

Thermal, X-ray and dynamic mechanical properties of thermoplastic elastomeric natural rubber–polyethylene blends

N. Roy Choudhury, T. K. Chaki, A. Dutta and A. K. Bhowmick*

Indian Institute of Technology, Kharagpur 721302, India

(Received 2 December 1988; accepted 24 February 1989)

Differential scanning calorimetry (d.s.c.), X-ray and dynamic mechanical studies were carried out on a series of natural rubber–polyethylene (PE) thermoplastic elastomeric blends of various levels of interactions. The chemical structure of rubber and its composition in the blend do not influence significantly the melting temperature (T_m) of PE. The decrease in percent crystallinity (x_c) with the rubber content is related to incomplete crystallization observed from lower heat of fusion values (ΔH). The glass transition temperatures (T_g) of the blend do not change substantially and this indicated incompatibility. From the X-ray diffraction patterns d values were calculated. With the addition of rubber there was a tendency for the d values to increase in all the systems. The same trend was observed for the interplanar distance (R), which indicated the appreciable migration of rubber into the interchain space of polyethylene. The crystallinity was measured by X-rays and the results were in line with those of the d.s.c. measurements. The existence of separate T_g values for the blends, as observed from dynamic mechanical analysis, also leads to the conclusion that natural rubber and polyethylene are incompatible in the melt even with the physical as well as a chemical compatibilizer.

(Keywords: rubber–polyethylene blends; d.s.c.; X-ray analysis; dynamic mechanical analysis)

INTRODUCTION

In recent years, commercialization of thermoplastic elastomers has stimulated interest in studying their behaviour thoroughly. Various types of thermoplastic elastomers have been described in detail by several authors^{1,2}. One type of fast-growing thermoplastic elastomer which is easier to process is made by blending rubber and plastic in definite proportions. Characteristically, this is a family of material consisting of a rubber soft segment which gives rise to elastomeric properties and a crystalline hard segment which acts as cross-link and fillers. Several researchers have reported useful rubber–plastic blends^{3,4}. The mechanical properties of these blends will depend on properties of individual components, interaction between them and the morphology of blends. These factors were highlighted in our earlier communications with reference to natural rubber–polyolefin thermoplastic elastomers^{5–7}. However, to explore newer applications, important properties must be investigated. It is with this in mind, we have studied the thermal, X-ray and dynamic mechanical behaviour of the thermoplastic elastomers made from natural rubber and polyethylene (PE). Blends with varied levels of interactions using physical and chemical compatibilizers which we have reported earlier^{5,7} were used for the present investigation.

Martuscelli *et al.*^{8,9} reported a series of investigations on thermal behaviour and morphology of rubber–plastic blends. According to them fundamental information about miscibility of the blends and the phase diagram of the components in the melt state could be obtained from

these studies. Locke and Paul¹⁰ studied the dynamic mechanical properties, thermal analysis, adhesion studies and microscopy of ternary blends to examine the effectiveness of third component as a blend modifier. Smith *et al.*¹¹ carried out a d.s.c. study of low density polyethylene and a certain crystalline ethylene propylene diene rubber (EPDM) blend to find out the causes for tensile strength synergism.

EXPERIMENTAL

Materials

The formulation of various mixes is given in Table 1. Mixing and moulding were carried out as reported elsewhere^{5,7}.

Natural rubber (NR) ISNR 5, was supplied by the Rubber Board, Kottayam, India. Molecular weight $M_w = 780\,000$. Intrinsic viscosity $\eta = 4.45$ (benzene, 30°C dl/g). Wallace plasticity $\rho_0 = 59.0$

Polyethylene (PE) Indothene 16 MA 400, was supplied by IPCL, Baroda. Density 0.916 g/cm³. Melt flow index (MFI) = 40 g/10 min.

PE_m is PE modified by benzoyl peroxide and maleic anhydride⁷. Polypropylene (PP) Koylene M0030, was supplied by IPCL, Baroda. Molecular weight $M_w = 530\,000$. Density 0.910 g/cm³. Melt flow index MFI = 10 (230°C and 2.16 kg).

Chlorinated polyethylene (CPE) 36% chlorine, was supplied by Dow Chemicals, USA. Specific gravity = 1.16. Mooney viscosity $ML_{(1+4)} = 80$ at 121°C.

Chlorosulphonated polyethylene was supplied by Du Pont. Specific gravity = 1.18; solubility parameter $\delta = 9.0 \text{ cal}^{1/2} \text{ cm}^{3/2}$.

* To whom all correspondence should be addressed

Table 1 Formulation of the mixes

Blend	Physically modified systems											Chemically modified systems				Dynamically cured systems		
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
NR	90	70	70	70	70	70	70	50	50	30	30	70	70	70	70	70	70	—
PE	30	30	30	30	30	30	30	50	50	70	70	27	27	27	27	30	30	30
PE _m	—	—	—	—	—	—	—	—	—	—	—	3	3	3	3	—	—	—
EPDM	—	—	20	—	—	—	—	—	—	—	—	20	—	—	—	—	—	70
CPE	—	—	—	20	—	—	—	—	20	—	20	—	20	—	—	—	—	—
CSPE	—	—	—	—	20	—	—	—	—	—	—	—	—	—	—	—	—	—
ENR	—	—	—	—	—	20	—	—	—	—	—	—	—	20	—	—	—	—
S-EPDM	—	—	—	—	—	—	20	—	—	—	—	—	—	—	20	—	—	—
ZnO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5	—	5
Stearic acid	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1	—	1
Sulphur	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.5	—	2
CBS	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.8	—	—
MBT	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.5
TMT	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1
DCP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.5	—

Sulphonated EPDM (S-EPDM) Ionomer 2590, was supplied by Uniroyal Chemical Co., USA, Density = 1.12 g/cm³. Mooney viscosity $ML_{(1+4)} = 45-50$ at 100°C. Percent by weight of ionic group = 2.7.

Ethylene propylene diene rubber (EPDM) Keltan 520, was supplied by DSM, Holland through SBM Chemicals, India. Specific gravity = 0.86. Mooney viscosity $ML_{(1+4)} = 46$ at 125°C.

Epoxidized natural rubber (ENR) ENR 25, was supplied by MRPRA, UK. Density = 0.99 g/cm³. Epoxidation level 25 mol%, Mooney viscosity $ML_{(1+4)} = 110$ at 100°C.

DCP, Dicumyl peroxide was supplied by Hercules Incorporated, Wilmington, USA. ZnO, zinc oxide, specific gravity = 5.55. S, Sulphur, density = 1.9 g/cm³.

CBS, cyclohexyl benzothiazyl sulphenamide was supplied by IEL, Rishra, Hooghly. Specific gravity = 1.30 at 25°C; melting point = 101°C.

MBTS, 2-benzothiazyl disulphide was supplied by IEL, Rishra, Hooghly. Specific gravity = 1.54 at 25°C; melting point = 167°C.

TMTD, tetramethyl thiuram disulphide, was supplied by IEL, Rishra, Hooghly. Specific gravity = 1.42 at 25°C; melting point = 140°C.

The blends were characterized by differential scanning calorimetry (d.s.c.), X-ray and dynamic mechanical analysis (DMA) techniques.

Differential scanning calorimetry study (d.s.c.)

The thermal behaviour of the polymer blends was studied with the help of a Dupont 910 thermal analyser. A series of compositions ranging from 70/30 to 30/70 rubber/plastic proportion, with varied levels of interactions was used for the study. The samples were programmed cooled at 10°C/min to -150°C, then heated at 10°C/min to about 200°C in nitrogen atmosphere. The cycle was repeated with cooling at 10°C/min and heating at the same rate for a second time. The glass transition temperatures of the samples were taken as the mid-point of the step in the scan. The peak maximum from the d.s.c. melting thermograms was considered as the melting point.

X-ray study

In order to determine the degree of crystallinity and the amorphous content of different samples, X-ray diffraction patterns of the samples were recorded with a Philips X-ray diffractometer (Type PW 1840) using Ni-filtered CuK α radiation from a Philips X-ray generator (Type PW 1729). The angular range was from 5 to 35° (2 θ). The samples were of the same thickness and the same area was exposed. The operating voltage and current of the tube were kept at 40 kV and 20 mA respectively, throughout the entire course of investigation.

The X-ray diffraction patterns of the samples were separated into two parts, crystalline and amorphous by taking natural rubber to be fully amorphous. The areas under the crystalline and amorphous portions were measured in arbitrary units and the degree of crystallinity (x_c) and amorphous content (x_a) of the samples were measured using the relations

$$x_c = \frac{I_c}{I_c + I_a} \quad x_a = \frac{I_a}{I_c + I_a} \quad (1)$$

where I_c and I_a represent the integrated intensity corresponding to the crystalline and amorphous phases respectively, i.e. areas under the respective curves.

Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were carried out on a dynamic mechanical analyser (Rheovibron DDV III EP) consisting of a temperature programmer and controller. It measures dynamic moduli (both storage and loss moduli) and damping of a specimen under oscillatory load as a function of temperature. The experiment was conducted in tension mode from -150 to 200°C at a frequency of 11 Hz at 0.125% dynamic strain with a programmed heating rate of 3°C/min. Liquid nitrogen was used to achieve sub-ambient temperature. The mechanical loss factor $\tan \delta$ and dynamic moduli (E' , E'') were calculated with a microcomputer.

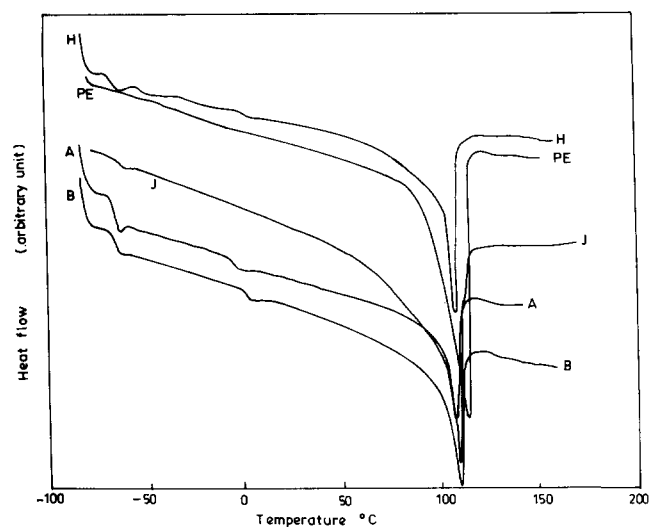
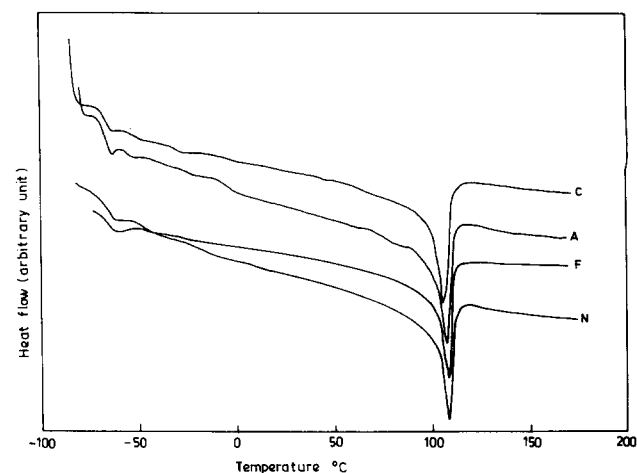
RESULTS AND DISCUSSION

Thermal analysis

The thermal properties of the homopolymers and the blends were analysed by d.s.c. The melting temperature

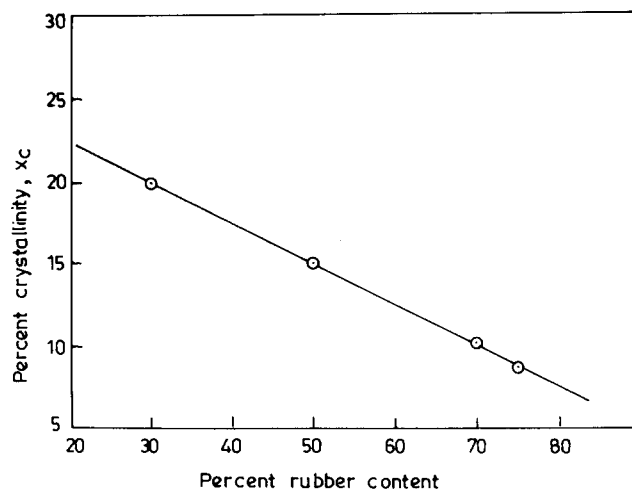
Table 2 Thermal properties

Sample reference	PE	PE _m	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	NR	EPDM	ENR
Parameters measured																				
Peak temperature																				
T_m (°C)	110	106.5	106.8	107.4	105.2	107.1	106.4	107.0	107.1	108.3	107.0	107.9	107.2	105.0	106.7	107.2	107.1	-	-	-
Heat of fusion ΔH (J/g)	86	80	24.4	29.0	23.15	25.15	24.0	26.9	26.22	43.37	34.5	56.9	48.6	21.9	23.48	24.6	24.2	-	-	-
Percent crystallinity (%)	30	25.0	8.4	10.0	8.3	8.7	8.5	9.3	9.0	15.0	12.0	19.6	17.0	7.7	8.1	8.8	8.5	-	-	-
Glass transition temperature, T_g (°C)	-120	-100	-66	-65	-63	-65	-65	-66	-65	-66	-67	-68	-67	-63	-64	-63	-62	-70	-56	-45


Figure 1 D.s.c. thermograms of NR/PE blends of different blend ratios and polyethylene. See Table 1 for details of blends

Figure 2 D.s.c. thermograms of NR/PE blends with varied levels of interactions. See Table 1 for details of blends

(T_m), fractional crystallinity (x_c), heat of fusion (ΔH) and the glass transition temperature (T_g) of the blends are reported in Table 2.

D.s.c. results of the thermoplastic elastomers at various weight fractions of the components and different levels of interactions are shown in Figures 1 and 2. The detectable onset of melting behaviour of PE is around 65°C and spans a range of 45°C before the main peak is detected at 110°C. The peak point temperature of the thermogram was taken as the melting point (T_m). The broad range of melting indicates that there are small crystals in the system which melt before 110°C. It is interesting to note from Table 2 that the value of T_m is almost independent of composition and chemical structure of the rubber.


Figure 3 Plot showing the effect of variation of rubber content (%) in the blend on percent crystallinity

There is, however, a slight decrease in melting point from 110°C for pure PE to 106–107°C for various blends.

The area of the melting endotherm is also calculated and reported as the heat of fusion ΔH . The fractional crystallinity x_c was calculated assuming a heat of fusion for 100% crystalline PE and taken as 290 J/g (ref. 10).

As expected, the values of x_c decrease with the increase in rubber content (Figure 3) under similar conditions of crystallization. The crystallinity of PE was found to be 30%. With gradual incorporation of rubber (30 parts, 50 parts, 70 parts) it comes down to 19.6% for 30/70; 15% for 50/50 and 10% for 70/30 NR/PE blends. Crystallinity is affected by blend composition and crystallization conditions⁸ such as temperature, pressure, orientation, molecular weight and diluent. Figure 4 shows a plot of percent crystallinity x_c vs. blend composition. The degree of crystallinity is almost independent of chemical composition of the amorphous phase. The crystallization of the PE segment is controlled by the segmental diffusion rate of other polymeric chains. The separation is enhanced as rubber content is increased. Incomplete crystallization thus leads to decrease in ΔH and hence in crystallinity. For a 90/30 NR/PE blend the crystallinity is 8.4%. With physical modification (NR/EPDM/PE or NR/CPE/PE or NR/ENR/PE), depending on the nature of the third component it increases or decreases slightly. However, for chemically modified systems (NR/ENR/PE_m/PE) there is a decrease in the overall crystallinity. This may be attributed to lower crystallinity of PE_m and the fact that the interaction of various components inhibits the crystal growth in PE.

The glass transition temperature for polyethylene in the present investigation is expected to be complicated by the restriction on motion that the crystalline regions exert on the amorphous region. The glass transition

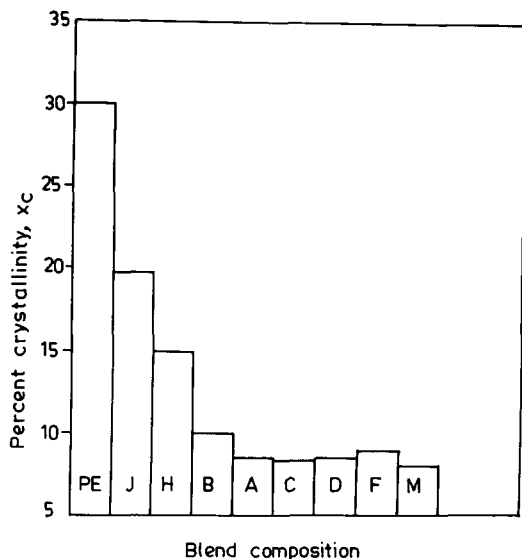


Figure 4 Plot showing variation of percent crystallinity with blend composition. See Table 1 for details of blends

temperatures as obtained from d.s.c. are reported in Table 2 for pure PE and NR. The T_g values are found to be at -120°C and -70°C , respectively. When natural rubber is blended with PE, a sharp glass transition around -65 to -66°C was observed. As the volume fraction of rubber increases the glass transition temperature remains almost constant, but the transition broadens. However, the T_g of the polyethylene phase cannot be detected in the blends. It seems that the T_g of the two phases in the blends do not undergo substantial variation. These observations, coupled with the result that T_m remains more or less constant with the increase in the rubber content, confirms the fact that the blends are incompatible. It was reported earlier^{12,13} that natural rubber-polyethylene systems are incompatible. It is important to note that even with the addition of technological compatibilizer, the blends are thermally incompatible.

X-ray diffraction analysis

Figure 5 depicts the X-ray diffraction pattern of pure PE and the blends. The results of X-ray analysis of the same samples are given in Table 3. In addition to the blends reported earlier, two samples crosslinked with dicumyl peroxide and sulphur (mixes P and Q) were studied. From Table 3 it can be seen that the degree of crystallinity, x_c , of PE is 39.68%. This is higher than that determined by d.s.c. The value of x_c depends very much on the method of preparation of the sample and the technique of measurement¹⁴. The lower value of crystallinity from d.s.c. as compared to X-ray has been reported before¹⁰. The decrease in crystallinity with the addition of natural rubber (mix B) is due to the addition of an amorphous component which migrates into the crystalline phase of pure PE, reducing the crystalline domains of the pure PE sample. Further reduction of the value of x_c takes place on addition of EPDM (mix C), another amorphous component. The crystallinity value is lowest for the chemically modified system (mix N) due to the addition of ENR/PE_m. The results of X-ray measurements are in line with those of d.s.c. measurements. The degree of crystallinity in the S-cured NR/PE system is 16.52%, which is less than that of pure PE and NR/PE

systems. Sulphur crosslinks the NR phase in NR/PE system. It retards the crystallization of PE from the melt and thereby reduces the regular arrangement of crystalline region within the samples. The same phenomenon occurs in the peroxide-cured NR/PE blend. The crystallinity reduces still further because dicumyl peroxide can react with polyethylene in the melt, unlike the sulphur system.

The d values are reported in Table 3. The h, k, l planes are also calculated assuming polyethylene to be ortho-

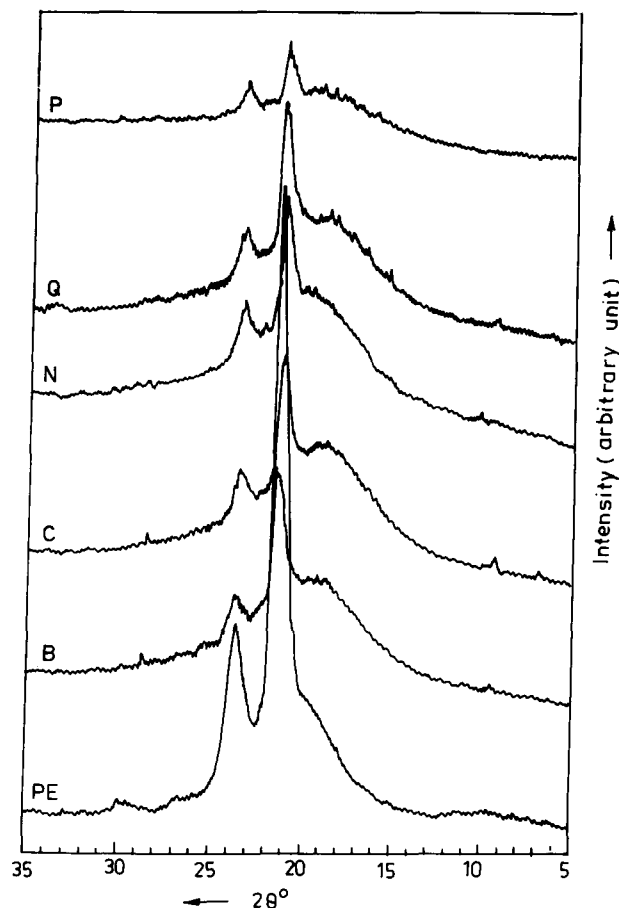


Figure 5 Variation of the X-ray diffraction pattern from different NR/PE blends and polyethylene. See Table 1 for details of blends

Table 3 X-ray study

Sample reference	Percent crystallinity, x_c (%)	d value (Å)	(h, k, l)	R
PE	39.68	4.143	(110)	4.598
		3.754	(200)	
		2.998	(210)	
B (NR/PE)	17.7	4.143	—	4.598
		3.769		
		3.110		
C (NR/EPDM/PE)	12.46	4.171	—	4.629
		3.785		
N (NR/ENR/PE _m /PE)	8.27	4.181	—	4.640
		3.802		
Q (NR/PE/dynamic curing by DCP)	15.44	4.152	—	4.608
		3.777		
P (NR/PE/dynamic curing by sulphur)	16.52	4.142	—	4.597
		3.767		

rhombic and using equation (2)

$$d = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2} \quad (2)$$

where, $a = 7.40 \text{ \AA}$; $b = 4.93 \text{ \AA}$; $c = 2.53 \text{ \AA}$ (ref. 15).

There are three d values observed corresponding to [110], [200] and [210] planes. With the addition of rubber (both crosslinked and uncrosslinked) there is a tendency for the d values to increase in all the systems. The interplanar distance R , calculated as [$R = 1.1d_0$] also follows the same trend. The increase in interplanar distance shows that appreciable migration of rubber into the interchain space of PE takes place.

Dynamic mechanical properties

The dynamic mechanical properties of a few systems are reported here. In order to have an adequate modulus for correct measurements some systems were crosslinked. Figures 6–8 show the dynamic mechanical properties of the blends and pure PE. The glass transition temperature was selected as the peak position of the $\tan \delta$ when plotted vs. temperature. The loss modulus E'' shows a trend basically similar to the mechanical loss factor $\tan \delta$. The T_g values for all the systems are reported in Table 4.

Pure PE exhibits transition at -131 and -10°C , respectively. For PE the transition at (-131°C) is attributed to the glass transition¹⁵ temperature. The peak

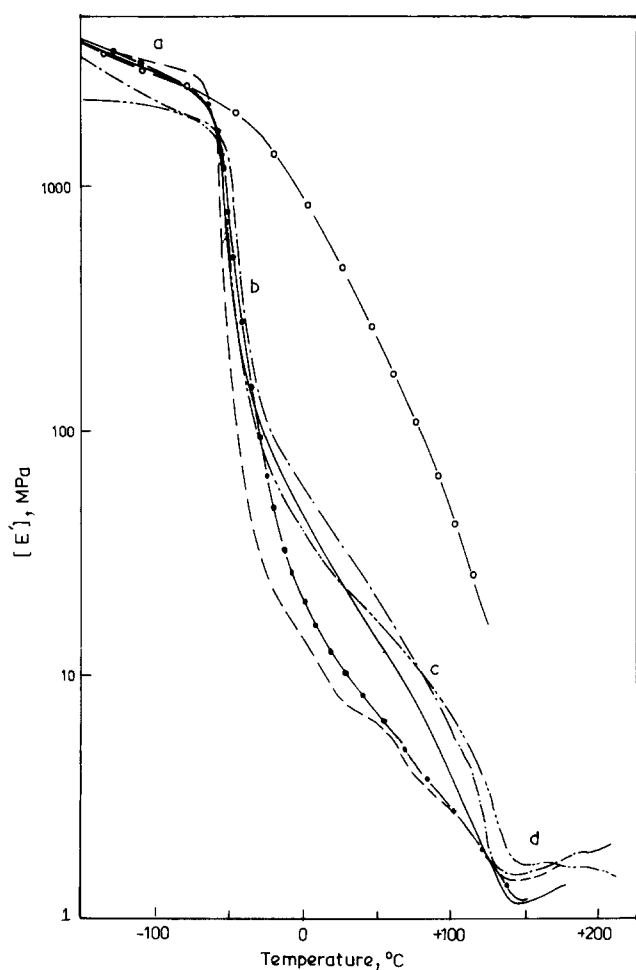


Figure 6 Effect of temperature on storage modulus of different NR/PE blends and polyethylene. —, P; —, A; —, C; —●—●—●, N; —●—●—●, R; —○—○—○, PE. See Table 1 for details of blends and text for details of curve regions

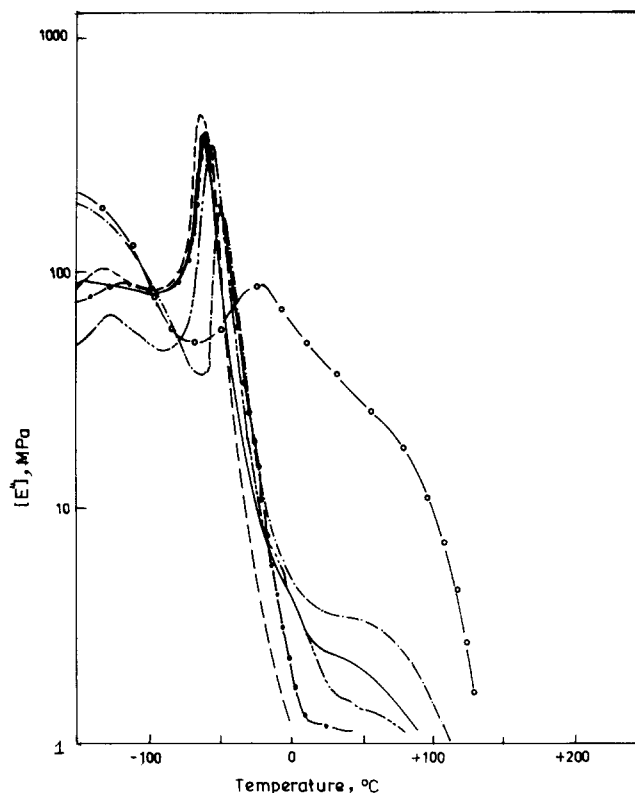


Figure 7 Effect of temperature on loss modulus of different NR/PE blends and polyethylene. —, P; —, A; —, C; —●—●—●, N; —●—●—●, R; —○—○—○, PE. See Table 1 for details of blends

at -10°C is due to β -relaxation process which is associated with the unfreezing of segmental motion of the main chain in amorphous region¹⁶. For pure NR, the glass transition is detected at -53°C . In the NR/PE blends the transition of PE is not so prominent. In fact, some authors^{17,18} reported earlier that the T_g of PE is masked by its crystallinity and also observed the suppression of the secondary relaxation due to the interaction of the blend components.

In contrast to the d.s.c. results the DMA thermograms exhibit transition at lower temperatures, indicating the different nature of response of the molecular segments of the samples towards DMA and DSC analysis conditions.

Figure 6 illustrates the elastic modulus E' of various systems over a wide range of temperatures. The curves for all the compositions are very similar and consist of four distinct regions: a glassy region (a); a transition region (b); a rubbery region (c); and a high temperature region (d). The storage modulus changes from a very high value to a much lower value with increase in temperature due to the decrease in stiffness of the sample. The way in which this transition takes place for different blends in different positions is shown in Figure 6. The transition (b–c) for NR/PE (90/30) (mix A) blend takes place at the lowest temperature. On crosslinking there is a shift towards the higher temperature region as in the case of 70/30 blends (mix P). As expected, the loss modulus and damping sharply increase in the transition zone until they attain maxima, and then fall off with the rise in temperature.

It is interesting to note from Table 4 that the low temperature transition for $\tan \delta$ (T_{g1}) and E'' (E''_1) occur

at the same temperature for all the systems, whereas the second transition (T_{g2}) temperature varies from E'' . The first transition occurs at -124.5°C (from both $\tan \delta$ and E'') and the second transition at -50°C (from $\tan \delta$) and -58.7°C (from E'') for the NR/PE system. The value of $\tan \delta_1$ remains almost the same for the NR/PE blends (0.029–0.031) but that of $\tan \delta_2$ varies. The EPDM/PE system shows $\tan \delta_1$ close to that of PE, which may be due to the similarity in chain structure (methylene group)

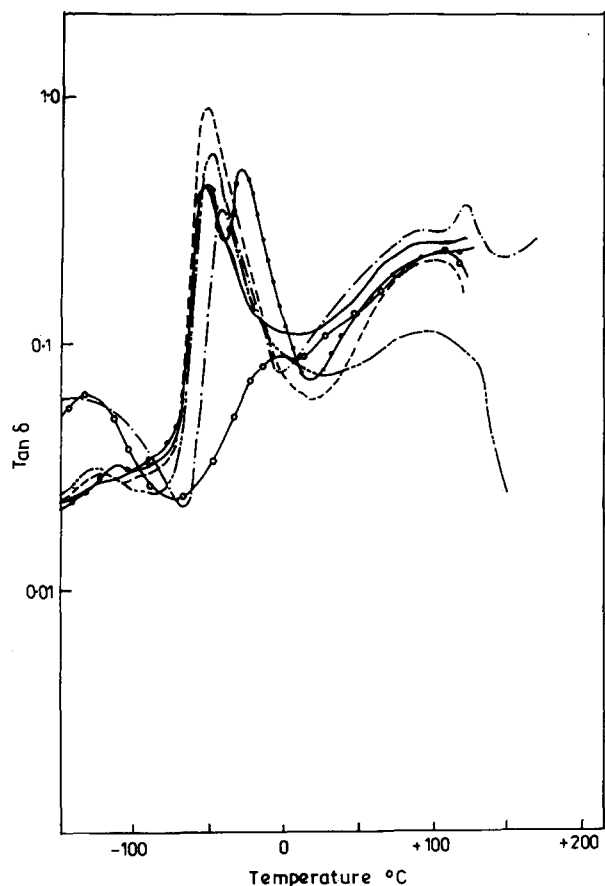


Figure 8 Effect of temperature on damping ($\tan \delta$) of different NR/PE blends and polyethylene. —, P; —, A; —, C; —●—●—, N; —●—, R; —○—○—, PE. See Table 1 for details of blends

between EPDM and PE. However, the 90/30 NR/PE blend (mix A) shows the $\tan \delta_2$ value of 0.885 whereas the EPDM/PE system (mix R) shows the lowest $\tan \delta_2$ value 0.352 among the blends studied. In fact, Koleske *et al.*¹⁷ reported that the height of loss peak at transition will depend on the degree of crystallinity and would be greater than unity for a completely amorphous polymer. The existence of the separate peaks at (-131°C) and (-50°C) for the binary blends indicates the incompatibility of the systems. Akhtar *et al.*¹⁹ also reported the incompatibility of the NR/PE blends. With the incorporation of EPDM (third component) the peak position remains unaltered, probably due to the close T_g values of both NR and EPDM. It was reported earlier²⁰ that the T_g values of the two components in a blend should be well separated in order to detect them separately by two distinct peaks on the damping curve. However, the chemically modified system with ENR shows two distinct T_g values at -53°C and -26°C for NR and ENR phases, respectively, besides the T_g of PE. This is clearly evidence for the existence of a multiphase, and hence incompatible, system.

ACKNOWLEDGEMENT

The authors are grateful to the Department of Science and Technology, New Delhi for funding the project.

REFERENCES

- 1 Wells, S.C. 'Handbook of Thermoplastic Elastomers' (Ed. B. M. Walker) Van Nostrand Reinhold, New York, 1979, p. 103
- 2 Morris, H. L. 'Handbook of Thermoplastic Elastomers' (Ed. B. M. Walker) Van Nostrand Reinhold, New York, 1979, p. 5
- 3 Coran, A.Y. 'Handbook of Elastomers - New Development and Technology' (Eds A. K. Bhowmick and H. L. Stephens) Marcel Dekker, New York, 1988, p. 249
- 4 Kresge, E. N. 'Polymer Blends', Vol. 2 (Eds D. R. Paul and S. Newman) Academic Press, New York, 1978, p. 293
- 5 Roy Choudhury, N. and Bhowmick, A. K. *J. Mater. Sci.* 1988, **23**, 2187
- 6 Roy Choudhury, N. and Bhowmick, A. K. *J. Adhesion Sci. Technol.* 1988, **2**, 167
- 7 Roy Choudhury, N. and Bhowmick, A. K. *J. Appl. Polym. Sci.*, in press
- 8 Martuscelli, E., Riva, F., Sellitti, C. and Silvestre, C. *Polymer* 1985, **26**, 270
- 9 Martuscelli, E. *Polym. Eng. Sci.* 1984, **24**, 563

Table 4 Dynamic mechanical properties

Sample reference	T_{g1}^a ($^\circ\text{C}$)	T_{g2}^b ($^\circ\text{C}$)	$\tan \delta_1$	$\tan \delta_2$	E''_1 (peak temperature), $^\circ\text{C}$	E''_2 (peak temperature), $^\circ\text{C}$
NR/PE/S-cure 70/30	-128	-47	0.031	0.564	-128	-53
NR/PE 90/30 75/25	-124.5	-53	0.030	0.885	-124.5	-58.7
NR/EPDM/PE 70/20/30	-119	-52.9	0.029	0.429	-119	-58.8
NR/ENR/PE _m /PE 70/20/3/27	-113	-52.8 -26.0	0.031	0.420	-113	-55.9
EPDM/PE/S-cure 70/30	-136.7	-43	0.062	0.352	-136.7	-47
PE	-131	-10	0.058	0.086	-131	-20

^a T_{g1} is the glass transition temperature of the polyethylene phase

^b T_{g2} is the glass transition temperature of the rubber phase

- 10 Locke, C. E. and Paul, D. R. *Polym. Eng. Sci.* 1973, **13**, 308
- 11 Lindsay, G. A., Singleton, C. I., Carman, C. J. and Smith, R. W. 'Multiphase Polymers, Advances in Chemistry Series' (Eds S. L. Cooper and G. M. Estes) American Chemical Society, Washington, DC, 1979, p. 367
- 12 Kraus, S. 'Polymer Blends', Vol. 1 (Eds D. R. Paul and S. Newman) Academic Press, New York, 1978, p. 16
- 13 Ecker, R. *Rub. Chem. Technol.* 1957, **30**, 200
- 14 Herman, P. H. and Weidinger, A. *Makromol. Chem.* 1961, **24**, 44
- 15 Brandrup, J. and Immergut, E. H., Eds. 'Polymer Handbook, III-1', Wiley Interscience, New York, 1975
- 16 Boyer, R. F. *Polym. Eng. Sci.* 1968, **8**, 161
- 17 Koleske, J. V. and Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Edn.* 1969, **7**, 795
- 18 Hickman, J. J. and Ikeda, R. M. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 1713
- 19 Akhtar, S. and Bhagawan, S. S. *Rub. Chem. Technol.* 1987, **60**, 1591
- 20 Trexler, H. E. and Lee, M. C. H. *Kautschuk Gummi Kunststoffe* 1987, **40**, 945