

New polymeric blends from hydrogenated styrene–butadiene rubber and polyethylene

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New thermoplastic elastomeric blends based on hydrogenated styrene–butadiene rubber (HSBR) and low-density polyethylene (LDPE) were prepared by the melt blending technique. The rheology, structural and mechanical properties were measured as a function of blend composition. The HSBR/LDPE blend had a higher tensile strength, modulus, and work-to-break with low elongation at break compared with those of pure HSBR. X-ray diffraction studies demonstrated co-crystallisation and a remarkable increase in the degree of crystallinity. The improvement in the mechanical properties and the uniform morphology were correlated with the interfacial adhesion and compatibilisation of the HSBR/LDPE blend through ethylene segments. The experimental results for the HSBR/LDPE blends were compared with those for HSBR/high-density polyethylene (HDPE) and SBR/LDPE blends. The mechanical properties of the HSBR/LDPE blend were found to be superior. The results were explained on the basis of morphology and interaction. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Hydrogenated styrene–butadiene rubber (HSBR) has been reported in the literature^{1,2}. It has been claimed that this polymer is thermoplastic-elastomeric in nature as a result of the generation of crystalline ethylene segments in the backbone on hydrogenation². However, the crystallinity of HSBR having 17% styrene and a 92% hydrogenation level has been determined in our laboratory to be only 7–8%. As a result, significant improvements in the mechanical properties are not obtained on hydrogenation. An attempt is made here to increase the crystallinity and the properties of HSBR, retaining its thermoplastic elastomeric character, by physically blending it with olefinic plastics. It is expected that there is a possibility of ethylenic segments interacting with the olefins. Thermoplastic elastomers from rubber–plastic blends have been reported widely in the literature³. Natural-rubber-based thermoplastic elastomers have been prepared by blending natural rubber with polyolefins (polyethylene and polypropylene)⁴. However, such blends need physical and chemical compatibilisation in order to enhance the properties to the level of rubber vulcanisates. The objective of the present study is to blend HSBR with low-density polyethylene (LDPE) in different proportions in order to prepare thermoplastic elastomers and to understand their behaviour. For comparison purposes, we have also used high-density polyethylene (HDPE) as the plastic, and SBR, in place of HSBR, as the rubber in the blends.

EXPERIMENTAL

Materials

Hydrogenated styrene–butadiene rubber (92% saturated) was prepared by diimide reduction of SBR latex with a 17%

styrene content⁵, obtained from the Nippon Zeon Co. Ltd., Japan. The low-density polyethylene (LDPE), Indothene 22 FA002, was supplied by IPCL, Baroda. It had the following specifications: specific gravity (23°C), 0.92 g cm⁻³; MFI (190°C, 2.16 kg), 0.2 g per 10 min; melting temperature range, 108–112°C. The high-density polyethylene (HDPE), Hostalene GA 7260 (specific gravity, 0.96 g cm⁻³; MFI, 16 g per 10 min; melting point, 128°C) was obtained from Polyolefin Industries Ltd., Bombay.

Blend preparation

Binary blends were prepared by melt mixing the polymers in a Brabender Plasticorder (model no. PLE 330) fitted with a cam-type mixing head (N-50H) with a rotor speed of 60 rev min⁻¹. Mixer temperatures were set at 150°C for the LDPE blend and 160°C for the HDPE blend, respectively. Generally, the plastic was melted in the mixer for 1–2 min, then the rubber strips were allowed to blend for 4 min. The molten mass was immediately removed from the mixer and passed through a two-roll mixing mill at room temperature to obtain a sheet. The compositions of the investigated blends are given in *Table 1*.

Moulding of the samples

The premixed material (HSBR/LDPE or SBR/LDPE) was compression moulded in an electrically heated Labo Press between two aluminium foils at 150°C for 3 min at a pressure of 5 MPa to obtain sheets 1.75 ± 0.05 mm thick. The aluminium foil was used to reduce the shrink marks in the moulding. After completing the moulding, the sample (still under compression) was immediately cooled in water to avoid possible degradation of the rubber phase under high temperature exposure and to maintain overall dimensional stability. Similarly, HDPE blends were moulded at 160°C.

Measurement of rheological properties

The flow properties of the compounds were measured in a

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Table 1 Formulation of blends

Blend designation	HSBR (parts by weight)	SBR (parts by weight)	LDPE (parts by weight)	HDPE (parts by weight)
HL ₀	100	—	0	—
HL ₂₀	80	—	20	—
HL ₃₀	70	—	30	—
HL ₄₀	60	—	40	—
HL ₅₀	50	—	50	—
HL ₆₀	40	—	60	—
HL ₇₀	30	—	70	—
HL ₈₀	20	—	80	—
HL ₁₀₀	0	—	100	—
SL ₃₀	—	70	30	—
HD ₃₀	70	—	—	30

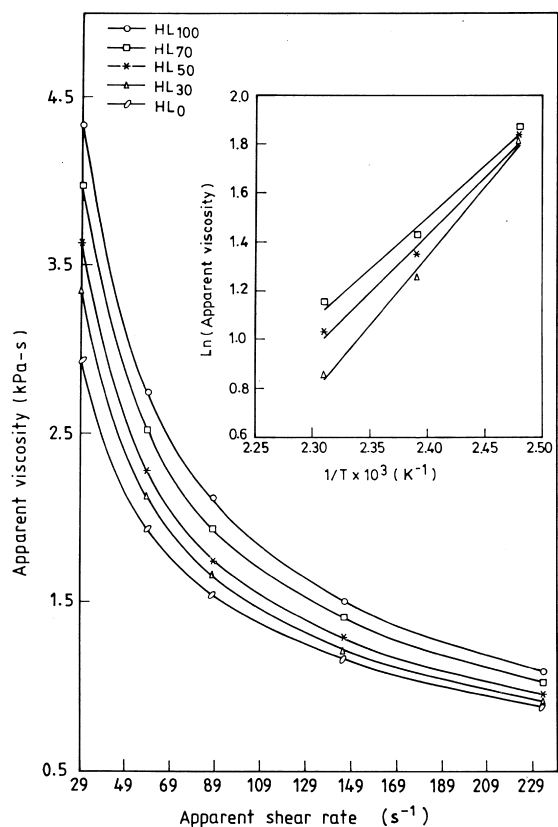


Figure 1 Variation of apparent viscosity with shear rate and composition of some HSBR/LDPE blends and pure components at 145°C. The inset shows $\ln(\text{apparent viscosity})$ against reciprocal temperature at a 29.21 s^{-1} shear rate for HSBR/LDPE blends

Monsanto processability tester (MPT) which was a fully automatic high-pressure capillary viscometer. The barrel and the capillary were electrically heated with a micro-processor-based temperature controller system. The capillary used possessed a length-to-diameter ratio of 30:1, having multiple cone entry with a compound entrance angle of 45° and 60°. The preheating time for the samples was constant at 4 min at the extrusion temperature. The change in shear rate was achieved by changing the plunger speed. For calculating the activation energy, extrusion was carried out at different temperatures: 130, 145 and 160°C for the LDPE blends, and 160, 180 and 200°C for the HDPE blends.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical spectra of the pure materials and the blends were obtained using a dynamic mechanical thermal analyser (DMTA MK II) from Polymer Laboratories Ltd.,

UK. All the samples ($43.5 \times 13.3 \times 1.7 \text{ mm}^3$) were analysed in the dual cantilever bending mode with a strain of 64 μm (peak-to-peak displacement) in the temperature range from -130 to 120°C . The frequencies selected were 0.1, 1 and 10 Hz. The heating rate was 2°C min^{-1} . The low temperatures were attained by slow cooling with liquid nitrogen. DMTA MK II software (version 1.2) was used for data acquisition and analysis. The data were analysed using a COMPAQ computer. The experimental error was $\pm 2^\circ\text{C}$.

D.s.c. studies

Differential scanning calorimetry (d.s.c.) studies were carried out using a Dupont 9000 thermal analyser (model 910). The samples were initially cooled to -150°C and then heated to 150°C with a heating rate of $10^\circ\text{C min}^{-1}$. Liquid nitrogen was used to achieve subambient temperatures. The thermograms were recorded during the second heating.

Morphology study

The phase morphology of the blends was studied by examining the surface of the blends with use of a scanning electron micrograph (Hitachi SEM model S 415A) with an emission current of 80 μA and an accelerating voltage of 25 kV. For the blend morphology study, one approach took advantage of the enhanced solubility of HSBR and SBR in organic solvents compared to polyethylene. A thin section of the blends was exposed to chloroform for 48 h at room temperature, which selectively extracted the rubber part and effectively etched the samples. The solvent-extracted sections were dried to room temperature inside a desiccator. Subsequently, the etched surfaces were sputter-coated with gold. The voids in the samples indicated the locus of HSBR/SBR.

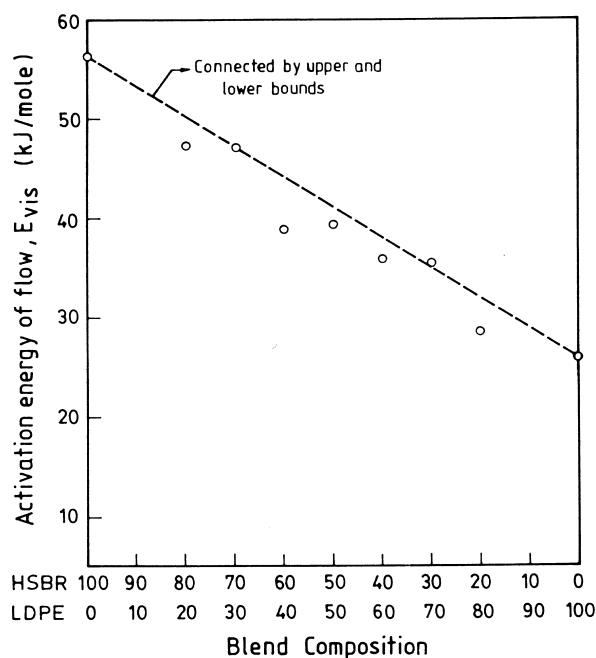
Wide-angle X-ray diffraction studies (WAXS)

The pure materials and the blends containing various proportions and types of plastics were subjected to iron-filtered $\text{Co K}\alpha$ radiation generated from a Philips PW 1719 X-ray generator at an operating voltage and current of 40 kV and 20 mA, respectively. The diffraction patterns of the samples were recorded with use of a Philips X-ray diffractometer (PW-1710). Samples of the same thickness and area were exposed. The diffraction patterns were recorded over the angular range $10^\circ < 2\theta < 50^\circ$ at a scanning speed of 3° min^{-1} . The amorphous reflection contributions were subsequently resolved with use of curve fitting by a non-linear least-squares method assuming that the intensity peak profile could be approximated by a Gaussian function⁶. The degree of crystallinity was determined from the ratios of the areas under the crystalline peaks and the amorphous halo. For the purpose of indexing the reflections, the interplanar spacing d_{hkl} was calculated

Table 2 Rheological properties of HSBR/LDPE blends

Sample reference	Pseudoplasticity index, n		Viscosity index, k		Activation energy (kJ mol ⁻¹)	
	145°C	160°C	145°C	160°C	29.21 s ^{-1a}	146.05 s ^{-1a}
HL ₀	0.44	0.47	20.09	14.05	56.2	44.9
HL ₂₀	0.39	0.46	23.17	15.98	47.3	39.1
HL ₃₀	0.38	0.46	28.70	18.13	47.2	35.5
HL ₄₀	0.38	0.41	30.85	20.09	38.9	34.5
HL ₅₀	0.37	0.41	32.33	21.57	39.4	33.6
HL ₆₀	0.36	0.40	35.55	23.17	35.9	30.6
HL ₇₀	0.36	0.40	38.21	24.89	35.5	29.1
HL ₈₀	0.34	0.38	41.02	33.12	28.6	26.6
HL ₁₀₀	0.29	0.36	41.92	35.57	26.0	22.3

^aShear rate


Figure 2 Plot of the Activation energy of flow (E_{vis}) against blend composition for HSBR/LDPE blends

using the known cell parameters of polyethylene⁷ ($a = 7.4 \text{ \AA}$, $b = 4.93 \text{ \AA}$, $c = 2.534 \text{ \AA}$ with $\alpha = \beta = \gamma = 90^\circ$) using the relationship⁸

$$d_{hkl} = [(h^2/a^2) + (k^2/b^2) + (l^2/c^2)]^{-1/2} \quad (1)$$

It is worth mentioning that the unit cell size of polyethylene is not unique, but can vary among polyethylene samples differing in their structural details⁹. Indexing of the reflections was carried out by comparing the d_{hkl} values corresponding to the different reflection peaks with the theoretically calculated d_{hkl} values. The interchain distance (R), crystallite size (P) and r.m.s strain value ($\langle e^2 \rangle^{1/2}$)¹⁰ of the pure materials and their blends were calculated using the relationships

$$R = \frac{5\lambda}{8 \sin \theta} \quad (2)$$

$$P = \frac{K\lambda}{\beta_{2\theta} \cos \theta} \quad (3)$$

$$\langle e^2 \rangle^{1/2} = \frac{\beta_{2\theta}}{5 \tan \theta} \quad (4)$$

where $\beta_{2\theta}$ is the peak width, θ is the Bragg angle, λ is the

wavelength of the X-radiation ($\lambda = 1.790 \text{ \AA}$ for Co $K\alpha$) and K is a constant close to unity (commonly taken as 0.89).

Measurement of physical properties

The tensile strength, elongation at break and modulus at 100 and 300% elongation were measured on dumb-bell specimens ((BS-E) type; cut with a hollow punch from the test slab) according to ASTM D 412-80 in a Zwick-1445 universal testing machine at a strain rate of 500 mm min^{-1} at $30 \pm 2^\circ\text{C}$. The averages of three data points were taken and the experimental error was $\pm 5\%$ (deviation from the median value).

The tension set was measured according to ASTM D 412-80. A dumb-bell specimen was stretched to 100% elongation at a rate of 500 mm min^{-1} and held at that elongation for 10 min. It was then quickly released and allowed to rest for 24 h. The distance between two benchmarks was measured to the nearest 1% of the original distance and the tension set was calculated as a percentage of the original unstretched distance.

A hysteresis test was also performed on a dumb-bell specimen at room temperature ($30 \pm 2^\circ\text{C}$) in a Zwick UTM instrument. The testing rate for both loading and unloading was 500 mm min^{-1} and the strain was 300%.

RESULTS AND DISCUSSION

Rheological characteristics

Figure 1 shows the variation of viscosity with shear rate and composition of a few binary blends of HSBR/LDPE along with the pure polymers at 145°C . In all the samples, the viscosity decreases with increase in shear rate, demonstrating a pseudoplastic character. The viscosity values of the blends lie between that of the pure components. Pure polyethylene exhibits a viscosity of 4.33 kPa s at a 29.21 s^{-1} shear rate. This value decreases to 1.10 kPa s at a 233.7 s^{-1} shear rate. This is almost a 75% decrease. HSBR under the same conditions displays a 70% decrease. As usual, the viscosity of all the blends decreases with increase in temperature. As the temperature increases, the segmental mobility of the chains increases and the interchain force decreases. To further understand the effect of temperature on the viscosity of the blends, the logarithm of the viscosity is plotted as a function of reciprocal temperature (Arrhenius plot; shown as an inset in Figure 1). Values of the activation energy of flow (E_{vis}) calculated from the slopes of the lines are given in Table 2. In the case of HSBR/LDPE blends, the activation energy values decrease with increase in LDPE content. HSBR-rich blends show higher values of activation energy due to the lower mobility. Polyethylene-rich blends are more mobile,

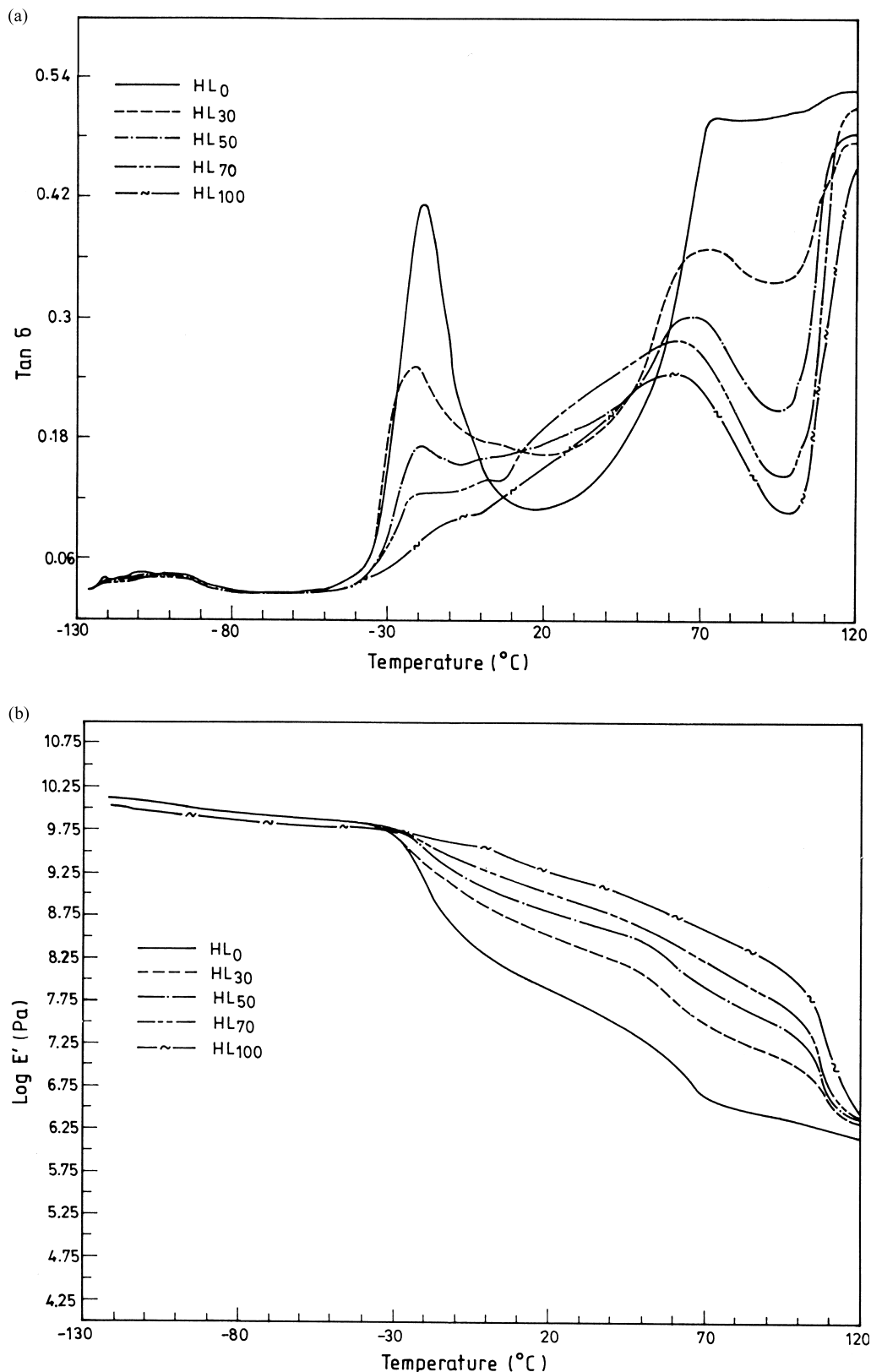


Figure 3 Temperature dependence of (a) the loss tangent ($\tan \delta$) and (b) the storage modulus (E') for some HSBR/LDPE binary blends and pure components at a frequency of 10 Hz

as indicated by lower values of the activation energy. The absence of bulky side groups might be the reason for the highest mobility (lowest activation energy) for pure LDPE. For compatible blends, it has been proposed that the additivity of E_{vis} is preserved¹¹. Figure 2 shows a near-linear dependence of E_{vis} on the blend composition,

indicating compatibility of the systems. The effects of temperature and blend ratio on the pseudoplasticity index of the system are given in Table 2. The extent of non-Newtonian behaviour of the system can be judged from the n values. Pseudoplastic materials are characterised by $n < 1$. Therefore, a high value of n demonstrates a low

Table 3 Dynamic mechanical properties of HSBR/LDPE blends

Sample reference	Transition temp. T_1 (°C)	$\tan \delta_1$	Transition temp. T_2 (°C)	$\tan \delta_2$	Transition temp. T_3 (°C)	$\tan \delta_3$
HL ₀	-106	0.05	-18	0.42	— ^a	—
HL ₂₀	-107	0.05	-18	0.31	— ^a	—
HL ₃₀	-106	0.04	-21	0.26	72	0.37
HL ₄₀	-104	0.04	-19	0.22	66	0.32
HL ₅₀	-108	0.04	-20	0.18	64	0.31
HL ₆₀	-105	0.04	-20	0.15	64	0.27
HL ₇₀	-103	0.04	-21	0.13	64	0.28
HL ₈₀	-105	0.04	-15	0.10	65	0.27
HL ₁₀₀	-108	0.04	-6	0.10	64	0.25

^aAbsent

pseudoplastic nature of the material. From *Table 2*, it is clear that the pseudoplasticity index increases with increase in HSBR content.

Structural characteristics

DMTA. The dynamic mechanical properties of pure polymers and their blends are displayed in *Figure 3a* and *3b*. Pure polyethylene shows three peaks at 64°C, -6°C and -108°C corresponding to the α -, β - and γ -transitions, respectively. The peak values at the β - and γ -transitions are in accordance with the values reported earlier⁴. However, the α -transition is obtained at a much lower temperature. Ribbs and Diaz¹² noted that the relaxations in LDPE are related to the melting peaks and the temperature is governed by the crystallite thickness, which differs due to the different moulding conditions used in different investigations. The γ -transition is due to crankshaft motion in the molecular chain of -CH₂- units of polyethylene¹³, while the β -transition arises from the branching of polyethylene units. Pure HSBR displays a strong transition at -18°C with a $\tan \delta$ value of 0.42. The peak is ascribed to the glass transition temperature of HSBR. The γ -transition shows a weak $\tan \delta$ peak maximum at -106°C. On blending LDPE and HSBR, the height of the glass transition temperature peak of HSBR is lowered. The higher the PE content, the lower is the value of the peak $\tan \delta$ (*Table 3*). The peaks at -18 to -21°C indicate some sort of compatibility of HSBR and PE through the -CH₂- chain segments. It is interesting to note that the α -transition temperature of polyethylene is shifted towards higher temperatures (64°C for pure LDPE to 72°C for HL₃₀) on incorporation of HSBR. $\tan \delta$ peak values are also raised from 0.25 to 0.37 in this temperature region. This also reveals that HSBR and PE interact with each other. For the γ -transition, there is no significant change in the peak temperature or peak $\tan \delta$ value. This peak arises due to polyethylene segments common to both HSBR and LDPE when they are frozen.

In the $\log E'$ against temperature plot (*Figure 3b*), the transitions for polyethylene are not distinct. There is a gradual drop in modulus with increasing temperature up to 107°C. Beyond this temperature, there is an abrupt reduction in the modulus due to the melting of LDPE. HSBR, on the other hand, shows a distinct transition corresponding to the glass transition temperature. There is one more transition at about 57°C, where a drop in the modulus is observed. These may be ascribed to the melting of the crystalline segments of HSBR. The modulus of HSBR is much lower than that of PE over the whole range of temperatures. The blends show an intermediate behaviour. For the blends with higher HSBR content ($\geq 50\%$), distinct transitions are observed. The high peak value of $\tan \delta$ of HSBR in the transition region is due to

low values of the storage modulus, as the loss modulus peak values in the range -50° to 0°C (not shown in the figure) are 0.22×10^{-9} Pa to 0.03×10^{-9} Pa, respectively. Similarly, the PE segments show higher loss modulus values (0.17×10^{-9} Pa to 0.32×10^{-9} Pa) in the same temperature range. However, $\tan \delta$ of LDPE, which is the ratio E''/E' , is lower because of the higher value of E' . These results are in line with the rheological behaviour of the materials at 145°C (*Figure 1*), where the apparent viscosity of PE or the viscous components of PE are shown to be much higher.

D.s.c. studies. The transitions in DMTA are further confirmed from the d.s.c. studies. HSBR shows a distinct glass transition temperature at -28°C and a melting endotherm with a peak melting temperature at 57°C (*Figure 4*). These temperatures are shifted on the incorporation of polyethylene; the value of T_g is lower at a higher polyethylene content. The area of the melting endotherm at 57°C decreases as usual at a higher PE content, as there is no transition of PE in this region. PE reveals a sharp melting peak at 113°C, the area of which decreases with increasing HSBR content. The crystallinity values calculated from the HSBR and the PE melting peaks are 6.8% and 39%, respectively. The blends register intermediate values (*Table 4*).

SEM studies. The morphology of the blends was investigated by using a microscope technique. *Figure 5* shows the morphology of HSBR/LDPE blends at 70:30, 50:50 and 20:80 ratios (HL₃₀, HL₅₀ and HL₈₀, respectively). It is interesting to note the laminate structure in all the blends. HSBR, which has been etched out with solvent, corresponds to the dark portion in the micrograph. Such structures were obtained by the authors earlier for natural rubber/polyolefin blends under similar processing conditions³.

XRD results. Wide-angle X-ray diffractograms were recorded in order to characterise the structure of the pure materials and their blends. X-ray diffraction patterns for HSBR, LDPE and the HSBR/LDPE blends are shown in *Figure 6*. A broad halo in the region from 15 to 30° 2θ represents the amorphous part. Two sharp peaks for PE at 25.1° and 27.7° 2θ corresponding to the d_{hkl} values 4.13 Å and 3.74 Å represent the (110) and (200) reflections, assuming PE to be orthorhombic. HSBR (92% saturated) shows three reflections at 13.1° 2θ , 24.6° 2θ and 36.9° 2θ corresponding to the (100), (110) and (210) planes respectively, which may be due to crystalline polyethylene segments. On the introduction of LDPE, the peak intensities along the (110) and (200) planes increase. For the blends with LDPE ($\geq 50\%$), a new peak at 41.8° 2θ ($d = 2.51$ Å)

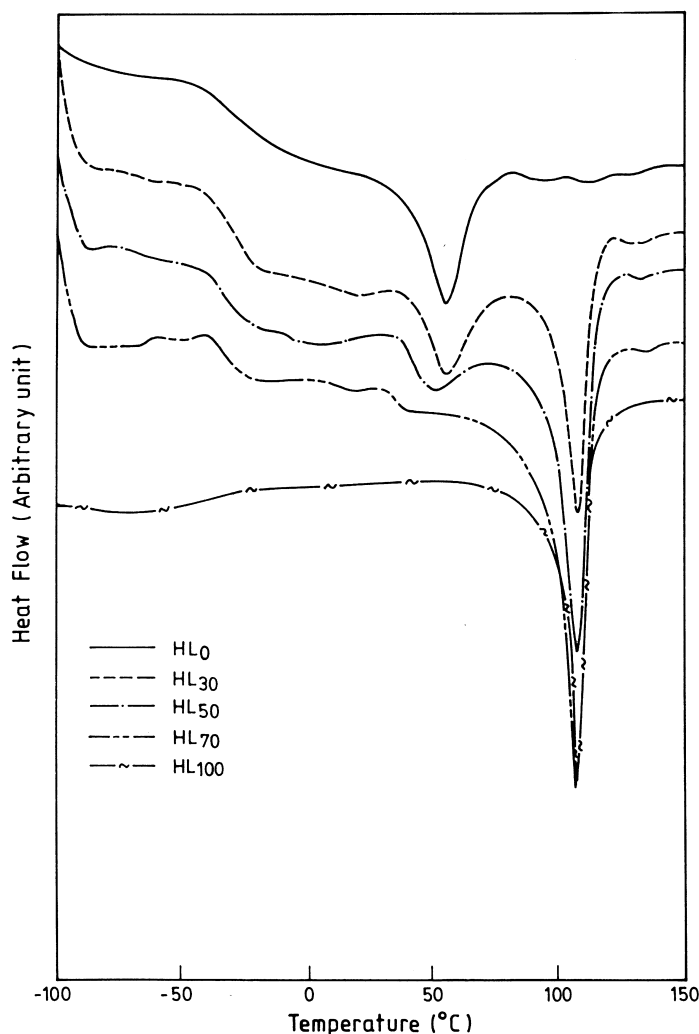


Figure 4 D.s.c. thermograms of some HSBR/LDPE blends and pure components

Table 4 Thermal properties of HSBR/LDPE blends

Sample reference	Glass transition temp. of rubber phase, T_g (°C)	Melting peak temp., T_m (°C)		Crystallinity (%)
		Rubber phase	Polyethylene phase	
HL ₀	-28	57	- ^a	6.8
HL ₂₀	-26	56	108	13.2
HL ₃₀	-31	56	110	16.9
HL ₄₀	-32	55	110	19.8
HL ₅₀	-32	54	111	22.4
HL ₆₀	-32	52	111	27.3
HL ₇₀	-33	- ^a	112	29.4
HL ₈₀	- ^a	- ^a	112	36.0
HL ₁₀₀	- ^a	- ^a	113	39.0

^aAbsent

appears, which may be due to the reflection along the (001) plane. The parameters evaluated from the X-ray diffractograms of various blends are reported in Table 5. With the addition of HSBR, there is a tendency for the interplanar distance (d_{hkl} values) to increase in all the systems. The interchain distance (R) also follows the same trend. The increase in interplanar and interchain distances indicates an appreciable migration of HSBR into the interchain space of PE. As a result, the unit cell of PE must expand and the a and b dimensions must increase to accommodate them. These results corroborate our earlier

observation on rheological, dynamic mechanical and calorimetric measurements. The degree of crystallinity of pure PE is 43.5%, which decreases steadily with an increase in the HSBR content. The decrease in crystallinity is due to the addition of an amorphous component, which migrates into the crystalline phase of pure PE, and the reduction of the total amount of PE. The crystallite size (R), when plotted against the per cent HSBR content (Figure 7) shows a deviation from the median value, which is indicative of mixed crystallite formation or co-crystallisation. To determine the relative degree of a -axis orientation in the blend samples,

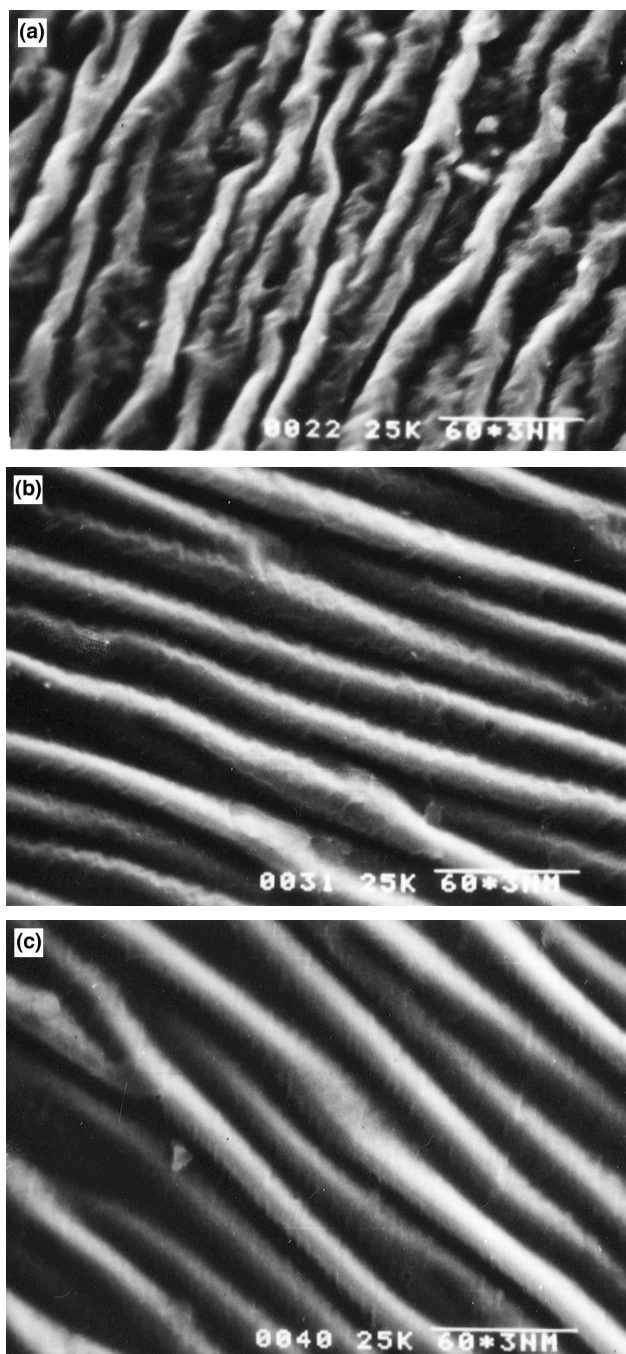


Figure 5 Scanning electron micrograph showing a laminated morphology for the HSBR/LDPE blends (a) HL₃₀, (b) HL₅₀ and (c) HL₈₀. Magnification, 500 ×

the ratio of meridional intensities from the (200) and (110) planes is measured. The higher the ratio of meridional intensities (I_{200}/I_{110}), the higher the orientation of the crystallites along the *a*-axis. It is seen that the *a*-axis orientation steadily increases along with larger *R* and d_{hkl} values with increase in HSBR content. It is also noteworthy that the r.m.s. strain becomes larger on incorporation of HSBR.

Mechanical properties. Figure 8 shows the stress-strain behaviour of the pure materials and their blends. Pure LDPE shows a tensile strength and yielding/necking tendency typical of tough plastics, as reported earlier³. A small Hookean elastic extensibility is followed by a localized plastic deformation process or bulk deformation which may take the form of a neck. HSBR, on the other hand,

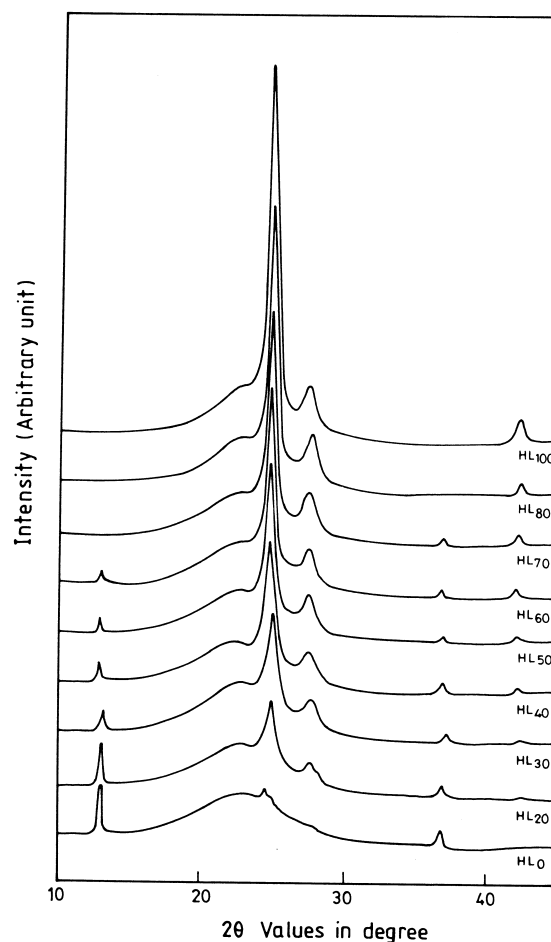


Figure 6 X-ray diffraction patterns of HSBR/LDPE binary blends and pure components

displays typical rubbery characteristics with low values of the 100% and 300% moduli and high elongation at break. The addition of HSBR considerably changes the stress-strain behaviour of LDPE; the moduli of the samples are considerably reduced. The necking tendency characteristic of plastic disappears and a rubbery behaviour is exhibited. The effect of the blend ratio on the physical properties of HSBR/LDPE is shown in Table 6. All the blends display an increase in tensile strength, work-to-break and modulus with the introduction of LDPE, whereas the elongation-at-break value shows a decrease. The increase in the tensile strength of HSBR with increase in LDPE can be explained satisfactorily in terms of increasing crystallinity. The crystallites can act in the dual role of multifunctional physical cross-links and filler particles. As the number and/or size of the crystallites increases with the incorporation of LDPE, the tensile strength increases. It has been shown^{14,15} that the blends of compatible polymers exhibit good mechanical properties; the tensile strength especially shows a near linear dependence with composition. In contrast, blends of incompatible polymers exhibit broad minima. The results of the present investigation (Figure 9) suggest that the HSBR/LDPE blend is compatible.

The tensile sets of pure materials and their blends were determined in order to give an indication of their elasticity. It is found (Table 6) that the tensile set increases with increase in LDPE content. At intermediate blend ratios, the set values are in line with those of typical thermoplastic elastomers.

Table 5 X-ray diffraction results

Sample reference	2θ	Interplanar distance, d_{hkl} (Å)	Interchain distance, R (Å)	Crystallite size, P (Å)	R.m.s strain $10^{-3} (e^{-2})^{1/2}$	Degree of crystallinity (%)	$\langle I_{200}/I_{110} \rangle$
HL ₀	24.6	4.21	5.26	90	16.7	7.6	—
HL ₂₀	24.7	4.19	5.24	123	12.2	14.3	0.38
HL ₃₀	27.3	3.80	4.75	132	11.3	17.6	0.36
	24.7	4.19	5.23				
HL ₄₀	27.4	3.78	4.72	143	10.3	20.6	0.30
	24.8	4.17	5.21				
HL ₅₀	27.4	3.78	4.72	146	10.1	24.2	0.29
	24.9	4.16	5.20				
HL ₆₀	27.5	3.77	4.71	150	9.8	28.5	0.25
	24.9	4.15	5.19				
HL ₇₀	27.6	3.75	4.69	155	9.5	32.3	0.24
	25.0	4.14	5.18				
HL ₈₀	27.7	3.75	4.68	156	9.4	36.5	0.23
	25.0	4.14	5.17				
HL ₁₀₀	27.7	3.74	4.67	158	9.3	43.5	0.16
	25.1	4.13	5.16				
	27.7	3.74	4.67				

Table 6 Mechanical properties of HSBR/LDPE blends

Property	HL ₀	HL ₂₀	HL ₃₀	HL ₄₀	HL ₅₀	HL ₆₀	HL ₇₀	HL ₈₀	HL ₁₀₀
Tensile strength (MPa)	5.7	7.0	8.4	8.6	9.0	10.5	11.4	13.2	14.4
Elongation at break (%)	957	743	735	600	580	560	555	511	498
Work to break (kJ m^{-2})	12.1	13.9	15.5	15.8	15.8	16.8	19.3	21.5	23.2
<i>Modulus (MPa)</i>									
100%	1.5	2.7	3.3	3.8	4.7	5.7	6.2	7.1	8.6
300%	2.3	3.7	4.4	5.0	5.8	7.0	7.5	8.8	10.2
Set at 100% elongation (%)	2.0	6.3	7.5	10	12.5	15	17.5	22.5	45.0
Hysteresis loss (J cm^{-3})	3.04	6.14	7.43	9.73	11.55	13.58	14.13	17.26	24.37

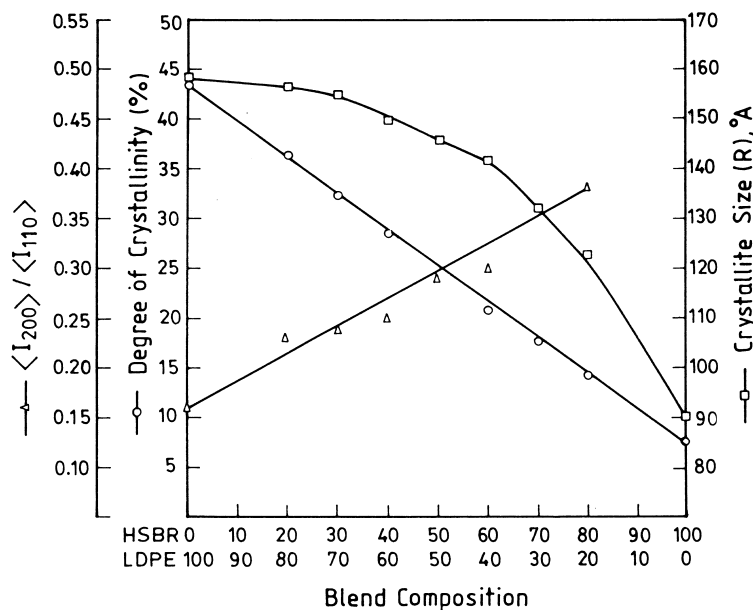


Figure 7 Composition dependence of the degree of crystallinity, crystallite size and intensity ratio for HSBR/LDPE systems

The hysteresis properties of various HSBR/LDPE blends are also reported in Table 6. It is observed that for the HSBR/LDPE blends, the hysteresis loss values show a regular increasing trend with increase in LDPE content.

Influence of the nature of plastics and rubbers

The influence of the nature of the plastic and the rubber has been investigated with the following blends: HSBR:LDPE, HSBR:HDPE and SBR:LDPE at a weight ratio of 70:30. Figure 10 shows the variation of apparent

viscosity with shear rate at 180°C for different systems. The rheological behaviour of the blends containing HSBR and different polyolefins (namely LDPE, HDPE) over a wide range of shear rates, specially at high shear rates, is similar. The blend containing SBR and LDPE (SL₃₀) behaves quite differently. The decrease in viscosity with shear rate is more prominent for the SBR/LDPE system compared with the other systems. Table 7 compares the rheological parameters for different systems. The pseudoplasticity index n for the HSBR/LDPE system (HL₃₀) is higher than that for the

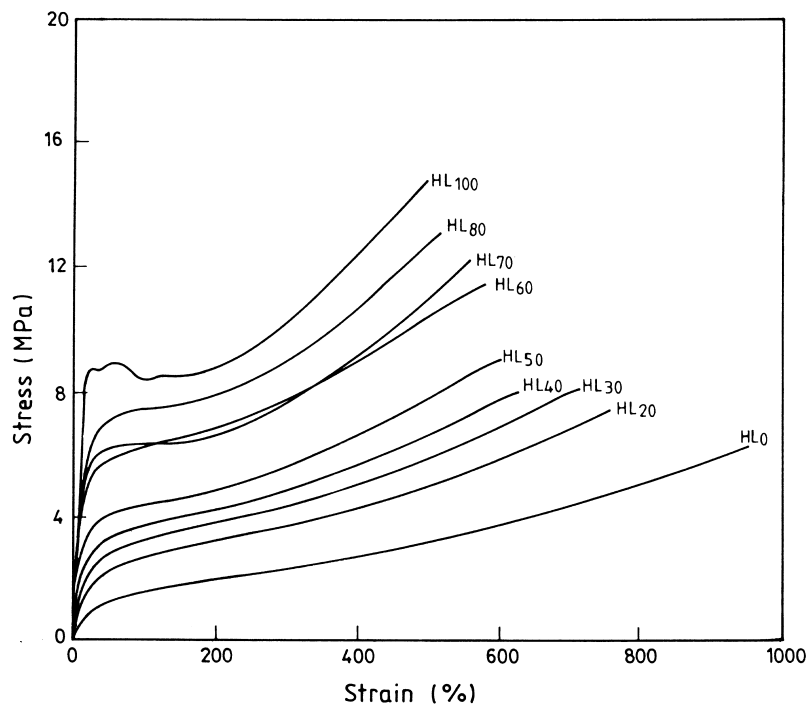


Figure 8 Stress-strain curve for HSBR/LDPE blends and pure components

Table 7 Influence of the nature of the plastics and rubbers on rheological properties

Sample reference	Pseudoplasticity index n			Activation energy of flow, E_{vis} (kJ mol ⁻¹)	
	160°C	180°C	200°C	29.21 s ^{-1a}	146.05 s ^{-1a}
SL ₃₀	0.29	0.33	0.34	14.7	13.7
HL ₃₀	0.40	0.44	0.47	47.2	35.5
HD ₃₀	0.52	0.56	0.59	24.0	19.4

^aShear rate

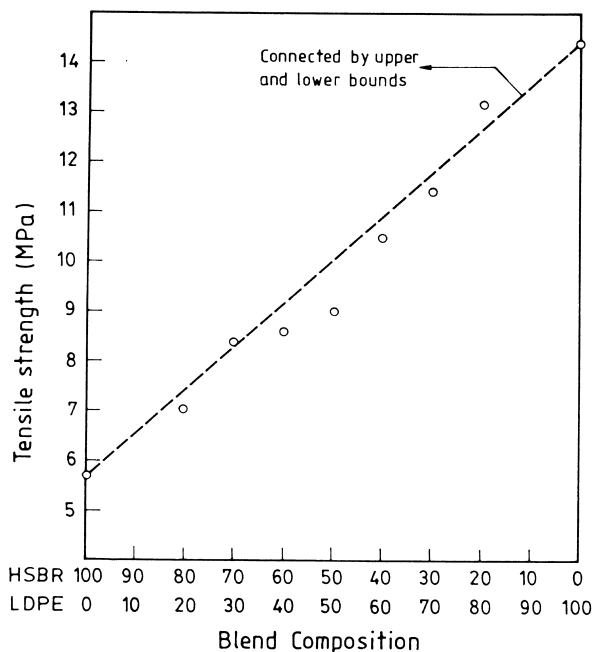


Figure 9 Dependence of the tensile strength on the blend composition of HSBR/LDPE systems

SBR/LDPE system (SL₃₀). The lower value of n of the SBR/LDPE system compared to that of the HSBR/LDPE system is due to the higher pseudoplastic characteristic of SBR than HSBR. Table 7 shows that the activation energy of viscous flow (E_{vis}) for blends with LDPE is almost double that of HDPE. The difference in the E_{vis} value between LDPE and HDPE is due to chain branching in LDPE¹⁶. Long-chain branches may be expected to increase the size of the flow unit (the average length of the polymer chain that moves as a single entity during the flow) and hence to increase the activation energy of the flow.

The morphology is a major determinant of the properties of heterogeneous polymer blends. It is known that for the same processing history, the composition ratio and melt viscosity differences between the components determine the morphology. The larger viscosity difference between SBR and LDPE leads to the gross segregation of SBR to form globules or pores on the LDPE surface (Figure 11a). The morphology of HSBR/HDPE (Figure 11b) is quite different from that of HSBR/LDPE (Figure 5a) for the same blend ratio. There are no lamellae in the HSBR/HDPE system.

Dynamic mechanical properties of the various systems are reported in Figure 12. The SBR/LDPE blend exhibits a lower glass transition temperature (-28°C) of the rubber phase compared with the HSBR/LDPE system (-21°C) (Figure 12a). We have reported earlier that the glass transition temperature of HSBR is higher than that of SBR⁵.

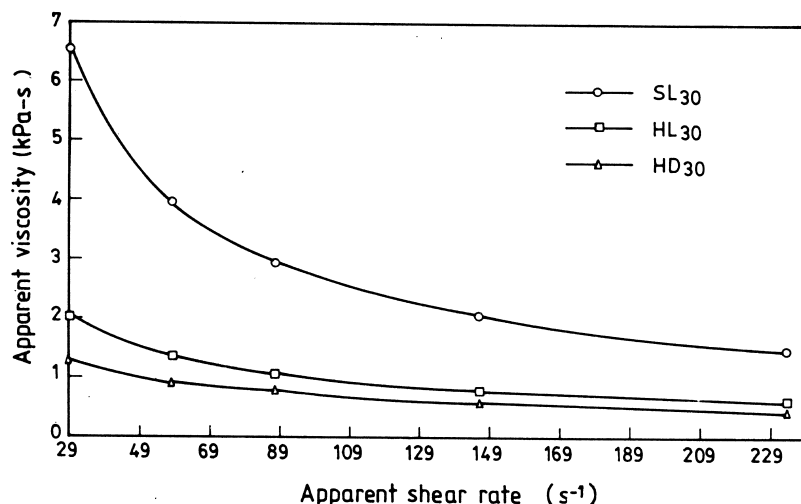


Figure 10 Variation of the apparent viscosity with shear rate for the SBR/LDPE (SL₃₀), HSBR/LDPE (HL₃₀) and HSBR/HDPE (HD₃₀) blend systems

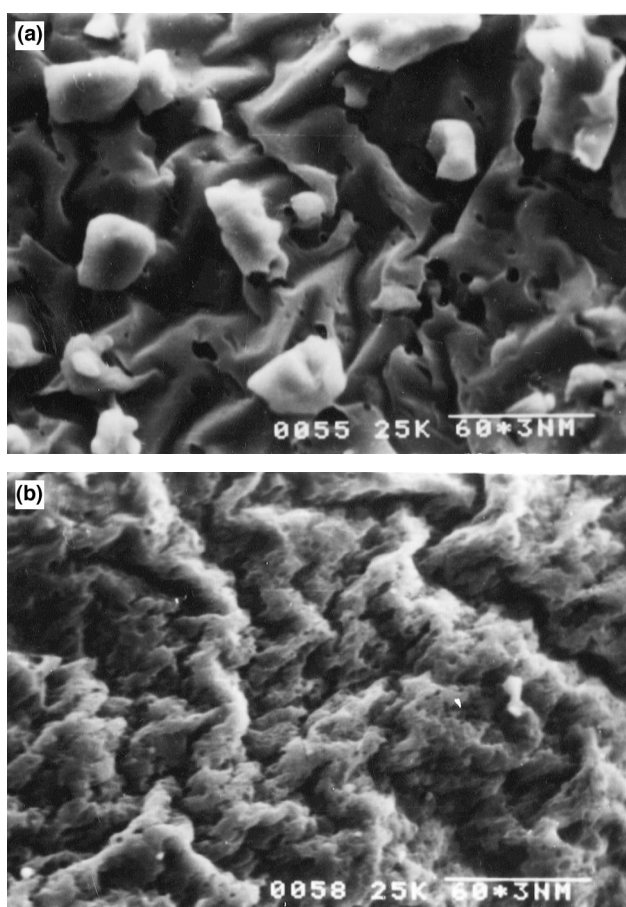


Figure 11 Scanning electron micrographs of (a) SBR/LDPE (SL₃₀) and (b) HSBR/HDPE (HD₃₀) blend systems

The same glass transition temperature of -21°C is recorded for the HSBR/HDPE system. However, it is interesting to note that the peak $\tan \delta$ value of the HSBR/HDPE systems is much lower in height than that of HSBR/LDPE, possibly because of the higher crystallinity of HDPE. In the γ -transition region, HD₃₀ and HL₃₀ display a peak at -106°C with a peak $\tan \delta$ value of 0.04. SBR/LDPE does not register any peak in this region. This indicates that the γ -transition arises predominantly from the

motion of $-\text{CH}_2-$ units of HSBR. In the α -transition region, a peak appears at 65°C which may be ascribed to the melting of HSBR, as the SBR/LDPE blend does not show this transition. This is, of course, further reflected in the d.s.c. melting peak of HSBR at 57°C , as reported in an earlier section. The storage modulus is highest for the HSBR/HDPE system (HD₃₀) (Figure 12b) and all the samples display a transition at around -33°C .

The tensile strength of HL₃₀ is 8.4 MPa as compared to 4.3 MPa and 2.4 MPa for the HD₃₀ and SL₃₀ blends, respectively. A similar trend is followed for the values of the work-to-break (Figure 13). It is interesting to note that the HL₃₀ system registers the highest elongation at break. It is clearly evident from the values of the tensile strength, work-to-break and elongation at break that the morphology and the rubber-to-plastic adhesion play a dominant role in deciding the mechanical properties. The DMTA, d.s.c. and X-ray data give an indication that the drop in crystallinity (77% for SL₃₀; 60% for HL₃₀; 62% for HD₃₀) normalised with respect to the crystalline plastic is at a maximum with SL₃₀.

CONCLUSIONS

New polymer blends from HSBR/polyolefins have been developed.

- (1) All the blends show non-Newtonian pseudoplastic behaviour. The viscosities of the blends lie between those of the pure components at all temperatures and shear rates. The activation energy of the flow decreases with increase in LDPE content due to enhanced mobility of the chains.
- (2) The phase morphology of the blends does not change with variation of the blend ratio for the HSBR/LDPE systems, which reveal a laminated structure. HSBR/HDPE or SBR/LDPE show a different morphology.
- (3) X-ray studies indicate appreciable migration of HSBR into the interchain space of low-density polyethylene. The degree of crystallinity and crystallite size increase with increase in polyethylene content, indicating co-crystallisation.

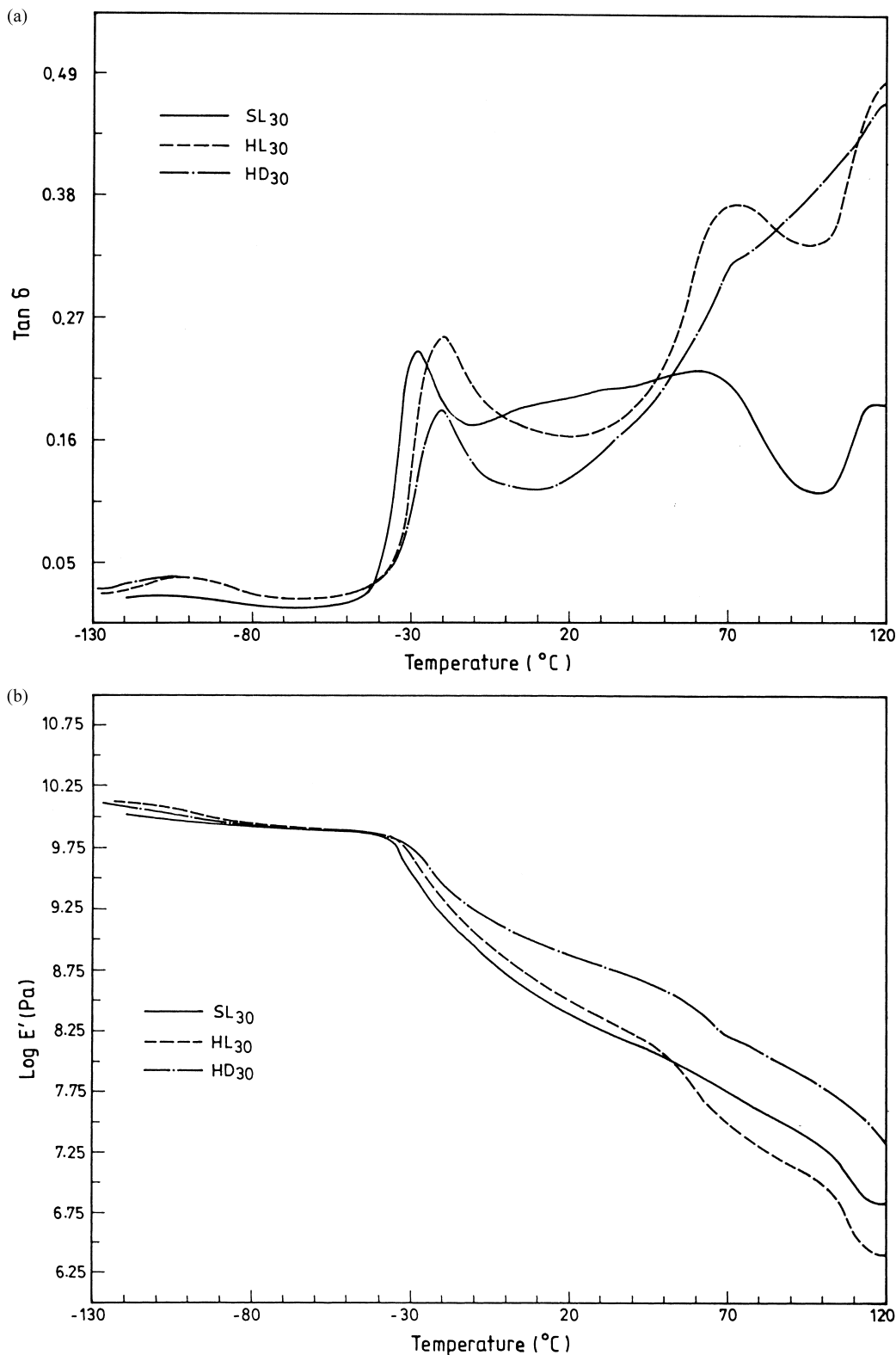


Figure 12 Temperature dependence of (a) the loss tangent ($\tan \delta$) and (b) the storage modulus (E') for the SBR/LDPE (SL₃₀), HSBR/LDPE (HL₃₀) and HSBR/HDPE (HD₃₀) blend systems

(4) The mechanical properties of HSBR can be improved by blending with LDPE, retaining its thermoplastic elastomeric behaviour. The tensile strength, work-to-break and 100% modulus values indicate a maximum increase of 132%, 78%, 373%, respectively, for the 20:80 blend (HL₈₀); the elongation at break, however, decreases with increase in LDPE.

(5) HSBR/LDPE blends have superior mechanical properties to HSBR/HDPE or SBR/LDPE. The results are explained on the basis of a change in the morphology, interaction between the components, and crystallisation.

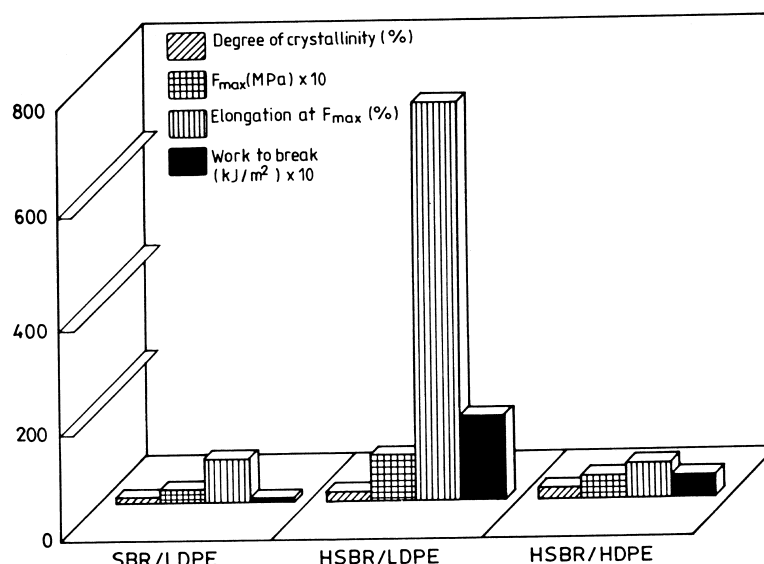


Figure 13 Plot showing the variation of the degree of crystallinity, tensile strength (F_{max}), elongation at break, and work-to-break for the SBR/LDPE (SL₃₀) HSBR/LDPE (HL₃₀) and HSBR/HDPE (HD₃₀) blend systems

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