APPENDIX
LIST OF PUBLICATIONS

I. Papers published in International Journals

(a) Morphology, mechanical and viscoelastic behaviour of blends of nitrile rubber and ethylene-vinyl acetate copolymer.

(b) Tearing behaviour and recyclability of nitrile rubber/poly(ethylene-co-vinyl acetate) blends.

(c) Melt rheology and extrudate morphology of nitrile rubber and ethylene-vinyl acetate copolymer blends.

(d) Effect of blend ratio, crosslinking systems and fillers on the morphology, curing behaviour, mechanical properties and failure mode of acrylonitrile butadiene rubber and poly(ethylene-co-vinyl acetate) blends.

(e) Thermogravimetric analysis and thermal ageing of crosslinked nitrile rubber/poly(ethylene-co-vinyl acetate) blends.

(f) Transport properties of crosslinked acrylonitrile-butadiene rubber/poly(ethylene-co-vinyl acetate) blends.

(g) Dynamic mechanical and thermal analyses of acrylonitrile-butadiene rubber/poly(ethylene-co-vinyl acetate) blends.
2. **Papers presented in International/National Conferences**

(a) Dynamic mechanical analysis of nitrile rubber/ethylene-vinyl acetate copolymer blends.
   H. Varghese (81st Session of Indian Science Congress Association).

(b) Correlation of morphology with the mechanical properties of nitrile rubber/ethylene-vinyl acetate copolymer blends.

(c) Viscoelastic behaviour of crosslinked nitrile rubber/poly(ethylene-co-vinyl acetate) blends

3. **Conferences attended**

(a) Professor Sankarlal Memorial National Seminar, IIT, Kharagpur, Jan. 29, 1993.

(b) 81st Session of Indian Science Congress Association, Rajasthan University, Jaipur, Jan. 3-8, 1994.

(c) Sixth Kerala Science Congress, Thiruvananthapuram, Jan. 27-29, 1994.

(d) Seventh Kerala Science Congress, Palakkad, Jan. 27-29, 1995.


(f) Eighth Kerala Science Congress, Kochi, Jan. 27-29, 1996.

(g) MACRO '98, IUPAC International Seminar on Polymers, CLRI, Chennai, Jan. 5-9, 1998.
CURRICULUM VITAE

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(i) Polymer blends: Characterisation and properties.

(ii) Interpenetrating networks: Latex IPNs and characterisation.

(iii) Polymer composites: Fabrication and properties-polymer fibre interface adhesion, fibre surface modification and characterisation, transcrystallisation.

(iv) Transport process through polymers, its kinetics and thermodynamics.
MORPHOLOGY, MECHANICAL AND VISCOELASTIC BEHAVIOUR OF BLENDS OF NITRILE RUBBER AND ETHYLENE–VINYL ACETATE COPOLYMER

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Abstract—Nitrile rubber/ethylene–vinyl acetate copolymer (NBR/EVA) blends with different ratios were prepared by using a two roll mixing mill. The morphology of the blends was studied using optical and electron microscopies. The morphology of the blends indicated a two phase structure in which the minor phase is dispersed as domains in the major continuous phase. However, between 40 and 50 wt% of NBR content both NBR and EVA exist as continuous phases and generate a co-continuous morphology. The viscoelastic properties have been determined using a Rheovibron Viscoelastometer at 35 Hz over a wide range of temperatures. The effect of blend ratio on the mechanical properties such as tensile strength, elongation at break, stress–strain behavior and hardness has been investigated. The mechanical properties increase with the increase of EVA content in the blend. Attempts have been made to correlate the variation of properties with morphology of the blend. Various composite models have been used to fit experimental mechanical and viscoelastic data.

INTRODUCTION

The scientific and commercial progress in the area of polymer blends during the past two decades has been tremendous and was driven by the realizations that new molecules are not always required to meet needs for new materials and that blending can be implemented more rapidly and economically than the development of new chemistry [1]. Extensive studies have been carried out in the area of polymer blends. The blends of poly(methyl methacrylate), poly(ethyl methacrylate) and poly(vinyl acetate) with poly(vinylidene fluoride), polycarbonate/poly(e-caprolactone), polyethylene terephthalate/polycarbonate etc. are reported by Paul and coworkers [2–6]. Blends of poly(methyl methacrylate)/poly(styrene-co-acrylonitrile), poly(e-caprolactone)/poly(styrene-co-acrylonitrile), polystyrene/poly(vinyl methyl ether), isotactic polypropylene/ethylene–propylene rubber, natural rubber/low density polyethylene and 1,2-polybutadiene/natural rubber are also reported [7–12].

Nitrile rubber compounds (NBR) have excellent oil resistance, abrasion resistance and mechanical properties but poor ozone resistance. The oil resistance of nitrile rubber is due to the polarity of the acrylonitrile group. Nitrile rubber is highly resistant to non-polar oils and solvents. Ethylene–vinyl acetate copolymers (EVA) are random structured polymers which offer excellent ozone resistance, weather resistance and mechanical properties [13]. Several polymers have been blended with EVA and NBR to make high performance materials. The blends of EVA/silicone rubber have unique heat shrinkable characteristics, good mechanical properties and lower cost [14]. Several other blends based on EVA are also reported [15–21]. A flame resistant conveyor belting was developed from NBR/PVC blends [22]. Blends of NBR/EPDM show better oil swelling resistance [23]. Hot oil resistant blends of NBR with polyethylene and polypropylene have been developed by Coran and Patel [24]. Blending of nitrile rubber with EVA leads to a new class of materials having excellent oil resistance, ozone resistance and mechanical properties. However, no attempt has been made so far to develop blends of nitrile rubber and EVA. Recently, Thomas and coworkers have developed blends of EVA with polypropylene and natural rubber. Miscibility, morphology, crystallization, mechanical properties and aging behaviour of these blends have been studied in detail [25–31]. Blends of NR/EVA have been successfully used for the manufacture of microcellular foams [13].

A blend morphology wherein one component is dispersed within a continuum of the other has received great attention in the literature. It has been reported that the properties of polymer blends are strongly influenced by the morphology of the system [32, 33]. Baer [33] found mechanical and dynamic properties to be dependent mainly on particle size, independent of the processing methods used. The mechanism of toughening was correlated with particle size and size distribution by Ricq et al. [34]. Cimmino et al. [35] have related the mechanical properties of binary polyamide 6/rubber blends with the blend morphology. By the characterization of

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blend morphology. Yang et al. [36] analysed the compatibility of polypropylene with ethylene-propylene diene rubber, polybutadiene rubber and styrene–butadiene rubber. A 70:30 blend of NBR/PP shows a co-continuous morphology. The co-continuity exhibited in this blend composition is due to the high volume fraction of NBR and low viscosity of PP compared to the other component [37]. Transmission electron microscopy was employed to identify the morphology of the poly(styrene-b-isoprene) diblock copolymer/poly(styrene-homopolymer blend and it was found that the morphology generated depends on the magnitude of diblock copolymer molecular weight [38]. The impact behaviour observed for iPP/EP-55 and iPP/EP-88 blend samples is explained in terms of the different mode and state of dispersion of the two copolymers in the isotactic polypropylene (iPP) matrix [39]. Scanning electron microscopy is used to study the change in morphology of NBR/HDPE blends during the time of extrusion [40].

Miscibility and phase behaviour of polymer blends are of crucial importance in many applications. Miscibility in polymer blends can easily be investigated by dynamic mechanical analysis in terms of changes in $T_g$ (glass transition temperature) of the components of the blend. Miscible blends will have a single and sharp glass transition temperature intermediate between those of the individual polymers. In the case of borderline miscibility broadening of the transition will occur whereas two separate transitions between those of the constituents may result in the case of complete immiscibility [41]. One of the main disadvantages of EVA based blends is the low maximum service temperature which is dependent on the crystalline melting point of EVA. Cyclic stressing during service generates heat and hence the study of viscoelastic behaviour of these blends become important.

In this paper we report the results of our studies on morphology, mechanical and viscoelastic properties of nitrile rubber/ethylene-vinyl acetate copolymer (NBR/EVA) blends. More specifically the influence of composition on morphology, mechanical properties and viscoelastic behaviour has been analysed. Morphology of the blends has been related to the properties. Various models such as parallel model, series model and Halpin-Tsai equation have been used to fit the experimental mechanical and viscoelastic data.

**EXPERIMENTAL**

**Materials used**

NBR (Aparone N-553NS) having 34% bound acrylonitrile content was supplied gratis by Gujarat Apar Polymers Ltd, Bombay. EVA (Plene-1802) having 18% vinyl acetate content was procured from PIL, Madras. The basic characteristics of NBR and EVA are given in Table 1.

**Preparation of blends and test samples**

The blends of NBR/EVA were prepared on a two roll mixing mill having a friction ratio 1:1.4. The blends are designated as $N_x$ ($x = 0, 10...100$), where the value of $x$ indicates the weight percentage of NBR in the blend. Nitrile rubber and EVA were separately masticated for 2 min. The masticated rubbers were then mixed together. The total mixing time was 7 min in all cases. The sheeted out stock was compression moulded in an electrically heated press at 150°C for 2 min. No significant degradation of the materials has been occurred during processing techniques. The mould was specially designed in such a way that it could be cooled immediately after moulding, keeping the samples still under compression. The samples for tensile test, dynamic mechanical analysis were punched along the mill grain direction from the moulded sheet.

**Morphology studies**

Moulded samples of the blend were broken after freezing the samples using liquid nitrogen. This was done to avoid any possible deformation of the phases. For studying the morphology of the blends NBR was preferentially extracted from EVA rich blends using toluene and EVA from NBR rich blends using CCl$_4$. From the 50/50 blend NBR was extracted. The microtomed edge of the sample was kept immersed in the solvent for about 48 hr at ambient temperature for the preferential extraction of one of the phases. The samples were then dried in an air oven at 40 ± 1°C for 24 hr. The dried samples were then preserved in a desiccator for SEM studies. The solvent extracted samples were then sputter coated with Au/Pd alloy and SEM observations were made using JEOI-JSM-T330A SEM. Morphological studies were also carried out on thin films of these blends using optical microscope.

**Mechanical properties**

Tensile testing of the samples was done at 25 ± 2°C according to ASTM D-412-87 method using dumb bell shaped test pieces at a cross head speed of 500 mm/min.

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<th>Table 1: Details of materials used</th>
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<td><strong>Materials</strong></td>
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Fig. 1. Optical micrographs showing the blend morphology of different blend compositions: (a) N₁, (b) N₂, (c) N₃, (d) N₄, (e) N₅, (f) N₆, (g) N₇, (h) N₈, and (i) N₉.
The blend morphology is determined by the composition ratio and melt viscosity differences of the components. Continuity of a phase is favoured by high volume fraction and low viscosity relative to that of the other component.

The optical micrographs of the blends are shown in Fig. 1. In N_{10}, N_{30} and N_{50} [Fig. 1(a-c)], NBR is dispersed in the EVA matrix. Correspondingly in N_{50}, N_{70} and N_{90} [Fig. 1(i), (h) and (g)], EVA is the dispersed phase but with a larger domain size. This is due to the clustering of EVA domains as reported in the case of NR/EVA blends [13]. Occurrence of coalescence at higher concentrations of one of the components has been reported by many authors [32, 43-45]. In the case of polyethylene/polystyrene blends, the increase in domain dimension of PE at its higher concentration is caused by coalescence [43]. Thomas et al. [16, 44] have reported similar

**Fig. 3. Effect of blend composition on the dispersed particle size.**

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phenomenon in the case of hytrel/PVC and EVA/PP blends. In N₀, N₁ and N₂ [Fig. 1(d-f)] both the phases exist as continuous phases. The elongated nature of the dispersed particles in N₀ is also observed in scanning electron micrograph. The SEM of some blend compositions are given in Fig. 2. In N₆₀ and N₈₀ [Fig. 2(a and c)] the minor NBR component is dispersed within a continuum of the major EVA component. N₆₀ [Fig. 2(b)] is showing a co-continuous morphology where both the components are continuous. The average particle size vs blend composition is shown in Fig. 3. In the blends with high EVA content, NBR is the dispersed phase and the average particle size of the dispersed domains increase with the increase in NBR content. In the NBR rich blends the average particle size of the dispersed EVA domains increase with the increase in EVA content. The increase in domain size of EVA or NBR with increasing proportion of that component is associated with the coalescence or recombination of the domains [13, 32, 43-45]. Between 40 and 60 wt% of NBR a co-continuous morphology is exhibited. The particle size distribution curve (Fig. 4) is drawn by measuring the size of 100 particles from the optical micrographs. N₀ is having a broader distribution curve than N₁₀ which is as a result of the clustering of EVA particles.

Mechanical properties

The stress–strain curves of the samples are shown in Fig. 5. The differences in deformation characteristics of homopolymers and blends under an applied load are evident from the stress–strain curves. Pure

![Graph](image_url)
EVA and EVA rich blends show higher initial modulus with a yield point. At higher strains these blends show a gradual increase in stress which can be attributed to the orientation of the polyethylene crystalline hard segments of EVA, the continuous phase, in the direction of applied stress. The stress-strain curves of pure EVA and high EVA blends have distinct elastic and inelastic regions. In the inelastic region, the samples undergo yielding and strain induced crystallization. The stress-strain curve of NBR (N, EVA) is the typical one for uncrosslinked rubbers. If the blends N, and N, where NBR is the continuous phase a similar stress-strain behaviour as that of NBR is obtained. N, with a co-continuous morphology shows a stress-strain behaviour which is intermediate between those of the other blend compositions.

In Fig. 6 Young's modulus and modulus at 100% elongation are plotted as function of blend composition. Young's modulus of the blends increase with EVA content. The increase in modulus at 100% elongation is less marked at the extreme ends of the curve compared to the middle portion. Elongation at break, tensile strength and hardness increase with the weight percentage of EVA (Figs 7 and 8). In all these
Morphology, mechanical and viscoelastic behaviour

curves the properties increase more sharply when the EVA content is more than 40%. This is due to the fact that when the weight percentage of EVA is more than 40%, it tends to become the continuous phase. The mechanical properties of these blends are given in Table 2.

Viscoelastic properties

Figure 9 shows the loss tangent (tan δ) values of the blends and homopolymers as a function of temperature. Nitrile rubber and EVA show the glass transitions at -10°C, i.e. glass transition temperatures of both the polymers are same. In the case of blends there is a single, sharp transition which shifts slightly towards the lower temperature region with blend ratio. However, miscibility cannot be ascertained by the Tg measurements since the glass transition of both the components are at the same temperature. The peak width at half height of the tan δ curve is measured and given in Table 3. It is seen that the peak widths of the blends take intermediate values between those of the pure components, i.e. some variations in broadening of the glass transition zone with respect to blend composition. The relative peak width of tan δ curve against blend composition is plotted in Fig. 10. The curve shows positive and negative deviation depending on the composition. A similar variation is reported by Varghese et al. [46] for miscible blends from plasticized poly(vinyl chloride) and epoxidized natural rubber. This indicates some marginal level of compatibility in some of the blend compositions. Figure 11 is a graph showing the variation of tan δ, with the weight percentage of NBR. It can be noticed that the damping properties of the blends increase with increasing nitrile rubber content. The tan δ, values show a regular increase up to 50% of NBR followed by a sharp increase at higher content of NBR. This is due to the fact that
there occurs a phase inversion in the morphology of the blend from $N_{50}$ onwards. This is clearly evident from the SEMs.

The influence on temperature on the storage modulus of the samples is shown in Fig. 12. The curves for all the compositions have three distinct regions: a glassy region, a transition region and a rubbery region. Blends with higher proportions of NBR show higher values of storage modulus at lower temperatures (below $-20^\circ C$). But at higher temperatures the trend is reversed which is evident from the lower modulus of NBR rich samples. Interestingly all the curves intersect around the glass transition region of the blends. At higher temperatures (above $T_g$) NBR changes from glassy state to amorphous state. Also on increasing the NBR content the crystallinity is reduced. Therefore the modulus of NBR rich blends decrease at higher temperatures. A similar trend is reported in the case of miscible hytrel/PVC blends by Thomas et al. [44]. In the plot of loss modulus ($E''$) against temperature there is also a similar behaviour as in the case of storage modulus curve observed around the glass transition region (Fig. 13). Below glass transition region ($T < T_g$) NBR rich blends show higher values of loss modulus. As the temperature is increased and the EVA rich blends exhibit higher loss modulus. The $T_g$ values obtained from $E''$ vs temperature plots are always lower than those obtained from $\tan \delta_{\max}$ values (Table 3). The storage and loss modulus at $0^\circ C$ as a function of wt% of NBR is presented in Fig. 14. It is seen that both storage and loss moduli decrease with the increase of NBR content.

Reprocessability/degredation of the material

One of the important advantages of thermoplastic elastomer is their recyclability and reprocessability. The recyclability of the blends has been analysed by

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**Fig. 13.** Effect of temperature on the loss modulus of NBR/EVA blends.
Morphology, mechanical and viscoelastic behaviour

Fig. 14. Variation of storage and loss moduli with blend composition at 0°C.

Fig. 15. Applicability of various models on tensile strength of the blends.

Fig. 16. Applicability of various models on hardness of the blends.

Fig. 17. Applicability of various models on storage modulus of the blends at 10°C.
repeated moulding (four times) at 150°C. The properties of the recycled blends have been measured. It is interesting to note that the properties of the recycled blends remain constant. This indicates that there was no substantial degradation during processing of these blends. However, this is a subject of our future publication.

Model fitting

Applicability of various composite models such as the parallel model, series model and Halpin-Tsai equation (47, 48) have been examined to predict the mechanical and viscoelastic behaviour of these blends. The upper bound of modulus is given by the rule of mixtures

\[ M = M_1 \phi_1 + M_2 \phi_2 \]  

where \( M \) is the modulus of the blend, \( M_1 \) and \( M_2 \) are the moduli of the components 1 and 2 respectively, \( \phi_1 \) and \( \phi_2 \) are the volume fraction of the components 1 and 2 respectively. This equation is applicable for models in which the components are arranged parallel to the applied stress. The lower bound of the modulus holds in which the components are arranged in series with the applied stress and the equation is

\[ \frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2} \]

According to Halpin-Tsai equation

\[ M_1/M = (1 + A,B,\phi_2)/(1 - B,\phi_2) \]  

\[ B = (M_1/M_2 - 1)/(M_1/M_2 + A). \]

In the Halpin-Tsai equation subscripts 1 and 2 refer to the continuous and dispersed phase respectively. The constant \( A \) is defined by the morphology of the system. For elastomer domains dispersed in a continuous hard matrix, \( A = 0.66 \). The applicability of these models to mechanical and viscoelastic properties is presented in Figs 15-17. In all cases it is seen that the experimental data are close to the parallel model.

CONCLUSION

The morphology of NBR/EVA blends indicates a two phase structure in which the minor component is dispersed within a continuum of the major component. A co-continuous morphology was obtained when the NBR content was between 40-60%. The mechanical properties such as tensile strength, elongation at break and hardness increase with the increase in EVA content. The increase was sharper when the EVA content was more than 40% where it formed a continuous phase. The stress-strain curves of EVA rich blends have a similar behaviour as that of pure EVA. NBR rich blends as that of pure NBR and the 50/50 blend with a co-continuous morphology showed an intermediate stress-strain behaviour. The viscoelastic behaviour of these blends have been studied with special reference to the effects of blend ratio and temperature. At lower temperatures (below \( T_g \)) NBR rich blends showed higher values of storage moduli because of its glassy nature below glass transition temperature. But the trend is reversed at higher temperatures. This is due to the higher proportion of NBR in the blends which is in its amorphous state at higher temperatures (above \( T_g \)). The damping properties of the blends decreased with the increase of EVA content. The changes in dynamic properties could be related to the morphology of the system. All the blends showed a single glass transition temperature. However, miscibility of the system cannot be ascertained by this technique since the glass transition temperature of both the pure components are at the same temperature. Various theoretical models have been used to predict the mechanical and viscoelastic behaviour of these blends. It was found that the experimental results could be predicted by the parallel model.

Acknowledgements—The authors are grateful to Mr. Fidley T. Baby, Botany Department, CMS College, Kottayam for his assistance given for carrying out the optical analysis of the blends.

REFERENCES

Morphology, mechanical and viscoelastic behaviour

Tearing behavior and recyclability of nitrile rubber/poly(ethylene-co-vinyl acetate) blends

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Aims
Materials Letters is a fast publication journal on the science and technology of materials. The journal provides a rapid communication forum for scientists and engineers engaged in the field of ceramics, metals and alloys, composites and novel materials. The rapid publication of advances in these fields contributes to their further development and stimulates cross-fertilisation and interdisciplinary studies.

Scope
Contributions include, but are not restricted to, a variety of topics such as:

Materials:
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Novel materials:
Microstructures, nanostructures, thin films and fullerences.

Characterisation:
Analytical, microscopic, acoustic, optical, spectroscopic and diffraction.

Properties:
Mechanical, magnetic, optical, electrical, interfacial, phase transformational and transport.

Applications:
Structural, opto-electronic, magnetic, smart materials, ferroelectrics, novel semiconductors, environmental materials.

Processing:
Crystal growth, beam processing, sol-gel processing and deformation processing.

Synthesis:
High pressure, powder preparation, explosive forming, rapid quenching, extrusion and milling.

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Tearing behavior and recyclability of nitrile rubber/poly(ethylene-co-vinyl acetate) blends

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Abstract

The tear strength of nitrile rubber/poly(ethylene-co-vinyl acetate) (NBR/EVA) blends was measured as a function of blend composition in an Instron universal testing machine. An increase in tear strength was observed with increasing EVA content. The variation in this property was correlated with the microstructural morphology of the system. The tear failure mechanism of these blends as a function of blend composition was studied by examining the failure surfaces and the fracture patterns correlated with the strength and failure of these materials. Various models such as parallel model, series model and the Halpin-Tsai equation were used to fit the experimental tear strength values. In order to analyze the reprocessability of these blends, the blends were recycled up to three times and the mechanical properties were measured. It was found that the properties of the blends were little affected by recycling.

1. Introduction

Thermoplastic elastomers are a rapidly growing class of materials due to their improved properties, easy processability and economical advantages. These materials bridge the gap between conventional elastomers and thermoplastics by combining the excellent processing characteristics of thermoplastics at higher temperatures and the wide range of properties of elastomers at service temperature [1–3]. One of the main advantages of thermoplastic elastomers is their reprocessability.

A miscible thermoplastic elastomer blend from plasticized PVC/ENR was reported by Varughese et al. [4–6]. Thermoplastic elastomers find uses in a variety of applications. During service these materials may undergo tearing and hence a thorough understanding of the fracture mechanism is important to predict the service life of the products. Recently, Thomas et al. [7,8] reported on the tearing behavior of thermoplastic elastomers from isotactic polypropylene (iPP)/ethylene–vinyl acetate (EVA) and isotactic polypropylene (iPP)/nitrile rubber (NBR) blends.

In this paper we report on the tearing behavior of NBR/EVA blends with special reference to the effect of blend ratio. The tear properties were correlated with the morphology of the blend. The tear fractographs were examined using a scanning electron microscope. The recyclability of this system has also been analyzed.

2. Experimental

2.1. Materials used

Nitrile rubber (NBR) (Aparene N553 NS) was supplied gratis by Gujarat Apar Polymers Ltd., Bombay
Table 1
Details of the materials used

<table>
<thead>
<tr>
<th>Material</th>
<th>Characteristics</th>
<th>Source</th>
</tr>
</thead>
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<tr>
<td>nitrile rubber (Aparene N553 NS)</td>
<td>volatile matter (%) = 0.130</td>
<td>Gujarat Apar Polymers Ltd., Bombay</td>
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<tr>
<td></td>
<td>antioxidant (%) = 1.400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>organic acid (%) = 0.250</td>
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<td></td>
<td>soap (%) = 0.004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mooney viscosity (ML(1+4), 100°C) = 40.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>bound acrylonitrile (%) = 34.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>intrinsic viscosity (dl/g) = 1.527</td>
<td></td>
</tr>
<tr>
<td>poly(ethylene-co-vinyl acetate) (Pilene 1802)</td>
<td>melt flow index (g/10 min) = 2.000</td>
<td>PLL, Madras</td>
</tr>
<tr>
<td></td>
<td>density (g/cm³) = 0.937</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Viscous softening point (°C) = 59.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>vinyl acetate (%) = 18.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>intrinsic viscosity (dl/g) = 0.170</td>
<td></td>
</tr>
</tbody>
</table>

and poly(ethylene-co-vinyl acetate) [EVA (Pilene 1802)] was procured from PLL, Madras. The basic characteristics of the materials are given in Table 1.

2.2. Preparation of the blends and test samples

The blends of NBR/EVA were prepared on a two roll mixing mill having a friction ratio 1:1.4. The blends are designated as \( N_x \) (\( x = 0, 10, \ldots, 100 \)) where the value of \( x \) indicates the weight percentage of NBR in the blend. Nitrile rubber and poly(ethylene-co-vinyl acetate) were masticated separately for 2 min. The masticated materials were then mixed together. The total mixing time was 7 min in all cases. The sheeted out stock was compression molded in an electrically heated press at 150°C for 2 min. The mold was specially designed in such a way that it could be cooled immediately after molding while keeping the sample under compression. The samples for the tear and tensile tests were punched along the mill grain direction from the molded sheet.

2.3. Physical testing of the samples

The tear strength (load at failure/thickness) of the samples was determined using unnotched 90° angle test pieces at a cross head speed of 500 mm/min in an Instron universal testing machine (model 1121) according to ASTM D-624-81. To analyze the reprocessability, these blends were remolded up to 3 times at the same temperature (150°C) and the tensile measurements repeated. The tensile testing was done in accordance with ASTM D412-87 using dumbbell shaped test pieces at a cross head speed of 500 mm/min.

2.4. Scanning electron microscopy studies

For morphology studies, the NBR extracted samples of \( N_{10} \) and \( N_{50} \) (toluene was used for the preferential extraction of the NBR phase) and the EVA extracted sample of \( N_{70} \) (CCl₄ was used for the preferential extraction of the EVA phase) were sputter coated with gold. These samples were examined by SEM. The tear failure surfaces of \( N_0, N_{10}, N_{50}, N_{70} \) and \( N_{100} \) were examined by scanning electron microscopy.

3. Results and discussion

The properties of polymer blends depend on the blend composition, the mode of dispersion of one component within the other and the interactions at the interfaces. The morphology of NBR/EVA blends is shown in Fig. 1. In \( N_{10} \) blend, the minor NBR phase is dispersed in the major EVA phase and in \( N_{70} \), the minor EVA phase is dispersed in the major NBR phase. \( N_{50} \) is showing a continuous morphology.

Fig. 2 shows the tear strength of the blends as a function of composition. It is seen that the tear strength values increase with the weight percent (wt%) of EVA. The strength of NBR/EVA blends depends on the strength of EVA which in turn depends on the crystal-
Thus, the observed decrease in tear strength in NBR-rich blends may also be attributed to the decrease in crystallinity of the EVA phase. The NBR-rich region shows a negative deviation from the additivity line, i.e. there is a clear change in slope from 40 wt% of EVA onwards. This is due to the phase inversion in the morphology of the system [12]. Up to 30 wt% of EVA, NBR is the continuous phase and EVA the dispersed phase. From 40 to 60 wt% of EVA, both phases exist as continuous phases and thereafter EVA tends to become the continuous phase. The tear curves (load versus displacement) of the samples are given in Fig. 3. EVA tears at the highest load and at the smallest displacement as observed in Fig. 3. This indicates that EVA enhances the resistance to tearing of all samples. It is seen that the tearing force decreases and displacement increases with the decrease in EVA content. Thus, NBR with the lowest tear strength shows the highest displacement and lowest tearing force. The high displacement is due to the yielding of the rubber phase. To follow the tear failure proc-

Fig. 1. Scanning electron micrographs showing the microstructure morphology of (a) \( N_{10} \), (b) \( N_{20} \) and (c) \( N_{30} \).

Fig. 2. Variation of tear strength as a function of blend composition.
The average distance between the two adjacent sinusoidal foldings is approximately equal to 13 μm. The tear strength of the blends decreases with the addition of nitrile rubber. In N_90, the sinusoidal wavy pattern disappeared (Fig. 4b). It exhibits some fibrillar structure indicating a certain extent of plastic deformation. In N_60 the fibrillar structure diminishes and shows a relatively rough surface (Fig. 4c). The torn surface becomes somewhat smooth in the case of N_30 (Fig. 4d). The tear front of N_100 exhibits very smooth torn areas which is the characteristic feature of weak materials (Fig. 4e).

3.1. Model fitting

Applicability of various composite models such as the parallel model, series model and Halpin-Tsai equation [18] were examined to predict the tear strength of the blends. The upper bound of tear strength (parallel model) is given by the rule of mixtures,

\[ M = M_1\phi_1 + M_2\phi_2, \]

where \( M \) is the tear strength of the blends, \( M_1 \) and \( M_2 \) are the tear strengths of the components 1 and 2 respectively, \( \phi_1 \) and \( \phi_2 \) are the volume fractions of components 1 and 2 respectively. This equation is applicable for models in which the components are arranged parallel to the applied stress. The lower bound of the modulus (series model) holds for models in which the components are arranged in series with the applied stress and the equation is

\[ \frac{1}{M} = \frac{\phi_1}{M_1} + \frac{\phi_2}{M_2}. \]

According to the Halpin-Tsai equation

\[ M_1/M = (1 + AB_1\phi_2)/(1 - B_1\phi_2), \]

where \( B_1 \) is a constant defined as,

\[ B_1 = (M_1/M_2 - 1)/(M_1/M_2 + A_1). \]

In the Halpin-Tsai equation, subscripts 1 and 2 refer to the continuous and dispersed phases respectively. The constant \( A_1 \) is defined by the morphology of the system. For elastomer domains dispersed in a hard continuous matrix, \( A_1 = 0.66 \).

The applicability of these models to predict tear strength of NBR/EVA blends is shown in Fig. 5. It is
observed that the experimental data are close to the parallel model.

3.2. Reprocessability of the blends

One of the important advantages of thermoplastic elastomers over conventional elastomers is their reprocessability or recyclability. To study the recyclability, the blends were remolded (compression molded as described in Section 2) up to 3 times at 150°C and the properties such as tensile strength, elongation at break and modulus were measured. In compression molding, the shear is of low order (1–10 s⁻¹) and hence the effect of shear on the properties of NBR/EVA blends is negligible. The variation in properties against the
Fig. 5. Applicability of various models on tear strength of the blends.

Fig. 6. Effect of recycling on tensile strength of NBR/EVA blends.

Fig. 7. Effect of recycling on elongation at break of NBR/EVA blends.

Fig. 8. Effect of recycling on modulus at 100% elongation of NBR/EVA blends.
number of cycles is presented in Fig. 6–8. The tensile strength and elongation at break increase for the second cycle and thereafter remain constant. This is due to the homogeneity in mixing achieved during recycling. The modulus values remain constant in all the recycling process. These results suggest that the blends can be recycled and reprocessed several times without adversely affecting the properties.

4. Conclusion

The tearing behavior of NBR/EVA blends has been studied as a function of the blend ratio. It was observed that the tear strength of the blends increases with the increase in EVA content. The variation in property was related to the morphology of the system. The tear failure mechanism was investigated using scanning electron microscopic examination of the failure surfaces. The fracture patterns could be related to the strength and nature of the failure mode of these materials. The high tear strength of EVA was evidenced by the presence of sinusoidal foldings and striations. Various theoretical models were used to predict the tear strength of the blends and it was found that the parallel model fits the experimental results. The recyclability of the system was analyzed. Finally, it was interesting to note that the properties of the blends were little affected by the recycling process.

References

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