Scanning Electron Microscopy Studies on Tensile Failure of Polyethylene-Filled Natural Rubber Vulcanizates

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Synopsis

The tensile properties of high-density polyethylene (HDPE)-filled natural rubber (NR) vulcanizates have been studied. It was found that HDPE was incompatible with NR and lower loadings of HDPE had no influence on the tensile strength of the vulcanizate. At higher loadings of HDPE, the size and shape of HDPE domains in the vulcanizate changed and the tensile strength of the vulcanizate decreased. Fracture surface studies using scanning electron microscope were carried out to correlate the test results with tensile properties.

INTRODUCTION

Thermoplastic elastomers (TPEs) can be produced by the melt mixing of thermoplastics with elastomers. TPEs have properties of the vulcanized elastomers, but can be processed like thermoplastics.[1-5] Addition of thermoplastics as a filler, in comparatively small amounts, to elastomers contributes toward the betterment of processing properties. Enhanced green strength, smooth extruded and calendered profiles and reduced die swell of the compounds are possible by using thermoplastics as fillers. Several patents in literature deal with composites in which thermoplastic semicrystalline materials have been blended with elastomers. The blended compound is then vulcanized to obtain composites with improved properties.[6-9] Literature also reveals the potential use of these composites.[10,11] In addition, these thermoplastic-filled composites show good aging resistance and chemical resistance depending on the thermoplastic component used. However, the flex fatigue life and high temperature properties are affected adversely.

In this article, we report the results of our studies on high-density polyethylene (HDPE)-filled natural rubber (NR) vulcanizates, with special reference to the tensile failure mechanism. Mechanical properties of the TPEs from NR and HDPE have already been reported.[12,13] Failure characteristics of thermoplastic-filled rubber vulcanizates have not been studied extensively. De and co-workers[14-20] have used scanning electron microscopy (SEM) studies to explain the failure mechanism in natural rubber and in different synthetic rubber composites, including some thermoplastic elastomers. In the present

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study postfracture analysis was conducted using SEM to explain the failure mechanism.

EXPERIMENTAL

Formulations of the mixes are given in Table I. The mixes vary in HDPE content. NR and HDPE were melt mixed in a Brabender Plasticorder model PLE 330 using cam-type mixer with a rotor speed of 60 rpm at 150°C. HDPE was melted in the mixer for 4 minutes and then NR was added. The mix was allowed to blend for 4 minutes. This mix was taken out and sheeted through a laboratory two-roll mill. These sheets were then mixed with the other compounding ingredients in the two-roll mill as per ASTM D 3184-80. The optimum vulcanization time of the mixes were determined using Monsanto Rheometer R-100 at 150°C.

The mixed composites were cured at 150°C under 45 kg/cm^2 pressure to the respective optimum cure times. The dynamic mechanical properties of the composites were measured using Rheovibron DDV-III-EP in the temperature range $-150°$ to $0°$C. The samples were tested at a frequency of 35 Hz and a strain amplitude of 0.0025 cm. The heating rate of the sample was 1°C/min. The differential scanning calorimetric (DSC) study of the composite was carried out in N$_2$ atmosphere using a Du Pont 9000 thermal analyser. The heating rate used was 10°C/min. The midpoint of the glass to rubber transition was taken as the T_g of the mix.

Tensile testing of the samples was done at 25°C as per ASTM D 412-80 test procedure at a crosshead speed of 500 mm/min using an Instron 1195 universal testing machine. Aging of the test samples was conducted at 100°C in a cellular aging oven in an atmosphere of air.

The SEM observations of the tensile rupture surfaces were made using a Philips 500 model scanning electron microscope. The fracture surfaces of the test samples were carefully cut out from one of the failed test specimens without touching the surfaces and then sputter-coated with gold within 24 h

TABLE I
Formulations

Ingredients	Mix 1	Mix 2	Mix 3	Mix 4
Natural Rubber[a]	100.00	100.00	100.00	100.00
Zinc Oxide	5.00	5.00	5.00	5.00
Stearic Acid	1.50	1.50	1.50	1.50
Sulfur	2.50	2.50	2.50	2.50
Vulkacit CZ[b]	1.00	1.00	1.00	1.00
HDPE[c]	0.00	10.00	30.00	50.00
Optimum cure time (min)	12	12.5	13.5	13

[a] ISNR-5 supplied by Rubber Research Institute of India, Kottayam.
[b] Cyclohexyl benzothiazyl sulfenamide, supplied by Bayer (India) Limited, Bombay.
[c] High Density Polyethylene-HOSTALEN GA 7260, density at 23°C (g/cm^3) 0.960; melting point (°C) 128–132; melt flow index (g/10 min) 16.
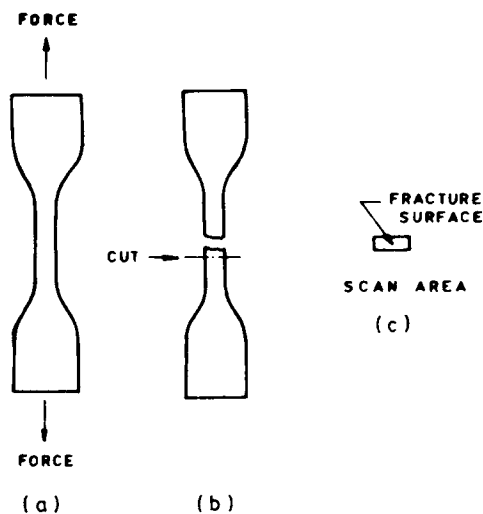
Fig. 1.   (a) Tensile test specimen; (b) broken specimen; (c) scan area.

of testing. A line drawing of the sample and area scanned for SEM is shown in Figure 1.

RESULTS AND DISCUSSION

The vulcanization behavior of the composites is shown in Figure 2. It can be seen that the torque response of the composites decreases with increase in HDPE loading. This is due to the low viscosity of the HDPE in the molten state (150°C) since HDPE does not take part in the vulcanization reaction. Cure time and scorch time are only marginally affected with HDPE loading. The respective optimum cure times obtained are given in Table I.

Figures 3 and 4 show the DSC thermograms of the HDPE-filled NR composites in the temperature range of −100 to 0°C and 50 to 150°C, respectively. In the former, glass transition of NR could be observed and for the vulcanizates studied, it was −62°C. The T_g of the vulcanizates was independent of the thermoplastic content. The transition was sharpest in the case of unfilled NR. Since the T_g of the vulcanizates did not change with the thermoplastic content, it may be concluded that the two polymers are essentially incompatible.[21] Figure 4 shows the melting endotherm of the vulcanizates. The melting point (T_m) is found to be 128°C corresponding to that of HDPE. It was found that the area under the endotherm peak corresponds to the percentage of HDPE in the mix. This implies that there is no change in the crystallinity of HDPE in the mix.

Figure 5 shows the plot of storage modulus versus temperature. The vulcanizates showed the same behavior below the glass transition temperature of NR. In the temperature range studied, T_g of HDPE could not be detected. The storage modulus decreased sharply near the T_g of NR and the rubbery plateau region started from nearly −25°C. It was found that incorporation of up to 30 phr HDPE into the rubber mix had no effect on the storage modulus. However, 50 phr HDPE-filled vulcanizate showed significant increase in
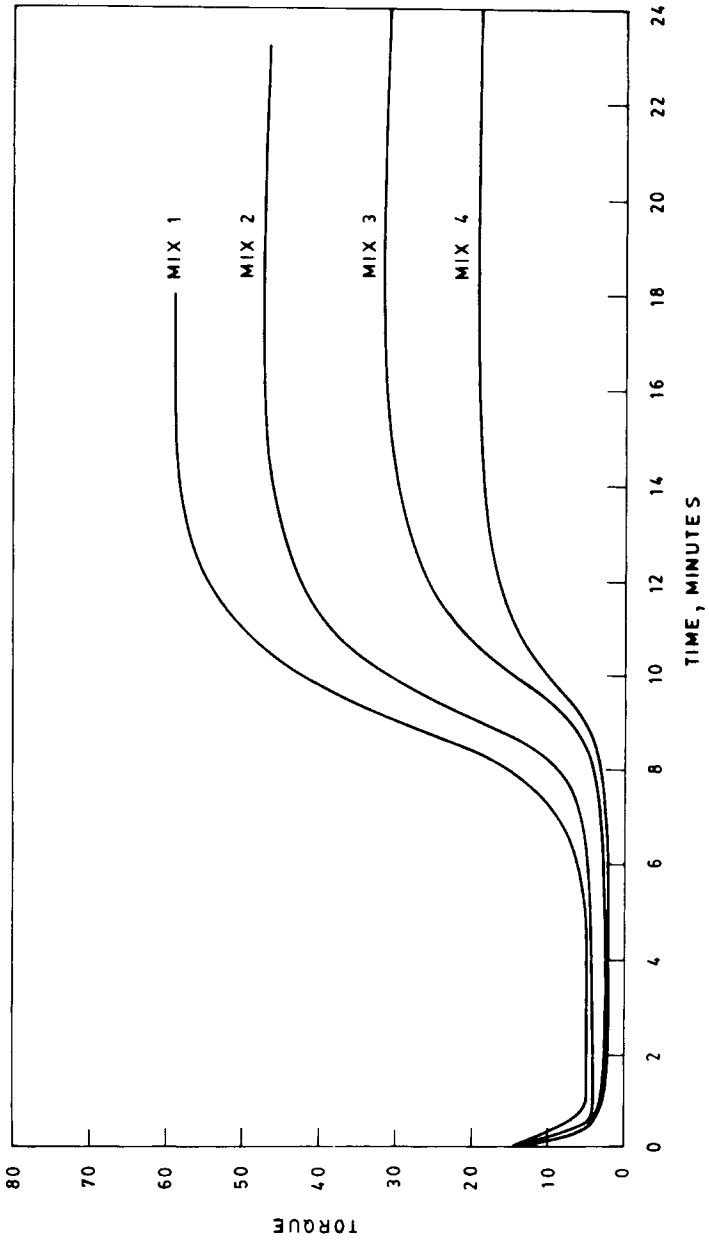
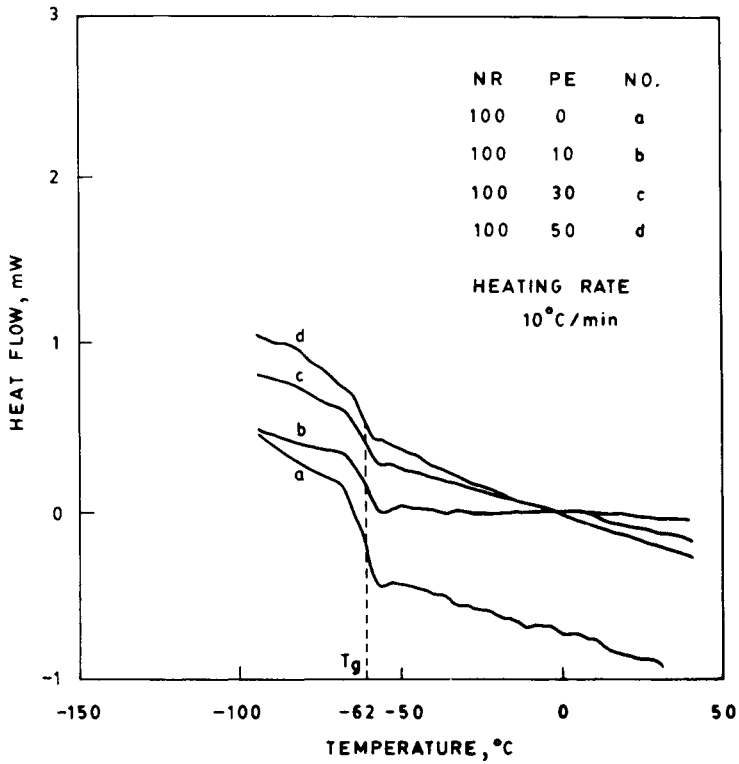Fig. 2. Vulcanization behavior of the mixes.

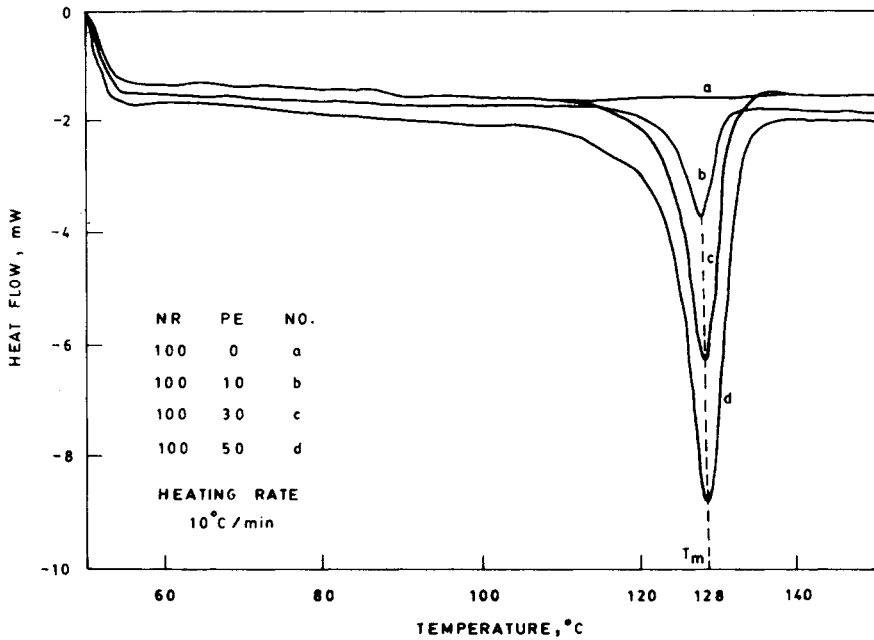Fig. 3. DSC thermograms of HDPE-filled NR vulcanizates.

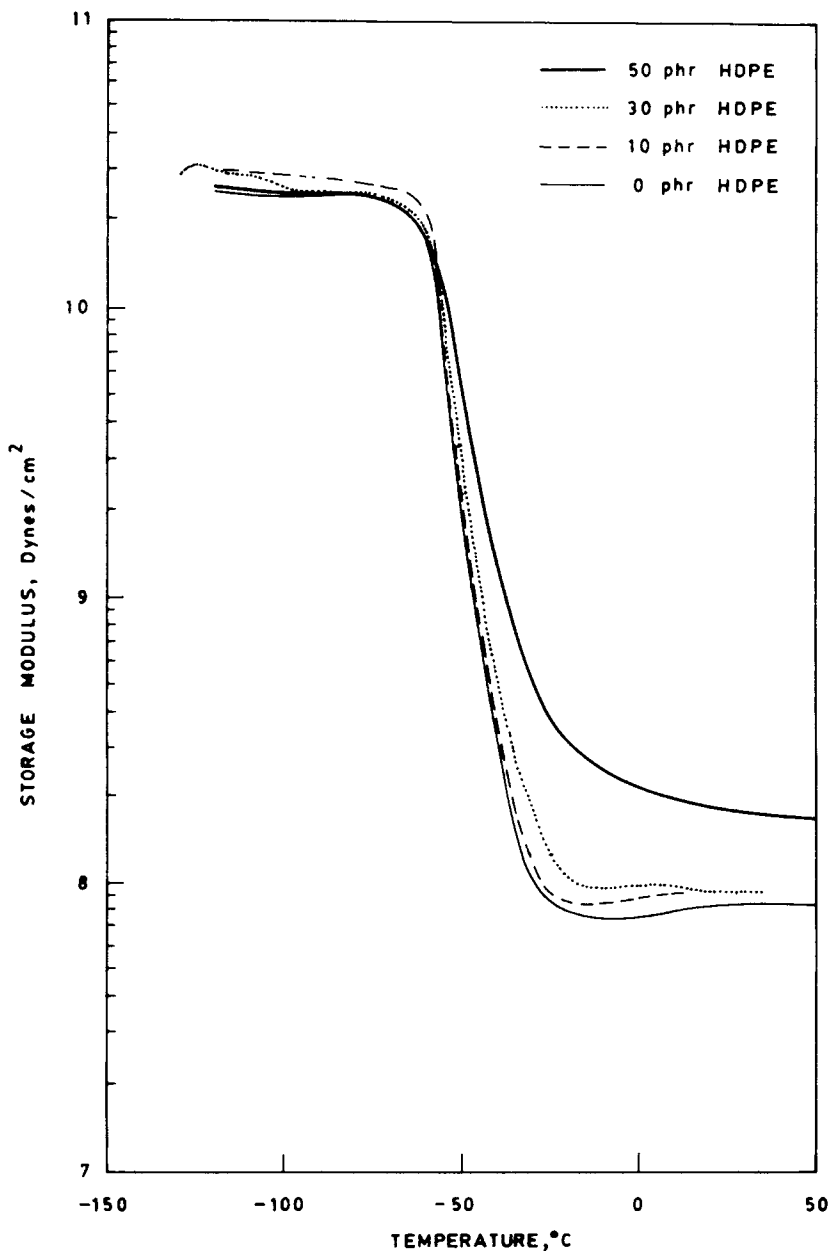Fig. 4. DSC thermograms of HDPE-filled NR vulcanizates.

Fig. 5.   Plot of storage modulus vs. temperature for HDPE-filled NR vulcanizates. — 50 phr;
··· 30 phr, --- 10 phr; — 0 phr.

storage modulus in the plateau region. At this loading (33% HDPE), the curve deviated from that of 0, 10, and 30 phr-filled mixes. Since there is no chemical interaction between NR and HDPE this deviation indicates that there is a definite change in the size and shape of the HDPE domains in the vulcanizate even though the crystallinity of HDPE does not change.[22] The loss moduli of the mixes showed a peak at the T_g of NR (Fig. 6). It was found that the T_g of the vulcanizates is independent of the HDPE loading up to 50 phr.
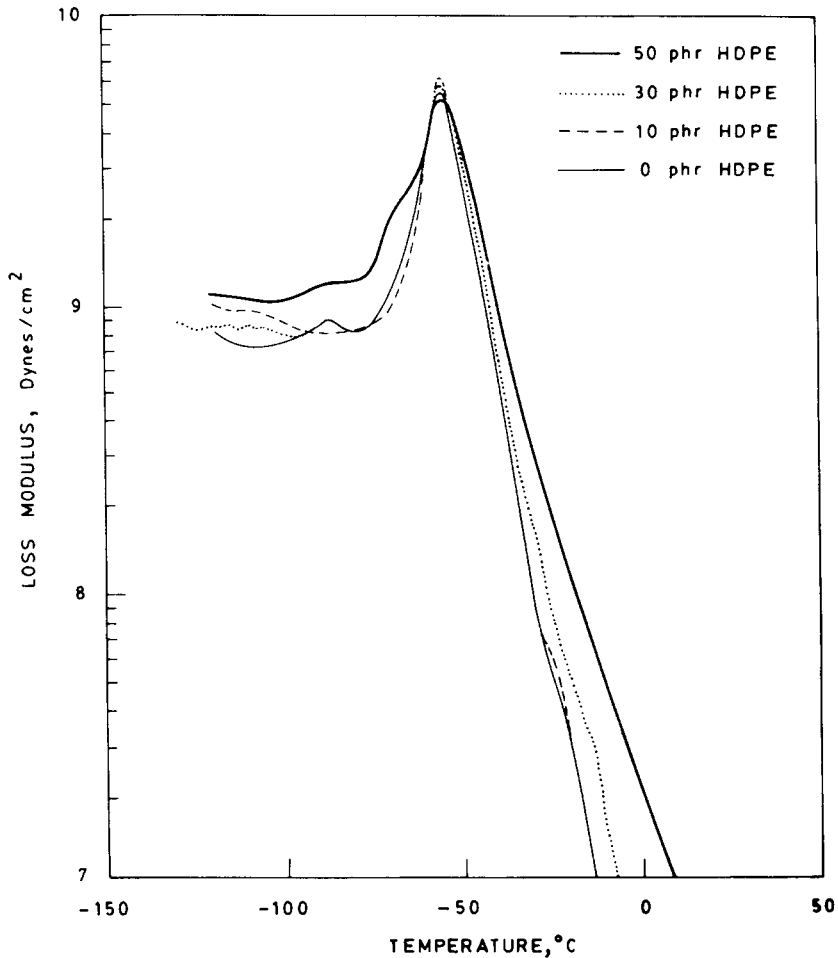
Fig. 6. Plot of loss modulus vs. temperature for HDPE-filled NR vulcanizates. — 50 phr; ··· 30 phr; --- 10 phr; — 0 phr.

Figure 7 shows the tan δ peaks of the vulcanizates which correspond to the T_g of NR. It is clear that T_g of NR is not affected by the incorporation of HDPE in the mix up to 50 phr. The unfilled, 10 and 30 phr-filled vulcanizates showed no significant difference in the nature of the curves, while the 50 phr-filled one showed a lower tan δ maximum and a broadening of the tan δ peak above −10°C. The lowering of tan δ maximum can be attributed to the dilution of NR matrix with HDPE. The broadening of the tan δ peak is related to the change in the size and shape of thermoplastic domains which lead to mechanical interaction between the thermoplastic domains and rubber matrix.[23]

Since the T_g of NR does not depend on the amount of HDPE in the mix, it can be concluded that the two polymers are incompatible and there is no chemical interaction between them under the conditions of mixing and moulding. The shape and size of HDPE domains in the mix should therefore account for the broadening of tan δ curve and increase of storage modulus in the rubbery plateau region.
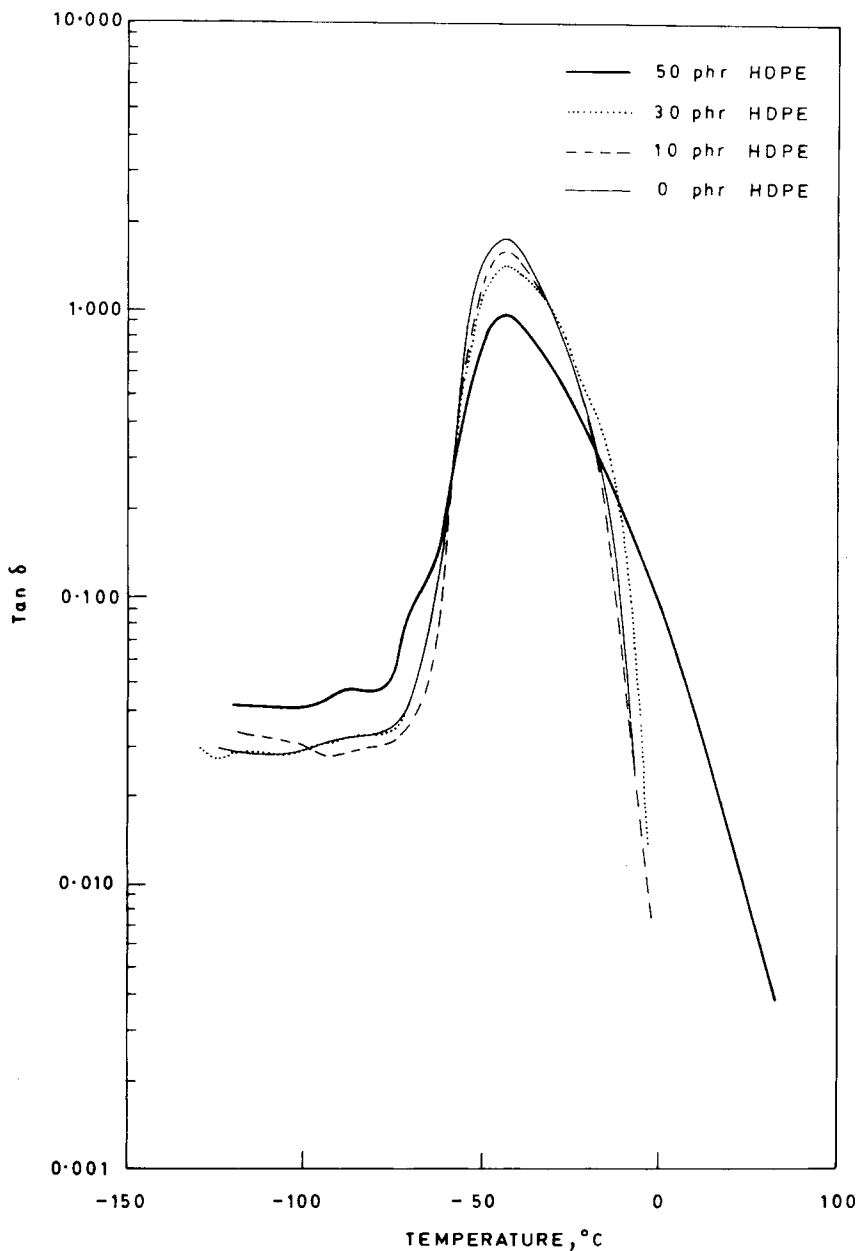
Fig. 7. Dependence of loss tangent on temperature for different loadings of HDPE. — 50 phr,
··· 30 phr; --- 10 phr; — 0 phr.

Figure 8 shows a plot of tensile strength of the vulcanizates against HDPE loading. It can be seen that up to a loading of 30 phr, the tensile strength was not significantly affected by HDPE but at 50 phr loading the strength decreased considerably. However, the modulus at 300% elongation increased steadily with HDPE loading (Fig. 8). Figure 9 shows the elongation at break and tension set after failure against the filler loading. The elongation at break
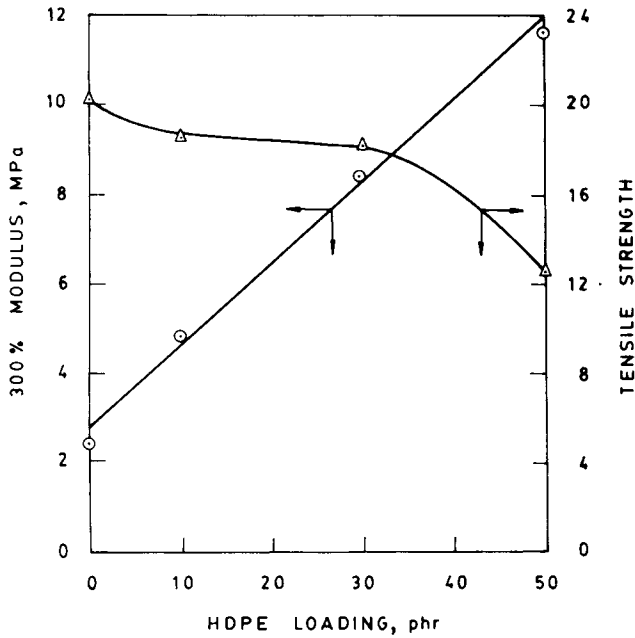
Fig. 8. Effect of HDPE loading on tensile strength and modulus at 300% elongation for HDPE-filled NR vulcanizates.
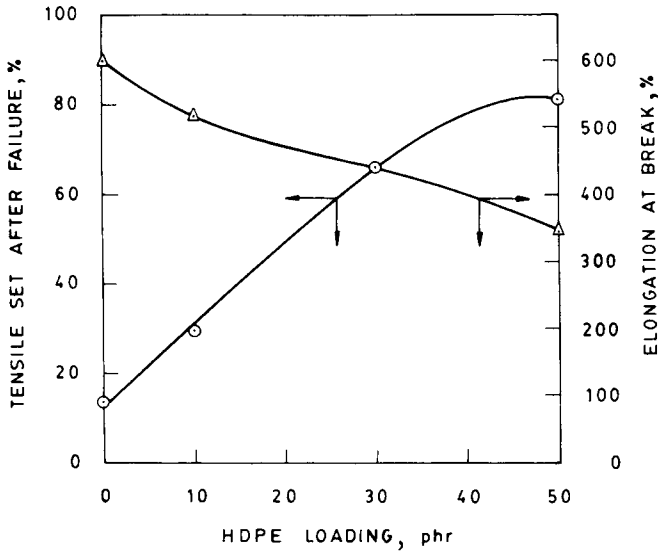
Fig. 9. Effect of HDPE loading on set property and elongation at break of HDPE-filled NR vulcanizates.
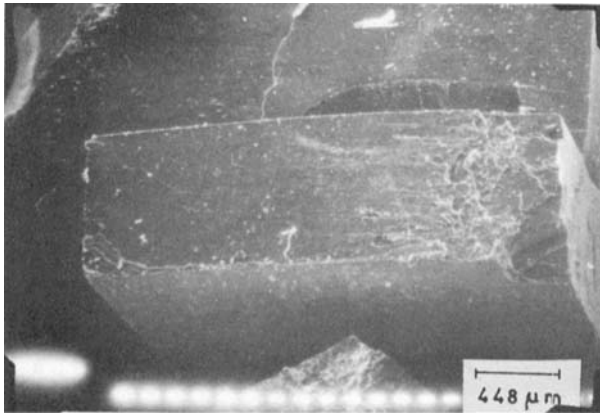
Fig. 10.   SEM fractograph of unfilled NR vulcanizate (×25).

decreases and tension set increases with increasing HDPE loading implying that the rubbery character of the composite was disappearing with increasing HDPE loadings.

Figures 10, 11, and 12 show the SEM fractographs of 0, 10, and 30 phr HDPE-filled vulcanizates at low magnifications. All the photographs show distinct rough and smooth regions on the fracture surfaces. In the case of 30 phr HDPE-filled vulcanizate, the fracture surface is comparatively uneven. Figures 13 and 14 show a magnified view of the fracture surfaces of unfilled and 10 phr-filled vulcanizates. These show the rubbery and ductile nature of failure with dimples and rounded fracture ends. Figure 15 is the magnified view of the fracture surface of 30 phr HDPE-filled NR vulcanizate. This is obviously quite different from that of the unfilled and 10 phr-filled vulcanizates. A large number of small, smooth elongated domains are distributed throughout the matrix. These smooth domains are assumed to be the HDPE. Small smooth cavities visible on the matrix are formed due to the removal of these HDPE domains during the tensile fracture.
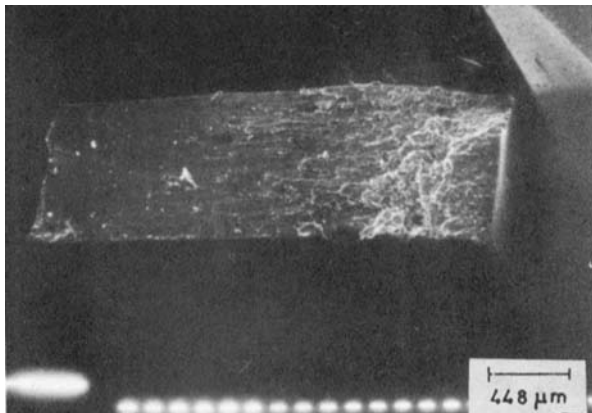

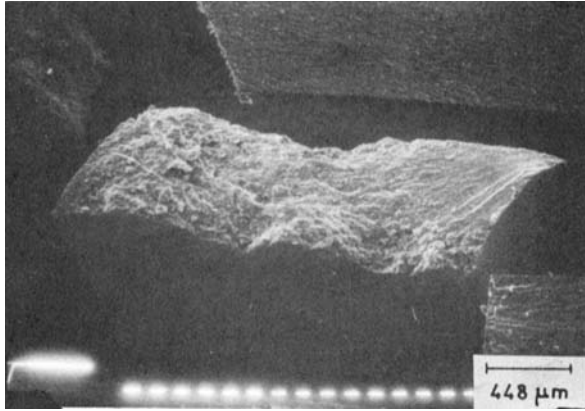Fig. 11.   SEM fractograph of 10 phr HDPE-filled NR vulcanizate (×25).

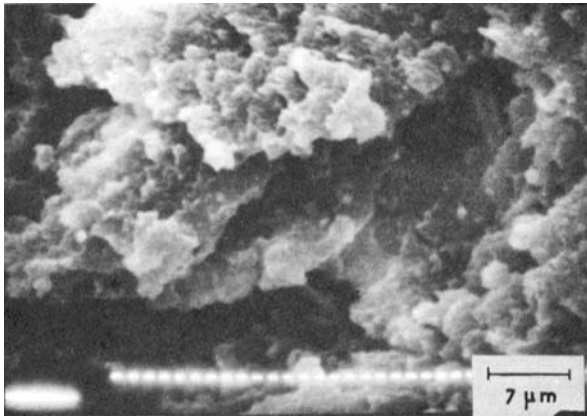Fig. 12. SEM fractograph of 30 phr HDPE-filled NR vulcanizate (×25).

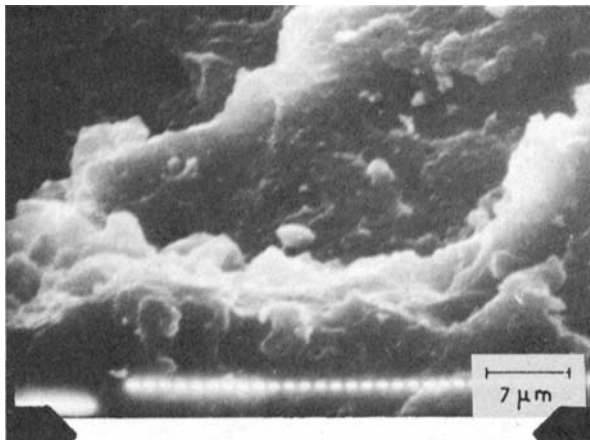Fig. 13. Magnified view of the fracture surface of unfilled NR vulcanizate (×1600).

Fig. 14. Magnified view of the fracture surface of 10 phr HDPE-filled NR vulcanizate (×1600).
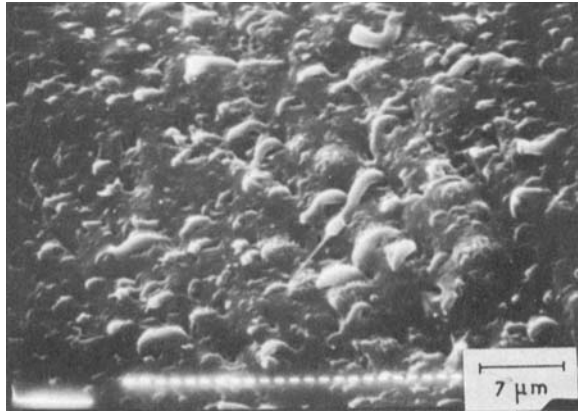
Fig. 15.   Magnified view of the fracture surface of 30 phr HDPE-filled NR vulcanizate (×1600).

Figure 16 shows the fracture surface of 50 phr HDPE-filled vulcanizate at a lower magnification. This is evidently different from that of the other filled composites in that there are no separate rough and smooth regions, the surface is rough throughout. At a higher magnification (Fig. 17), it shows large hollow cavities of different shapes. At places, fibrils are also seen, representing ductile failure. These cavities may be formed due to the removal of loosely bonded HDPE domains. From the irregular shape of the cavities, it can be presumed that the size and shape of domains of HDPE at 50 phr loading is different from that at 10 and 30 phr loading. This is supported by the observations from the dynamic mechanical analysis. The more thermoplastic nature of failure of 50 phr HDPE-filled composite can be seen from the stress–strain curve (Fig. 18) of the composites. The initial modulus of the composite increases considerably with HDPE loading. This may be due to the reinforcement of NR matrix by HDPE, obviously due to the size and shape of HDPE domains.
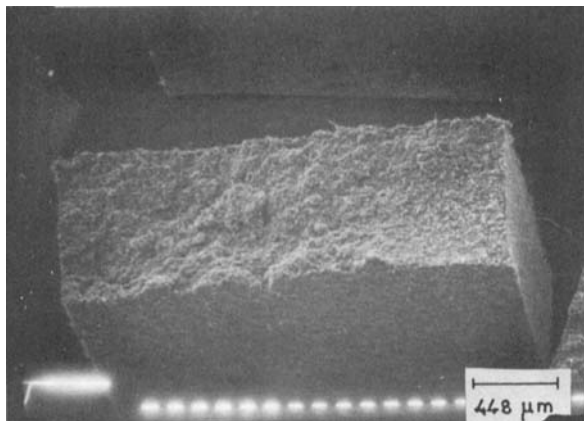

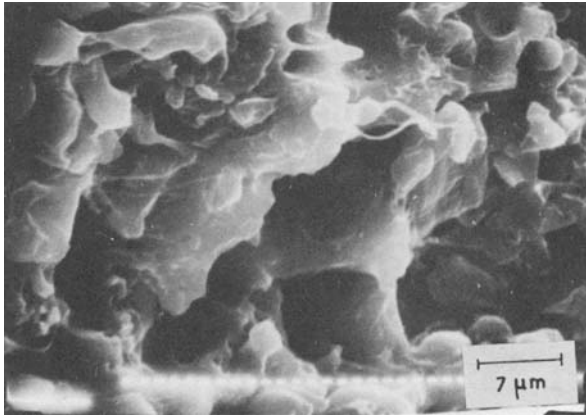Fig. 16.   SEM fractograph of 50 phr HDPE-filled NR vulcanizate (×25).

Fig. 17. Magnified view of fracture surface of 50 phr HDPE-filled NR vulcanizate (×1600).

It was found that after aging at 100°C for 48 h the tensile strength of the vulcanizates decreased. Figure 19 shows the retention of tensile strength against HDPE loading indicating that up to 30 phr, the retention is better, but at 50 phr, the retention in strength is low. Figures 20 and 21 show the magnified view of the fracture surfaces of 30 and 50 phr HDPE-filled samples aged for 24 h. In the case of 30 phr-filled vulcanizates, spherical- and elliptical-shaped HDPE domains can be seen scattered all over the surfaces. A large number of cavities can also be seen adjacent to the displaced HDPE domains. The base NR matrix undergoes brittle failure, characteristic of aged NR vulcanizates.[24] Figure 21 shows the fracture surface of 50 phr-filled vulcanizate where fibrils along with elongated domains of HDPE and long irregular-shaped cavities are seen. Here also the fracture surface of NR is smooth and the failure was brittle. The brittle nature of the NR matrix after
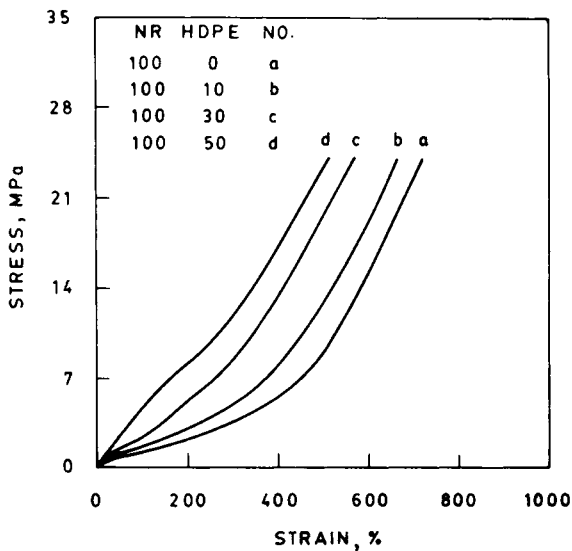

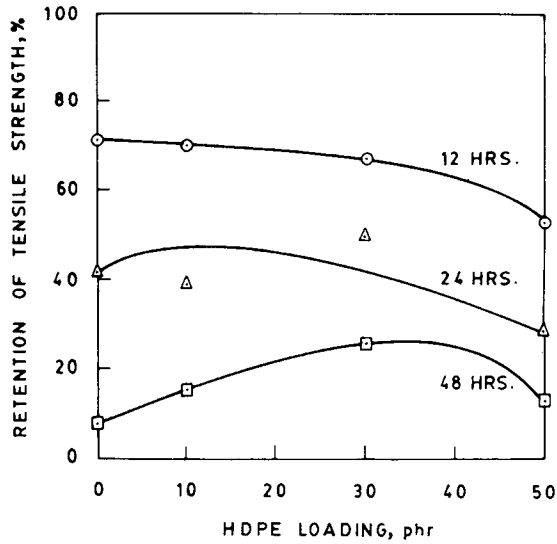Fig. 18. Tensile stress-strain curves for HDPE-filled NR vulcanizates.

Fig. 19. Effect of HDPE loading on retention of tensile strength of HDPE-loaded NR vulcanizates. ⊙ 12 h; ▲ 24h; ⊡ 48 h.

aging and the large domains of HDPE account for the poor retention in tensile strength in the case of the 50 phr HDPE-filled vulcanizate.

CONCLUSIONS

1. High-density polyethylene (HDPE) is incompatible with natural rubber (NR). The tensile strength of the vulcanizate is not influenced by lower loadings of HDPE.
2. At high loadings of HDPE in NR, the size and shape of the HDPE domains in the vulcanizate changes, but the crystallinity of HDPE remains unaffected.
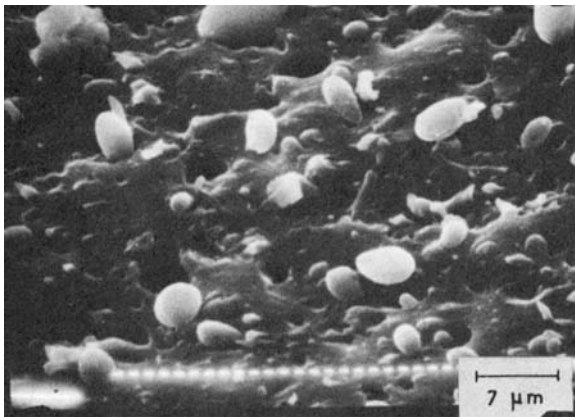

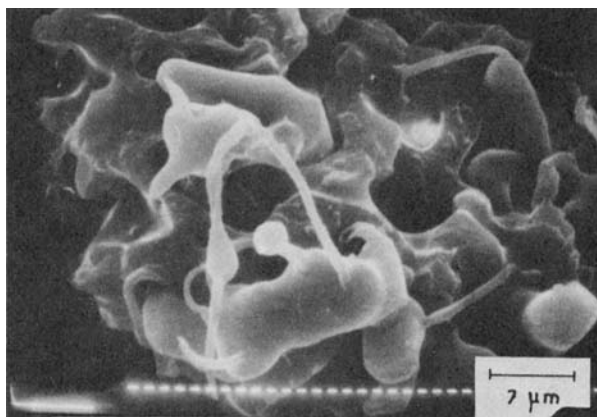Fig. 20. SEM fractograph of 30 phr HDPE-filled, 24 h aged NR vulcanizate (×1600).

Fig. 21. SEM fractograph of 50 phr HDPE-filled, 24 h aged NR vulcanizate (×1600).

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