Structure and properties of rubber-toughened polyethylene-based blends

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The preparation, thermal behaviour, mechanical properties and morphology of a family of binary blends composed of components each containing ionic functionalities are examined. One component is a semicrystalline copolymer, metal-neutralized ethylene–methacrylate (M-EMA), and the other an elastomeric component, metal-neutralized sulphonated ethylene–propylene diene copolymer (M-SEPDM). These polymeric materials contain low levels of ionic groups ($\leqslant$10 mol%) which are capable of coulombically associating together into microphase-separated regions. These regions contain non-stoichiometric levels of ionic groups. A general characteristic of these blend systems is that the mechanical properties and morphology are directly influenced by the specific composition ratio of rubber to semicrystalline component. Without the associating units on one (or both) of the components, the resulting blends have grossly phase-separated components. The interfacial adhesion is weak, as indicated by poor tensile properties. The inter-relationship between structure and mechanical properties is discussed in terms of changes in the initial spherulitic morphology of the M-EMA component with the addition of increasing levels of the coulombically associating elastomeric component, M-SEPDM.

(Keywords: rubber–polyethylene blends; coulombic interactions; carboxylate–sulphonate interactions; small-angle light scattering; tensile properties)

INTRODUCTION

Over the past several decades, polymer blend technology has achieved an important position in the field of polymer science from both a scientific and technological viewpoint. With regard to binary component blends, a large number of possibilities exist in which either miscibility or immiscibility is observed. Superimposed on these myriad of possibilities is the likelihood that one or both of the components are crystalline.

Typically, blends with crystallizable components are generally heterogeneous below the melting temperature. In fact, as noted by Martuscelli[1], compatible blends within these systems would require the formation of mixed crystals in which both polymer chains would cocrystallize. Therefore, if miscibility would occur, it would occur in the amorphous phases since cocrystallization is an unlikely occurrence.

It was noted recently[1–15] that tough amorphous-type blends could be formed with the 'addition' of low levels of interacting functionalities. Ionic groups, especially transition-metal-neutralized sulphonate[14] or carboxylate[15] groups, are able to coordinate with a wide variety of bases, such as 4-vinylpyridine, contained within a separate copolymer structure. The initial thrust focused on the incorporation of rubbery materials into an amorphous, brittle matrix. The physical properties, especially toughness, were dramatically enhanced through these coordination-type interactions. More recently[15], a similar approach was utilized to enhance the properties of semicrystalline polymers, especially polyethylene. In both of the above-mentioned family of blends, interactions between otherwise immiscible components resulted in markedly improved properties. The level of functionality was typically less than 10 mol%, which is not sufficient to form completely miscible systems. As expected, the nature of the transition-metal counterion had a marked influence on the blend properties. Non-transition-metal counterions, such as sodium, form blend systems having poor properties closely approximating to those found in unfunctionalized, non-interacting blends.

The unblended metal-neutralized ionomeric materials previously described also have interesting solution and bulk properties. The incorporation of even very low levels of ionic groups profoundly influences properties through both intra- and inter-molecular associations. As noted by Eisenberg[16], it is now virtually indisputable that low-order aggregates and clusters exist in some form in the bulk state. The exact nature of the ion-rich regions, however, are still an object of considerable debate. It is certain that in ion-containing polymers with low ion concentration, the ionic groups aggregate as multiple ion pairs, which give the polymer properties similar to a crosslinked system. The junction points are due to physical interactions (and not to chemical bonding). Furthermore, a critical concentration is reached where the properties become dominated by ionic clusters or aggregates of multiplets.

In this work, solution blending was used to prepare semicrystalline blends containing an ionomeric polyethylene, specifically metal-neutralized ethylene–methacrylate copolymer, and an amorphous component, specifically metal-neutralized sulphonated ethylene–propylene diene rubber. Melt blending was also an effective blending technique. The present investigation was undertaken to study blend formation through the interaction of ion-containing copolymers. The ionically associating units are located on otherwise immiscible blend systems. In the blends described here, the ionomeric

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associations are purely coulombic in nature and not specific interactions as in blends formed through coordination-type complex[14] formation. We further seek to assess whether this is a general blending approach to form tough olefinic-based polymers. In this regard, the stress–strain behaviour is detailed over the entire composition range with and without coulombically interacting moieties.

EXPERIMENTAL

Materials and blending

The semicrystalline component of the blends were salts of ethylene–methacrylate (EMA), specifically the zinc and sodium salts. These copolymers were kindly supplied by the Allied Signal Corporation. Elemental analysis (oxygen) was used to determine the carboxylate content, i.e. ionic content. The nominal carboxylate levels were 4.6 and 2.9 mol% for the sodium (Na-EMA) and zinc (Zn-EMA) salts, respectively.

The elastomeric component was sulphonated ethylene–propylene–diene polymer (SEPDM), which can be neutralized with a large variety of metal counterions, but in this instance zinc is preferred. The material is identified as Zn-SEPDM (TP-319). This material was prepared by sulphonating an EPDM terpolymer of 90 000 weight-average molecular weight which contained 55 wt% ethylene, 40 wt% propylene and 5 wt% ethylidinenorbornene (ENB). The nominal sulphonation level is 20 meq/100 g of polymer (approx. 0.65 mol%) for TP-319. Neutralization was accomplished with zinc acetate. An excess of neutralization agent was used (200%) in order to ensure complete neutralization of all sulphonic acids present. The specific details relating to the sulphonation and neutralization procedures have been described by Makowski *et al.*[17].

The sodium salt was produced in a similar manner except neutralization was effected with the appropriate amount of sodium acetate.

The blends of metal-neutralized EMA with metal-neutralized SEPDM were prepared by dissolving each component (70°C) into 95/5 (weight percentage) xylene/methanol solution at 10.0 g dl^{-1}. Dissolution occurred within 24 h. The appropriate solution volumes were mixed in order to produce blends spanning a broad composition range. The mixtures were subsequently isolated through evaporation of the solvent mixture. The powders were further dried under vacuum at 120°C.

The powders were formed into final form via compression moulding into approximately 2″ × 2″ × 0.02″ (5 cm × 5 cm × 0.5 mm) pads by using the following conditions: 2 min preheat at 350°F (177°C), followed by a 3 min press cycle at 29 tons (350°F) and finally 4 min cooling to room temperature (again at 29 tons pressure). The appropriate size sample for the tensile testing measurements were cut from these pads.

The unassociated blend analogues, i.e. one component without interacting groups, were formed with unfunctionalized EPDM (Socabu 55) and the metal-neutralized polyethylene derivatives. These blends were prepared via the previously described solution blending of the two individual components and subsequent compression moulding. Pads could not be formed with greater than 50 wt% EPDM due to the very gummy characteristics of these particular blends.

Mechanical properties

Stress–strain properties were tested at room temperature with an Instron Tensile Tester Model 1222. Samples used were microdumbbells, which were cut with a die from the compression-moulded pads. A crosshead speed of 1.0 in (2.54 cm) min^{-1} was used in all the tensile measurements.

Differential scanning calorimetry (d.s.c.)

D.s.c. measurements were made with a Perkin–Elmer DSC-2 instrument. All measurements were made under nitrogen at a scanning rate of 10°C min^{-1}. The enthalpy of fusion was determined in the conventional manner.

Small-angle light scattering (SALS)

Light-scattering measurements were made by using a small-angle photographic light-scattering apparatus similar to that described by Stein and Rhodes[18]. Briefly, the instrument consists of a light source (Spectra Physics Model 155 He–Ne gas laser) operating at a wavelength of 635.8 nm, a rotatable polarizer on a Gaertner rotary filter holder, a fixed analyser and a photographic-film holder. The exposure time was regulated by a camera-type shutter. Typical exposure times ranged from 0.25 to 30 s. Longer exposure times were required with low ethylene–methacrylate levels. The SALS patterns were recorded on Polaroid film type 55. The sample–film distance was 9.75 cm and 14.0 cm for the sodium and zinc salt, respectively. The spherulitic size (if measurable in a particular blend composition) is obtained from the intensity maximum at an azimuthal angle of 45° in the H_v scattering pattern[18].

Polarized-light microscopy

Thin films of each blend were melt-pressed between glass slides and examined under crossed polars on a Nikon microscope. The morphological features were recorded on Polaroid film 667 at 40× magnification (exposure times ranged from 1 to 5 s).

RESULTS AND DISCUSSION

The current body of evidence[19–26] convincingly shows that the ionic functionalization in semicrystalline ionomers, specifically polyethylene-based copolymers containing low levels of ion-containing monomers, are located in the amorphous regions of the superstructure. The tight crystalline structure is unable to accommodate the relatively large ionic structures. In fact, as more ionic groups are introduced into the chain structure, the lower the degree of crystallinity becomes, i.e. the larger the amorphous character.

Extensive wide-angle X-ray scattering (WAXS) performed in this laboratory also shows that the crystalline structure of these polyethylene-based ionomers (Na and Zn salts) is identical to its unfunctionalized precursor. Similar WAXS results were obtained on all blends containing even low levels of the polyethylene ionomer. These X-ray results strongly suggest that the ionic groups in these materials also reside in the amorphous phase and, therefore, addition of non-crystallizable, incompatible macromolecules capable of interacting with these ionic groups will also reside in the amorphous phase with little or no effect on the crystal structure or the degree of crystallinity.

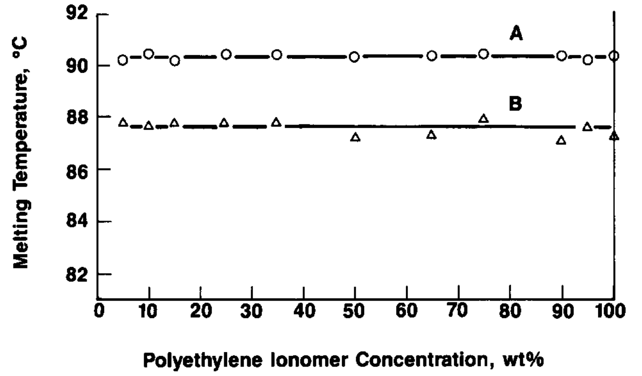


Figure 1 Melting temperature as a function of the M-EMA copolymer (○ and △ designate Zn and Na salts, respectively) content for blends spanning a broad composition range. The other component is an elastomeric copolymer, Zn-SEPDM

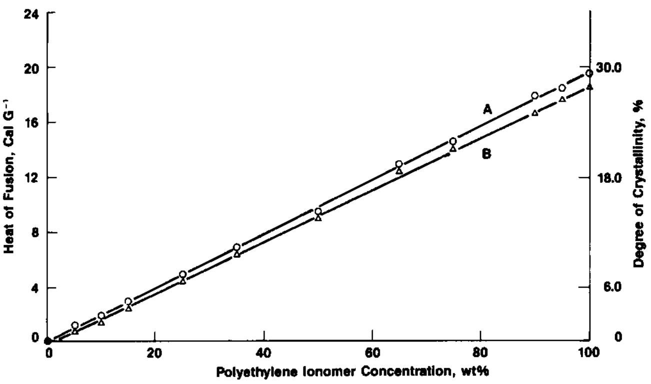


Figure 2 Heat of fusion (and the corresponding degree of crystallinity) as a function of the metal-neutralized (○ and △ designate Zn and Na salts, respectively) EMA copolymer content for blends spanning a broad composition range. The other component is Zn-SEPDM

D.s.c. measurements were made on all the blends produced for this study. The specific compositions and the detailed results are presented in *Figures 1* and *2*. An examination of these data clearly confirms that the degree of crystallinity and melting temperature remains invariant over the entire composition range. Minor variation is found in the behaviour due to the counterion structure. In some aspects these data closely follow the trends observed in semicrystalline blends formed through coordination-type interactions[15]. It is clear that these purely coulombic interactions do not perturb the lamellar structure.

It should be noted, however, that to a first approximation the properties of the amorphous phase in coulombically associating copolymers may closely parallel the properties of the previously detailed wholly amorphous blends.

It is quite likely, however, that the crystalline lamellae will impose structural restrictions which could be severe at high crystallinity levels. For example, in completely amorphous blends, the zinc counterion interacts with vinylpyridine in 1 : 1 ratio[14]. This may not be possible in semicrystalline blends due to the steric hindrance of the impenetrable crystallites. At present, the morphological details strongly indicate that the 1 : 1 relationship is still valid in these blends[15].

With regard to the purely coulombically interacting systems, the number of associating moieties is nonspecific with regard to stoichiometry and therefore these interactions can be used broadly in blending relatively large quantities of either blend component. A detailed investigation of semicrystalline blends formed via coordination-type bonding confirms that the morphology and physical properties begin to deteriorate rapidly at a stoichiometry greater than 1 : 1 with either component in excess.

A broader perspective of the blend morphology containing the zinc salt of EMA and Zn-SEPDM is presented in *Figure 3*. As compared to the highly demixed non-associating blends (not shown), this blend shows a significantly finer dispersion of the two blend components. It is noteworthy that the morphology does not become coarse at any composition as compared to blends based on stoichiometrically controlled interactions. It is readily apparent that the ionic microphase separation phenomenon is effective in blending these binary components. Furthermore, it is noted that identical micrographs are formed with Na-EMA/Zn-SEPDM blends.

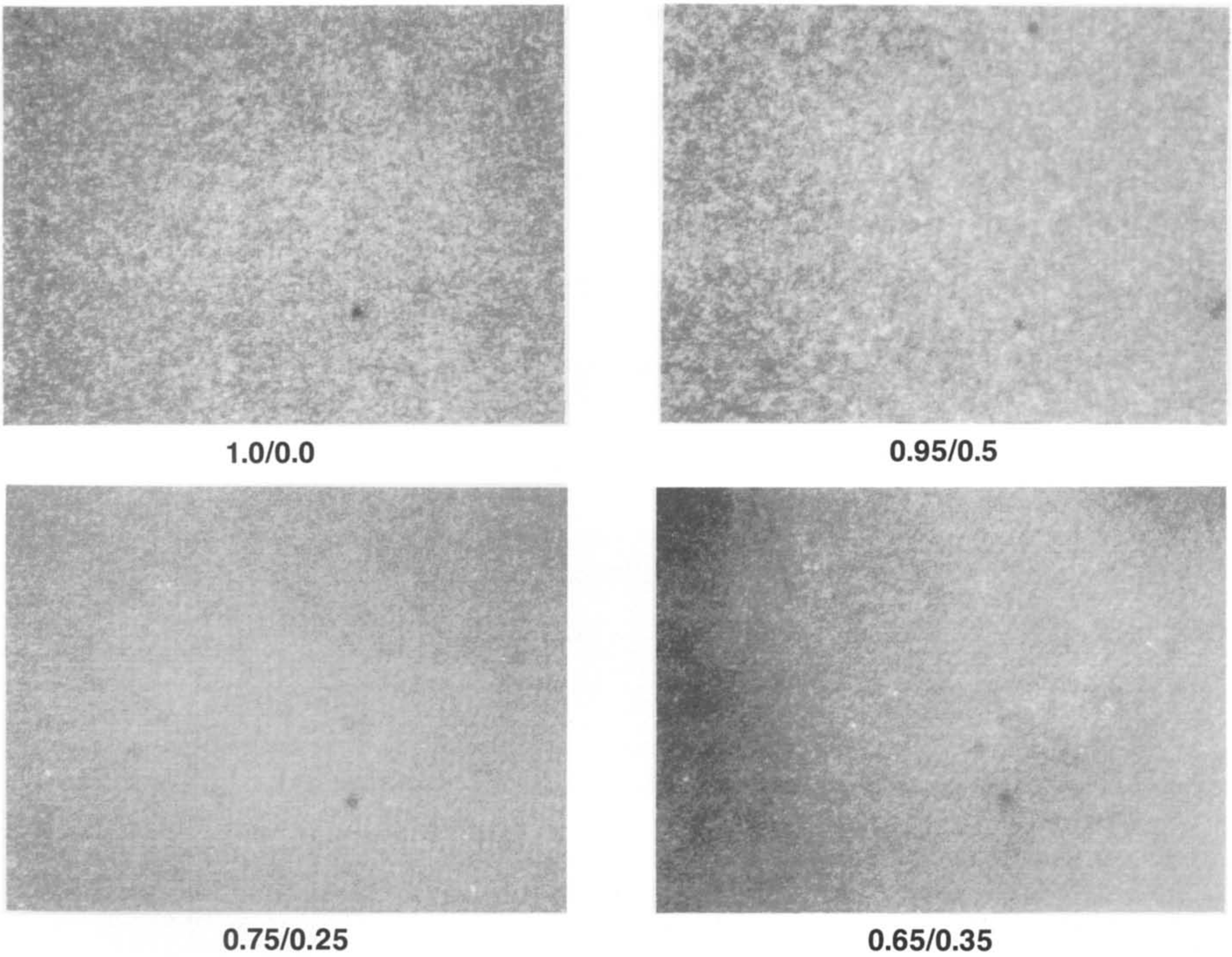
A number of morphologies from a binary blend with one crystallizable component are possible[27]. Crystals of the crystallizable component can be dispersed within the amorphous phase or, alternatively, spherulites (formed from the crystallizable component) may grow in the amorphous matrix. The amorphous component may be incorporated in the interlamellar space (i.e. amorphous phase) within the spherulite or, finally, the amorphous component could be dispersed in large domains within the spherulite structure.

In order to qualitatively examine the morphology, SALS measurements were made on each blend composition. The results are shown in *Figures 4* and *5* in which the H_v SALS patterns were recorded at a constant sample to detector distance.

The H_v polarization component is vertically polarized incident light and detection of the horizontally polarized scattered light. The theory of light scattering by crystalline polymers using a model approach was originally developed by Stein and coworkers[18,28–32]. A three-dimensional model of an isolated homogeneous anisotropic sphere with its optic axis fixed to the radius of the sphere, i.e. spherulite morphology, produces a four-leaf clover pattern (H_v scattering). This model precisely fits the results of unblended polyethylene ionomers. The only significant difference is the influence of counterion structure on spherulitic size, which for the Zn (*Figure 4*) and Na (*Figure 5*) salts are 3.6 and 4.6 μm, respectively.

In all blends reported, the H_v pattern has lobes at 45° to the polarization direction, which implies that the optic axis is oriented perpendicular or parallel to the spherulite radius. For the polyethylene-based blends under consideration, the former case is anticipated.

With increasing amounts of Zn-SEPDM, the spherulitic size decreases from 4.6 to 1.9 μm for Zn-EMA-type blends with the addition of 50 wt% Zn-SEPDM (*Figure 4*). A decrease of 1.5 μm occurs with the initial addition of 25 wt% Zn-SEPDM. A similar trend is observed in the Na-EMA based blends (*Figure 5*). Beyond these compositions, a rod-like aggregate morphology is noted, as indicated by the disappearance of the H_v scattering maximum at the 45° azimuthal angle. It is possible that in these blend compositions, i.e. 0.35/0.65 and 0.25/0.75 for Zn-EMA/Zn-SEPDM (*Figure 4*) and 0.65/0.35 and 0.5/0.5 for Na-EMA/Zn-SEPDM (*Figure 5*) mixtures, one is observing the remnants of spherulites which are now clusters of lamellae with correlated orientations.



1.0/0.0

0.95/0.5

0.75/0.25

0.65/0.35

Figure 3 Polarized light micrographs (40 ×) of the pure Zn-EMA copolymer (1.0/0.0) and several blends containing varying amounts of Zn-SEPDM

These patterns are characterized by a maximum intensity at the centre of the pattern and a steady intensity decrease along the 45° azimuthal angle in moving out from the centre[33]. It is worth noting that the rate of intensity fall-off with scattering angle increases with increasing rod length. Again, it is apparent that the optic axis remains invariant with composition.

With increasing amounts of the rubbery component, the patterns become even more diffuse and less azimuthally dependent. This is a characteristic of a greater degree of disorder[34]. With a still larger rubbery component, azimuthal dependence is completely eliminated, which may be explained by theories of random-orientation correlation[35], as arising from crystals randomly dispersed in an amorphous matrix, i.e. Zn-SEPDM. In the latter patterns, the markedly intense H_v scattering, as compared to V_v (parallel polarizers), confirms that the scattering arises predominantly from anisotropy or orientation fluctuations rather than density fluctuations. Therefore, the structure in this case can be viewed as a relatively uniform dispersion of anisotropic crystals dispersed in an amorphous, isotropic matrix. SALS clearly confirms the complete elimination of the spherulitic morphology with increasing Zn-SEPDM component concentrations. These results are in sharp contrast to coordination-type blends in which the stoichiometric ratio of interacting groups is important and the spherulitic morphology is preserved over essentially the entire composition range[15].

Finally, it is again important to note that the d.s.c. and WAXS data confirm that the purely coulombic interactions strongly influence morphology, but not the internal structure of the individual lamella.

The mechanical properties of these associating polyethylene–EPDM blends are reported in *Figures 6–8*. The modulus–composition relationship for both types of coulombically associating blends and their non-associating analogues are shown in *Figure 6*. A continuing increase in modulus is observed as the polyethylene ionomer component is increased. At approximately 90/10 composition, the modulus remains invariant with composition up to 100/0. It is noteworthy that the spherulite size also remains approximately constant in this composition range. This result can be attributed to the notion that the spherulite integrity is not grossly influenced by the initial modest additions of rubber into the interlamellar space within the spherulite itself. The data also show that the nature of the counterion has a negligible effect.

Representative tensile strength and elongation at break data are presented in *Figures 7* and *8*. Blends containing either the sodium or zinc salts show substantially enhanced properties over the entire composition range

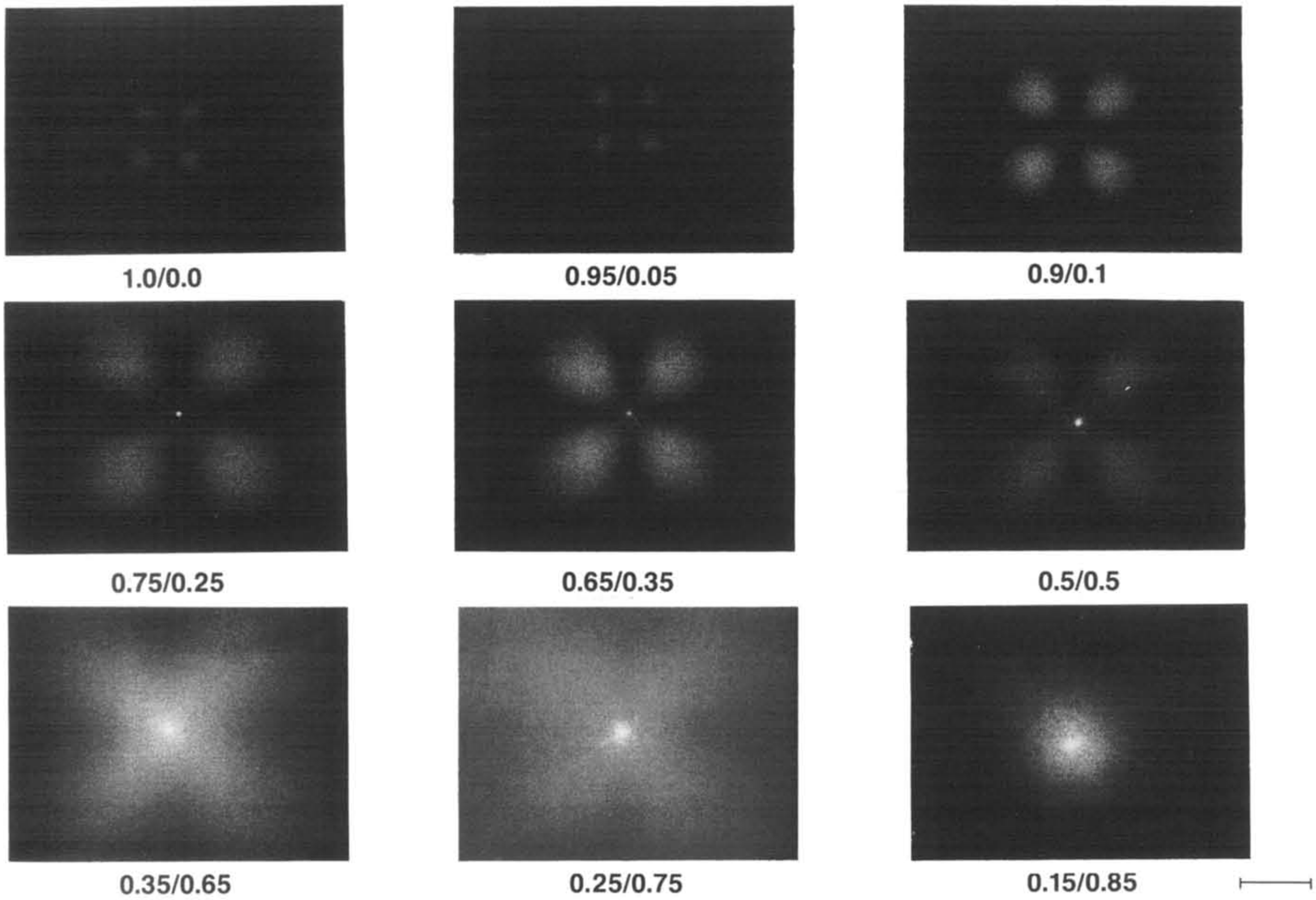


Figure 4 H_v light-scattering patterns obtained from blends containing various ratios of Zn-EMA copolymer and Zn-SEPDM

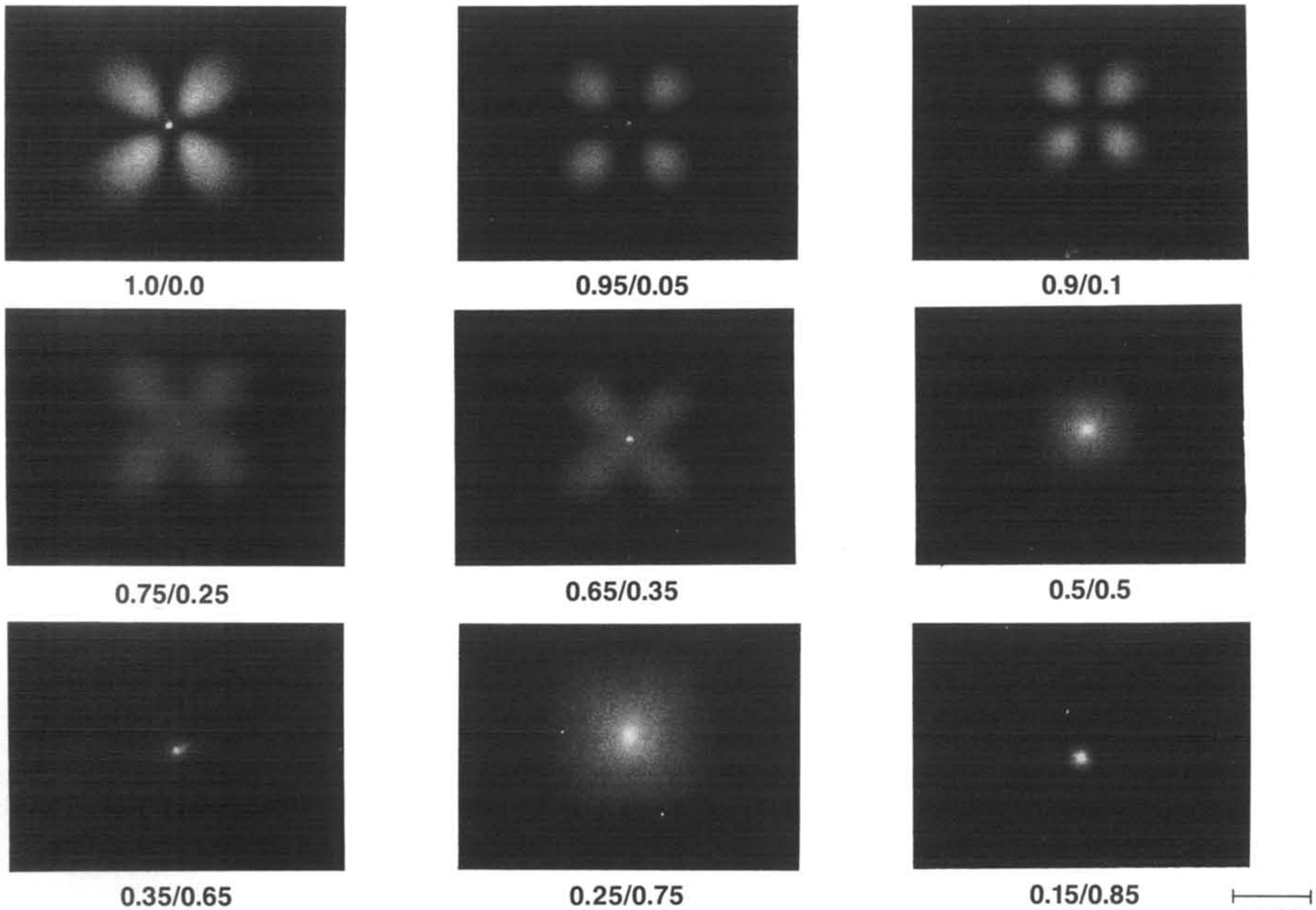


Figure 5 H_v light-scattering patterns obtained from blends containing various ratios of Na-EMA copolymer and Zn-SEPDM

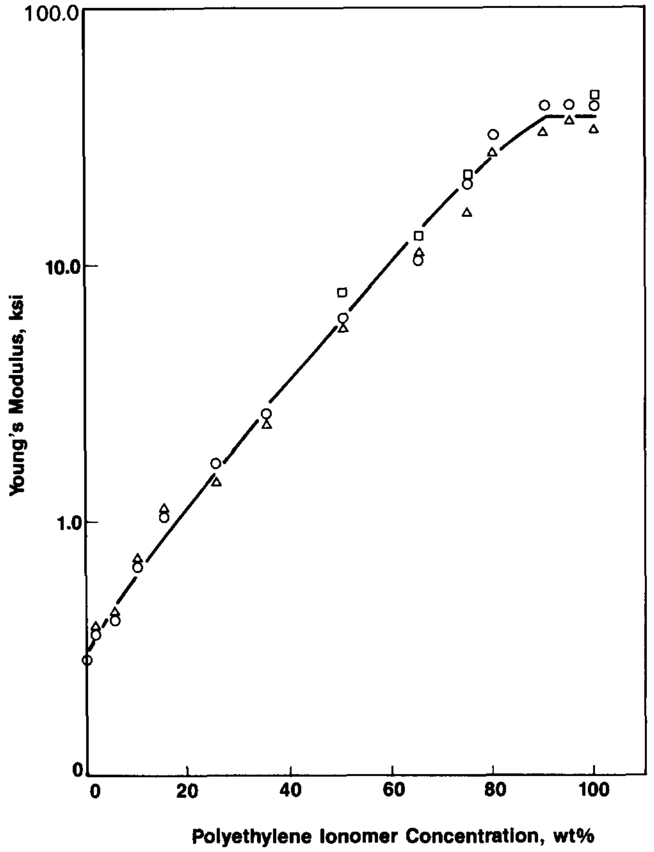


Figure 6 Young's modulus as a function of Na- and Zn-EMA copolymer content (○ and △ designate Zn and Na salt, respectively). Zn-SEPDM is the other component of the blend and □ denotes the binary mixture of unfunctionalized EPDM with Zn-EMA

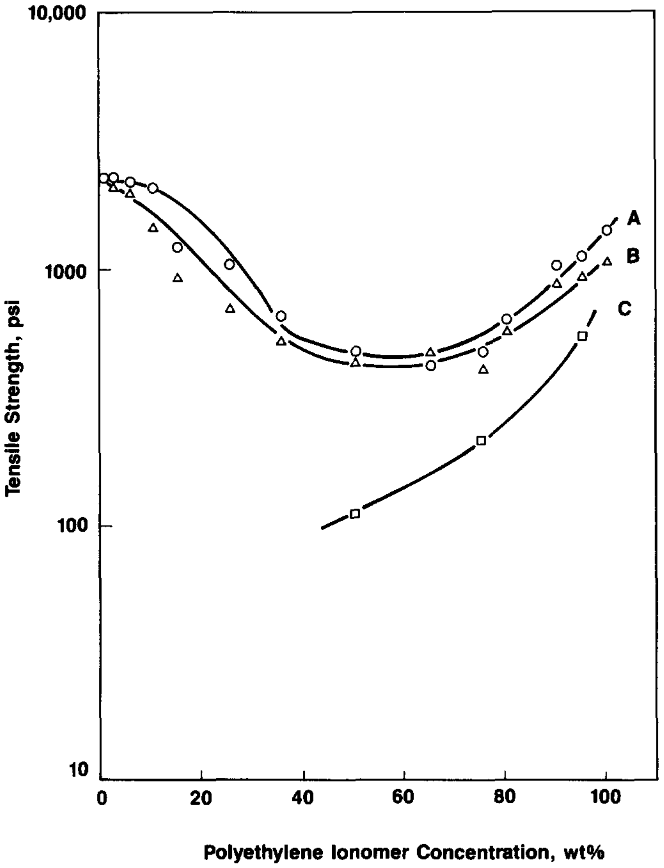


Figure 7 Tensile strength plotted against Na- and Zn-EMA copolymer content (○ and △ designate Zn and Na salt, respectively). Zn-SEPDM is the other component of the blend and □ denotes the binary mixture of unfunctionalized EPDM with Zn-EMA

as compared to the non-associating blend. The behaviour can be rationalized by the fact that the coulombic attractions between the metal-neutralized carboxylate and sulphonate groups are of sufficient magnitude to ensure good 'interfacial adhesion' between the otherwise phase-separated components. Poor 'interfacial' adhesion results when one component of the blend lacks even low levels of ionic functionality. This factor is certainly reflected in the substantially reduced properties, as noted in curve C of *Figures 7* and *8*. Furthermore, the data confirm that, to a first approximation, the blending of increasing levels of the associating elastomeric component reduces the tensile strength and elongation at break by a considerable amount. It is also noteworthy that the initial morphology appears to have an effect on these latter properties. A straightforward correlation is not apparent at present.

CONCLUSIONS

A distinguishing characteristic of these blend systems is that in the absence of coulombic-associating groups on either of the chains of these binary mixtures, poor mechanical properties result. If, however, even low levels of ionic functionality are present on both blend components, enhanced mechanical properties are observed over the entire composition range. This is due to the fact that good interfacial adhesion occurs through the microphase separation of the ionic units, even though the blends are still immiscible on a gross length scale. By comparing with rather similar blends that interact in a stoichiometric fashion (through transition-metal coordination chemistry), these latter microphase phase-separated regions can contain a number of ionic units. As a result, non-stoichiometric relationships are noted in both the tensile properties and morphology. In fact, the properties are continually modified over the complete composition range.

It should be noted that these binary blends can be distinguished from those blends in which one component is crystalline, but which exhibit a single compositionally dependent glass transition temperature and a compositionally dependent melting point. In these blends, the interacting groups are more numerous, typically one or more per monomer unit, as opposed to relatively low levels of interacting groups in the blends described in this work.

It should be further noted that there is broad interest in the mixing of elastomers with a large number of polymeric matrices (specifically polyolefin thermoplastics). The major thrust of this effort is to enhance the toughness of the latter materials. Typically, these binary blends are immiscible, but the structure-property relationships can be controlled through micro-rheological considerations[36], modification in the chemistry of the rubber component[37], use of block copolymers[38], grafted acidic and basic monomer units on each blend component[39], spinodal decomposition followed by crystallization[40], or grafting reactive functionalities on each blend component[41]. The approach described with regard to elastomer–semicrystalline-polymer blends is general and can be used effectively with a relatively large number

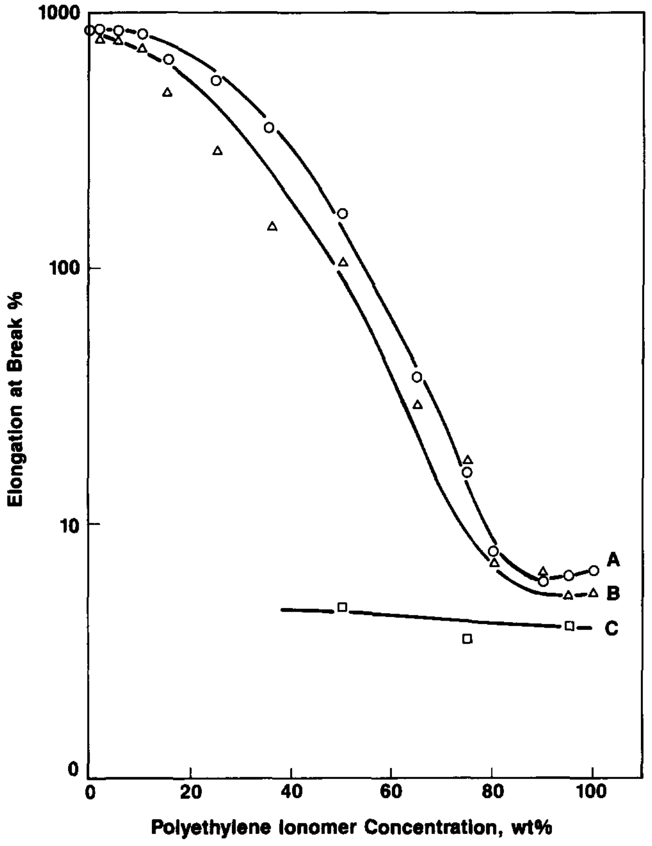


Figure 8 Elongation at break plotted against Na- and Zn-EMA copolymer content (○ and △ designate Zn and Na salt, respectively). Zn-SEPDM is the other component of the blend and □ denotes the binary mixture of unfunctionalized EPDM with Zn-EMA

of binary and multicomponent blends. Selected examples of general families of these coulombic-associating blends will be described in a number of future publications.

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