Polymer, 1991, Vol. 32, 95–102

Polymer blends with two kinds of elastomeric ionomers

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(Received 3 July 1989; revised 25 December 1989; accepted 20 January 1990)

Mechanical properties and structure relationships of polymer blends of sulphonated butyl rubber ionomer (IIR ionomer) or poly(butyl acrylate-*co*-acrylic acid) ionomer containing uniform poly(methyl methacrylate) grafts (BAM ionomer) with several kinds of polymers were studied. The results showed that blends of IIR ionomer with polypropylene or styrene–butadiene–styrene rubber and blends of BAM copolymer with poly(vinyl chloride) exhibited synergistic behaviour with respect to tensile strength. The melting point of polypropylene as measured by differential scanning calorimetry is lowered with increase of ionomer content. Transmission electron microphotographs indicated that two co-continuous phases existed in the blends of IIR ionomer with styrene–butadiene–styrene rubber. IIR ionomer/high-density polyethylene blends followed additive relationship between tensile strength and composition, while IIR ionomer/epichlorohydrin rubber, IIR ionomer/*cis*-1,4-polybutadiene, BAM ionomer/polypropylene or BAM ionomer/low-density polyethylene blends exhibited antagonistic behaviour. These results indicate that synergism for strength is not only induced by the enhanced compatibility due to the interpenetrating networks, but also dependent on the degree of similarity between structure of components.

(Keywords: ionomer; graft copolymer; blend; thermoplastic interpenetrating polymer networks; mechanical behaviour; synergism)

INTRODUCTION

Recently elastomers that contain ionic clusters or ionic domains as physical crosslinks have become of greater interest. Besides their attractive properties, they also produce some interesting blends with certain polymers. There have appeared in several patents blends of sulphonated ethylene–propylene–diene rubber (EPDM) ionomers with several polymers. For instance, the sulphonated EPDM ionomers were mixed with amino end-groups containing polyester to obtain a novel blend with good compatibility[1]. Blends of poly(styrene-*co*-vinyl pyridine) with sulphonated EPDM ionomer possessing improved rheological and mechanical properties were described in another US patent[2]. Blending elastomeric ionomers with polymers that contain glassy domains such as styrene–butadiene–styrene (SBS) or its hydrogenated product, styrene–ethylene–butylene–styrene (SEBS), or with polyolefins that contain crystalline regions leads to thermoplastic interpenetrating polymer networks (IPNs). In a US patent[3] a thermoplastic interpenetrating polymer network formed from blends of sulphonated EPDM ionomer with SEBS was reported. Siegfried and Sperling[4] described a series of thermoplastic interpenetrating polymer networks based on SEBS and poly(styrene–isoprene–sodium methacrylate) ionomer. Recently we reported the blends of sulphonated EPDM ionomer with polypropylene (PP), high-density polyethylene (HDPE), poly(vinyl chloride) (PVC), polyoxyethylene (PEO) and sulphonated butyl rubber (IIR) ionomer and showed that EPDM ionomer/PP and EPDM ionomer/HDPE blends exhibited synergistic behaviour with respect to tensile strength, while EPDM ionomer/PVC and EPDM ionomer/PEO blends showed antagonistic behaviour and EPDM ionomer/IIR ionomer blends followed an additive relationship between tensile strength and composition of the blends[5].

This paper deals with the blends of sulphonated butyl rubber (IIR) ionomer with SBS, PP, HDPE, epichlorohydrin rubber (CHR) and *cis*-1,4-polybutadiene (BR), as well as blends of the ionomers from poly(butyl acrylate-*co*-acrylic acid)-*g*-poly(methyl methacrylate) (BAM ionomer) with PEO, PP, low-density polyethylene (LDPE) and PVC in order to find out the factors affecting the synergism or the antagonism with respect to the tensile properties of the blends.

EXPERIMENTAL

Materials

HDPE of 7750 type with *MI* of 1.6 was manufactured by Liaoyang Chemical Factory. LDPE of 112A type with *MI* of 2 and PP of 1300 type with *MI* of 1 are products made by Yanshan Chemical Factory. Thermoplastic elastomer SBS of YH-762 type with molecular weight of 12×10^4 and *cis*-1,4-polybutadiene of DJ-9000 type with molecular weight of 25×10^4 were produced by Yuyang Synthetic Rubber Factory. Epichlorohydrin rubber is of homopolymer type with molecular weight of 60×10^4 obtained from Wuhan Organic Synthetic Materials Factory. PVC of XJ type with molecular weight of 5.3×10^4 was manufactured by Tianjin Chemical Factory.. Polyoxyethylene with molecular weight of 6.9×10^5 was self-made according to the procedure described in the literature[6].

IIR ionomer was made from a butyl rubber of 268 type with Mooney viscosity of 70 and unsaturation degree

0032-3861/91/010095-08

of 1.6–2.0% through sulphonation in petroleum ether solution using acetyl sulphate made *in situ* from sulphuric acid and acetic anhydride as the sulphonating agent at a concentration of 16 g IIR/100 ml of petroleum ether at 25°C for 1 h. After termination with 3% (v/v) ethyl alcohol the sulphonated product was neutralized through adding metallic acetate or ethylamine in ethyl alcohol/water mixture with stirring at room temperature for 1 h. The solvent was removed by solvent flashing in hot water and the ionomer was dried. Zinc ionomer with 25.1 meq/100 g of sulphonate groups was used in blending, while lead ionomer was used in TEM examination.

BAM ionomer was synthesized using macromer technique as follows[7]: Poly(methyl methacrylate) (PMMA) macromer was obtained by free-radical polymerization of MMA using azobisisobutyronitrile (AIBN) as initiator and thioglycollic acid as chain transfer agent, followed by termination with glycidyl methacrylate. Then the PMMA macromer was copolymerized with butyl acrylate (BA) and acrylic acid (AA) in benzene followed by purification and neutralization in acetone with methanolic solution of zinc acetate at 50°C. Composition of the copolymer used in blending is PMMA/BA/AA = 22.4/74.6/3.0 by weight.

Melt blending

One of the ionomers was mixed with a certain proportion of one of the above-mentioned polymers (sometimes in the presence of zinc stearate) in a Brabender mixer at 160–170°C until the recorded torque value reached equilibrium. The blend was then compression moulded under a hot press.

Test and characterization of the blends

Mechanical properties were determined on a DL-250A tensile tester at 20–25°C with a stretching rate of 300 mm min^{-1}. Permanent set was measured as percentage elongation after the specimen was broken and reunited after 3 min.

D.s.c. curves were obtained using a Rigaku TAS 100 apparatus combined with a computer with a heating rate of 20°C min^{-1}.

Microphotographs of the blends were taken by JEM 1000C transmission electron microscope. Some of the samples were stained with vapour of 1% OsO_4 solution and cut by microtome.

Dynamic mechanical properties were measured by means of DDV-III-EA viscoelastometer with a frequency of 110 Hz and a heating rate of 3°C min^{-1} using a sample of 0.3 mm thickness.

RESULTS AND DISCUSSION

Blends of sulphonated IIR ionomers with SBS

Change of torque values at 160°C and 20 rpm with time during blending of the IIR ionomer with SBS in the Brabender mixer is shown in *Figure 1*. It can be seen that in the presence of 10% zinc stearate the two components mixed more smoothly and with much lower torque than in the absence of zinc stearate. Obviously zinc stearate acts as an ionic plasticizer for the ionomer. Equilibrium torque value decreased with increasing SBS content.

Table 1 lists the mechanical properties of the IIR ionomer/SBS blends of different composition and *Figure*

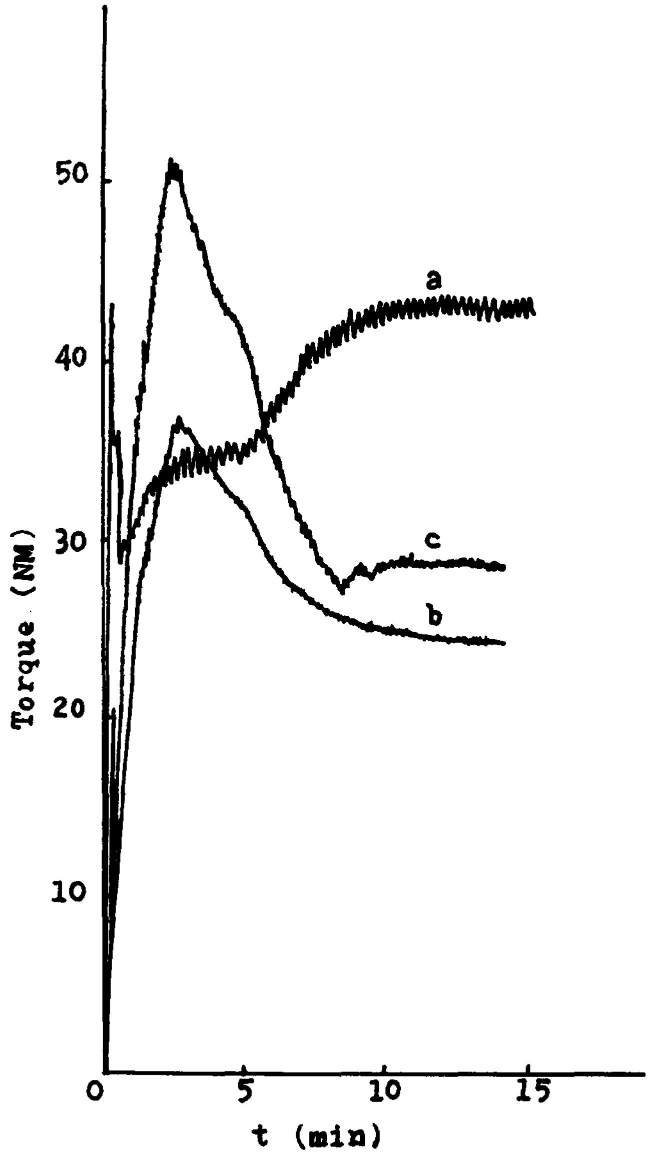

Figure 1 Torque–time curves of blending IIR ionomers with SBS: (a) IIR ionomer/SBS = 50/50 (w/w); (b) IIR ionomer/SBS = 50/50 (w/w) with 10% zinc stearate; (c) IIR ionomer with 10% zinc stearate

Table 1 Mechanical properties[a] of different IIR ionomer/SBS blends in the presence of 10% zinc stearate

IIR ionomer[b] (wt%)	SBS (wt%)	*TS* (MPa)	*M* (MPa)	*UE* (%)	*PS* (%)
100	0	18.7	4.3	940	150
90	10	18.6	4.2	950	131
66.7	33.3	19.5	4.3	960	115
50	50	18.5	4.3	820	100
33.3	66.7	18.2	3.7	860	96
10	90	11.0	2.8	780	54
0	100	8.8	3.2	780	42
50[c]	50	15.3	4.1	870	56
50[d]	50	17.6	2.0	970	23
35[e]	65.0	14.6	3.7	980	85

[a] *TS* denotes tensile strength, *UE* ultimate elongation, *M* modulus at 300% elongation, *PS* permanent set

[b] Most of IIR ionomers are zinc-sulphonated IIR ionomers except the last two

[c] Without zinc stearate

[d] Ethylamine-neutralized IIR ionomer in the absence of zinc stearate

[e] Lead-sulphonated IIR ionomer in the presence of 10% zinc stearate

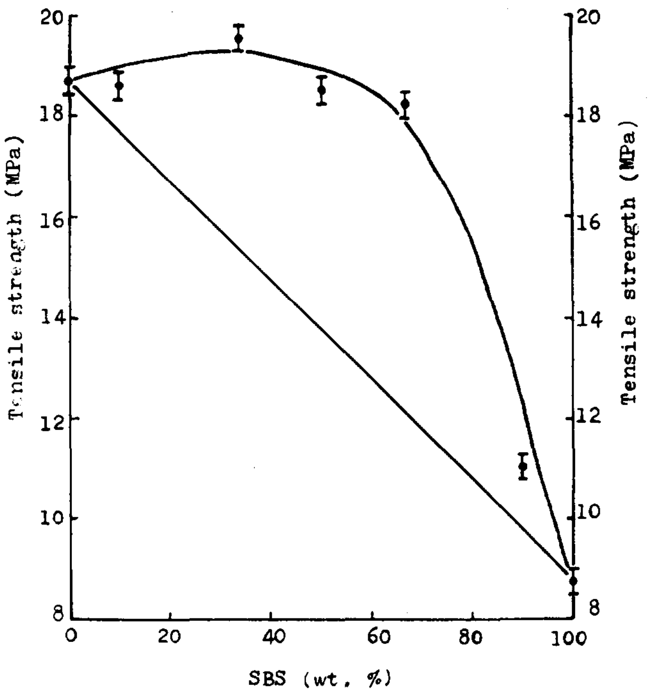

Figure 2 Relationship between tensile strength and composition of IIR ionomer/SBS blends

2 shows the relationship between tensile strength and composition of the blends. The straight line represents the theoretical additive relationship. Obviously, a synergism was observed for tensile strength of the IIR ionomer/SBS blends, i.e. tensile strength of the blend is higher than the calculated sum of tensile strength contributed by the two components. The blend with weight ratio of IIR ionomer/SBS = 66.7/33.6 possesses tensile strength even higher than that of either individual component. Since both the ionomer and SBS are physically crosslinked (the former contains ionic domains, while the latter contains glassy polystyrene domains), the blend may form a thermoplastic IPN. There is some similarity between the CH_3-groups-containing polyisobutylene of the IIR ionomer and the vinyl-side-groups-containing polybutadiene of SBS. This provides a necessary condition for the two physical interpenetrating networks to enhance the compatibility of the two components, thus resulting in better adhesion of interface between phases and efficient transfer of stress between phases. The synergistic effect is more obvious when the ratio of the two components approaches to near unity. This is probably due to more interpenetrating networks formed in the blends with equal weight of components.

Table 1 indicates that the blends containing metallic-ions-neutralized ionomer possess large ultimate elongation and permanent set. Zn IIR ionomer/SBS blends exhibit higher tensile strength and larger permanent set in the presence of 10% zinc stearate than those in the absence of zinc stearate. Lead IIR ionomer blend seems to have lower tensile strength and larger ultimate elongation than that of zinc IIR ionomer blend. However, if the ionomer used is an ethylamine-neutralized one, then the blend shows the same tensile strength but lower permanent set even in the absence of zinc stearate, as shown in *Table 1*.

In order to study the morphology of the blends, lead IIR ionomer/SBS (35/65) blends with or without staining with OsO_4 were examined under TEM. It appears from microphotograph (a) in *Figure 3* that two co-continuous phases exist; the light phase represents SBS, while the dark phase with black spots is the ionomer. From the microphotograph (b) of the blend stained with OsO_4, light domains of polystyrene can be seen in the dark background of both ionomer and continuous phase of polybutadiene. The appearance of co-continuous phases is coincident with the morphology of thermoplastic interpenetrating polymer networks, indicated by Gergen[8] as very special properties. Each of the continuous phases can withstand stress, resulting in synergism in strength.

Blends of sulphonated IIR ionomer with polypropylene

Torque–time curves of blending zinc IIR ionomer with PP in the presence of 10% zinc stearate at 170°C and 20 rpm are shown in *Figure 4*. Since the torque value is proportional to the melt viscosity, the equilibrium torque value or melt viscosity decreases with increasing PP content from 50 wt% to 90 wt%.

Figure 5 represents the tensile strength–composition relationship for the zinc IIR ionomer/PP blends. It can be noted that the blends in the presence of 10% zinc stearate show synergistic behaviour with respect to the tensile strength. When PP content is 50–70% of the blend, the tensile strength of the blend is even higher than that of PP alone. It may be attributed to the thermoplastic IPN formed in the blend, because both the ionic domains in the ionomer and also crystalline regions or crystallites of the PP can be considered as physical crosslinks. Since there are some similarities between methyl-groups-containing amorphous phase of PP and

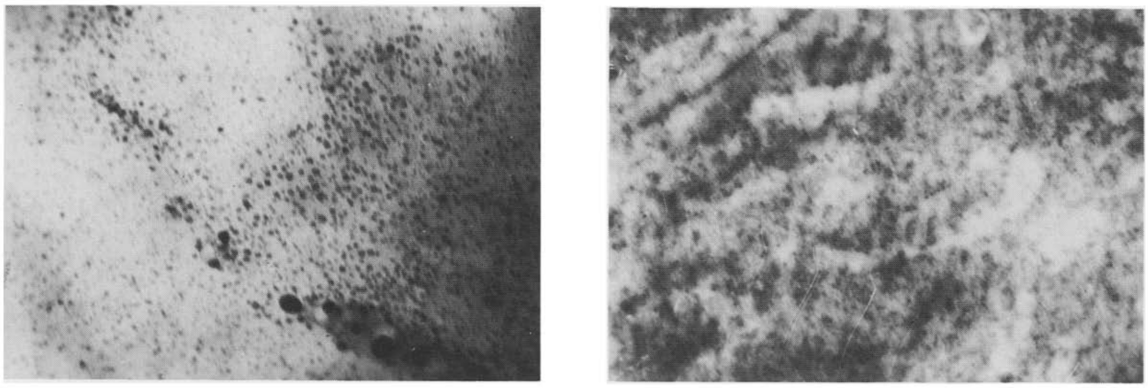

Figure 3 TEM microphotographs of lead IIR ionomer/SBS: (a) without staining, 100000 × ; (b) stained with OsO_4, 270000 ×

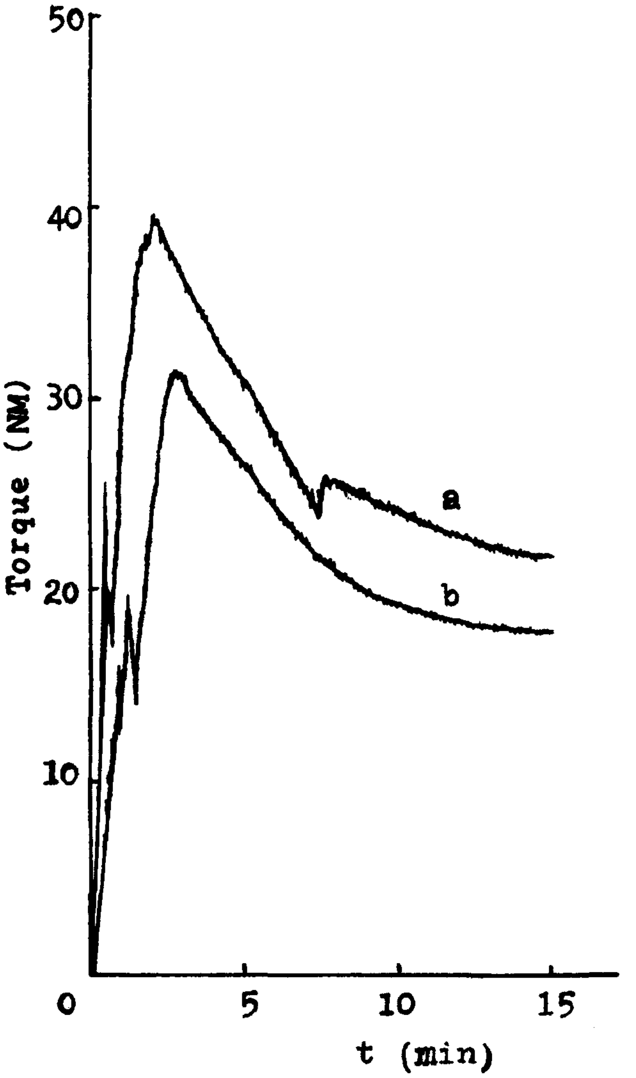

Figure 4 Torque–time curves of blending IIR ionomers with PP: (a) IIR ionomer/PP = 50/50 (w/w) with 10% zinc stearate; (b) IIR ionomer/PP = 10/90 (w/w) with 10% zinc stearate

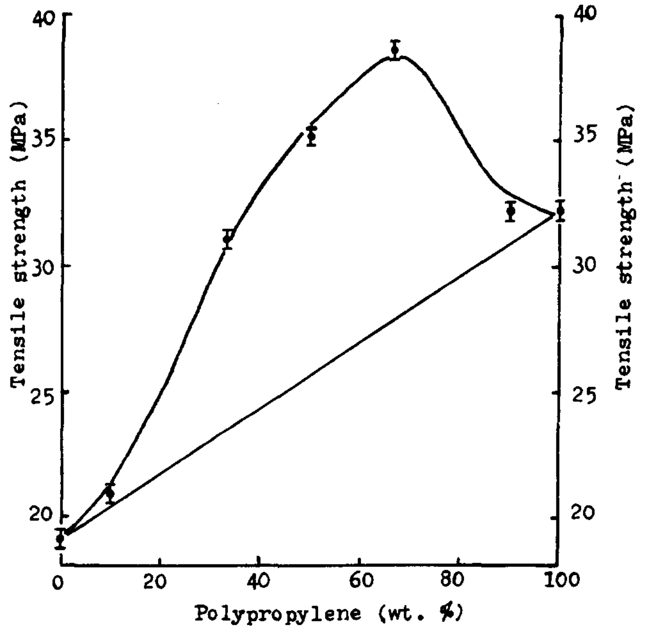

Figure 5 Relationship between tensile strength and composition of IIR ionomer/PP blends

methyl-groups-containing butyl rubber phase, the components show certain affinity for each other, and the segments of different macromolecules diffuse into each other, especially at interfaces between the two phases, where the two physical crosslinks penetrate into each other and enhance compatibility of the two components, thus increasing the interfacial adhesion and the ability to transfer stress through phases, resulting in synergism in strength.

Melting point as measured by d.s.c. is lowered with increase of ionomer content, as denoted in *Table 2*. This demonstrates that the crystalline regions or crystallites of PP in the blend were partially destroyed by the partial compatibilization of the isobutylene segments in the ionomer with the amorphous parts of PP, enhanced by the physical interpenetrating networks.

Table 3 summarizes the ultimate elongation and permanent set of IIR ionomer/PP blends with different compositions. It can be seen that the blends behave like toughened plastics at PP content larger than 33.1%.

Blends of sulphonated IIR ionomer with HDPE

Blending of the IIR ionomer with HDPE also proceeded more smoothly in the presence of 10% zinc stearate than in the absence of it. Zinc stearate is not only beneficial to the lowering of melt viscosity, but also to the enhancement of tensile strength, probably due to more uniform distribution of ionic domains in the blend[9].

Tensile strength of the IIR ionomer/HDPE blends in the presence of 10% zinc stearate almost follows the additive relationship between properties and composition of the blends, except the blend containing 10% HDPE, as shown in *Figure 6*.

HDPE is also a semicrystalline polymer like PP, containing both crystalline and amorphous regions. The crystalline regions or crystallites play the role of physical crosslinks. However, owing to the much lower similarity between amorphous phase of HDPE and polyisobutylene phase of IIR ionomer, low affinity is expected between the two components. But due to the enhanced compatibilization caused by the two physical interpenetrating

Table 2 Melting point of polypropylene *versus* composition of the IIR ionomer/PP blends in the presence of 10% zinc stearate

IIR ionomer (wt%)	PP (wt%)	T_m[a] of PP in blend (°C)
0	100	186.6
33.3	66.7	182.8
66.7	33.3	170.3

[a] Determined by d.s.c.

Table 3 Mechanical properties of IIR ionomer/PP blends with different compositions in the presence of 10% zinc stearate

IIR ionomer (wt%)	PP (wt%)	*TS* (MPa)	*UE* (%)	*PS* (%)
100	0	18.7	940	150
90	10	20.4	970	131
66.7	33.3	30.5	54	4
50	50	34.5	35	2
33.3	66.7	37.8	19	2
10	90	31.4	10	2
0	100	31.6	0	0

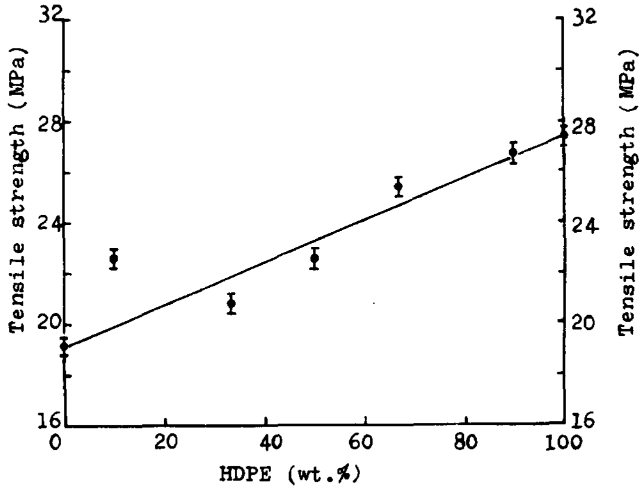

Figure 6 Relationship between tensile strength and composition of IIR ionomer/HDPE blends

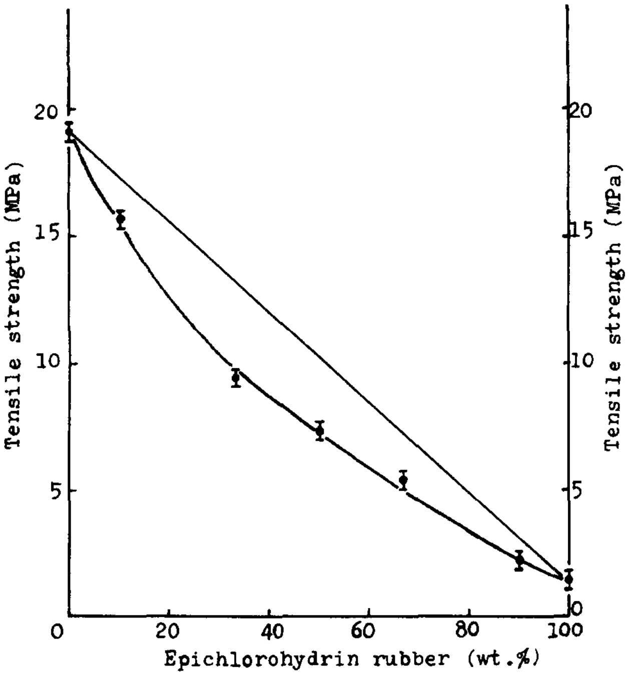

Figure 7 Relationship between tensile strength and composition of IIR ionomer/CHR blends

networks, not antagonism but an additive relationship occurs.

For the blends containing HDPE in the range of 33.3 to 66.7% neck formation appeared during stretching of the blend samples. This is somewhat similar to the EPDM ionomer/HDPE blends[5], but no obvious synergism with respect to tensile strength was noted, owing to the lower similarity in structure of the two components as compared to EPDM ionomer/HDPE blends.

Blends of sulphonated IIR ionomer with epichlorohydrin rubber (CHR)

Although the IIR ionomer can be well blended with CHR in a Brabender mixer at 160°C and 20 rpm, the tensile strength of the blends appears lower than that according to the additive relationship, as indicated in *Figure 7*. Since CHR without vulcanization is a linear polymer containing no crosslinks, only semi-IPN can be formed in the blend with IIR ionomer. There probably exists some interaction between oxygen atoms in CHR and Zn^{2+} of the ionomer, but the structure between the two components is very different and no interpenetrating networks will enhance the compatibility. Hence only antagonism for the tensile strength occurred in the blends.

Blends of sulphonated IIR ionomer with cis-*1,4-polybutadiene*

Results of blending IIR ionomer with *cis*-1,4-polybutadiene seem much poorer. As demonstrated in *Figure 8*, these blends exhibit evident antagonistic behaviour with respect to tensile strength. This can be interpreted as that *cis*-1,4-polybutadiene is a linear, double-bond-containing polymer without any crosslinks and is quite different in structure from IIR, which contains a lot of methyl groups around the main chain and also no interaction or interpenetrating networks exist between the two components.

Blends of BAM ionomer with polyoxyethylene (PEO)

Change of torque values with time during blending of the BAM ionomer with PEO at 160°C and 20 rpm is illustrated in *Figure 9*. Addition of 10% zinc stearate or increase of PEO content lowered the equilibrium torque. *Figure 10* shows the relationship between tensile strength and composition of the BAM ionomer/PEO blends with or without zinc stearate. In the presence of 10% zinc stearate the blends show antagonistic behaviour for tensile strength, while in the absence of zinc stearate the blends exhibit somewhat additive properties below 50% ionomer content and antagonistic behaviour above 50% ionomer content. These results indicate that zinc stearate can lower the melt viscosity of the blends containing ionomer, but inhibit the ion–dipole interaction between ionomer and PEO due to the competitive ion–dipole interaction between zinc stearate and PEO. In the absence of zinc stearate when PEO content is less than 50% and the continuous phase is probably the BAM ionomer, there exist both the ion–dipole interaction

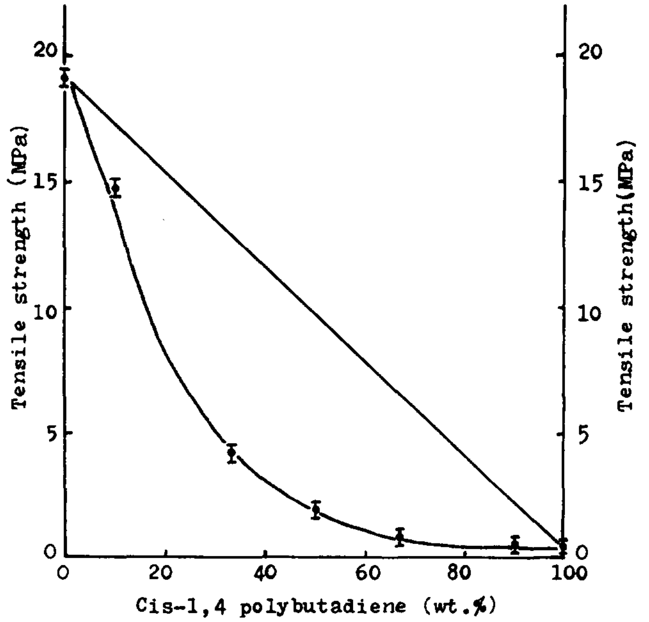

Figure 8 Relationship between tensile strength and composition of IIR ionomer/*cis*-1,4-polybutadiene blends

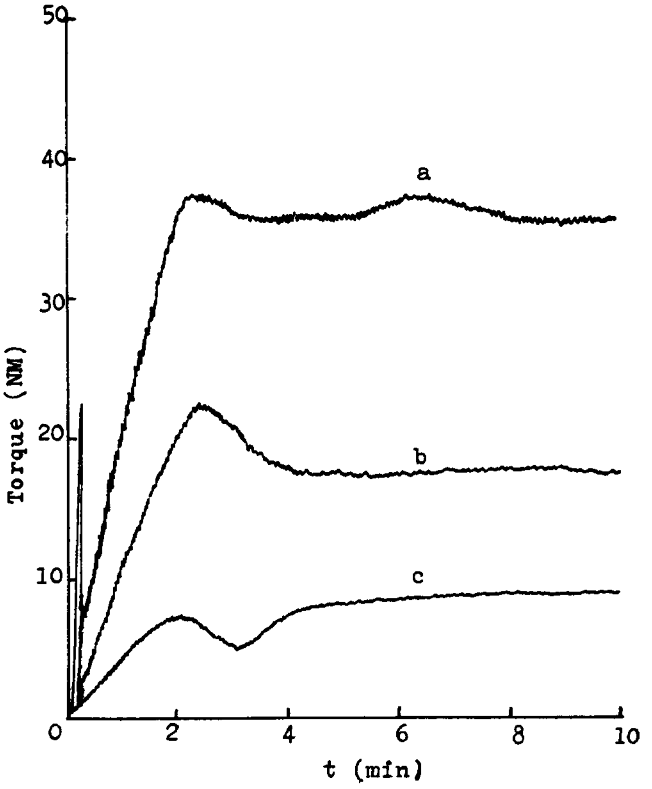

Figure 9 Torque–time curves of blending BAM ionomers with PEO: (a) BAM ionomer/PEO = 75/25; (b) BAM ionomer/PEO = 25/75; (c) BAM ionomer/PEO = 25/75 with 10% zinc stearate

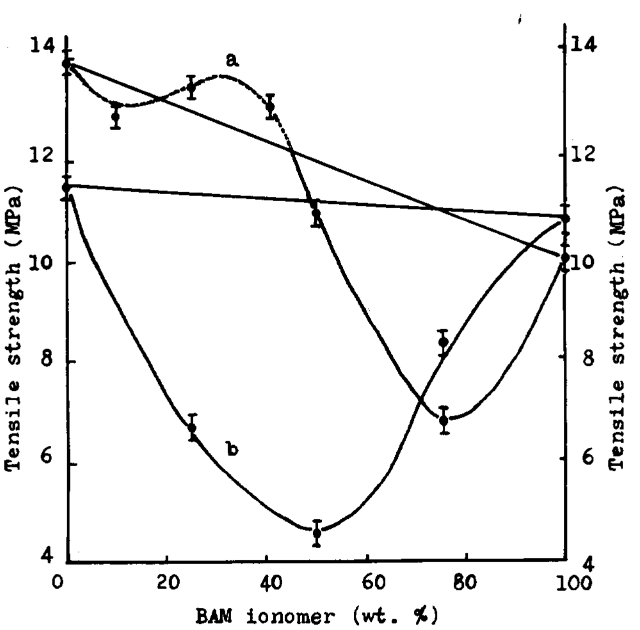

Figure 10 Relationship between tensile strength and composition of BAM ionomer/PEO blends: (a) without zinc stearate and (b) with 10% zinc stearate

between PEO and Zn^{2+} ions and also the compatibilization between PEO and PMMA grafts. The latter action may be stronger than the former, and may destroy the glassy PMMA domains. The destruction of PMMA domains as well as the incompatibility between PEO and PBA cause the strength to decrease. When PEO is more than 50% of the blend and becomes the continuous phase, the destruction of PMMA domains seems less important and the ion–dipole interaction and compatibility between PMMA and PEO compensate the incompatibility between PBA and PEO, resulting in the additive relationship between tensile strength and composition.

However, if the BAM copolymer instead of BAM ionomer is used in the blends without zinc stearate, synergism can be observed in the relationship between tensile strength and composition. This is attributed to the hydrogen-bond formation between hydrogen atoms of the acid groups in the BAM copolymer and oxygen atoms of the PEO chains, resulting in enhanced compatibility between the two components. The hydrogen-bond interaction seems to be much stronger than ion–dipole interaction and the compatibility between PMMA and PEO. Both the hydrogen-bond interaction and also the glassy domains of PMMA grafts induce the synergism for strength.

The dynamic mechanical spectrum of the BAM copolymer/PEO blend (*Figure 11*) shows that two loss peaks with a shallow valley exist over a wide range of temperatures and the two glass transition temperatures (−4°C and +94°C) shift inwards as compared to the BAM copolymer (−20°C and +98°C), indicating the enhanced compatibility of the BAM copolymer with PEO dur to the hydrogen-bond formation between PAA and PEO.

The blends of BAM copolymer with PEO in the presence of 10% zinc stearate, on the contrary, show an antagonistic effect, as shown in *Figure 12.* In this case tensile strength of the BAM copolymer is lower than that in the absence of zinc stearate. This is probably due to the fact that zinc stearate exchanges Zn^{2+} ions with acid groups of the BAM copolymer, forming stearic acid and some ionic domains in the BAM copolymer. The stearic acid formed could complex with PEO in the blend in competition with the acid groups of the BAM copolymer and thus make the compatibility between PEO and BAM copolymer diminish.

In the blends of PEO with BAM copolymer without zinc stearate ultimate elongation decreases from 600% to 100% and permanent set increases from 20% to 45% with increase of PEO content from 0 to 50%.

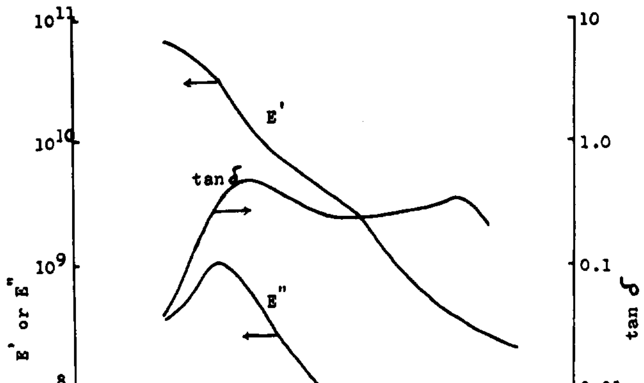

Figure 11 Dynamic mechanical spectrum of a BAM copolymer/PEO blend

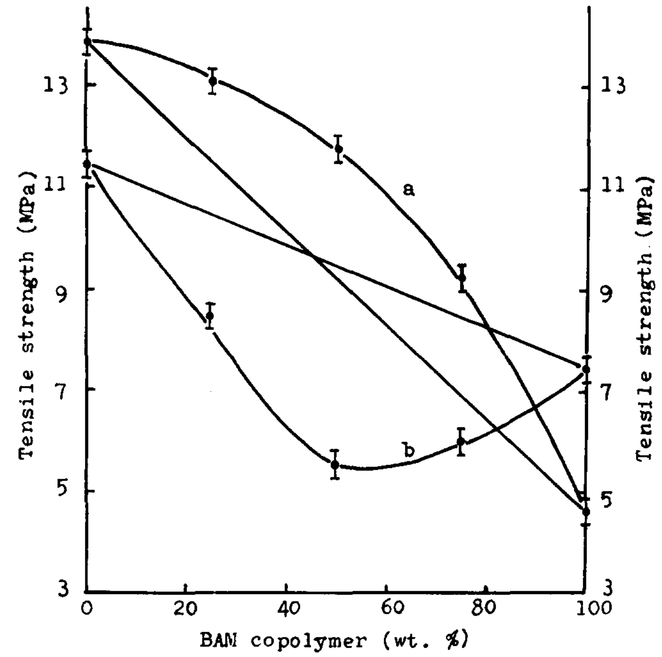

Figure 12 Relationship between tensile strength and composition of BAM copolymer/PEO blends: (a) without zinc stearate and (b) with 10% zinc stearate

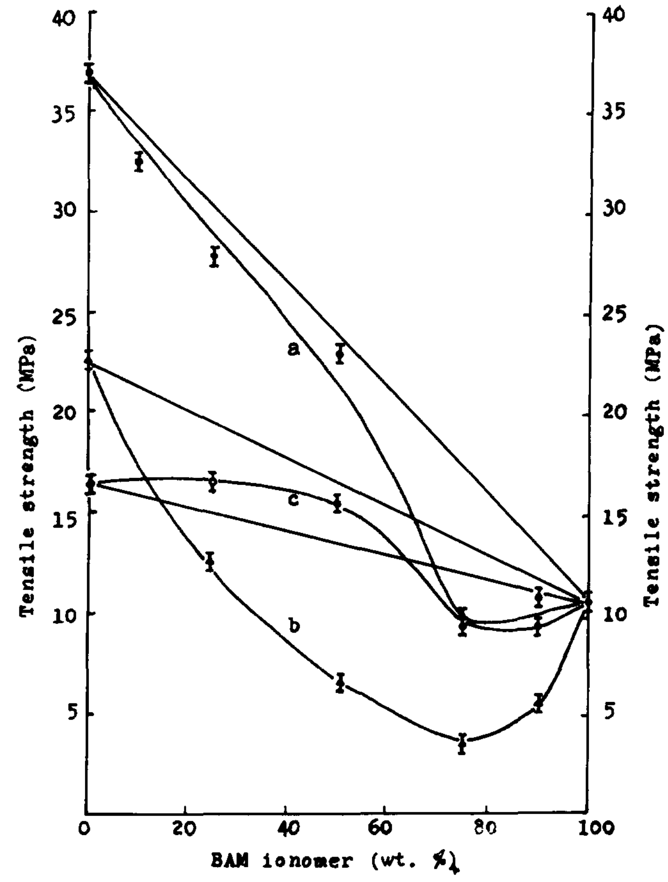

Figure 13 Relationship between tensile strength and composition of BAM ionomer blends in the presence of 10% zinc stearate with (a) PP, (b) LDPE, (c) PVC

Blends of BAM ionomers with polypropylene

Opposite to the results of the blends of IIR ionomer with PP, blends of BAM ionomer with PP show antagonistic behaviour with respect to tensile strength, especially with ionomer content of more than 50% in the presence of 10% zinc stearate, as shown in *Figure 13*. This may be explained by the fact that the structure of BAM copolymer is quite different from that of PP and the compatibility between them is very poor. The effect of incompatibility overcomes the effect of physical interpenetrating networks, resulting in an antagonistic effect.

Blends of BAM ionomer with low-density polyethylene

LDPE is not a semicrystalline polymer as HDPE owing to its high content of branches. Blends of BAM ionomer with it show very strong antagonism with respect to tensile strength, when 10% of zinc stearate is present, as illustrated in *Figure 13*. This is because their structure is very different from each other and also because no interpenetrating networks exist in the blend.

Ultimate elongation of the blends decreases from 500% to 180% and permanent set increases from 12% to >50% with increase of LDPE content from 10% to 50% in the blends.

Blends of BAM ionomer with poly(vinyl chloride)

It is interesting to note from *Figure 13* that blends which contain 50% or more of PVC exhibit synergism for tensile strength. Since tensile strength of the blend depends mainly on the continuous phase, when PVC content is over 50%, some parts of PVC in the continuous phase are compatible with PMMA grafts of BAM ionomer due to the interaction of α-hydrogen of PVC with carbonyl groups of PMMA[10] and also the close solubility parameters, resulting in good adhesion of the interface between the PVC and BAM ionomer phases, thus enhancing the tensile strength of the blends.

But if PVC occupies only 25% of the blend, then the tensile strength depends mainly on the continuous phase of BAM ionomer, the PMMA grafts of which interact with PVC molecules, resulting in destruction of PMMA glassy domains acting as physical crosslinks and thus lowering the tensile strength of the blend.

With increasing PVC content from 0 to 50% in the blend ultimate elongation is reduced from 500% to 80% and permanent set increases from 20% to 50%. At PVC content of 10–25% the blend behaves like a thermoplastic elastomer, yet the tensile strength is not so high.

CONCLUSIONS

The above results of polymer blends with two kinds of ionomers in combination with those of polymer blends with EPDM ionomers indicate that a synergistic effect is not only induced by the interaction of the two components in the blend or the enhanced compatibility caused by the interpenetrating networks, but also dependent on the similarity between the structure of components. Enhanced compatibility due to interpenetrating networks will be effective only when there is certain similarity between the structure of the components in the blend. This is why the thermoplastic interpenetrating polymer networks formed by EPDM ionomer/PP, EPDM ionomer/HDPE, IIR ionomer/PP or IIR ionomer/SBS blends show synergistic behaviour with respect to tensile strength, while IIR ionomer/HDPE follows the additive relationship and BAM ionomer/PP exhibits antagonism. Synergism existing in the blends of BAM ionomer/PVC or BAM copolymer/

PEO is mainly attributed to the interaction between the two components of the blend.

ACKNOWLEDGEMENT

This work was supported by National Natural Science Foundation Committee of China.

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