

Dynamically vulcanised thermoplastic elastomer blends of polyethylene and nitrile rubber

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Abstract

The effects of dynamic crosslinking on rheological, mechanical and dynamic mechanical properties of high density polyethylene (HDPE) and acrylonitrile butadiene rubber (NBR) blends have been evaluated with special reference to the effect of dosage of crosslinking agent. The morphology has been studied using scanning electron microscope. Both the microscopy and dynamic mechanical analysis indicate that the blends are immiscible and form two-phase structures. But it is evident that dynamic vulcanisation can be employed as a technological compatibilisation technique to get finer and stable morphology and improved mechanical properties. The rheological studies reveal that the dynamically vulcanised samples could be processed like thermoplastics. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dynamic vulcanisation; Blends; Morphology

1. Introduction

Elastomer–thermoplastic blends have become technologically useful as thermoplastic elastomers in recent years [1–3]. They have many of the properties of elastomers but they are processable as thermoplastics [4]. Thus, they offer a substantial economic advantage with respect to the fabrication of finished parts.

For many end uses, the ideal morphology is that the elastomer should be finely dispersed in a relatively small amount of the plastic. The elastomer particles should be crosslinked to promote elasticity. The favourable morphology should remain during the fabrication of the material into parts and in use. Because of these requirements for the ideal case, the usual methods of preparing elastomer–plastic blends by melt mixing, solution blending or latex mixing [5] are not sufficient.

The best way to produce thermoplastic elastomeric compositions comprising vulcanised elastomer particles in melt processable plastic matrices is by the method called dynamic vulcanisation. It is the process of vulcanising the elastomer during its melt mixing with the molten plastic [6–9]. Thus dynamic vulcanisation is a route to new

thermoplastic elastomers which have properties as good or even in some cases, better than those of block copolymers.

The improvement in properties resulting from dynamic vulcanisation are reduced permanent set, improved ultimate mechanical properties, greater resistance to attack by fluids, improved high temperature utility, greater stability of phase morphology in the melt, greater melt strength and more reliable thermoplastic fabricability.

Thermoplastic vulcanisate compositions have been prepared from a large number of plastics and elastomers; however only a limited number of elastomer–plastic combinations give technologically useful blends even after dynamic vulcanisation. The study of a large number of dynamically vulcanised elastomer plastic combinations shows that the best combinations are those in which the surface energies of the components are matched, when the entanglement molecular length of the elastomer is low and when the plastic component is 15–30% crystalline [10].

Eventhough acrylonitrile butadiene rubber (NBR) and high density polyethylene (HDPE) have a large difference in surface energy, the blend of these two is a good choice for hot oil-resistant applications. It has been found that dynamically vulcanised elastomers of high entanglement density (lower M_c values) gave the higher quality blends with plastics [11]. Also, it results in a fine and uniform morphology. With a view to achieve better and stable morphology and high entanglement density, a few compositions were analysed. The rubber/plastic blend ratio was maintained

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Table 1
Formulation of the mixes

Components	Designation				
	H ₅₀	H ₅₀ D ₁	H ₅₀ D ₂	H ₅₀ D ₃	H ₅₀ D ₄
HDPE	50	50	50	50	50
NBR	50	50	50	50	50
Stearic acid	0	2	2	2	2
ZnO	0	5	5	5	5
DCP	0	1	2	3	4

constant in all the cases while the concentration of the vulcanising agent varied. In this paper we report the effect of peroxide concentration on various properties of the blend system such as mechanical, dynamic mechanical and the flow properties. The morphology changes were also analysed.

2. Experimental

All the HDPE/NBR blends under investigation contain 50/50 plastic to rubber weight ratio. HDPE of density 0.958 g/cc and melt flow index of 7.5 was supplied by M/s Indian Petrochemicals Corporation Ltd., Vadodara. NBR of density 0.98 g/cc and acrylonitrile content of 33% was procured from M/s Synthetics and Chemicals, Bareilly, U.P. Rubber grade additives used were zinc oxide (ZnO), stearic acid and dicumyl peroxide (DCP). Melt mixing was carried out in a Brabender Plasticorder model PLE 331. HDPE was first melted for 2 min at 160°C followed by the addition of NBR. Mixing continued for 6 min. In dynamically vulcanised samples, the curatives were added 2 min after the rubber has been introduced. Mixing was stopped after 3 min. Details of the mixes are given in Table 1. Five different mixes were prepared and are designated as H₅₀, H₅₀D₁, H₅₀D₂, H₅₀D₃ and H₅₀D₄. In this H and D represent HDPE and DCP, respectively. The subscripts following H and D indicate the corresponding concentrations of HDPE and DCP in each blend. The amount of the curatives are based on the rubber phase only. The mixes were compression moulded at 180°C using thermoplastic mould. Specimens for testing were punched out from these moulded sheets.

2.1. Physical testing

Tensile testing was done following the ASTM D 412-80 test method using dumb bell shaped samples at a cross-head speed of 500 mm/min with a Universal testing machine (Zwick 1465). The tear strength was determined following the ASTM D 624-81 test method using unnicked 90° angle test pieces. The cross-head speed was the same as that of tensile test.

2.2. Determination of V_r

To estimate the extent of crosslinking the volume fraction, V_r of the rubber in chloroform swollen specimens was determined after 48 h using the relation:

$$V_r = \frac{(D - fT)\rho_r^{-1}}{(D - fT)\rho_r^{-1} + A_0\rho_s^{-1}} \quad (1)$$

where D the weight after drying out, f the fraction of insoluble components, T the weight of the sample, A_0 the weight of the absorbed solvent, ρ_r the density of the rubber and ρ_s the density of the solvent.

2.3. Rheological studies

Rheological measurements were carried out using a capillary rheometer attached to an Instron Universal Testing machine. After a warm-up period of 5 min, the melt was extruded through a specified capillary at pre-selected speeds of the cross-head. The force corresponding to different plunger speeds was recorded. The force and cross-head speeds were converted into apparent shear stress (τ_w) and shear rate at the wall ($\dot{\gamma}_w$), respectively, using the following equations involving the geometry of the capillary and plunger:

$$\tau_w = \frac{F}{4A_p(l_c/d_c)} \quad (2)$$

$$\dot{\gamma}_w = \frac{3n' + 1}{4n'} \frac{32Q}{\pi d_c^3} \quad (3)$$

where F the force applied at a particular shear rate, A_p the cross-sectional area of the plunger, l_c the length of the capillary and d_c the diameter of the capillary, Q the volume flow rate and n' the flow behaviour index.

The flow behaviour index n' was determined by regression analysis of the values of τ_w and $\dot{\gamma}_w$ obtained from the experimental data. The shear viscosity, η was calculated from τ_w and $\dot{\gamma}_w$. The die swell is calculated by measuring the diameter of the extrudate at several points using a travelling microscope. The swelling index is the diameter of the extrudate to that of the capillary (d_e/d_c).

2.4. Dynamic mechanical studies

The dynamic mechanical analysis of a few selected samples were carried out using a Rheovibron DDV-II-C. Samples of $50 \times 5 \times 0.5$ mm³ were used for the study. The samples were tested at a frequency of 35 Hz. The storage modulus (E'), the loss modulus (E'') and the dissipation factor ($\tan \delta$) were evaluated using the following equations:

$$E' = E^* \cos \delta \quad (4)$$

$$E'' = E^* \sin \delta \quad (5)$$

$$\tan \delta = E''/E' \quad (6)$$

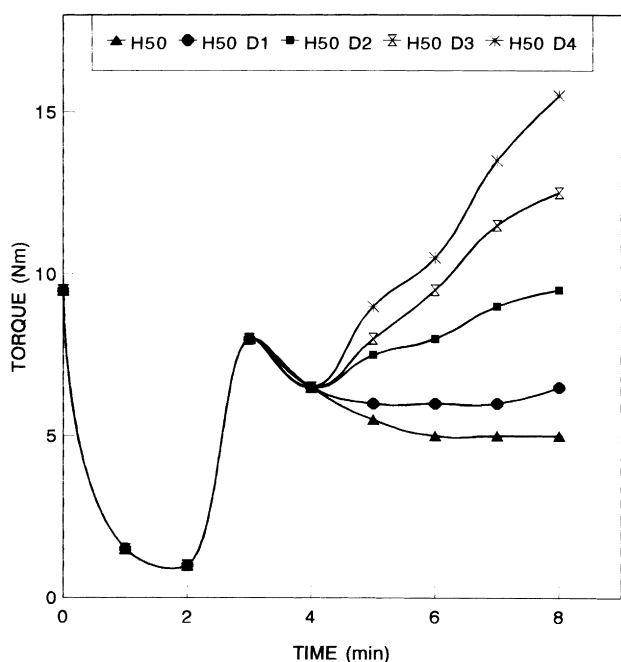


Fig. 1. Torque–time plots of 50/50 blend of HDPE and NBR containing different levels of crosslinking agent.

where E^* the complex modulus determined from the instrument reading and the sample dimensions.

2.5. Scanning electron microscopy studies

The morphology of H_{50} and $H_{50}D_4$ were analysed using liquid nitrogen fractured samples. The SEM observations were made using a Philips model 500C scanning electron microscope after sputter coating the surface with gold/palladium alloy.

3. Results and discussion

3.1. Brabender curves

The torque vs. time and temperature vs. time plots of different mixes are shown in Figs. 1 and 2, respectively. From Fig. 1 it is clear that at first the torque is high as we are introducing cold material to the hot chamber. Once the material attains the set temperature and gets melted, the torque comes down. Again it increases with the addition of NBR and comes down upon melting and levelling off can be observed in the torque values of the blend containing no crosslinking agent. However, DCP containing mixes register a substantial increase in torque with mixing time. The increase in torque is due to the crosslinking of the rubber phase and thereby exerting greater resistance to rotation. Thus the progress of the vulcanisation can be conveniently followed by monitoring mixing torque during mixing. The increase in torque with mixing time becomes more prominent in blends containing higher levels of DCP.

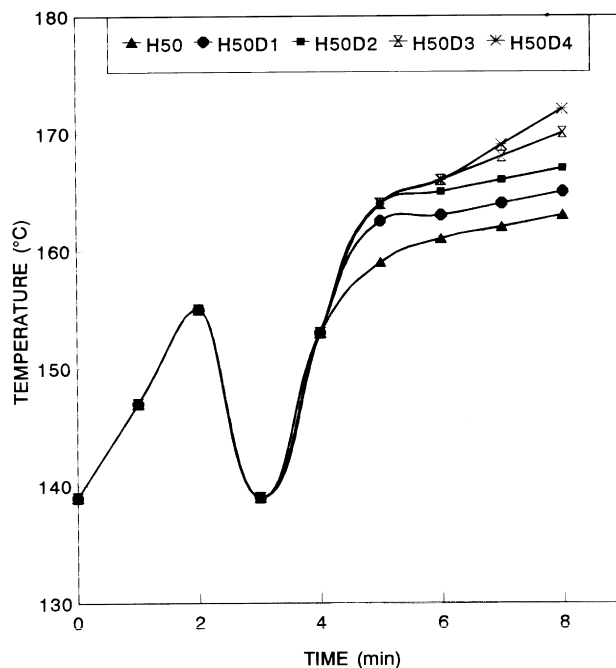


Fig. 2. Temperature–time plots of H_{50} containing different levels of DCP.

The temperature vs. time plots (Fig. 2) show that the set temperature is achieved at the end of mixing cycle in the case of uncrosslinked blend. But a substantial increase from the set values can be observed in dynamically vulcanised blends. This may be due to the resistance to rotation offered by the crosslinked rubber particles thereby resulting in frictional heat development.

The final torque values of unvulcanised and dynamically vulcanised blends containing four different concentrations of DCP is shown in Fig. 3. The final torque increases linearly with DCP content. The increase is comparatively less at 1% DCP because of insufficient crosslinking. But at a DCP content of 2% or above, the final torque values show a steep rise due to extensive crosslinking. The extent of crosslinking and final torque values are related.

3.2. Variation of crosslinking density

The extent of crosslinking of the elastomer phase in the blends containing different levels of DCP can be studied by measuring V_r values. The variation of V_r values with DCP concentration is shown in Fig. 4. The V_r values increase with extent of crosslinking as the restriction to swelling increases with increased network formation. From the above results it is clear that the crosslink density increases with DCP content.

3.3. Morphological changes

The analysis of the morphological changes during dynamic vulcanisation is quite interesting. The scanning electron micrographs of H_{50} and $H_{50}D_4$ are shown in Fig. 5(a) and (b), respectively. As HDPE/NBR blend is

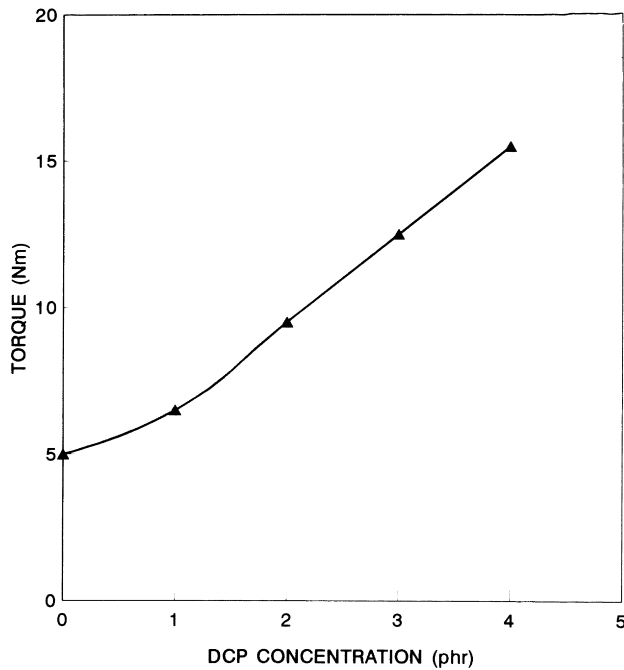


Fig. 3. Effect of DCP concentration on the final torque values of H_{50} containing different levels of the crosslinking agent.

incompatible a few number of coarsely distributed NBR particles can be observed in H_{50} . Dynamic vulcanisation results in crosslinking of the rubber phase. The crosslinked rubber particles exert more torque and results eventually in particle break-up and more effective mixing as observed in Fig. 5(b).

Fig. 6 shows the particle size distribution patterns of H_{50}

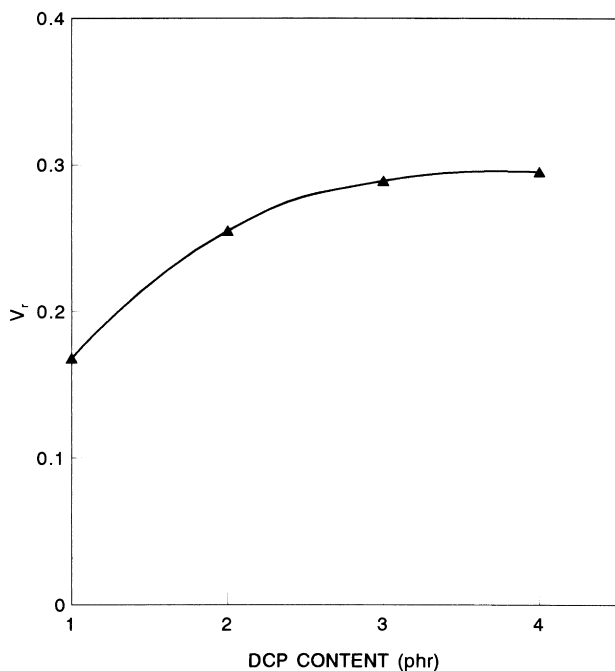


Fig. 4. Variation of V_r with DCP concentration showing the effect of extent of crosslinking on V_r values of H_{50} .

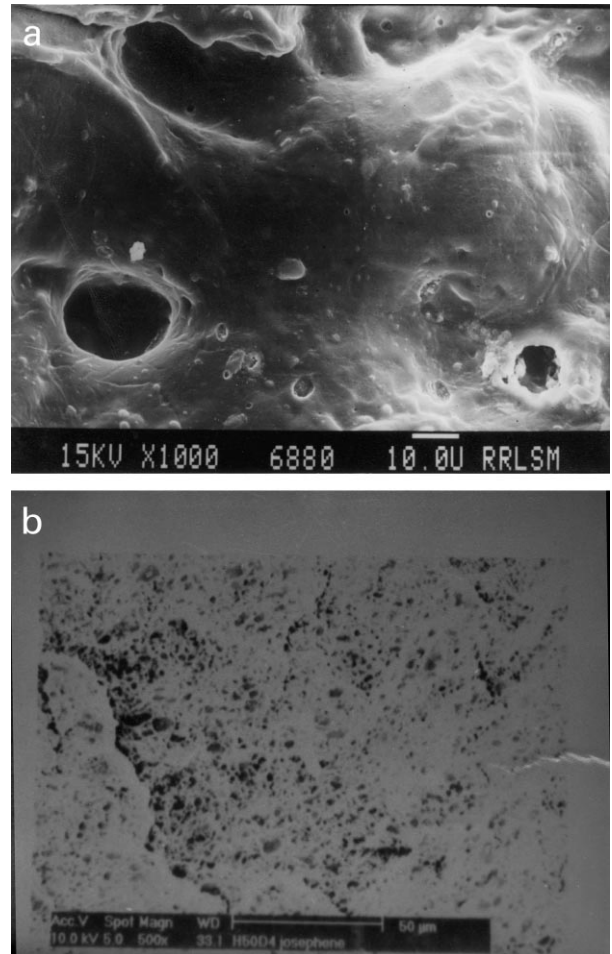


Fig. 5. SEM photomicrographs at high magnification illustrating the state of dispersion of the rubber phase of (a) unvulcanised and (b) dynamically vulcanised 50/50 blends of HDPE and NBR.

and $H_{50}D_4$. It is clear from the figure that the inherently broad distribution pattern of H_{50} is substantially narrowed down by dynamic vulcanisation. This is because of better particle break-up and improved stability against coalescence. Thus dynamic vulcanisation results in a drastic change in the morphology of H_{50} . The morphological changes can be correlated to the extent of dynamic vulcanisation. The extent of dynamic vulcanisation can conveniently be studied from the final torque values. As observed in Fig. 3, the final torque values increase with DCP content that means the extent of crosslinking increases with DCP content. The measurement of V_r values also give the same information. Based on the above considerations, a speculative model of the morphologies of unvulcanised and vulcanised H_{50} containing 1, 2, 3, and 4 phr DCP is shown in Fig. 7(a)–(e). A more or less spherical morphology can be observed in H_{50} and H_{50} containing 1% DCP. But at higher levels of DCP the spherical morphology changes to somewhat elongated pattern with further break-up into smaller spherical particles. In this case the system contains particles of different shapes such as spherical and elongated

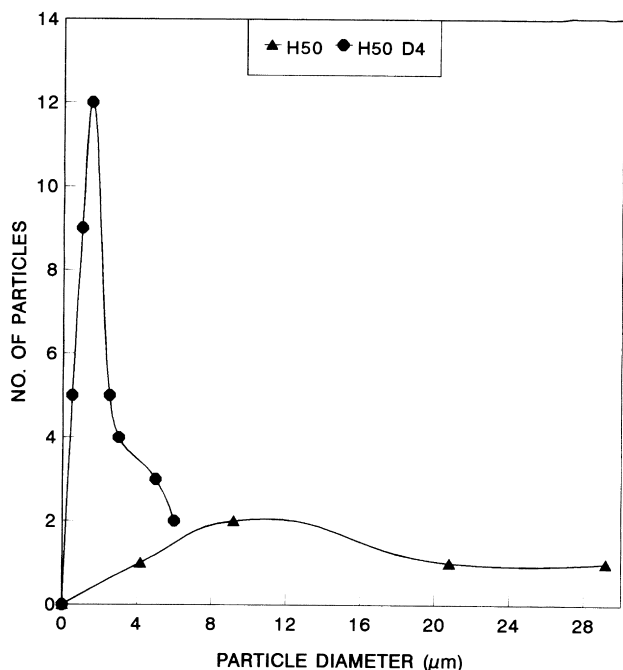


Fig. 6. Particle size distribution curves of unvulcanised and dynamically vulcanised H₅₀.

morphologies depending on the extent of curing and break-up. At higher extent of dynamic vulcanisation small spherical particles predominates because of effective particle break down.

3.4. Effect of crosslinking density on mechanical properties

3.4.1. Tensile properties

The stress–strain curves of the samples containing different levels of curative are shown in Fig. 8. It is evident from the figure that H₅₀ containing no crosslinking agent behaves like a weak brittle material as NBR domains are coarsely distributed in HDPE matrix. Upon the addition of DCP, the deformation pattern changes drastically. The weak brittle material gradually changes to a strong tough one as a result of dynamic vulcanisation. The addition of DCP results in crosslinking of the rubber molecules and thereby the viscosity increases. On subsequent shearing, more effective particle break-up occurs leading to a significant change in morphology. A large number of small, uniformly distributed crosslinked rubber particles can be observed in vulcanised sample. The entangled rubber molecules cannot slip past each other during loading and thereby resulting in higher tensile strength. Also, during loading the small crosslinked rubber particles can undergo deformation and hence relieves a portion of the applied stress whereas the large uncrosslinked rubber particles act as stress concentrating flaws. The net effect of dynamic vulcanisation is that the ultimate strength is improved.

The effect of DCP content on tensile strength and elongation at break are shown in Fig. 9. The tensile strength improves rather continuously as the DCP content increases. The increase is much pronounced at higher levels of DCP. This may be due to the increased crosslink density at higher levels of DCP. The elongation at break of H₅₀ is very low as

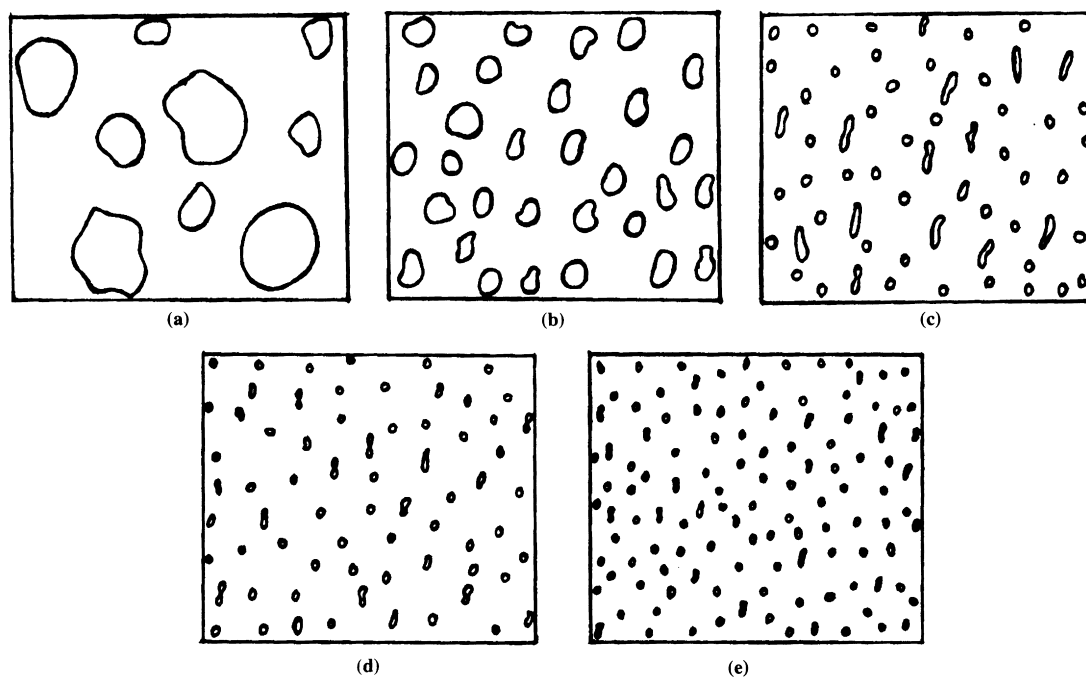


Fig. 7. Speculative models illustrating the distribution of the dispersed phase in the plastic matrix of a 50/50 blend of HDPE and NBR containing (a) 0%, (b) 1%, (c) 2%, (d) 3% and (e) 4% DCP based on the rubber phase.

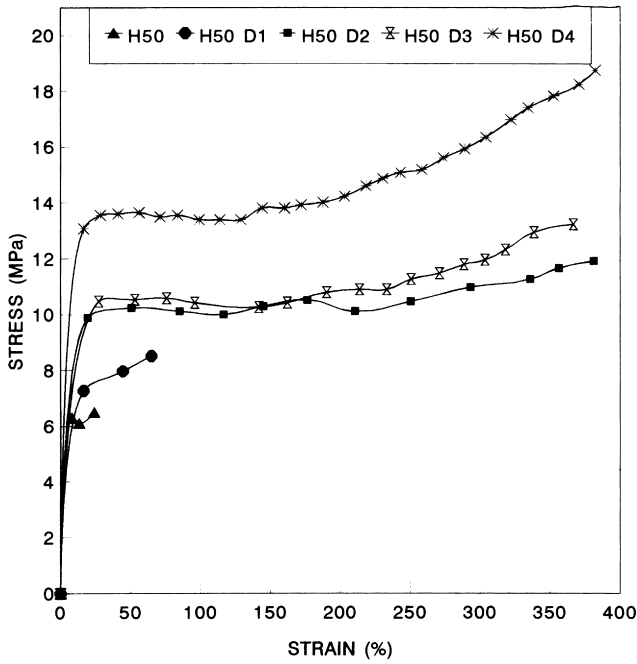


Fig. 8. Stress–strain plots of H₅₀ containing different levels of curatives.

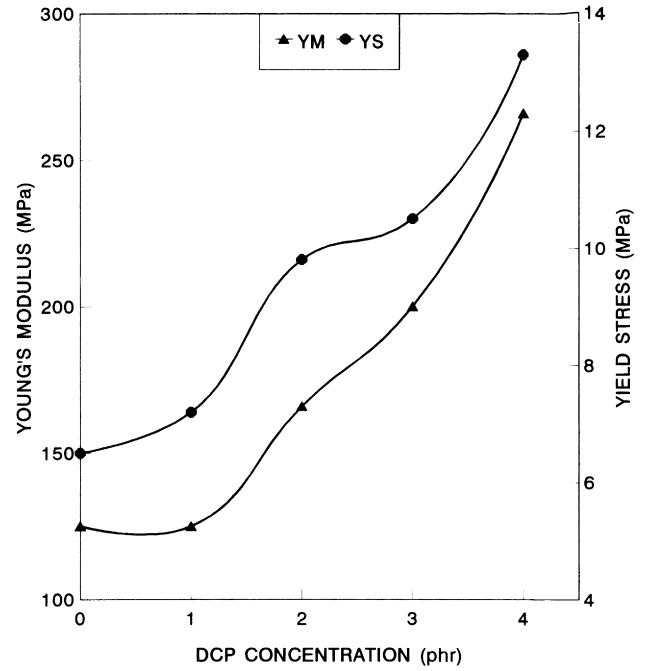


Fig. 10. Variation of Young's modulus and yield stress with DCP concentration.

the blend is incompatible and it increases with crosslink density as the crosslinked rubber particles can be strained to very large extensions before failure.

Variation of the yield stress and Young's modulus as a function of DCP concentration shown in Fig. 10 reveals that both the Young's modulus and yield stress increase with

DCP content which may be due to the increased extent of crosslinking.

3.4.2. Tear strength

Tear curves of unvulcanised and vulcanised blends containing different doses of curatives are shown in Fig.

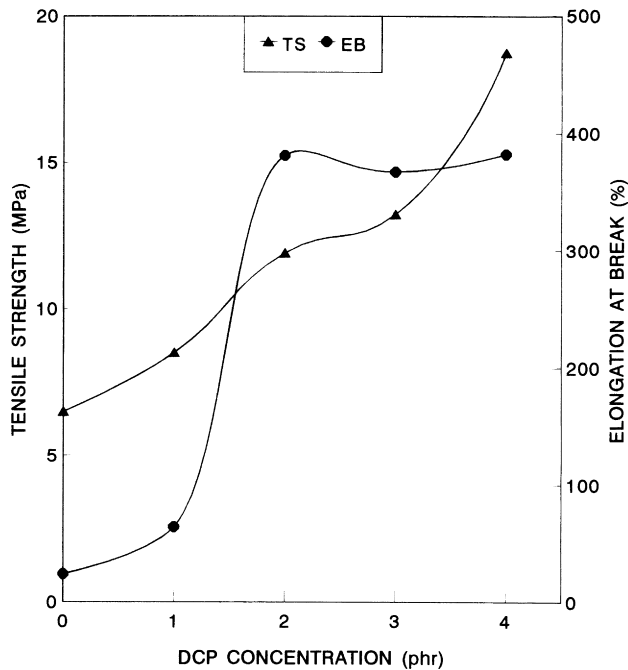


Fig. 9. Effect of DCP concentration on the ultimate properties of a 50/50 blend of HDPE and NBR.

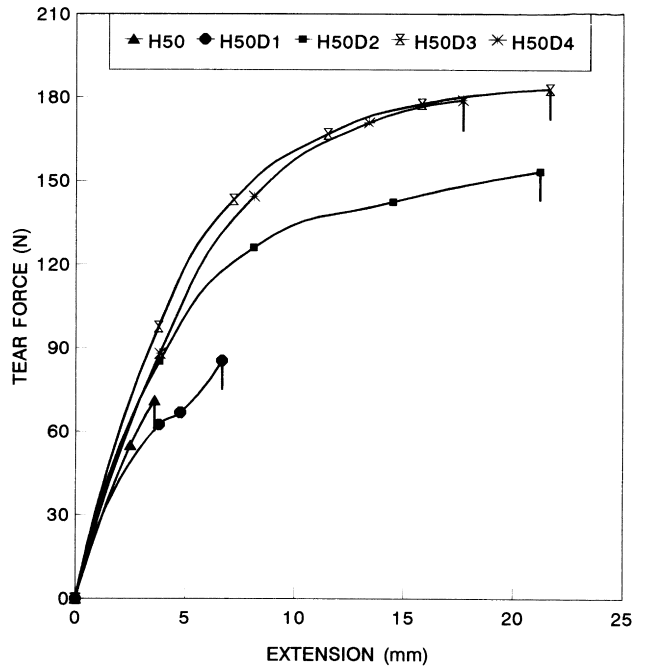


Fig. 11. Tear curves for a 50/50 blend of HDPE and NBR containing different levels of DCP.

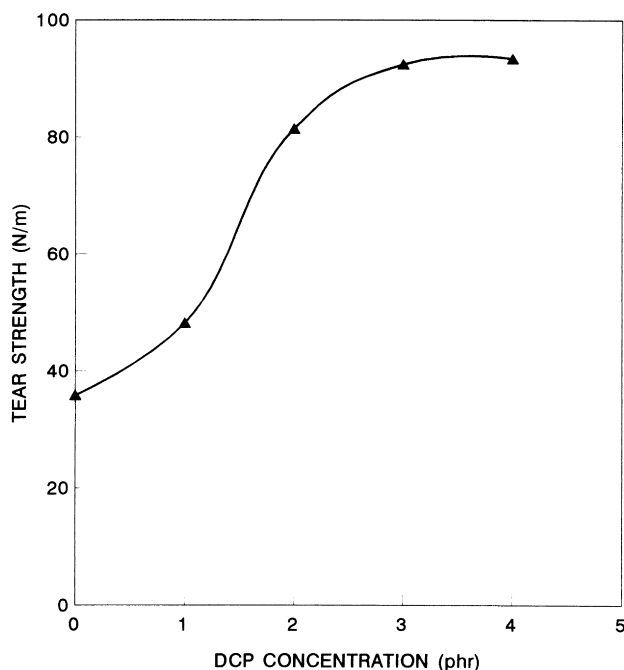


Fig. 12. Effect of DCP concentration on the tear strength values of H₅₀.

11. During tearing, rubber particles are subjected to very large tensile strains giving large extent of craze formation. In an incompatible blend (unvulcanised) a void would form at the interface and a crack might be initiated in response to an applied stress. Once a crack is formed it would run from one rubber particle to another with little hindrance. But in crosslinked samples the small crosslinked rubber particles which bridge the growing crack stretch to very large strains by fibrillation and also confers mechanical strength. The tearing strain of the rubber particle increases as its size is reduced [12]. Thus the increase in tear strength with extent of crosslinking of the elastomer phase as observed in Fig. 12

is due to the smaller size and higher elongation of the cross-linked particles.

The improvement in mechanical properties with vulcanisation can be explained on the basis of the morphological changes accompanying dynamic vulcanisation. The morphologies of H₅₀ and H₅₀D₄ are already discussed in a previous section. In unvulcanised H₅₀ (Fig. 5(a)) the large size and the smoothness of the holes created by the solvent etching of the rubber phase reveal that the degree of adhesion between the matrix and the rubber is very low. In vulcanised H₅₀ (Fig. 5(b)) the particle size exhibited a drastic reduction. Another interesting observation is that only a few particles are spherical while most of the others are elliptical or thread like. In thread-like structure, there is the possibility of interpenetration between adjacent rubber particles. Also, in vulcanised H₅₀ there is more effective mixing of the rubber particles with the matrix as the dispersed domains are small. A fracture path proceeds uninterrupted in unvulcanised blend, however, in vulcanised samples the small elastic rubber particles result in crazing and shear yielding of the matrix. They can hold together the opposite faces of a growing crack thereby enhancing the overall properties.

A speculative model illustrating the tearing behaviour of unvulcanised and vulcanised 50/50 blend of HDPE and NBR is shown in Fig. 13. In unvulcanised sample the crack propagation is easy because the propagation path experiences little hindrance from anywhere. In this case the fractured surface seems to be smooth. But in vulcanised sample the matrix near the vicinity of the crack propagation path undergoes some kind of yielding and its intensity decreases as the distance from the propagation path increases. Extensive crosslinking can bring down the tear strength values due to the inextensibility. In the present case the lightly crosslinked rubber particles can elongate in response to an applied stress and as the rubber particles

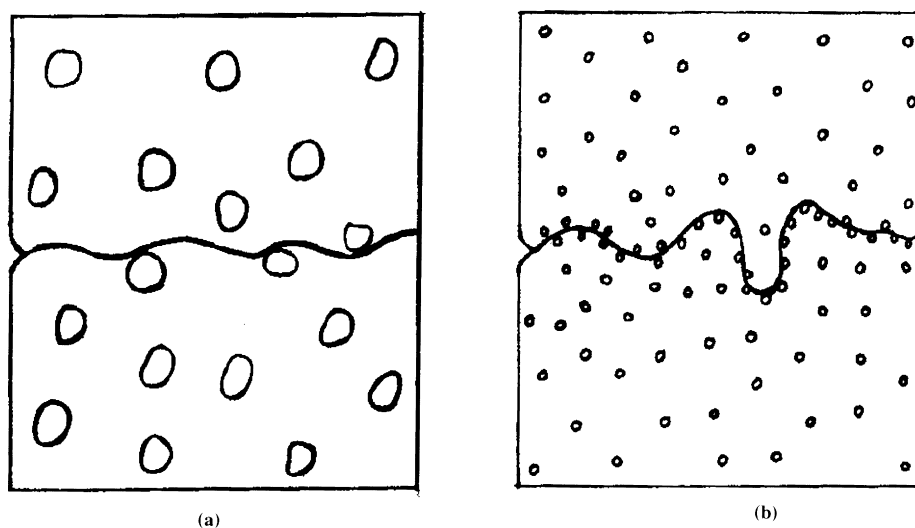


Fig. 13. Illustrative model for the tearing behaviour of (a) unvulcanised and (b) vulcanised 50/50 blends of HDPE and NBR.

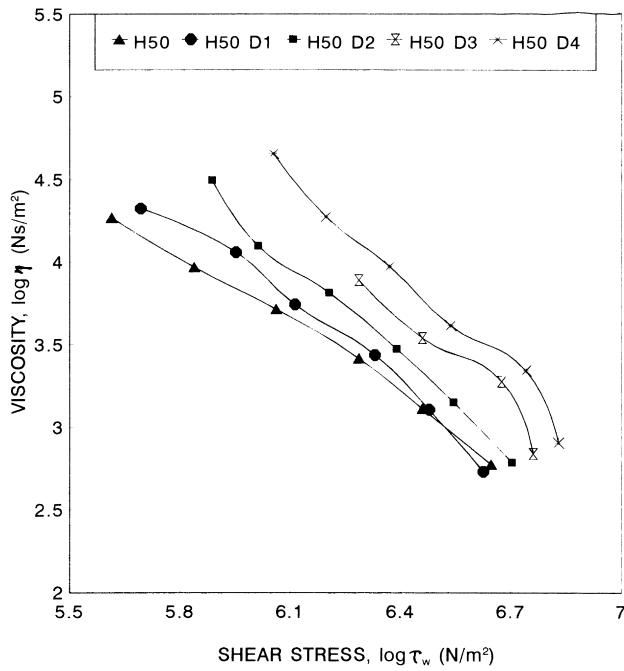


Fig. 14. Viscosity–shear stress plots of H₅₀ containing different levels of DCP.

are not continuous they transfer the applied stress to the matrix resulting in yielding of the matrix. Thus the extensibility of the crosslinked rubber particles and the yielding of the matrix imparts better tear strength to the vulcanised samples.

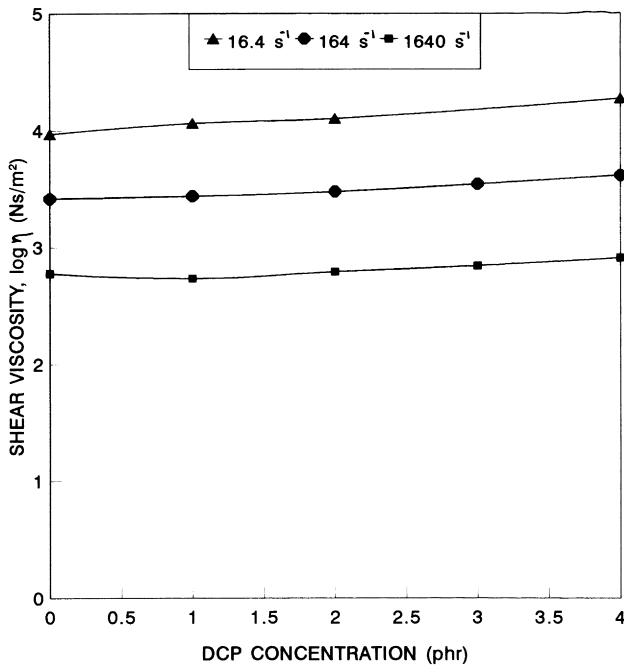


Fig. 15. Effect of DCP concentration on the shear viscosity of H₅₀ at three different shear rates.

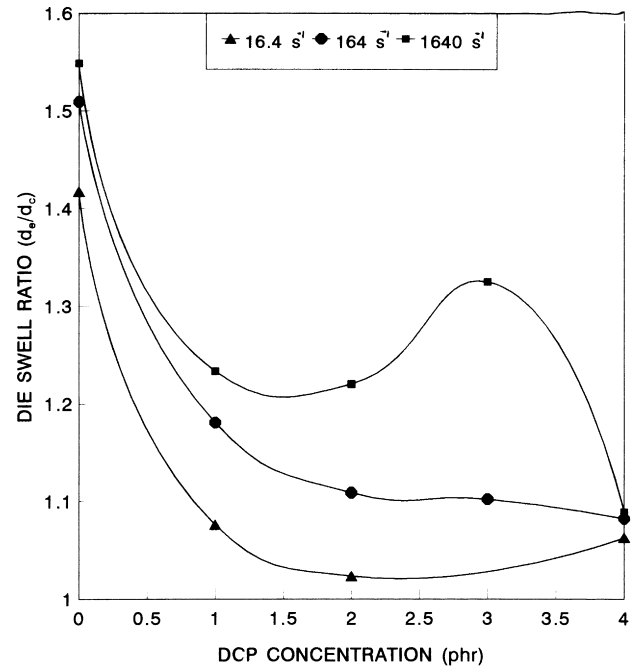


Fig. 16. Variation of die swell with DCP concentration illustrating the effect of extent of crosslinking on die swell values.

3.5. Rheological studies

The usual processing techniques for thermoplastic elastomers are extrusion, injection moulding, blow moulding, etc. Hence a thorough understanding of the flow behaviour of the polymer melts under high shearing action is important to make articles of good finish and dimensional tolerances. The melt elasticity and viscosity are two opposing factors that decide the overall processability. The different rheological properties of interest are discussed below.

3.6. Effect of shear stress and extent of dynamic crosslinking on shear viscosity

The effect of shear stress on shear viscosity of the mixes containing different levels of curatives at 175°C is shown in Fig. 14. In all the cases the viscosity decreases with shear stress indicating the pseudoplastic nature of the mixes. The viscosity increases with increasing concentration of DCP over the entire range of shear stresses. The increase in viscosity with DCP content is more pronounced at low

Table 2
Effect of extent of crosslinking on melt flow index (*n'*) of the mixes at 175°C

Sample code	<i>n'</i>
H ₅₀	0.41
H ₅₀ D ₁	0.37
H ₅₀ D ₂	0.33
H ₅₀ D ₃	0.32
H ₅₀ D ₄	0.32

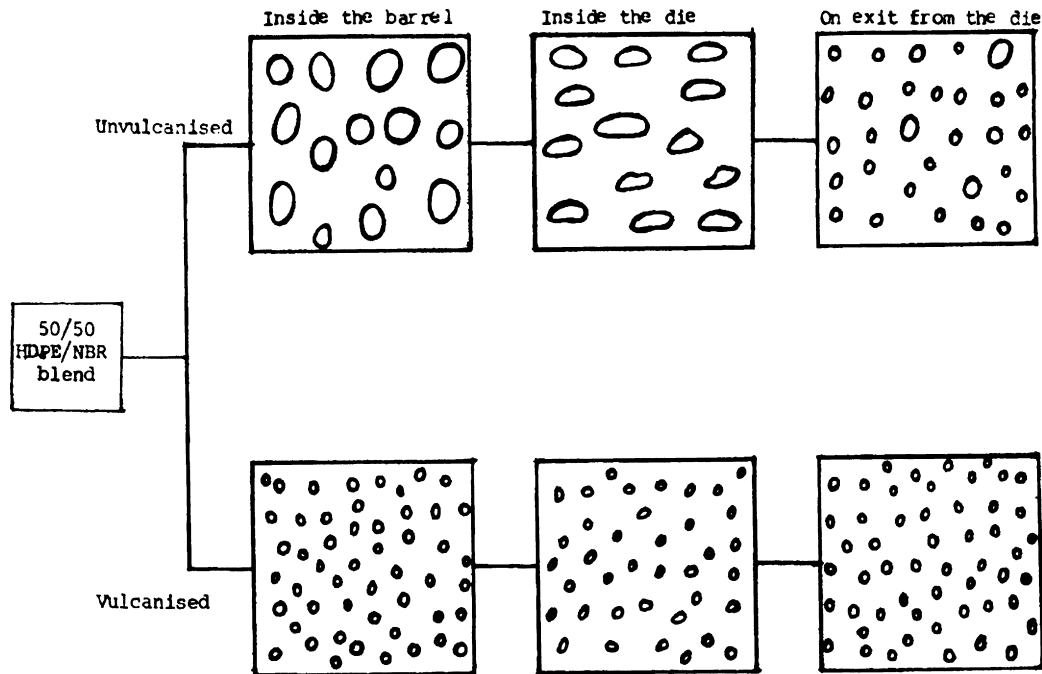


Fig. 17. Representation of the possible morphologies of unvulcanised and vulcanised 50/50 blend of HDPE and NBR during rheological measurements.

shear regions than at high shear regions as observed from the converging behaviour of the flow curves at high shear stresses. These results show that the dynamically vulcanised samples can be processed like thermoplastics by extrusion or injection moulding technique.

Fig. 15 shows the effect of DCP dosage on the viscosity of the mixes at different shear rates. At all shear rates there is a gradual increase of viscosity with the concentration of DCP indicating increased extent of crosslinking at higher levels of DCP. At a particular DCP content, the viscosity decreases as the shear rate increases.

3.7. Effect of extent of crosslinking on flow behaviour index (n')

The effect of extent of dynamic crosslinking on the flow behaviour index (n') is shown in Table 2. The unvulcanised blend shows the highest n' value. There is a marginal reduction in the n' values even with the addition of 1% DCP indicating the higher pseudoplastic behaviour of the vulcanised samples. The concentration of DCP has not much effect on the n' values as is evident from the data shown in this table.

3.8. Effect of shear rate and dynamic crosslinking on die swell ratio (d_e/d_c)

The swelling index of the mixes at three different shear rates are shown in Fig. 16. In all the cases the die swell ratio shows a substantial reduction even with 1% DCP and thereafter a levelling off is observed. The die swell occurs due to molecular relaxation upon emergence of the extrudate from

the capillary die. The results of the present study reveal that vulcanisation leads to network formation and thereby restricting the relaxation process. In a vulcanised sample, the molecules cannot slip past each other as in unvulcanised material. As expected, the die swell of vulcanised samples also increases with increase in shear rate.

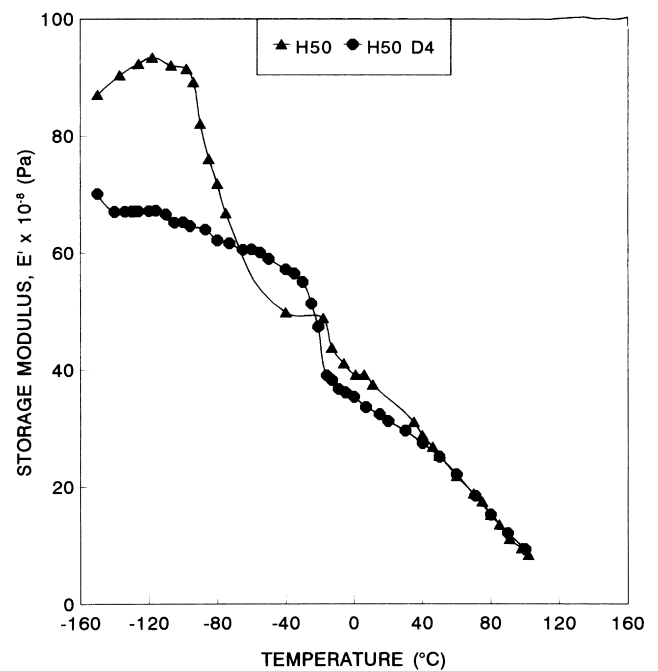


Fig. 18. Variation of storage modulus with temperature of unvulcanised and vulcanised 50/50 blends of HDPE and NBR.

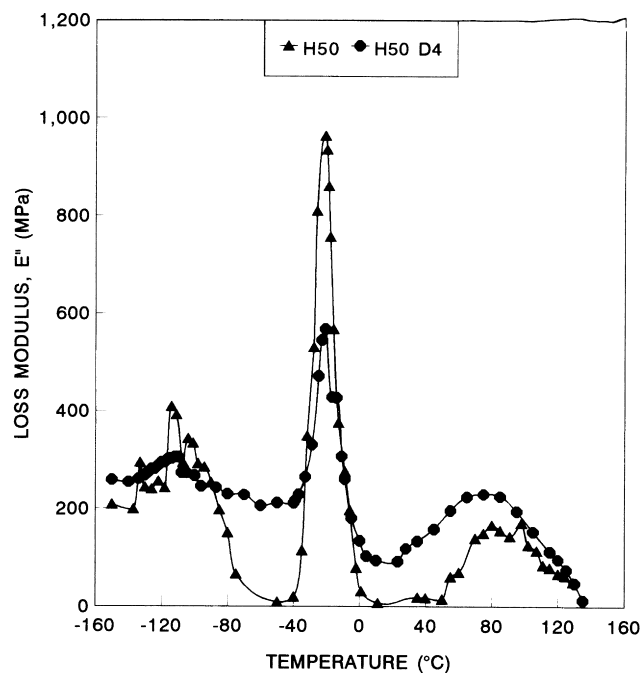


Fig. 19. Loss modulus vs. temperature plots of unvulcanised and vulcanised 50/50 blends of HDPE and NBR.

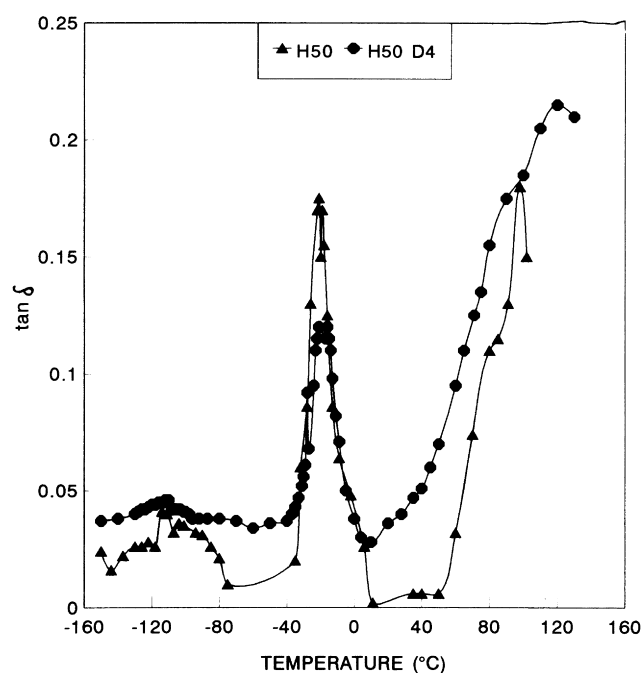


Fig. 20. Tan δ -temperature plots of unvulcanised and vulcanised 50/50 blends of HDPE and NBR.

In extrusion rheometer, the polymer sample taken in the extruder barrel is forced through a die of a very small diameter. Thus the sample is subjected to severe shearing force during its passage through the die and depending on its elasticity it can regain its original morphology. Based on this concept, an illustrative model for the morphology changes during rheological measurements is presented in Fig. 17. Thus in the extruder barrel the unvulcanised blend behaves like an incompatible one with large NBR particles in the HDPE matrix. During extrusion (in the die) severe particle deformation and break-up occur due to the high shearing force. Thus in the extruder die the shape of the dispersed phase changes drastically depending on the shear rate. The spherical particle becomes elliptical which then break down into small particles. On exit from the capillary, the stress is relieved and the rubber particles attain the spherical morphology. In vulcanised H_{50} the particle size is comparatively less and the morphological changes within the die is negligible because the crosslinked rubber particles cannot be broken down into finer dimensions. Also particle coalescence is completely suppressed in vulcanised compositions. Thus after extrusion, the particle size and its distribution are more or less unaffected in vulcanised samples.

3.9. Dynamic mechanical studies

Dynamic mechanical properties of polymers are highly dependent on the material structure. Thus the molecular level changes that occur in a polymer under the application of a sinusoidal stress is reflected in dynamic mechanical measurements.

The variation of storage modulus (E') with temperature of H_{50} and $H_{50}D_4$ is shown in Fig. 18. Three distinct regions of mechanical behaviour can be observed: (a) a glassy region; (b) a glass-rubber transition region; and (c) a flow region. In the glassy region at low temperatures the chain conformations are frozen into rigid network yielding high E' values and low loss. Some limited movement either within the main chain or within side groups attached to the chain is however possible giving rise to one or more secondary transitions of low magnitude.

The glass-rubber transition marks the onset of long range motions of amorphous polymer chain segments and is characterised by a large drop in modulus and a pronounced loss factor peak. The last region is the flow region, where the amorphous chains undergo net translatory motions relative to each other and a terminal fall off in modulus is accompanied by a continuous increase in loss factor.

From the above figure it is clear that in the case of uncrosslinked sample the reduction in modulus with temperature is high and it starts at a lower temperature. But in the case of dynamically crosslinked samples the fall in modulus with temperature is much less and the onset of segmental mobility starts at a higher temperature.

The variation of loss modulus (E'') and $\tan \delta$ values of H_{50} and $H_{50}D_4$ as a function of temperature are shown in Figs. 19 and 20, respectively. Two distinct peaks can be observed in Fig. 19. Below the T_g values the polymer chains are in tact and stress transfer is possible which is reflected in the more or less constant values of E'' . When the temperature is approaching the T_g , energy dissipation takes place and a corresponding peak is observed in the E'' values.

The variation of $\tan \delta$ values of H_{50} and $H_{50}D_4$ as a function of temperature is shown in Fig. 20. Here again two distinct peaks can be observed in both the cases indicating immiscibility between the phases in agreement with the microscopic studies. The peak between -120 and -105°C corresponds to the glass transition of polyethylene and the one between -30 and -15°C represents the corresponding transition in NBR. The damping peak values of HDPE in both crosslinked and uncrosslinked samples are more or less the same indicating that the plastic phase is unaffected by dynamic vulcanisation. However, a substantial reduction in $\tan \delta$ peak of NBR is observed in $H_{50}D_4$ indicating that crosslinking restricts the chain flexibility. The peak width at half height was measured and a value of approximately 6.5 mm was obtained in both unvulcanised and dynamically vulcanised samples. The similarity of the two values indicates that dynamic vulcanisation has no significant effect on miscibility.

4. Conclusion

Dynamic vulcanisation of 50/50 blends of HDPE and NBR was carried out using dicumyl peroxide. DCP dosage has a significant effect on the extent of crosslinking. As the DCP content increases the crosslink density also increases as observed from the increase in V_r values. The morphology changes drastically as a result of dynamic vulcanisation. A large number of small crosslinked rubber particles could be observed in vulcanised blend. The tensile and tear strength show substantial improvement upon vulcanisation which is attributed by the presence of crosslinked rubber particles. Speculative models have been suggested for the morphological changes during dynamic vulcanisation and also for the tearing behaviour of unvulcanised and vulcanised blends. The rheological studies reveal that the viscosity decreases

with shear stress indicating pseudoplastic nature of the mixes. Although viscosity increases with DCP dosage over the entire range of shear stresses it can still be processed like thermoplastics. The die swell ratio decreases with increase in DCP concentration indicating better dimensional stability of the extrudate. The flow behaviour indices show only a marginal decrease with extent of crosslinking. Dynamic mechanical studies indicated two separate transitions in both uncrosslinked and crosslinked blends corresponding to polyethylene and NBR phases. Although miscibility cannot be brought about by dynamic vulcanisation, the overall improvement in properties suggest that dynamic vulcanisation can be employed as a means of technological compatibilisation of HDPE/NBR blends.

References

- [1] Morris HL. In: Walker BM, editor. Hand book of thermoplastic elastomers. New York: Van Nostrand-Reinhold, 1979. p. 5.
- [2] Kresge EN. In: Paul DR, Newman S, editors. Polymer blends, vol. 2. New York: Academic Press, 1978. p. 293.
- [3] Kresge ENJ. Appl Polym Sci, Appl Polym Symp 1984;39:37.
- [4] O'Connor GE, Fath MA. Rubber World, December 1981, January 1982.
- [5] Gesner BD. In: Mark HF, Gaylord NG, editors. Encyclopedia of polymer science and technology, vol. 10. New York: Interscience, 1969. p. 694.
- [6] Gessler AM. US Patent 3037954, June 5, 1962.
- [7] Fischer WK. US Patent 3758643, September 11, 1973.
- [8] Coran AY, Das B, Patel RP. US Patent 4130535, December 19, 1978.
- [9] Coran AY, Patel R. Rubber Chem Technol 1980;53:141.
- [10] Coran AY. In: Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers: a comprehensive review. New York: Hanser Publishers, 1987.
- [11] Coran AY, Patel R, Williams D. Rubber Chem Technol 1982;55:116.
- [12] Kunz Donglass S, Beaumont PWR, Ashby MF. J Mater Sci 1980;15:1109.