparent that PVC and ENR react between themselves causing gradual increase in torque with time. That such an increase in torque is not due to thermo-vulcanization of PVC or ENR was confirmed by the fact that rheometer curves of PVC alone and ENR alone do not show any such increase in torque values at these temperatures. Furthermore, both PVC and ENR are soluble in tetrahydrofuran. Although the Brabender-mixed blend, before moulding, is soluble in tetrahydrofuran, the moulded PVC–ENR blend is immiscible in this solvent. The blend swells only to a limited extent in the same solvent. The high V_r value in both blends (see Table V) indicates high degree of cross-linking. PE-50 shows higher V_r value than PE-25 indicating that the cross-linking between PVC and ENR-50 is higher than that between PVC and ENR-25.

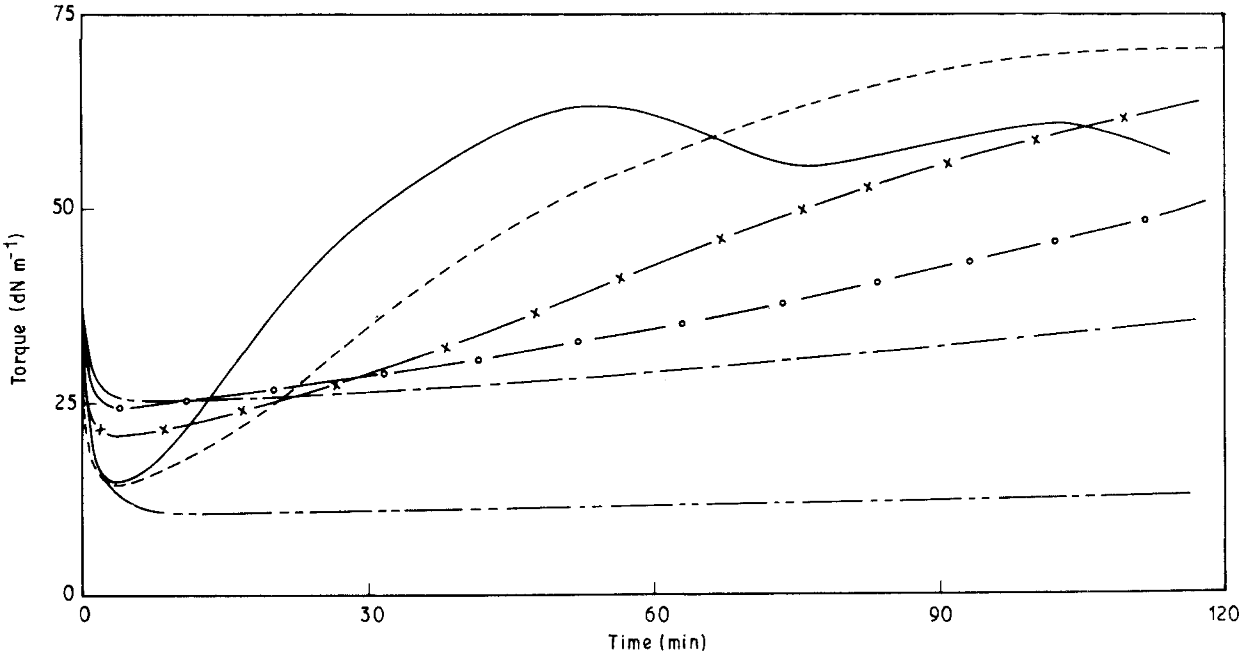

Figure 1 Rheographs of PVC–ENR-50 systems at different temperatures. PE-50: (—) 180 °C, (– – –) 170 °C, (— x —) 160 °C, (— o —) 150 °C, (— - —) 140 °C, (— - - —) with TBLS, 170 °C.

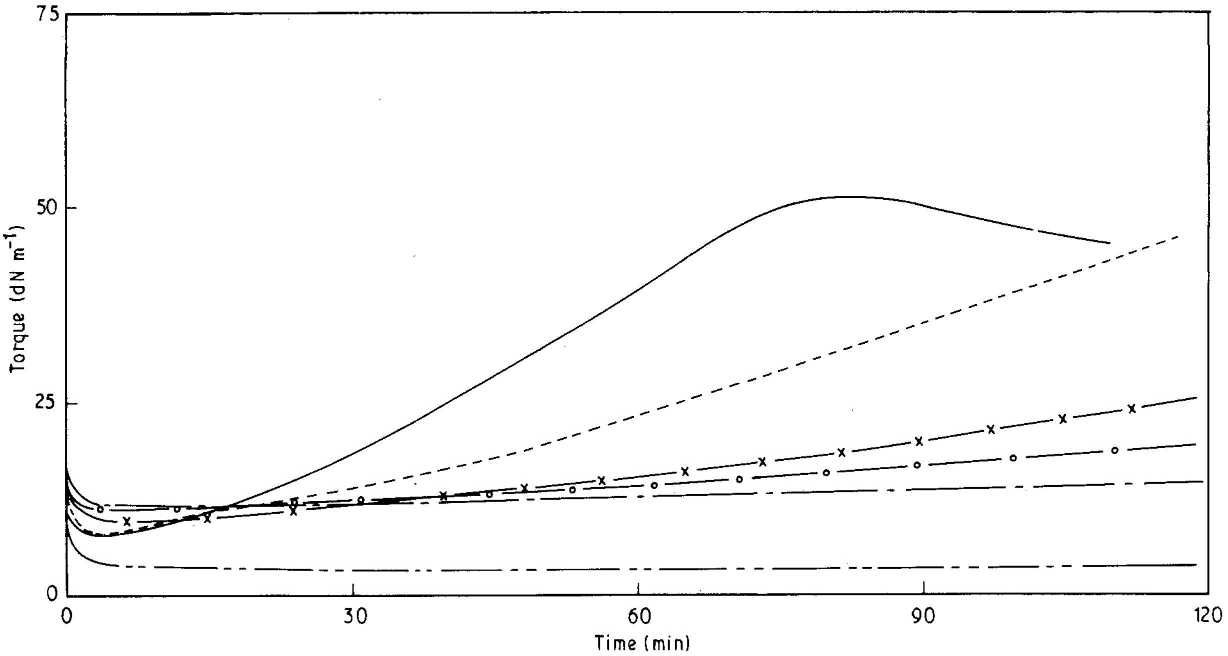

Figure 2 Rheographs of PVC–ENR-25 systems at different temperatures. PE-25: (—) 180 °C, (- - -) 170 °C, (— × —) 160 °C, (— o —) 150 °C, (— - —) 140 °C, (— - - - —) with TBLS, 170 °C.

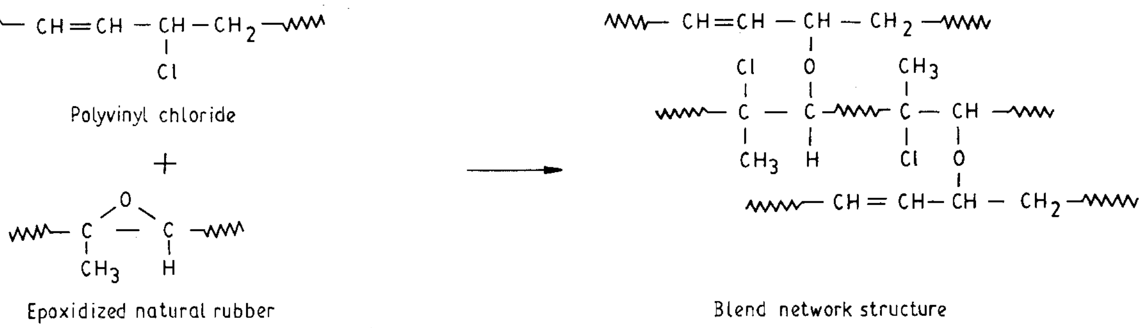

Figure 3 Plausible mechanism of cross-linking between PVC and ENR.

Furthermore, the per cent weight loss after equilibrium swelling in tetrahydrofuran is 13 for PE-25 and 14 in case of PE-50, indicating that both PVC and ENR exist mostly in the cross-linked form in the blends.

Another interesting observation is that when we mixed a stabilizer, namely tribasic lead sulphate, into the PVC–ENR blends, we observed no increase in the rheometer torque values even after 120 min at 170 °C. These stabilizer-mixed PVC–ENR blends were also found to be soluble in tetrahydrofuran indicating that no cross-linking has taken place. It is believed that the cross-linking reaction between PVC and ENR occurs through the allylic chlorine of PVC and by opening up of the epoxy ring in ENR. It is known that allylic and tertiary chlorine in PVC are labile and less stable [8]. A plausible mechanism of cross-linking between PVC and ENR is shown in Fig. 3. The stabilizer is believed to block the allylic chlorine in the PVC chain [9], thus preventing the cross-linking reaction between PVC and ENR.

Miscibility of the components in the two blends was examined by dynamic mechanical and differential scanning calorimetric studies. Fig. 4 shows the effect of temperature on storage modulus of the blends and the single components. It is apparent that the blends PE-50 and PE-25 exhibit two glass transitions indicating the immiscibility of the two phases. Dynamic storage modulus for the blends rapidly decreases at the T_g zone due to the decrease in the stiffness of the samples. Simultaneously, loss modulus and damping sharply rise until they attain maxima and then fall with further increase in temperature (Figs 5 and 6). The temperature corresponding to the maximum in damping or loss modulus is taken as the T_g of the blends (Table IV). Both PE-25 and PE-50 blends show characteristics of the individual components at the segmental level.

DSC thermograms of ENR-25, ENR-50, PVC and the blends are shown in Fig. 7. Results of thermal analysis are similar to that of dynamic mechanical analysis in the sense that the individual components were not miscible. Table IV summarizes the T_gs of different systems.

Fig. 8 shows the stress–strain curves of the two blends and Table V summarizes their physical

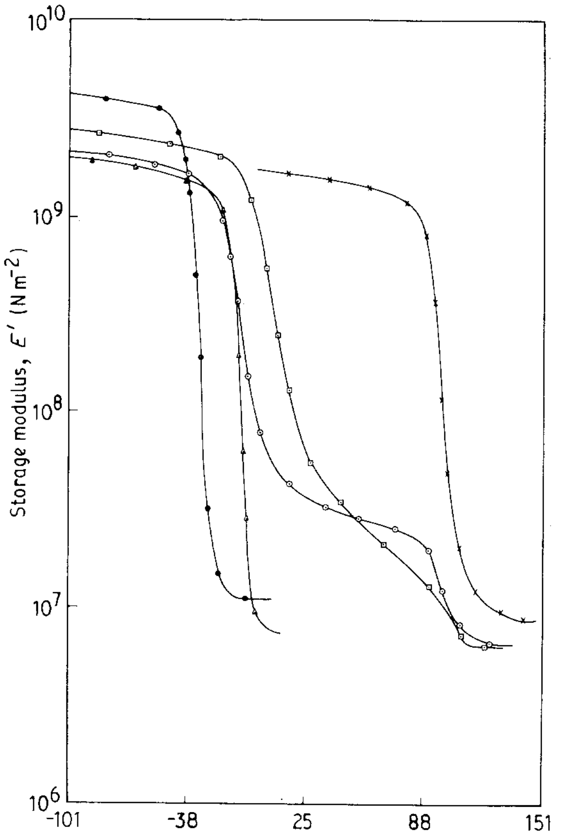

Figure 4 Effect of temperature on storage modulus, E', of PVC–ENR systems: (×) PVC, (●) ENR-25, (△) ENR-50, (○) PE-25, (□) PE-50.

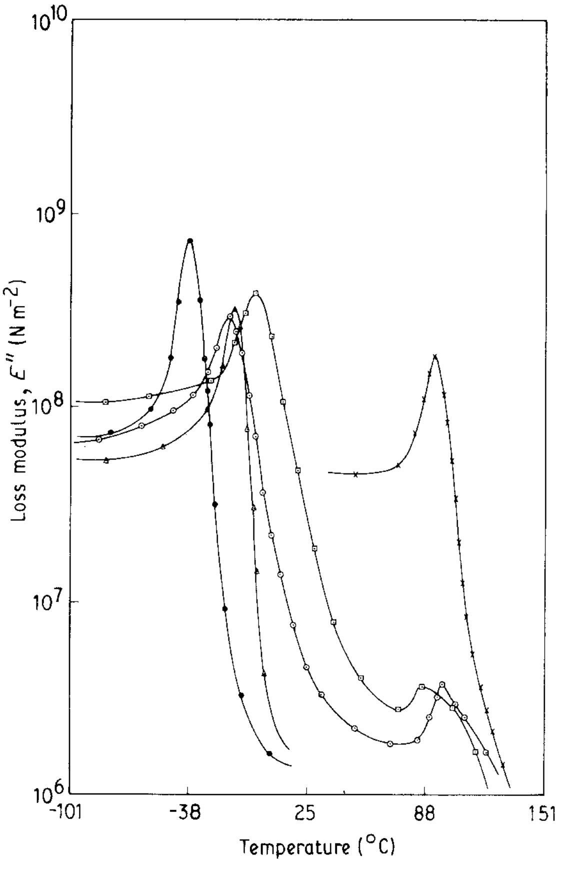

Figure 5 Effect of temperature on loss modulus, E'', of PVC–ENR systems: for key, see Fig. 4.

TABLE IV Glass transition temperatures, T_g, obtained from differential scanning calorimeter (DSC) and dynamic mechanical analysis studies

Sample	T_g (°C)		
	DSC	Dynamic mechanical analysis	
		Loss modulus (E'')	Damping (tan δ)
PVC	83	92.5	100.5
ENR-25	−41	−37.5	−25.4
ENR-50	−14	−13.2	−5.2
PE-25	−19, 88	−17.2, 97.5	−7.2, 105.2
PE-50	0, 81	−3.3, 84.9	8.7, 104.6

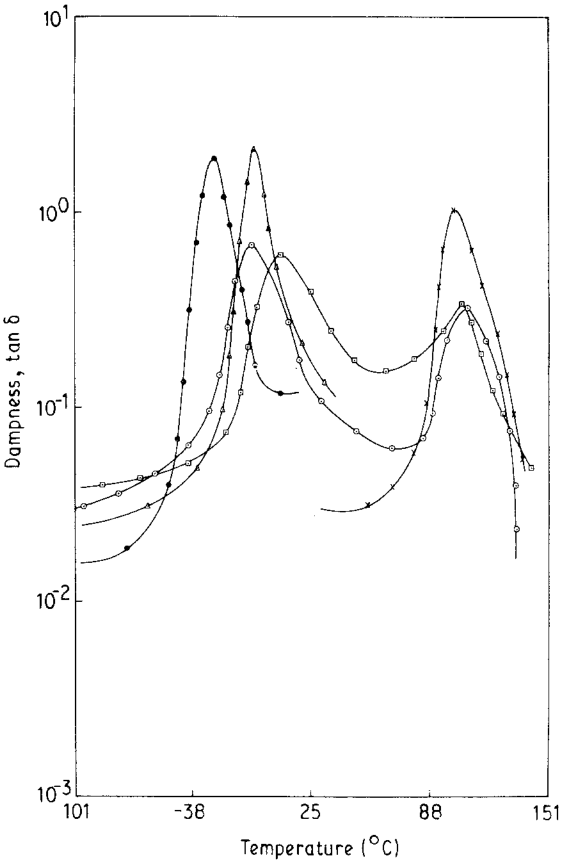

Figure 6 Effect of temperature on damping, tan δ, of PVC–ENR systems: for key, see Fig. 4.

properties. It is apparent that blends of PVC and ENR produce oil-resistant products which are abrasion resistant, have low resilience, and high modulus with moderate tensile and tear strength. The blend with ENR-50 registers higher hardness, modulus and tensile strength than the blend with ENR-25.

4. Conclusions

That PVC–ENR blend is "self-cross-linkable" in the absence of any cross-linking agent is evident from rheometer and swelling studies. PVC–ENR-50 blend was found to be more cross-linkable than PVC–ENR-25 blend and the degree of cross-linking increases with increasing curing temperature. Both PVC–ENR-50 and PVC–ENR-25 blends show an extraordinarily

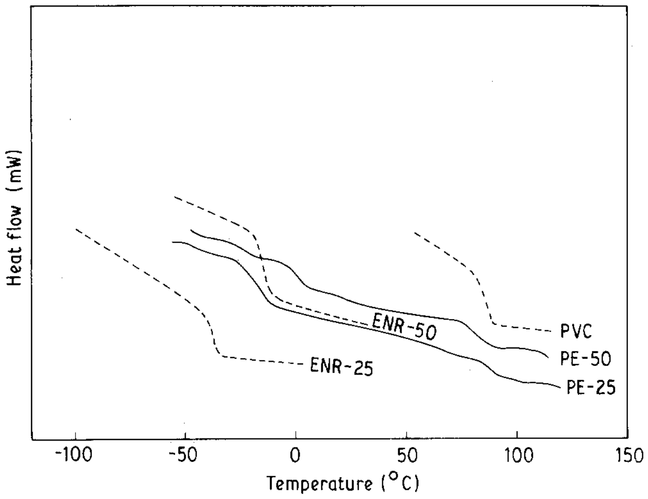

Figure 7 Differential scanning calorimeter thermograms of PVC, ENR-25, ENR-50, PE-25 and PE-50.

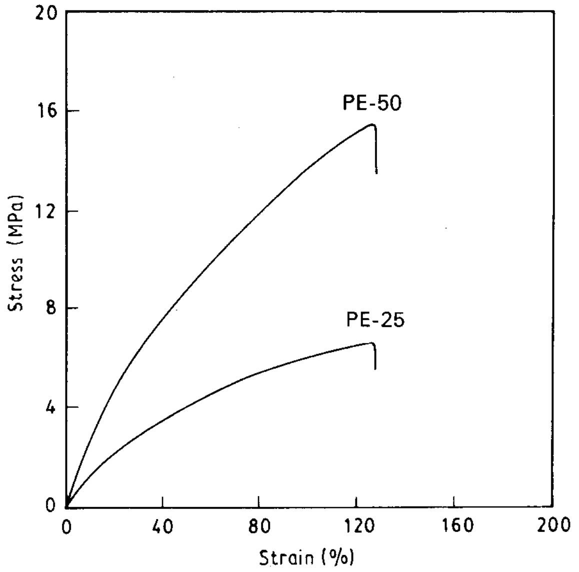

Figure 8 Stress–strain curves of PE-25 and PE-50 blends.

TABLE V Physical properties of PVC–ENR blends moulded at 180 °C

Properties	Blend	
	PE-25[a]	PE-50[b]
50% modulus (MPa)	3.80	8.08
100% modulus (MPa)	5.78	12.61
Tensile strength (MPa)	6.21	14.88
Elongation at break (%)	121	118
Tear strength ($\mathrm{N\,mm^{-1}}$)	15.67	28.80
Elongation at tear (%)	44.88	39.26
Abrasion loss ($\mathrm{cm^3\,h^{-1}}$)	1.02	0.98
Compression set at constant strain (%)	39	46
Heat build-up, ΔT (°C) (ambient temperature = 50 °C)	40	c
Dynamic set (%)	13	c
Resilience (%) (ambient temperature = 30 °C)	33	20
Hardness, Shore D	29	43
V_r, in tetrahydrofuran	0.08	0.12
Swelling in ASTM oil no. 3, % increase in weight	1.8	0.5

[a] Moulded for 60 min.
[b] Moulded for 32 min.
[c] Sample blown out at 5 min ($\Delta T = 28$ °C).

high degree of processing safety. The blends show two glass transition temperatures by dynamic mechanical analysis and differential scanning calorimetry. Such blends were found to have good oil resistance, high abrasion resistance, high modulus but low resilience with moderate tensile and tear strength.

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