JOURNAL OF MATERIALS SCIENCE **24** (1989) 3491–3496

Tensile and tear failure of plasticized poly (vinyl chloride)/epoxidized natural rubber miscible blends

K. T. VARUGHESE, G. B. NANDO, S. K. DE
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India
S. K. SANYAL
Chemical Engineering Department, Jadavpur University, Jadavpur 700 032, India

A study on the tensile and tear failure of miscible blends of plasticized poly (vinyl chloride), PVC, and epoxidized natural rubber (ENR) was carried out. Fractographs were taken in a scanning electron microscope in order to obtain an insight into the failure mechanism of the samples. It was found that low ENR blends failed by shearing in tensile testing, and they exhibited irregular stick–slip deformation and characteristics like vulcanizates in tear testing. Blends of plasticized PVC and ENR were more flexible than the individual components. As a result of the geometrical effect the tear fracture surface has rougher features than the tensile fracture surface. Sinusoidal wavy tear patterns in the form of a typical sine wave and rectified half sine wave of the fracture surface are characteristic features of tear resistant non-vulcanizates of rubber-like materials. Moreover, the study revealed that there were no features of phase separation of PVC and ENR due to incompatibility at any of the fracture surfaces examined.

1. Introduction

Miscible blends of polymers always find important industrial applications because of their improved properties, ease of preparation, and economical advantage. When the blend components are a thermoplastic and an elastomer, they have certain advantages. They are easily processable like a thermoplastic; they retain their rubbery properties at service temperature; they need no vulcanization; and they can be reprocessed and recycled.

In recent studies it has been reported that poly (vinyl chloride), PVC, and epoxidized natural rubber (ENR) are capable of forming miscible thermoplastic–elastomer blends in solution [1] as well as in melt states [2]. Studies based on melt blends have shown that both rigid [2] and plasticized [3] PVC blend miscibly with ENR in their entire range of composition.

Plasticized PVC–ENR blends are preferable in applications where flexibility and permanence in physical properties are required. Plasticization in PVC enhances the segmental motion and reduces the glass–rubber transition temperature. In addition, strength under tension decreases, elongation at break increases, and fracture surface morphology changes, with the appearance of several distinguishable fracture patterns. The present paper focuses attention on these aspects in miscible blends of plasticized PVC and ENR. Fracture surfaces have been characterized by scanning electron microscope to get an insight into the failure mechanism of samples. A similar study on the rigid PVC–ENR system has been reported previously [4].

2. Experimental procedure

Details of the materials used and the formulation of the mixes are given in Tables I and II respectively. Prior to the blending of plasticized PVC with ENR, the powdered resin was initially mixed with 6 phr of the stabiliser, tribasic lead sulphate (TBLS) and 40 phr of the plasticizer, dioctyl phthalate in a Brabender plasticorder (model PLE 330) at a rotor speed of 100 r.p.m. and at a temperature of 110° C for 15 min. The blending of plasticized PVC and ENR was performed in the Brabender plasticorder at 180° C maintaining the rotor speed 60 r.p.m. and the time of blending 6 minutes, for all cases, as described earlier [3].

Tensile testing of the samples was done at 25 ± 2° C according to the ASTM D 412-80 test method using dumb-bell shaped test specimens in an Instron Universal Testing Machine (model 1195) at a cross-head speed of 500 mm min^{-1}. Tear strength of the sample was determined according to the ASTM D 624-81 test method using unnicked 90° angle test specimens at the same conditions of temperature and cross-head speed as in the case of tensile testing.

The fracture surface of tensile and tear specimens was examined in a scanning electron microscope (SEM) as described earlier [4] where figures showing the test specimens, fracture surfaces and the area of SEM examination are also given.

3. Results and discussion

3.1. Stress–strain behaviour

The difference in the deformation characteristics of

TABLE I Details of materials used

Materials	Characteristics/Literature data	Source
Poly (vinyl chloride), PVC	Suspension polymerized poly (vinyl chloride)(NOCIL PVC polymer 567-311), K Value 66-69	NOCIL, Bombay, India.
Tribasic lead sulphate (TBLS)	Lead based stabilizer for PVC	Waldies Ltd., Calcutta, India.
Dioctyl phthalate (DOP)	Plasticizer for PVC	Perkin Chemical Industries, Calcutta, India
Epoxidized natural rubber (ENR)	50 mol % epoxidized natural rubber using peroxides at the latex stage. Mooney viscosity $ML_{(1+4)}$ 100° C, 140.	The Malaysian Rubber Producers' Research Association,Brickendonbury, UK

the samples under the uniaxial tensile stress is shown in Fig. 1. Plasticized PVC exhibits the deformation of a hard rubbery solid, without the appearance of any yield point until the final rupture occurs at a stress of 22.5 MPa. This deformation is linear elastic at lower strains and irreversible plastic at higher strains. ENR, being unvulcanized, has the viscoelastic deformation of a very soft rubber which breaks at the lowest values of strain and stress of all the samples. Stress–strain behaviour of blends range from the hard rubbery nature of plasticized PVC to the soft rubbery nature of ENR. As the proportion of ENR in blends increases, the breaking strain increases and the stress decreases. At higher strains every blend appears to undergo strain hardening.

The lowest value of breaking strain for ENR is due to its unvulcanized nature. In blends, however, the breaking strain of ENR increases. The miscibility of ENR with PVC results in the formation of a physical network between the two polymers. This physical network causes chain slippage and consequently high elongation at break for ENR in blends.

3.2. Tear force displacement

In Fig. 2, as shown in the tear force–displacement plots, plasticized PVC tears at the highest force and at the smallest displacement, indicating high resistance to tearing of all samples. The high resistance to tearing of plasticized PVC has also been reported by Gent and Shimizu [5]. They attributed it to the contributions from energy expended in a viscous process as the molecular strands are straightened and fractured. ENR undergoes considerably large displacements with the minimum tearing force. As the ENR content in blends increases, the tearing is followed by an increase in displacement and decrease in force.

The low ENR blends tear in an unstable manner as evident from the behaviour of PP_{70} in Fig. 2. From the fractographic studies, in this paper, it will be seen that this unstable deformation in tearing is due to an irregular stick-slip mode of failure.

3.3. Affect of blend composition on properties

The affect of blend composition on properties is generally studied with respect to their deviation from additive behaviour. In Fig. 3, it is seen that the elongation at break exhibits higher experimental values than the additive values for all compositions of plasticized PVC–ENR. The upward deviation is more pronounced beyond 30 wt % of ENR in the blend. A similar response of deviation in elongation at break has also been noted in the case of rigid PVC–ENR systems [4].

Tensile strength with respect to blend composition reveals an improvement for ENR and deterioration for the plasticized PVC in blends (Fig. 4). The experimental plot passes very close to the additive line with a slight downward deviation at the mid-composition region. The concavity noted for the corresponding plot in rigid PVC–ENR [4] is not prominent in the case of plasticized PVC–ENR. This may be due in part to the strain hardening effect in the plasticized PVC–ENR which breaks at a higher strain than rigid PVC–

TABLE II Formulation of the mixes

Blend code	PP_{100}	PP_{70}	PP_{50}	PP_{30}	P_0
Weight percentage of plasticized PVC*	100	70	50	30	–
Weight percentage of ENR	–	30	50	70	100

*Containing 6 phr of TBLS and 40 phr of DOP.

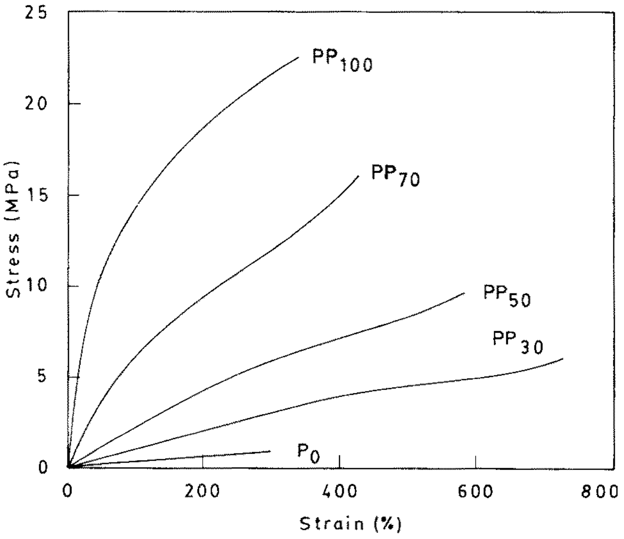

Figure 1 Stress–strain curves of plasticized PVC–ENR blends.

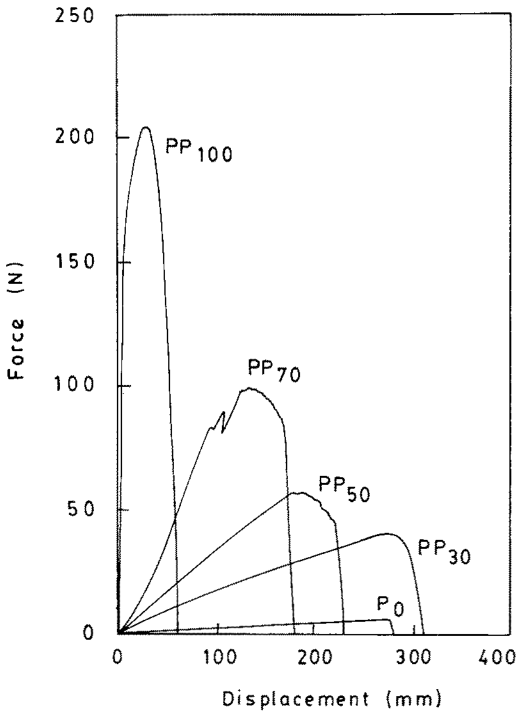

Figure 2 Tear force–displacement curves of plasticized PVC–ENR blends.

ENR. Strain induced crystallization of ENR [7, 8] may also contribute in increasing the ultimate tensile strength of the highly elongated plasticized PVC–ENR blends.

The experimental values of tear strength of plasticized PVC–ENR also lie below the additive plot as seen in Fig. 5. Maximum downward deviation in tear strength is noted for the 30 wt % composition of ENR in blends.

3.4. Fractographs

In tearing, the test specimen which is having an angular geometry is subjected to a tensile deformation. As the uniaxial tensile stress is applied, extensive stress is concentrated at the apex and the particles nearby and along the crack paths at the fracture surface undergo large plastic deformation. In the case of a dumb-bell tensile test specimen, stress concentration due to geometrical effect does not occur. Instead the stress is distributed uniformly along the entire neck portion till the fracture is developed from any of the growing cracks. Thus the tear fracture surface yields rougher features than the tensile fracture surface for any particular test sample. This situation is clearly understood from the further results of this paper.

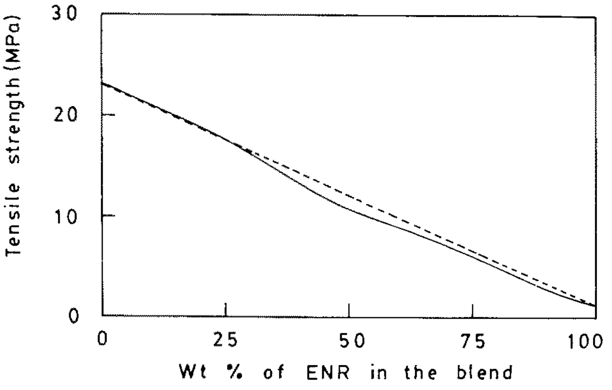

Figure 4 Affect of blend ratio on maximum tensile strength of plasticized PVC–ENR blends.

3.4.1. Tensile fractographs

Photomicrographs of the tensile fracture surface of plasticized PVC and blends are shown in Figs 6 to 8. Crack fronts in PP_{100} appear to have grown by tearing of the craze materials at the pointed tip of a diamond cavity. Diamond cavitation is believed to occur due to ductile failure prior to plastic deformation in PVC [9, 10]. The presence of peaks occurring from the stretching of the matrix along the stress axis also supports the tearing process in this fracture. Further, it is seen that the fracture propagates radially and some of the crack fronts appear to have advanced in a parabolic manner. The formation of a parabolic pattern is ascribed to the meeting of primary and secondary crack fronts growing at the same rate [11, 12]. In the highly magnified photomicrograph (Fig. 6b), PP_{100} exhibits plastically deformed features.

The initiation site as the origin of the radially advancing fracture and the appearance of features due to plastic deformation is still recognizable in the

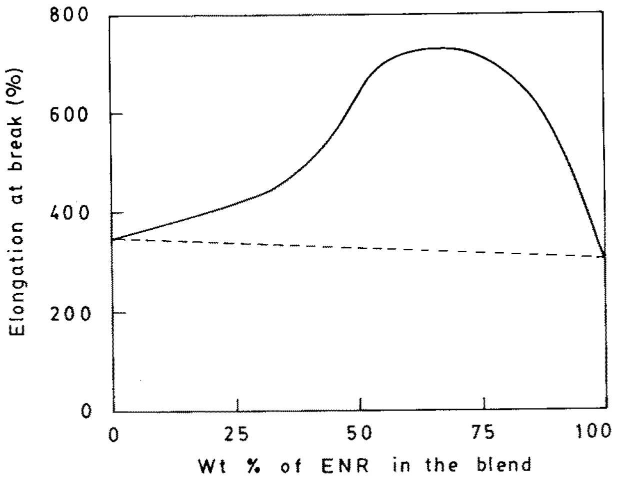

Figure 3 Affect of blend ratio on elongation at break of plasticized PVC–ENR blends.

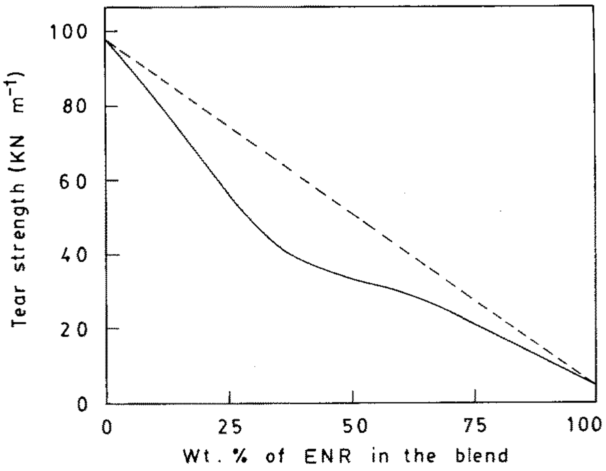

Figure 5 Affect of blend ratio on tear strength of plasticized PVC–ENR blends.

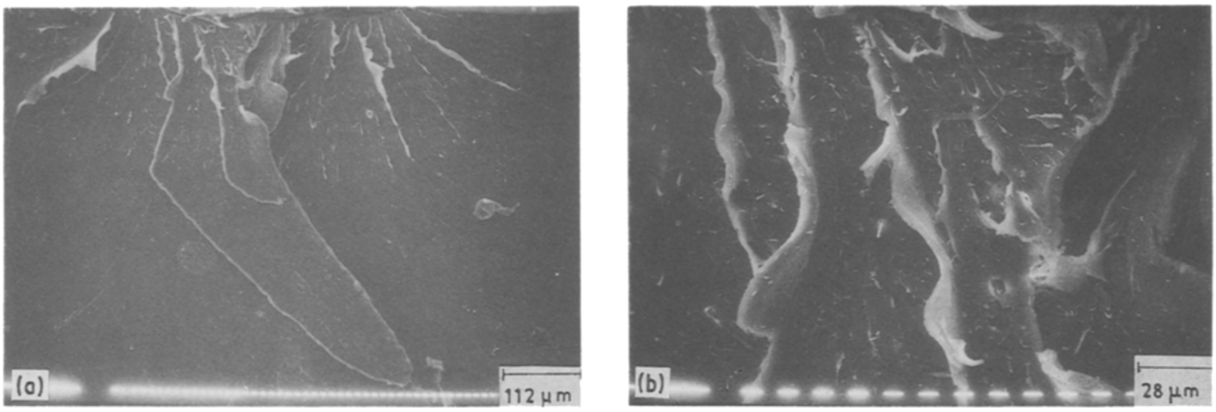

Figure 6 SEM of the tensile fracture surface of PP_{100} (a) low magnification, (b) high magnification.

fracture surface of blends, as for PP_{70}, in Fig. 7. The fracture profile in PP_{70} appears to have initiated from a single stress concentrated region. The matrix has drawn along the extrusion axis prior to the failure. Several concentric rings and the fibrils seen at the fracture initiation site give the impression that the final rupture has taken place by shearing and tearing. Concentric shear rings for the tensile failure and fibrils for tear failure have also been reported as fracture patterns for the 70:30 composition of rigid PVC–ENR [4].

The shearing and drawing of the matrix has not been observed at high ENR levels. Moreover, the features diminished with the appearance of a smooth fracture surface when the proportion of ENR was increased in blends (Fig. 8). This is understood in terms of the high strain and the low stress at the break of high ENR blends.

3.4.2. Tear fractographs

Plasticized PVC which is having the highest tear strength among the samples studied shows the fracture profile covering in a smooth zone of slow fracture and another rough zone of fast fracture (Figs 9a and b). Major surface features are (1) tearing along the wavy crests or troughs, (2) fine fibrous structures, and (3) peaks.

Tearing at the smooth zone in Fig. 9a shows tear fronts growing sinusoidally along wavy crests or troughs. Interestingly, the wavy tear fronts exhibit characteristics of a sine wave (Fig. 8a) or a rectified half sine wave (Fig. 9b). The length and the height of crests or troughs remain the same unless there is any perturbation due to secondary tearing. Fine fibrous structures present in the rough zone in Fig. 9a appear to be intrinsic crazes as reported for polycarbonates [13], poly (methyl methacrylate) [14] and rigid PVC [4]. These intrinsic crazes are capable of withstanding high load. Peaks are produced from excessively stress-concentrated regions due to stretching of the matrix with tremendous force. Wavy crests or troughs in the rough zone are closely spaced due to fast fracture.

Randomness in the tearing of plasticized PVC with the incorporation of ENR, as has been seen in the tear force–displacement curves, is followed by a marked change in the fracture surface morphology. The sinusoidal characteristics of wavy tear paths are diminished or damped for PP_{70} as seen in Fig. 10. New features due to steps and peeling of the matrix are observed at the fracture surface of PP_{70}. Steps in the torn surface have been reported as a characteristic feature of tear resistant rubber vulcanizates [15].

At high ENR compositions the decrease in the resistance to tearing is followed by the straightening of wavy tear fronts. This is evident from the more damped wavy tear patterns for PP_{50} in Fig. 11.

Polymer systems in which the sinusoidal wavy tear pattern has been reported are semicrystalline thermoplastic elastomers such as 1, 2 polybutadiene [16] and thermoplastic copolyester elastomers [17], plasticized PVC [17], plasticized PVC–thermoplastic copolyester elastomer miscible blends [18], and rigid PVC–ENR miscible blends [4]. The specific feature of a rectified

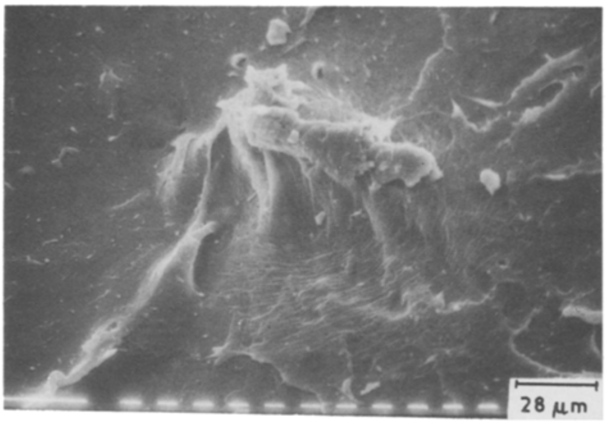

Figure 7 SEM of the tensile fracture surface of PP_{70} showing shearing and drawing of the matrix.

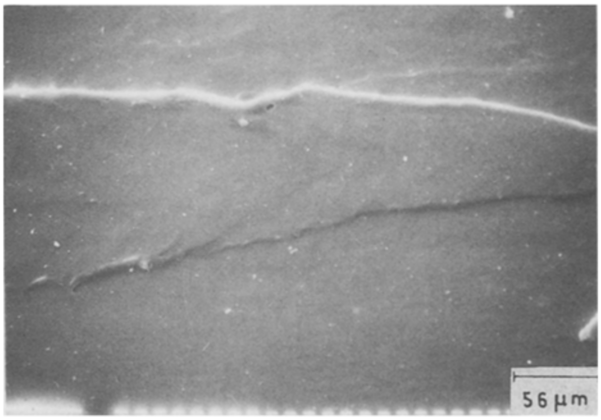

Figure 8 SEM of the tensile fracture surface of PP_{30}.

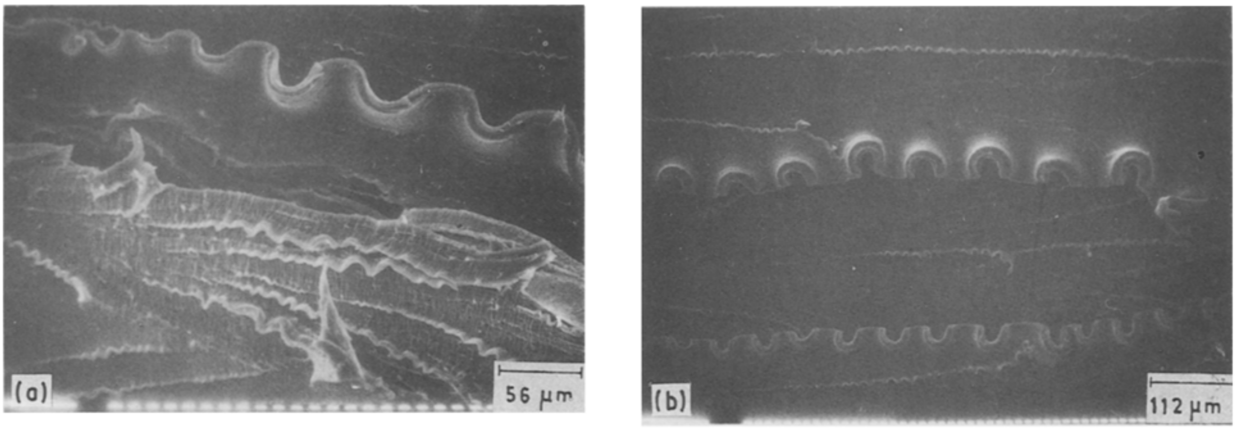

Figure 9 SEM of the tear fracture surface of PP_{100}. (a) fracture patterns of sine wave, peaks and intrinsic crazes, (b) rectified half sine wave pattern.

half sine wave tear pattern, however, is the first observation in the studies of fracture surface morphology using SEM. The wavy nature of tear paths is an indication of the instability of tear fronts due to crack blunting. It has been proposed that the amount of localized plastic deformation that occurs at the crack tip prior to crack propagation is the controlling factor in crack blunting [19, 20].

In rubber vulcanizates, a sinusoidal tear pattern is not a common feature. Instead, steps have been observed at the torn surface. Close spacing and great height in steps have been reported [15] as an indication of high resistance to the tearing of vulcanizates of rubber.

From the present study and the earlier reports [4, 16–18] it can be concluded that a significant sinusoidal wavy tear pattern at the fracture surface is a characteristic feature of tear resistant thermoplastic elastomers or rubber-like materials which do not require vulcanization. Sinusoidal wavy patterns at the torn surface appear in the shape of a sine wave or a rectified half sine wave. These patterns arise due to the extensive stretching of the matrix along the stress direction to yield large plastic deformation. Plastic deformation is high for thermoplastic materials which exhibit elastomeric character. The addition of a soft rubber into such materials results in a decrease in plastic deformation and an increase in rubbery deformation. Concomitantly, stress starts distributing uniformly all over the matrix; chances of extensive stretching of the matrix decrease. This situation is more pronounced in the fracture surface of a tear test specimen than that of a tensile test specimen due to the higher stress concentration occurring at the crack tip of the former than the latter.

The presence of significant sine wave or rectified half sine wave patterns is an indication of periodic stick–slip failure in tear resistant elastomer. The incorporation of a soft rubber into it causes disordering in the periodicity of stick–slip failure. As noted in the case of PP_{70}, low ENR blends show randomness in the tear force–displacement behaviour. This random deformation is associated with a random stick–slip pattern at the torn surface. In PP_{70}, this is evident from the absence of a rectified half sine wave and presence of a diffused sine wave as well as the appearance of new features such as steps and structures due to the peeling of the matrix. The appearance of steps in low ENR blends not only suggests the random stick–slip failure but also reveals, following the studies of Gent and Pulford [15], that they can behave like tear resistant rubber vulcanizates. Physical networks between PVC and ENR cause the blend to have a vulcanizate behaviour with respect to decreasing the level of plastic deformation and increasing the extent of rubbery deformation. The concurrent plastic and rubbery deformation is the reason for the random stick–slip deformation in low ENR blends. As the ENR content in blends increases, the tear strength decreases and thus, stick-slip deformation weakens. This is attributed

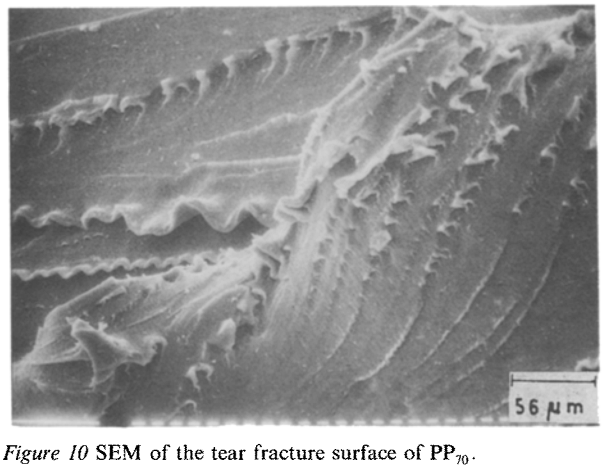

Figure 10 SEM of the tear fracture surface of PP_{70}.

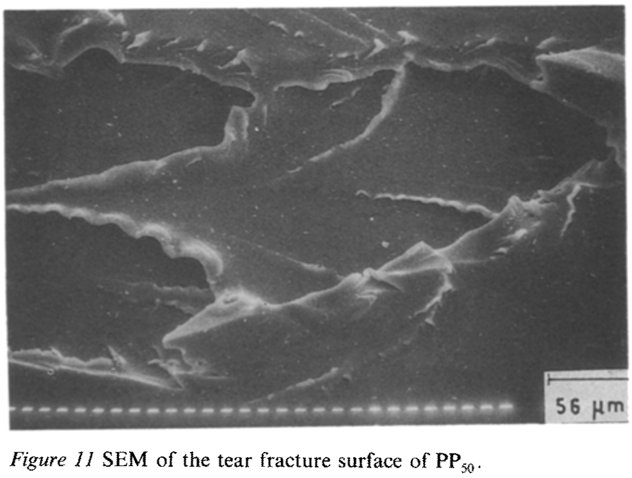

Figure 11 SEM of the tear fracture surface of PP_{50}.

to the decrease in plastic deformation. In high ENR blends, wavy tear paths are straightened and steps becomes widely spaced or diminished.

A comparison of the tensile and tear failure in this study shows more fracture surface roughness in the latter than the former. In both cases, however, a gradation in surface features is noted with respect to blend composition or resistance to tearing of blends. Phase separation of the individual components is not observed in any of the fractographs of blends. When phase separation occurs, the features at the fracture surface are expected to become severely rough due to a catastrophic failure. Consequently, the direction and growth of crack fronts may not be distinguished. Besides, various fracture patterns as observed in this study may not be identified. Such a situation will indicate incompatibility of polymer components in blends.

4. Conclusions

Incorporation of ENR into plasticized PVC affects the latter by decreasing plastic deformation and increasing rubbery–elastic deformation. Low ENR blends have some salient features. They fail by shearing and tearing in tensile testing. Also, they exhibit irregular stick–slip deformation and characteristics like vulcanizates in tear testing. The effect of blend composition on properties is such that experimental values of tensile and tear strength are lower and that of elongation at break is higher than the additive values of individual components. Thus blends of plasticized PVC and ENR are more flexible than the individual components. Due to geometrical effects the tear fracture surface has rougher features than the tensile fracture surface. Sinusoidal wavy tear patterns in the form of a typical sine wave and rectified half sine wave at the fracture surface are characteristic features of tear resistant non-vulcanizates of rubber-like materials. These features are also an indication of stick–slip failure due to high plastic deformation. Besides, there are no features of phase separation of PVC and ENR due to incompatibility at any of the fracture surfaces studied using SEM.

Acknowledgement

The authors are grateful to the Department of Science and Technology, New Delhi for financially supporting this research programme.

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Received 4 July 1988
and accepted 4 January 1989