# IONOMER BLENDS: MORPHOLOGY AND MECHANICAL PROPERTIES

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**Abstract** – Polymer blends, having one component as an ionomer, can develop an interesting combination of mechanical properties. These properties give such blends some specific advantages as compared to non-ionic homopolymers. Primary attention is given to blends involving an ionomer and the ionomer precursor polymer. In such blends, synergistic effects can occur in several of the mechanical properties, such as modulus, strength and fracture energy. The enhanced mechanical properties, which occur for relatively low concentrations of the ionomer in the blends, are well above values predicted by the rule of mixtures. This behavior is attributed to the presence in the ionomer component of a higher chain entanglement density and to good adhesion between the dispersed ionomer particles and the polymer matrix. Some discussion, with examples, is also given of other blends having an ionomer as one component and of blends in which a small amount of ionomer is added in order to enhance the miscibility of two otherwise incompatible polymers.

Key words: Ionomer Blends, Tensile Properties, Toughness

## INTRODUCTION

For the last several decades, considerable research and development activity has been devoted to the subject of polymer blends; and various review articles dealing with this topic have appeared in the literature [Manson and Sperling, 1978; Paul and Newman, 1979; Utraki and Weiss, 1989; Utraki, 1991]. One reason for the great interest in polymer blends is the need to develop new materials with enhanced properties compared to those of existing homopolymers. For example, many different homopolymers can be given much higher impact strength by adding, and preferably grafting, an elastomeric component to the more rigid homopolymer. Two well-known examples are high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) [Bucknall, 1977; Kinloch and Young, 1983]. The enhancement in impact strength of the rubber modified polymers arises both from increased crazing and/or shear banding of the matrix polymer in the vicinity of the stress-concentrating, dispersed rubber-rich particles and from rubber particle cavitation. However, the increase in impact energy of these materials is generally accompanied by a reduction in other mechanical properties such as stiffness and strength.

Considerable attention and research have also been given to blends of one rigid polymer with a second rigid polymer [Utraki and Weiss, 1989; Utraki, 1991; Olabisi et al., 1983]. In most such blends, the component polymers are incompatible with each other due to the very low entropy of mixing high molecular weight chains. Hence two separate phases, each of which has its own glass transition temperature, exist. Nevertheless, a number of such rigid-rigid blends show only a single $T_g$ which, depending on the blend composition, lies somewhere between the respective $T_g$'s of the individual com-

ponents [Olabisi et al., 1979; Krause, 1972]. One well-known example of a miscible blend is that formed by blending polystyrene (PS) and poly(2,6 dimethyl phenylene oxide) (PPO). This rigid-rigid blend, over wide ranges of blend composition, gives enhanced values of elastic modulus [Kleimer et al., 1979] and of tensile strength [Yee, 1977]. Other types of miscible blends may also develop synergism in certain mechanical properties such as modulus and yield strength but generally other mechanical properties such as ductility and toughness, are reduced in value [Hara and Sauer, 1998]. This situation arises because the favorable specific interactions that lead the component polymers to be miscible with each other also restrict molecular and segmental motions and thus reduce elongation to fracture and fracture energy.

In incompatible, two-phase, rigid-rigid blends, it is sometimes possible to enhance both the elastic properties, like modulus and yield stress, and also ultimate properties, such as fracture energy. This situation arises, for example, in blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) [Kyu et al., 1991]. Other examples of incompatible blends showing enhancement in one or more mechanical properties, frequently extending over all blend compositions, are cited in a recent review article [Hara and Sauer, 1998].

In the present paper, our concern is primarily with binary polymer blends in which one of the two components is an ionomer, defined as a hydrocarbon type polymer in which a relatively small number (up to 15%) of the monomer units consist of ionic moieties. As compared to the base polymer from which the ionomer is synthesized, it has a unique microstructure, briefly described in a subsequent section, and is stronger and more resistant to fracture than the non-ionic homopolymer, as a result of the presence of ionic-type crosslinking. The intermolecular ionic interactions cause an increase in chain entanglement density of the polymer; and this increase in the number of chain entanglements, as has been pointed

out by Kramer and coworkers [Kramer and Berger, 1990; Creton et al., 1991], raises the stress required for crazing and increases the resistance of the polymer to fracture. The specific degree of enhancement in mechanical properties depends on many factors, such as ion content, type of counterion, thermal history and degree of neutralization. The effect of these varied factors on mechanical performance of ionomers has been illustrated and described in a recent article [Hara and Sauer, 1994].

Our primary interest is to explore the concept that polymer blends, in which one component is an ionomer and the second component is the ionomer precursor polymer, will provide new materials with enhanced mechanical properties [Bellinger et al., 1997]. The morphology of such ionomers, when the ionomer constitutes the minor phase, consists of small, dispersed ionomer particles imbedded in the non-ionic polymer matrix. In such blends, the interfacial adhesion, which is one of the more important factors governing the mechanical properties of blends [Olabisi et al., 1979], should be good, as most of the monomer units of both the ionomer and the ionomer precursor polymer are identical. Hence we can expect some favorable penetration and intermixing of chains at the interfaces between the two phases [Bellinger et al., 1997]. The presence in these blends of the stronger, more-entangled ionomer phase should also lead to reinforcement of mechanical properties. The extent to which these expectations are realized will be explored by discussion of results obtained on several different ionomer/ionomer precursor polymer systems.

## IONOMERS: MICROSTRUCTURE AND PROPERTIES

Since our interest is in polymer blends in which one of the components is an ionomer, it is important to know how the properties of the ionomer vary with its ion content and how they compare with the properties of the non-ionic homopolymer. First however it is necessary to briefly discuss the microstructure of the ionomer as this can have a strong effect on properties. There exists an extensive literature concerning the synthesis, morphology and properties of ionomers, so only a brief discussion is given here [Utraki and Weiss, 1989; Hara and Sauer, 1994; Eisenberg and King, 1977; Fitzgerald and Weiss, 1988]. We limit our discussion essentially to amorphous ionomers, like those based on PS and PMMA, as these ionomers have been used in studies of deformation modes and mechanical properties of blends of an ionomer with the ionomer precursor polymer. Also, the microstructure of partly crystalline ionomers, like those based on low density polyethylene (LDPE) or high density polyethylene (HDPE), is more complex as a crystalline phase is present in addition to the ionic aggregates of the amorphous phase. One result of this difference in microstructure is that, in the partly crystalline ionomers, the optimum mechanical properties are generally realized at about 30 to 50% conversion of the originally acid-type copolymer from which the ionomer is formed, whereas in the amorphous ionomers, complete conversion to the ionomer form generally leads to the best balance of properties.

The polar ionic groups of the ionomer tend to form aggregates, commonly referred to as multiplets and clusters. Multiplets are considered to consist of a small number of interacting ion pairs; while clusters, which are thought to arise from overlapping regions of restricted mobility surrounding multiplets [Eisenberg et al., 1990], are ion-rich regions that constitute a second phase. This phase has its own glass transition which occurs at a significantly higher temperature than that of the multiplet-containing matrix phase. Dynamic mechanical measurements show that two separate loss peaks (tan $\delta$), indicative of the two glass transitions, occur in the temperature region above the $T_g$ of the homopolymer. When the intensity or loss peak height, of each of these two peaks is plotted against ion content one obtains results such as those shown in Fig. 1 for sodium salt, sulfonated polystyrene (Na-SPS) ionomer [Hara et al., 1991].

The data of Fig. 1 indicate that, as the multiplet phase reduces in loss peak intensity (and in volume fraction), the cluster phase increases. Hence, at some critical ion content (about 6 mol % for this ionomer), the cluster phase begins to dominate over the multiplet-containing matrix phase. A similar value of the critical ion content has also been obtained for another PS-based ionomer, viz. poly(styrene-co-sodium methacrylate) [Ma et al., 1996]. But in a PMMA-based ionomer, probably as a result of a. higher dielectric constant and a greater degree of chain flexibility in PMMA as compared to PS, the critical ion content for cluster domination of the microstructure appears to be about 12 mol % [Ma et al., 1995].

As the ion content of ionomers is increased, their properties can differ significantly from those of the homopolymer. One dramatic change is the marked increase (-1 to 2 decades or more) in the value of the rubbery modulus in the temperature region above the glass transition temperature of the homopolymer. Another is a more modest, but significant, change in the value of the glassy modulus at ambient temperature. An example of this is shown in Fig. 2 for the Na-salt of a PMMA-based ionomer [Ma et al., 1995].

Ionomers may also exhibit new deformation modes, particularly when the ion content is near to, or above the crit-
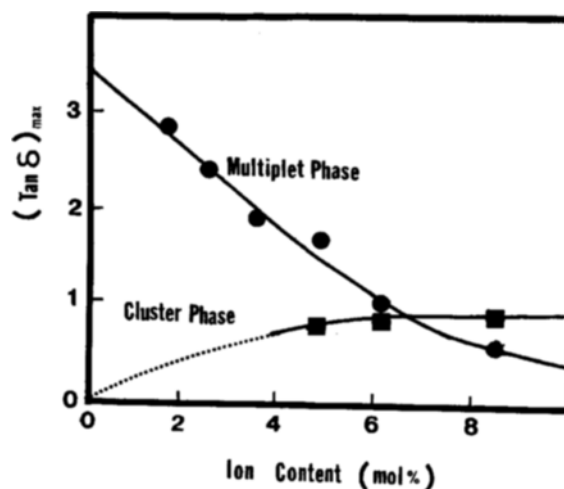


Fig. 1. Mechanical loss peak heights (tan $\delta)_{max}$ vs. ion content in Na-SPS ionomers [Data of Hara et al., 1991].
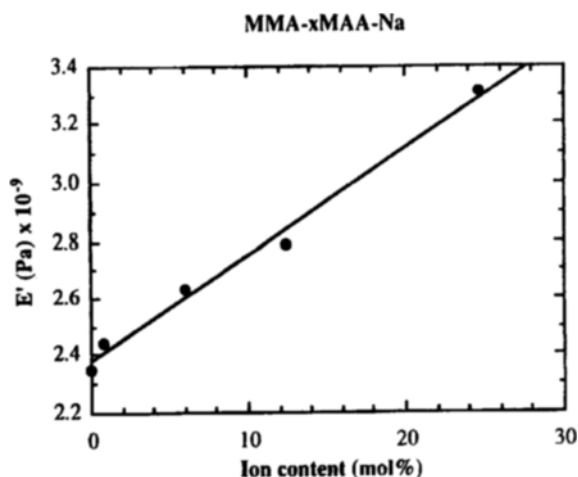
MMA-xMAA-Na



Fig. 2. Elastic modulus (30 °C) vs. ion content in the Na-salt of a PMMA-based ionomer [Data of Ma et al., 1995].

ical ion content. For example, at low ion contents below the critical value, the predominant deformation mode of glassy type ionomers is crazing; but as the ion content rises to or above the critical ion content, shear deformation competes with crazing and permits greater strains to occur prior to fracture. This type of behavior is illustrated in Fig. 3 which shows transmission electron micrographs (TEM scans) of strained thin films of poly(styrene-co-sodium methacrylate) ionomer [Ma et al., 1996]. For the sample with ion content below the critical value, Fig. 3a shows one of the typical crazes that have been produced in the tensile-strained thin films. Its morphology is similar to that of a craze in PS, with well-defined craze-bulk interfaces and with a central mid-rib section of higher fibril draw ratio. For the sample having an ion content above the critical value, Fig. 3b, the induced deformation shows both crazes and. interacting shear bands.

The development of shear deformation in strained thin films is an indication of a high chain entanglement density [Kramer and Berger, 1990]. This situation in ionomers arises from the presence of ionic-type crosslinking. The increased entanglement density raises the value of the craze stress and increases the resistance to fracture. As a. results in tensile test on macroscopic samples of Na-SPS ionomers having various ion contents, it was found that both the tensile strength and the energy to fracture increased significantly when the ion content approached and exceeded the critical value [Hara and Sauer, 1994; Hara et al., 1990]. In the range of ion contents from 6 to 8 mol %, the tensile strength increased by more than 50 % and the fracture energy or toughness, by about 80 %.

It may be concluded from this brief survey of the properties of ionomers that use of an ionomer in a polymer blend might well provide certain advantages. The ionomer is stronger and. tougher than the homopolymer, or copolymer, from which it is formed and, if the ion content is high enough to permit an appreciable fraction of the more chain entangled cluster phase to be present, shear modes of deformation may arise and restrict the growth and breakdown of crazes. Another possible advantage, depending on the nature of the second polymer component to which the ionomer is blended, is that
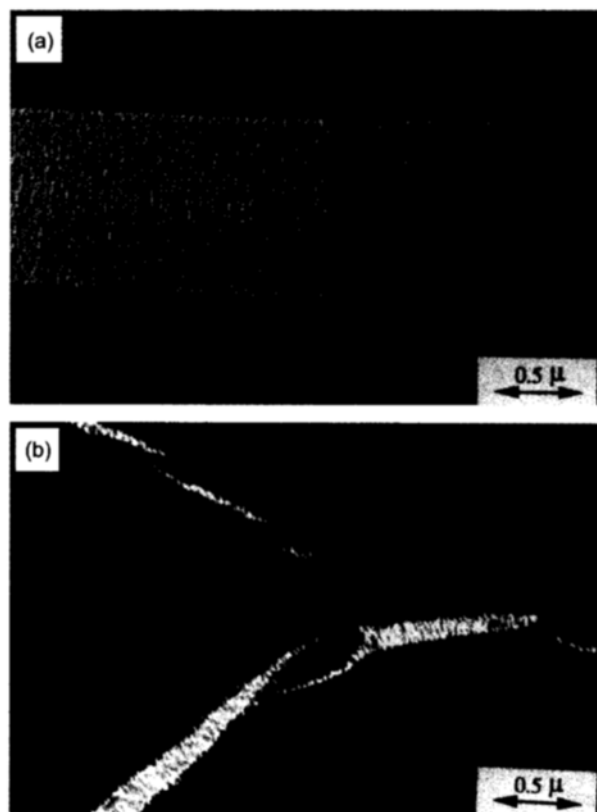


Fig. 3. Transmission electron micrographs of strained thin films of poly(styrene-co-sodium methacrylate) ionomer cast from THF [Ma et al., 1996].
(a) Ion content 4.8 mol %, (b) Ion content 8.2 mol %

the interfacial adhesion should be enhanced either by athermal interaction and intermixing of common chain segments or by interactions between the ionic groups of the ionomer phase and dipolar units of the other polymer component.

## IONOMER/IONOMER PRECURSOR POLYMER BLENDS

### 1. Morphology

Due to differences in polarity between an ionomer and the non-ionic homopolymer binary blends of these two polymers generally consist of two distinct phases. This is evident, for example, from the TEM micrograph of Fig. 4, which shows the 2-phase morphology of a cast film of a 5/95 blend of a PMMA-based ionomer and PMMA [Tsou, 1997]. The dark particles represent the ionomer phase which has. a higher electron density as a result of the presence of Na-metal counterions. Hence no staining agent is needed to bring out the morphological features. The ionomer is present as small spherical particles dispersed, in an essentially random manner, in the homopolymer matrix. The ionomer particles vary in size with the blend composition. For the 5/95 blend, there is a. range of sizes from about 0.2 μm to about 5 um, with an average particle size of about 2 μm. For a 10/90 blend, the average particle size increased to about 5 um and for a 30/70 blend to about 7 μm.

Fig. 4. TEM scan of a thin film, cast from DMF, of a 5/95 blend of PMMA ionomer (6 mol %)/PMMA [Tsou, 1997].



Fig. 5. Optical views of samples of PS, SPS ionomer, and two of their blends. All samples overlay grid lines [Bellinger, 1992].

An increase in size of the dispersed ionomer particles with increasing concentration of ionomer has also been noted in blends of SPS ionomer with PS [Hara et al., 1991]. In these blends, the morphology was examined over wider ranges of blend composition and, for a given composition over a series of different ion contents for the ionomer component. As the blend composition ratio rises above 30/70, the ionomer phase no longer exists as discrete, spherical particles. Instead, it was found that for a 50/50 composition involving a LI-SPS (4.95 mol %) ionomer, the ionomer was present as large, irregularly shaped domains. At still higher ionomer content, a phase inversion takes place and, when the ionomer is the predominant component, the morphology consists of PS particles imbedded in the ionomer matrix.

The influence of ion content of the ionomer component has been examined for Na-SPS ionomer/PS blends with a blend ratio of 30/70 [Hara et al., 1991]. For low ion contents (-1 mol %), the two components of the blend are essentially miscible as there is no evidence of phase separation in the TEM micrographs. With increase of ion content to 2-5 mol % or so, phase separation is evident. Upon further increase of the ion content of the ionomer component to 5.6 mol % and then to 7.45 mol %, it was noted that the size of the dispersed phase increased. Upon subjecting thin films of these blends to tensile stress, TEM examination showed that the larger size particles were more effective in inducing multiple crazes in the surrounding matrix and thereby increasing the total deformation prior to fracture.

One TEM observation, of importance to mechanical properties, is that in the ionomer/ionomer precursor polymer blends there is no evidence of debonding at the particle matrix interfaces. Hence the dispersed ionomer phase, though more rigid than the matrix polymer in view of its ionic type cross-linking and greater entanglement density, participates in the deformation process and shares in carrying the applied load. The good adhesion at the interfaces between the two phases is attributed to the fact that the majority of the chain units in both the ionomer and in the non-ionic homopolymer are identical. Hence there is considerable intermixing of chain
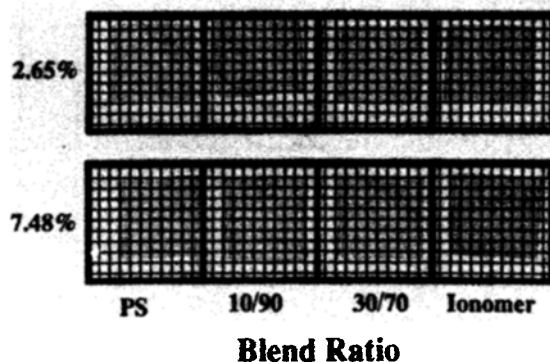
segments at interfaces.

Another interesting observation is that, although the size of the dispersed rigid ionomer particles is greater than the wavelength of light, the blends retain optical clarity. This is evident from Fig. 5 which shows visible grid lines underlying samples of PS, SPS ionomer, and blends of the ionomer and PS of two different blend ratios [Bellinger et al., 1992]. Optical clarity is also retained in PMMA ionomer/PMMA blends [Tsou et al., 1998]. The transparency of blend samples, in these rigid-rigid blends of an ionomer and the ionomer precursor polymer is due to the fact that, at the relatively low values of the ion content of the ionomer used in these blends, the refractive indices of the two blend components are similar.

The results obtained from study of strained thin films of these blends gives promise that there may be enhancement of the mechanical properties and of the resistance to fracture of bulk specimens. This possibility is explored by considering the results of tensile tests carried out on both SPS ionomer/PS blends and on PMMA ionomer/PMMA blends.

## 2. Mechanical Properties

The mechanical properties of interest in many applications are modulus, strength and fracture energy or toughness. New materials with enhanced resistance to impact loading and to fracture can be obtained by blending an elastomeric polymer with a rigid polymer but this is accomplished at the expense of a reduction in stiffness and strength. Also one can enhance the stiffness and possibly strength by blending a homopolymer with a more rigid polymer, or hard particles such as glass beads, but then a lower ductility or toughness results. This latter effect is usually caused by poor adhesion at the interfaces between the respective components. Therefore, in rigid-rigid polymer blends it is generally necessary to add a so-called compatibilizing agent, such as a block copolymer of the two components of the binary blend [Barlow and Paul, 1994]. The presence of the copolymer at the interface lowers the interfacial tension, raises the adhesion and leads to a finer dispersion.

However, in blends of an ionomer with the ionomer precursor polymer, TEM examination of strained thin films has shown that good adhesion already exists between the ionomer particles and the homopolymer matrix. This allows the ionomer particles that are involved with matrix crazes to change their shape from spherical to ellipsoidal and to share in carrying the applied stress. Hence, in such blends, some enhancement in mechanical properties is anticipated even without use of a compatibilizing agent. Hopefully, this enhancement will come in both modulus and strength, as the ionomer phase is stronger and stiffer than the matrix polymer, and also in resistance to fracture due to the higher strand entanglement density of the ionomer and to its good adherence to the non-ionic homopolymer.

The changes that take place upon blending an ionomer with the ionomer precursor polymer can be illustrated by comparison of the tensile stress-strain curves of the homopolymer and of the blends. Two typical stress-strain curves are shown in Fig. 6 for PS and for a 5/95 blend of PS and SPS ionomer [Bellinger, 1992]. Even though the blend possesses only 5 % by weight of the ionomer, it develops a. higher tensile strength and a greater fracture energy, or toughness, as measured by the area under the stress-strain curve. Another example, in this case over a. wider range of blend compositions, is shown in Fig. 7 which depicts comparative stress-strain curves for PMMA and for blends of PMMA with PMMA ionomer [Tsou, 1997]. With an increasing amount of ionomer in these blends, the modulus increases, the tensile strength rises and the strain to fracture and the fracture energy are enhanced.

The specific effects of blend composition on tensile strength are illustrated in Fig. 8 for SPS/PS blends [Bellinger, 1994] and on modulus in Fig. 9 for blends of PMMA ionomer/PMMA [Tsou et al., 1998]. The dotted lines, in these and subsequent graphs, indicate the behavior expected based on the rule of mixtures. It is evident from the data of Figs. 7 and 8 that both sets of blends display synergy, as the values of tensile strength and modulus of all the blends show a positive deviation from the rule of mixtures.
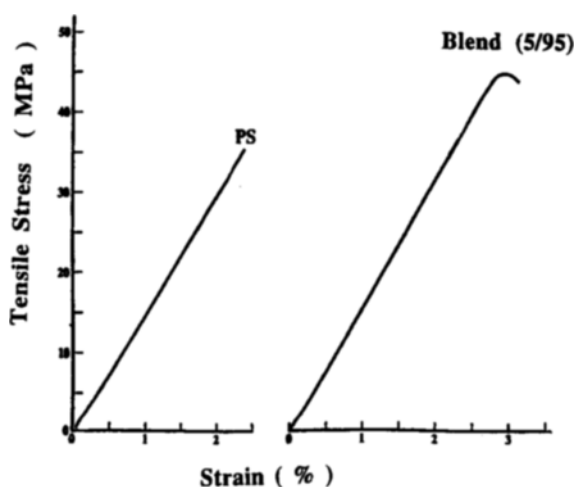


Fig. 6. Typical stress-strain curves of PS and a 5/95 blend of Na-SPS ionomer (5.26 mol %) and PS [Bellinger, 1992].
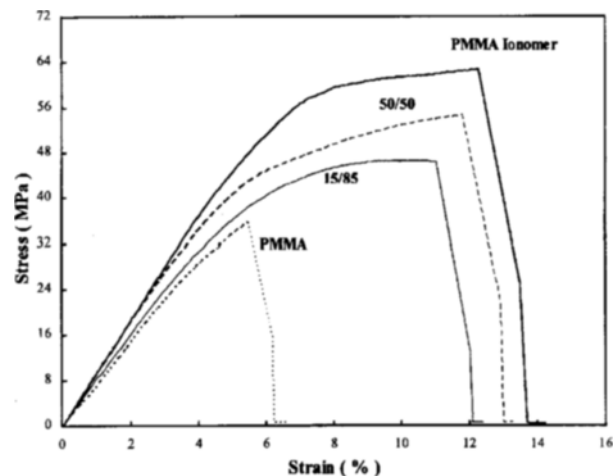


Fig. 7. Typical stress-strain curves of blends of Na-PMMA ionomer (6 mol %) and PMMA of different blend compositions [Tsou, 1997].
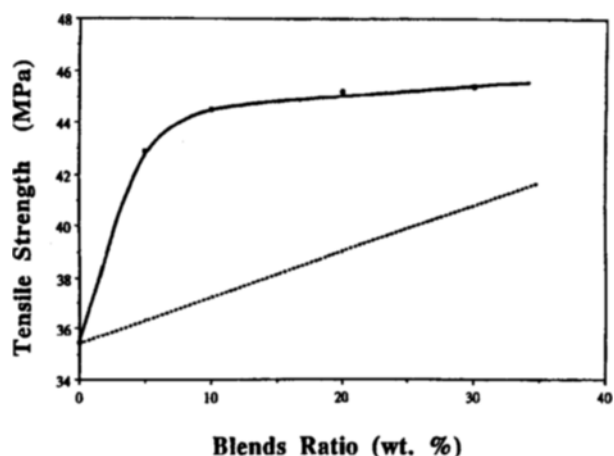


Fig. 8. Tensile strength vs. ionomer content for Na-SPS ionomer (5.26 mol %)/PS blends [Bellinger, 1994].

A positive deviation from the additivity rule is considered to arise as the result of some specific interaction between the components of the blend and it is an indication that some degree of miscibility exists even though the two components of the blend are basically incompatible and form two distinct phases [Hara and Sauer, 1998]. This condition arises, in both the SPS ionomer/PS blends and in the PMMA ionomer/PMMA blends, as a result of athermal intermixing of common molecular segments at the ionomer/matrix interfaces. Also the greater strand entanglement density and resistance to fracture of the ionomer phase aids in enhancing the strength and stiffness of the blends. In addition, in the PMMA ionomer/PMMA blends, favorable interactions may also exist between the ionic units of the ionomer and the dipolar units of the molecular chains and contribute to the observed synergism and enhancement of properties.

The strain to fracture and the fracture energy, as is evident from Figs. 6 and 7, also show enhanced values for ionomer/ionomer precursor polymer blends. When values of each property are plotted vs. ionomer content, they exhibit positive deviation from the rule of mixtures. For example, the fracture
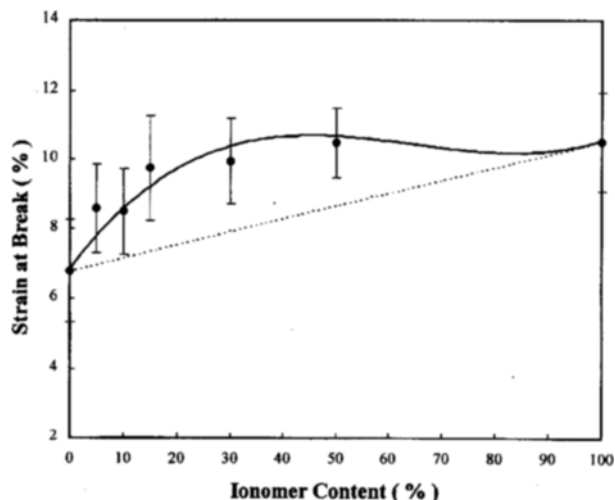
Fig. 9. Tensile modulus vs. ionomer content for Na-PMMA io-
nomers (6 mol %)/PMMA blends [Tsou et al., 1998].



Fig. 11. Fracture toughness, K$_{Ic}$, vs. ionomer content in blends
of PMMA ionomer (6 mol %) and PMMA [Tsou et
al., 1998].

energy, or toughness, of the SPS ionomer/PS blends varies
with blend composition in a similar manner to that shown for
tensile strength in Fig. 8 [Bellinger, 1994]. As another exam-
ple, the strain to fracture of PMMA ionomer/PMMA blends
also exhibit synergy, as indicated by the data shown in Fig.
10. The toughness of these blends behaves in similar manner
[Tsou, in publication]. Hence, synergistic effects, with specific
property values lying above those anticipated on the basis of
the additivity rule, appear to hold for all of the mechanical pro-
perties discussed so far.

Another mechanical property of importance in many appli-
cations is the so-called fracture toughness, K$_{Ic}$, which is the
value at fracture of the stress intensity factor, K, that can be
evaluated from tests on notched, and pre-cracked, specimens.
Materials may show high values of energy to fracture in sim-
ple tensile tests on unnotched specimens yet show poor per-
formance when the test samples contain sharp cracks. For-
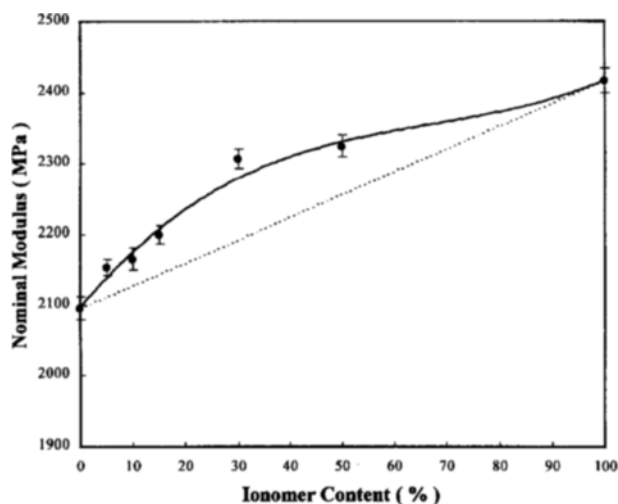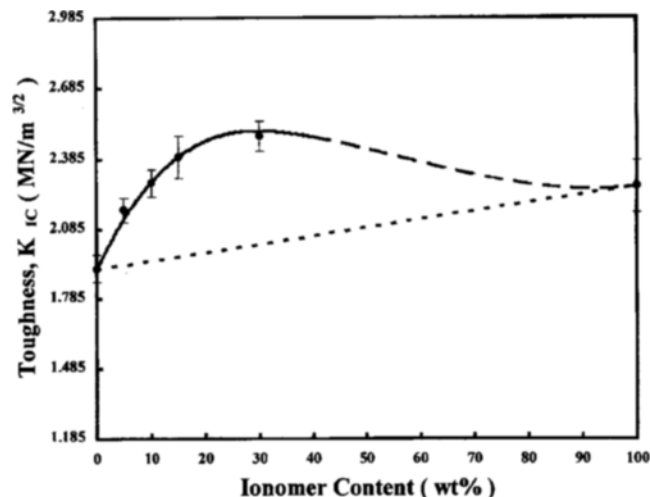tunately, values of K$_{Ic}$ have been determined as a function

of blend composition for one ionomer/ionomer precursor po-
lymer blend, viz. for PMMA ionomer/PMMA blends [Tsou
et al., 1998]. The results obtained are shown in Fig. 11. For
all blends tested, values of the fracture toughness exhibit po-
sitive deviation from the rule of mixtures. This beneficial ef
fect is attributed, in part, to good adhesion at the interfaces
between the two phases and to the presence of some degree
of miscibility between the components arising from their many
common chain units. Additional support for the presence of
favorable interactions between the components arises from
measurements of blend density. Here too, values obtained
for several different blend compositions were found to be high-
er than anticipated based on the additivity rule [Tsou, in pub-
lication].

In ionomer/ionomer precursor polymer blends, the micro-
structure of the ionomer plays a significant role. For example,
in blends of SPS ionomer/PS, data have been obtained on
the mechanical properties of blends possessing a relatively
low ion content of the ionomer phase and on blends having
ion contents near to and above the value of the critical ion
content. For ion contents of 2.65 mol % and above, syner-
gistic effects have been noted in strength and toughness for
all blend compositions investigated; but the best properties,
at any given blend ratio, were achieved when the ion con-
tent of the ionomer phase was above the critical value at
which the more heavily entangled cluster phase dominated
the morphology [Bellinger et al., 1994].

It may be concluded that blends of an ionomer with the
ionomer precursor polymer provide new materials with en-
hanced mechanical properties; and that even relatively small
addition of ionomer can lead to significant improvements in
properties such as strength, stiffness and resistance to fracture.
This conclusion, drawn from studies of amorphous glassy po-
lymers and their ionomers, apparently also applies to some
partially crystalline polymer blends. For example, in a recent
paper data have been presented concerning the mechanical
properties of blends of poly(ethylene-co-sodium methacrylate)
ionomer (Na-EMA) and low density polyethylene [Deanin and



Fig. 10. Fracture strain vs. ionomer content in blends of Na-
PMMA ionomer (6 mol %) and PMMA [Tsou, 1997].

Chu, 1997]. The data show that the elastic properties, modulus and yield stress, and the ultimate properties, tensile strength and fracture energy, all display synergy. Values of each property, for the three different blend composition studied, lie above the rule of mixture line. Also both the tensile strength and the strain to fracture of the Na-EMA/LDPE blends attained maximum values, higher than those for either component, at blend compositions close to 50/50. The enhanced properties imply some degree of miscibility between the components and good adhesion between the phases. Also, interpenetrating polymer networks, arising from ionic crosslinking and from crystalline domains, may play a significant role.

## OTHER IONOMER/POLYMER BLENDS

Various studies have been made of polymer blends in which the two components differ in chemical composition but in which one of the components has been converted to an ionomer. In many of these studies, emphasis has been placed on the influence of the ionic groups, and of the type of counterion present, on miscibility. Fewer studies have devoted attention to mechanical properties. In those that have, it is generally found that the presence of the ionic interactions enhances one or several properties of the blends but has an adverse reaction on other properties. Various examples illustrating these possible effects are presented and discussed in the following passages.

The tensile properties of blends of a slightly sulfonated polyacrylonitrile (S-PAN) and a polyurethane cationomer, containing soft segments of 600 molecular weight (PU-Cat) have been determined over a wide range of blend ratios [Oh et al., 1994]. The results obtained for tensile strength and modulus are shown in Fig. 12. For all blends, the modulus values fall slightly below values anticipated on the basis of simple additivity but the tensile strength values display synergy. They show a positive deviation from the rule of mixtures for all blends and a maximum value higher than that of either component, is attained at the 30/70 composition ratio. The synergistic increase in strength at this composition
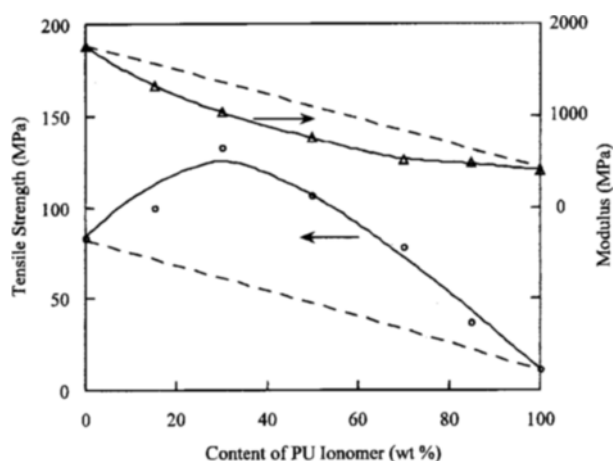
is a result of strong ionic interactions between the blend components, as, at this composition, the concentration of sulfonate anions in the S-PAN polymer is comparable to the concentration of cations in the PU ionomer.

In another study, it has been shown that the addition of a relatively small amount of an ionomer to a (50/50) blend of polypropylene (PP) and an ethylene-propylene-diene terpolymer (EPDM), can enhance both the modulus and the tensile strength [Kim et al., 1994]. The ionomer used was a 50 % neutralized (91/9) copolymer of ethylene-co-methacrylic acid (EMA) containing counterions of either Zn (Surlyn9520) or Na (Surlyn 8528). Fig. 13 illustrates the effect of the added Zn-EMA ionomer on the tensile strength and stiffness of the (50/50) PP/EPDM blends. As little as 5 wt% of the ionomer produces a slight increase in tensile strength and a significant increase (25 %) in modulus. Both properties also exhibited maximum values at this concentration in blends containing Na-EMA ionomer but values were not as high as for blends containing the doubly ionized Zn as the counterion. However, as frequently happens, when ionic interactions lead to an increase in stiffness, the elongation to fracture of the ionomer-modified blends decreased in value.

In one investigation, a wide variety of mechanical properties were reported for blends in which the major component was a polyamide, nylon 6 (N6) and the minor component was one of the following: low density polyethylene, chlorinated polyethylene, ethylene-acrylic acid copolymer and a Zn-EAA ionomer (Surlyn 9950) [Deanin et al., 1990]. A relatively small addition of any of these polymers led to an increase in impact strength but the best overall combination of properties was obtained for the N6/Zn-EAA blends. Some of the mechanical properties of these latter blends are shown as a function of ionomer content in Fig. 14. The yield stress $\sigma_y$ and the modulus E decrease with increasing ionomer concentration but the impact strength (I.S.) increases in an essentially linear manner, until at about 25 wt% of the ionomer it attains a value some 300 % higher than that of N6. The data show that the ionomer is an efficient impact modifier for the nylon polymer. For example, even at the low concentration



Fig. 12. Tensile strength and modulus vs. blend composition in blends of S-PAN and PU cationomer [data of Oh et al., 1994].
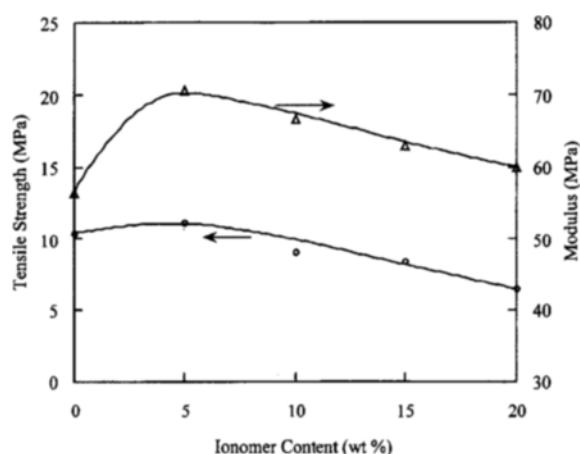


Fig. 13. Tensile strength and modulus vs. ionomer content in (50/50) PP/EPDM blends containing Zn-EMA ionomer [data of Kim et al., 1994].
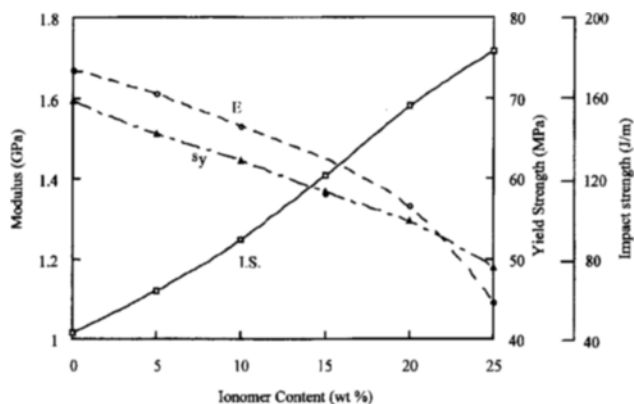
Fig. 14. Impact strength (I.S.), modulus (E) and tensile yield stress ($\sigma_y$) vs. ionomer content in blends of Zn-EAA ionomers/N6 [Data of Deanin et al., 1990]

of 10 wt% the impact strength rises over 100% while the reductions in modulus (-11%) and in tensile yield stress (-8 %) are relatively small. Evidently the reduction in crystallinity of the nylon, caused by the presence during melt mixing of the ionomer, more than outweighs any stiffening effect of ionic interactions.

The influence of ionic interactions on miscibility and on the Flory-Huggins interaction parameter, $\chi_{12}$, has been investigated for blends of a sulfonated, amorphous polyester ionomer (S-polyester) with poly(ethylene terephthalate) (PET) and with the polyamide, nylon 66 (N66) [Boykin and Moore, 1997]. For melt blends of the S-polyester, with Mn as the counterion, and PET, the interaction parameter was determined to have a large negative value. This is an indication of a high degree of miscibility between the two components which is attributed to a transesterification reaction that occurs during the melt-mixing process. In similar blends, with Na as the counterion, miscibility was not present ($\chi_{12}$=0), probably as a result of poor mixing due to high melt viscosity.

In the S-polyester/N66 melt blends, the interaction parameter was found to have values of -0.3, with Na as the counterion, and -1.3 with Zn as the counterion. The blends containing Zn counterions also exhibited a better dispersion and a smaller particle size. One would expect these factors to lead to enhanced mechanical properties but no data on such properties were reported. The enhanced miscibility in the S-polyester/N66 blends is attributed to the presence of specific interactions between the ionic groups of the ionomer and the polar amide groups of the nylon N66 component [Boykin and Moore, 1997].

The elastomer, EPDM, is known to be an effective impact modifier for high density polyethylene (HDPE) but properties can be significantly improved by replacing EPDM with a sulfonated EPDM ionomer (Zn-SEPDM) [Zeng et al., 1992]. To illustrate, for an HDPE/EPDM blend containing 10 wt% of the elastomer, the fracture strain was found to rise from 40% to 82% and the impact strength increased from 178 J/m to 420 J/m; and these changes were accompanied by a decrease in tensile strength from 32.8 to 21.9 MPa. However, for blends in which the 10 wt% of EPDM was replaced by 9 wt% of the SEPDM ionomer and 1 wt% of zinc stearate

(an ionic plasticizer used to reduce melt viscosity and provide more intimate mixing) the strain to fracture rose to over 450%, the impact strength to 541 J/m, and the tensile strength decreased only to 26.5 MPa. These beneficial results are attributed to effective load sharing and good adhesion between the phases as a result of interpenetrating networks (IPN'S), with one IPN arising from ionic crosslinking in the ionomer phase and the second IPN from the presence of crystallites in the HDPE phase.

Other examples of ionomer/polymer blends, in which properties are improved by the presence of two interpenetrating networks, are blends of a sulfonated butyl rubber ionomer (S-BR) with polypropylene or with styrene-butadiene-styrene elastomer (SBS), to which 10 wt% of zinc stearate has been added to improve mixing [Xie et al., 1991]. In these blends, the variation of tensile strength with ionomer content exhibited positive deviation from simple additivity; and at intermediate compositions near 30 wt% S-BR in the S-BR/PP blend and near 70 wt% S-BR in the S-BR/SBS blend, the tensile strength attained maximum values that were higher than those of either component. Here too, the enhanced properties arise from the formation of interpenetrating networks, with one IPN arising from ionic interactions in the ionomer phase and the second IPN from the presence of crystalline regions in PP or from the PS glassy domains in the SBS phase [Hara and Sauer, 1998; Xie et al., 1991].

If ionic groups are added to one component of a block copolymer, rather than to one component of a. polymer/polymer blend, they can also produce significant changes in mechanical properties. For example, in a polystyrene-polyisobutylene (PIB) block copolymer (PS-PIB-PS), a 50% increase in tensile strength, with only an 8% reduction in fracture strain, has been obtained by changing the PS end sequences to a PS ionomer (Zn-SPS) [Storey et al., 1997]. Hence the presence of ionic interactions in the modified block copolymer will also lead to an increase in the energy required to fracture.

## CONCLUSIONS

1. The concept of blending an ionomer with the ionomer precursor polymer to produce new materials with enhanced properties of stiffness, strength and fracture energy, has been confirmed by experimental data acquired on several different polymer blend systems.

2. In ionomer/ionomer precursor polymer blends, it appears that properties are enhanced when the ion content of the ionomer component is increased to the point where its morphology is dominated more by cluster-type aggregates than by nano-size multiplets.

3. In other ionomer/polymer blends, synergy may be achieved in some particular polymer property but other mechanical properties frequently display negative deviation from the rule of mixtures.

4. Some ionomer/polymer blends that show enhanced performance in one or more mechanical properties consist of interpenetrating polymer networks; one IPN arising from ionic crosslinking of the ionomer phase and the second IPN from

the presence of crystallites in a partially crystalline polymer or from glassy domains in an elastomeric-type polymer.

5. In incompatible polymer/polymer blends, addition of a relatively small amount of a suitable ionomer can provide some degree of miscibility, improve adhesion between the phases and increase the value of some mechanical properties.

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