ELSEVIER

Polymer 40 (1999) 1487–1493

polymer

The effect of zinc stearate on melt-processable ionomeric blends based on zinc salts of maleated high-density polyethylene and maleated EPDM rubber

Prince Antony, S.K. De*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India

Received 24 October 1997; revised 3 April 1998; accepted 7 May 1998

Abstract

An ionomeric blend of maleated ethylene–propylene–diene monomers (mEPDM) and maleated high-density polyethylene (mHDPE) exhibits higher melt viscosity than the corresponding non-ionomeric polyblend. The addition of zinc stearate decreases the melt viscosity of the ionomeric polyblend. The ionomeric polyblend shows superior physical properties to the corresponding non-ionomeric polyblend. The addition of zinc stearate causes an increase in tensile strength of the ionomeric polyblend. Infra-red studies show that an interionic interaction exists between the zinc stearate and ionomeric polyblend. Reprocessability studies reveal the thermoplastic elastomeric nature of the blend.

Keywords: Ionomer; Zinc salt of maleated HDPE; Zinc salt of maleated EPDM

1. Introduction

The incorporation of ionic groups into organic polymers yields ionomers [1–4]. The presence of a small amount of ionic groups exerts a profound effect on the physical and rheological properties of the polymer [5–7]. The ionic groups present in the polymers interact to form strong intermolecular ionic aggregates, which increase the melt viscosity due to stiffening of the adjacent polymer chains. The melt rheology of the ionomer depends on the type of ionic moiety, the counterion type, the degree of neutralization, the flexibility of the backbone polymer and the presence of plasticizers [5–8]. Lundberg et al. compared the rheological behaviour of carboxylated polystyrene and sulfonated polystyrene at the same molecular weight and ion level with the same cation and concluded that sulfonated ionomers are more strongly associated and possess higher melt viscosity than the corresponding carboxylate ionomers [9]. Makowski et al. have shown that ionomers based on sulfonated ethylene–propylene–diene monomers (EPDM) containing zinc cations exhibit a much lower melt viscosity than those containing other cations such as Mg^{2+} and Ca^{2+} [10]. Weiss and co-workers have also studied the effect of the counterion on the melt rheology of ionomers [11,12].

Polar plasticizers are able to interact with the ionic groups, thereby reducing the degree of ionic associations and causing a reduction in melt viscosity. It has been proposed that crystalline zinc stearate can act as an ionic plasticizer at elevated temperature (i.e., above its melting point, 128°C), but behave as a low reinforcing filler at room temperature in the case of the zinc salt of sulfonated EPDM (Zn-SEPDM) [13,14] and the zinc salt of maleated EPDM (Zn-mEPDM) [15]. Makowski and Lundberg studied the plasticization of metal sulfonated EPDM with various stearic acid derivatives [14]. The addition of zinc stearate lowers the melt viscosity of a Zn-SEPDM and polypropylene (PP) blend [16]. Bagrodia et al. have also studied the effect of plasticizers on the rheological behaviour of ionomers [17,18]. Tong and Bazuin reported the plasticization of a poly(ethyl acrylate) ionomer by an alkyl aniline [19]. Lundberg and co-workers studied the effect of polar and non-polar plasticizers on the melt viscosity of the sodium salt of sulfonated polystyrene [20].

Ionomeric blends of Zn-mEPDM and the zinc salt of maleated high-density polyethylene (Zn-mHDPE) in the ratios of 90/10 to 50/50 behave as an ionic thermoplastic elastomer [21]. The present investigation was undertaken to

---

* Corresponding author. Tel.: +91-3222-55221 ext. 4976; fax: +91-3222-55303/55239; e-mail: skd@hijli.iitkgp.ernet.in

0032-3861/98/$ - see front matter © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(98)00362-0

Table 1
Details of the materials used

Material	Properties	Source
Maleated HDPE, abbreviated as mHDPE (trade name, Polybond-3009)	Specific gravity, 0.95 Maleic acid/maleic anhydride content, 1% M_w, 97 000 Melting point, 127°C	Uniroyal Chemical Co., USA
Maleated EPDM abbreviated as mEPDM (trade name, Royaltuf-465)	Ethylene content, 55% Specific gravity, 0.89 Maleic acid/maleic anhydride content, 1% ML_{1+4} at 125°C, 60	Uniroyal Chemical Co., USA
Zinc oxide	Rubber grade Specific gravity, 5.6	E. Merck Ltd, Bombay, India
Stearic acid	Rubber grade Melting point, 76°C	Obtained locally
Zinc stearate	Rubber grade Melting point, 128°C	Obtained locally

determine the effects of an ionic plasticizer, namely zinc stearate, on the rheological and physical properties of the ionic thermoplastic elastomer based on a 60/40 Zn-mEPDM/Zn-mHDPE blend.

2. Experimental

Details of the materials used and their characteristics are given in Table 1.

2.1. Preparation of blends

Formulations used for preparation of the blends are given in Table 2. The masterbatch of mEPDM with 10, 20 and 30 phr (parts per hundred parts of resin) of zinc stearate were prepared by mixing in a two-roll mill at room temperature for 4 min. The blending of mHDPE with the mEPDM masterbatch was done in a model PLE-330 Brabender Plasticorder at 170°C and at a rotor speed of 60 rev min^{-1}. First mHDPE was added and allowed to melt for 2 min. Then the masterbatch of mEPDM with zinc stearate was added and mixed for an additional 2 min. Finally, stearic acid and zinc oxide were added and mixed for another 2 min. Stearic acid reacts with zinc oxide to produce water, which converts the anhydride groups into acid groups [15]. After mixing, the hot material was sheeted out in a two-roll mill. The mixes were then moulded at 170°C for 20 min in an electrically heated hydraulic press. After moulding was complete, the mixes were cooled to room temperature by circulation of cold water through the platens.

Table 2
Formulations of the mixes

Ingredient	Mix number				
	PM0	PM1	PM2	PM3	PM4
mEPDM	60	60	60	60	60
mHDPE	40	40	40	40	40
ZnO	10	10	10	10	0
Stearic acid	1	1	1	1	0
Zinc stearate	0	10	20	30	0

For preparation of the ionomeric polyblend without zinc stearate, pure mEPDM, instead of the masterbatch, was used and the mixing procedure was the same as described above.

2.2. Processability studies

The processability studies were carried out with a Monsanto Processability Tester (MPT) at shear rates of 61.5, 122.9, 245.8 and 491.6 s^{-1} and at a temperature of 190°C. The capillary length (30 mm) to diameter (1 mm) ratio, L/D, was 30. The preheat time for each sample was 5 min.

2.3. Measurement of physical properties

The stress–strain properties of the samples were obtained on dumb-bell samples according to ASTM D412 (1987) in a model 1195 Instron Universal Testing Machine (UTM) at a crosshead speed of 500 mm min^{-1}. Tear strength was measured in the model 1195 Instron UTM, using 90° nick-cut cresent samples according to ASTM D624 (1986). The hardness was determined as per ASTM D2240 (1986) and expressed in Shore A units. The tension set at 100% extension was determined as per ASTM D412 (1987).

2.4. Infra-red spectroscopic studies

Infra-red spectroscopic studies of compression-moulded thin films of the samples were performed with a Perkin–Elmer 843 spectrophotometer with a resolution of 3.2 cm^{-1}.

2.5. Reprocessability studies

The reprocessability studies were made by extruding the sample through the MPT at 190°C, using a die with $L/D = 30$ at a shear rate of 122.9 s^{-1}. The extrudate was re-extruded under similar conditions and the process was repeated for three consecutive cycles. The preheat time for the sample before each extrusion was 10 min. The tensile strength of the extrudate from each cycle was measured after a resting period of 24 h.

3. Results and discussion

3.1. Rheological properties

The log–log plots of apparent viscosity versus shear stress and shear rate are shown in Fig. 1. The non-linear variation of apparent viscosity with respect to shear stress shows the non-Newtonian behaviour of the mixes. The apparent viscosity is found to decrease with increase in shear stress. The decrease in apparent viscosity with increasing shear rate implies the pseudoplastic nature of the mixes. It is also found that the ionomeric polyblend exhibits higher melt viscosity at all shear rates than the corresponding non-ionomeric polyblend. The higher melt viscosity of the ionomeric polyblend is due to the reduction of chain mobilities resulting from the strong ionic interactions. The extrudates of the ionomeric polyblend show melt fracture at all shear rates. This is believed to be due to the presence of strong ionic crosslinks which resist the melt flow. There is a remarkable decrease in the melt viscosity of the ionomeric polyblend in the presence of zinc stearate. The decrease in melt viscosity of the ionomeric polyblend with the addition of zinc stearate at elevated temperature is presumably due to solvation of the carboxylate associations by the zinc stearate which weakens the ionic network structure [13,14] and by shear-induced exchange reaction during melt flow [15].

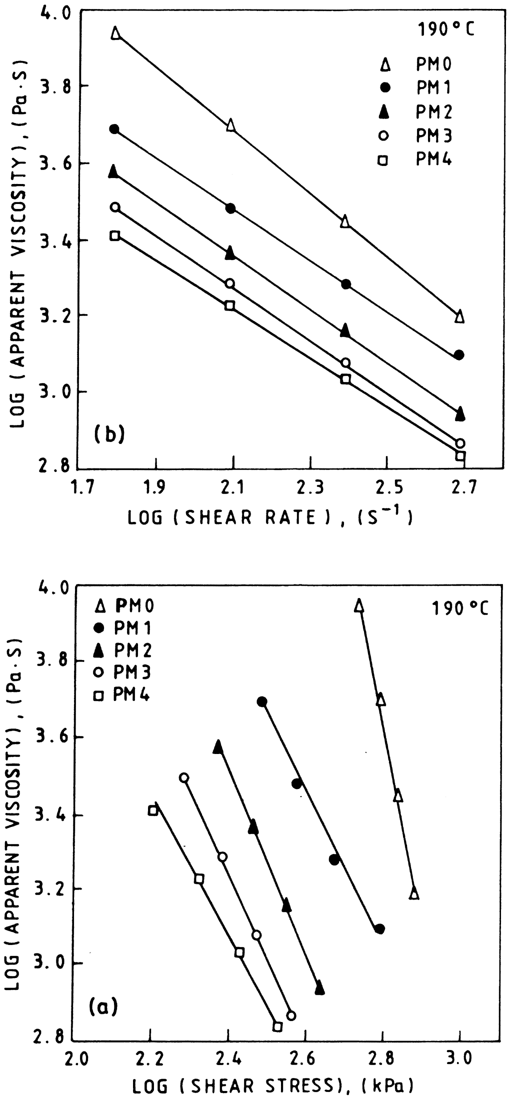

Fig. 1. (a) Log–log plots of apparent viscosity versus shear stress; (b) log–log plots of apparent viscosity versus shear rate.

Fig. 2 shows a plot of log(apparent viscosity) against concentration of zinc stearate. It is evident that at all shear rates the apparent viscosity decreases with increase in zinc stearate loading. At a particular zinc stearate level the viscosity decreases with increase in shear rates. Fig. 3 shows photomicrographs of the extrudates. The ionomeric polyblend in the absence of zinc stearate (mix PM0) shows melt fracture at all shear rates. With the addition of 10 phr and 20 phr zinc stearate, melt fracture is observed only at high shear rates. Furthermore, no melt fracture is observed for the ionomeric polyblend in the presence of 30 phr of zinc stearate (mix PM3) due to the marked reduction in melt viscosity.

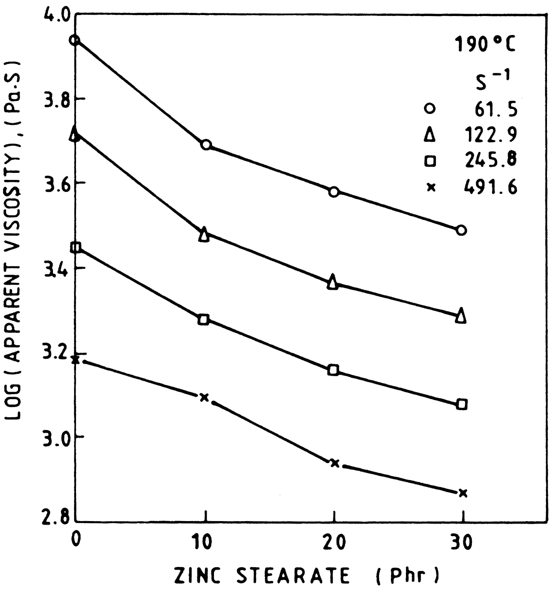

Fig. 2. Plots of log(apparent viscosity) versus zinc stearate loading at different shear rates.

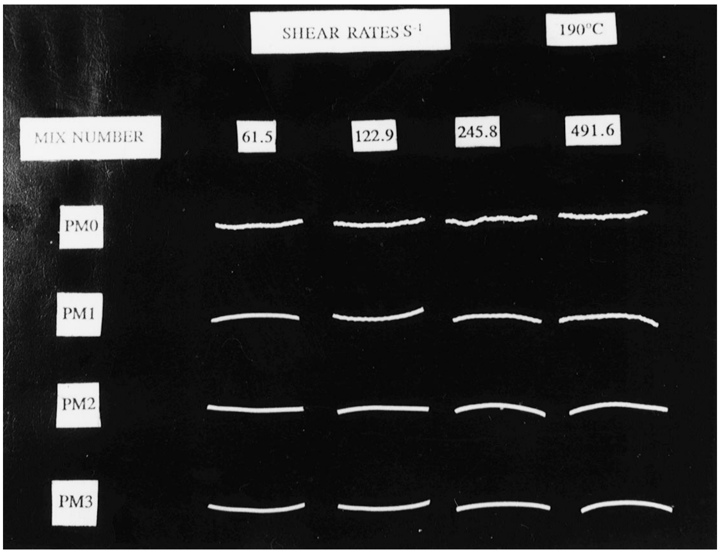

Fig. 3. Photomicrographs of the extrudates at 190°C and at different shear rates.

3.2. Physical properties

The stress–strain behaviour of all of the mixes is shown in Fig. 4. Physical properties measured at 25°C are summarized in Table 3. It can be seen from the table that the ionomeric polyblend (mix PM0) exhibits higher modulus, tensile strength and tear strength than the corresponding non-ionomeric polyblend (mix PM4). Therefore, it is apparent that the strong intermolecular ionic interaction enhances the compatibility of the polyblend. Mix PM0 shows lower tension set than mix PM4, because the ionic groups act as physical crosslinks and thereby decrease the set properties. Fig. 5 shows the effect of zinc stearate on the tensile strength and elongation at break of the ionomeric polyblend. It is apparent that the tensile strength and elongation at break of the ionomeric polyblend increase with the addition of zinc stearate. But there is a marginal decrease in modulus and marginal increase in tear strength. The improvement of tensile strength is believed to be due to low reinforcing ability of zinc stearate in the ionomers [14].

3.3. Infra-red spectroscopic studies

Fig. 6 shows the infra-red spectra of the non-ionomeric polyblend (mix PM4) and the corresponding ionomeric polyblend (mix PM0). Spectra for mix PM4 show two weak bands at 1894 and 1775 cm^{-1} arising from the C=O stretching of the non-conjugated five-membered ring (maleic anhydride group) [22]. The band at 1709 cm^{-1} accounts for the hydrogen-bonded carboxylic acid pairs [22,23]. The strong band observed at 1462 cm^{-1} is ascribed to $-CH_2-$ bending and the band at 1376 cm^{-1} corresponds to the $-CH_3$ symmetric deformation [22–24]. The spectrum of the ionomeric polyblend (mix PM0) shows a broad band centred at 1562 cm^{-1} in the asymmetric carboxylate stretching region due to the formation of ionomer. The disappearance of bands at 1709 and 1775 cm^{-1} indicates neutralization of the carboxylic acid groups. The spectrum of zinc stearate was taken by the KBr disc technique and the result is shown also in Fig. 6. The spectrum shows a sharp intense singlet band at 1534 cm^{-1}, which is believed to be due to the asymmetric carboxylate stretching of metal carboxylate ions present in the zinc stearate [22–24]. The band at 1463 cm^{-1} is attributed to the $-CH_2-$ bending vibration.

Fig. 7 compares the spectra of zinc-stearate-filled

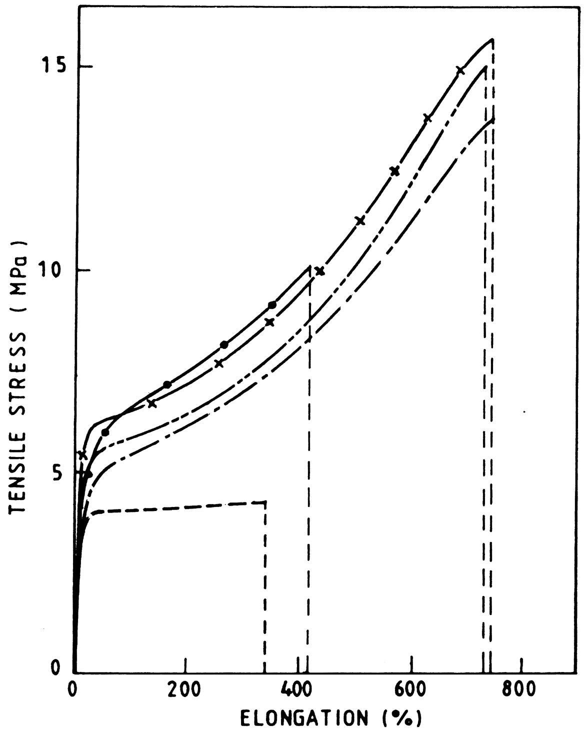

Fig. 4. Stress–strain plots of mix PM0 (– • –), mix PM1 (— - —), mix PM2 (— - - - —), mix PM3 (– × –) and mix PM4 (- - -).

Table 3
Physical properties at 25°C

Property	Mix number				
	PM0	PM1	PM2	PM3	PM4
Modulus at 100% elongation (MPa)	6.6	5.4	5.8	6.4	4.0
Modulus at 200% elongation (MPa)	7.6	6.1	6.5	7.1	4.1
Modulus at 300% elongation (MPa)	8.4	7.0	7.4	8.1	4.2
Tensile strength (MPa)	10.1	13.7	15.1	15.7	4.4
Elongation at break (%)	418	739	731	740	338
Tear strength (kN m^{-1})	79.1	79.6	81.2	80.5	65.6
Hardness (Shore A)	80	84	86	87	78
Tension set at 100% elongation (%)	15	22	32	37	45

ionomeric polyblends. It is apparent from the spectrum of mix PM1 that the addition of zinc stearate causes changes in the spectral features in the asymmetric carboxylate region of the ionomeric polyblend. The broad band at 1562 cm^{-1} is replaced by a sharp band at 1535 cm^{-1} with a shoulder at 1589 cm^{-1}. The changes in spectral features are associated with the strong interaction of zinc carboxylate ions present in the zinc stearate with zinc carboxylate ions present in the polyblend. The infra-red spectra of mix PM2 and mix PM3 show the occurrence of three bands around 1588, 1542 and 1532 cm^{-1} in the asymmetric carboxylate stretching region instead of a single sharp band at 1534 cm^{-1}, as observed in the case of zinc stearate, and a broad band centred at 1562 cm^{-1}, as observed in the case of the ionomeric polyblend. The intensity of the asymmetric carboxylate stretching band increases on addition of zinc stearate. From the infra-red spectroscopic studies, it can be concluded that there occurs a strong intermolecular interaction between zinc stearate and the ionic aggregates present in the ionomeric polyblend, which causes marked changes in the spectral features of the asymmetric carboxylate stretching region.

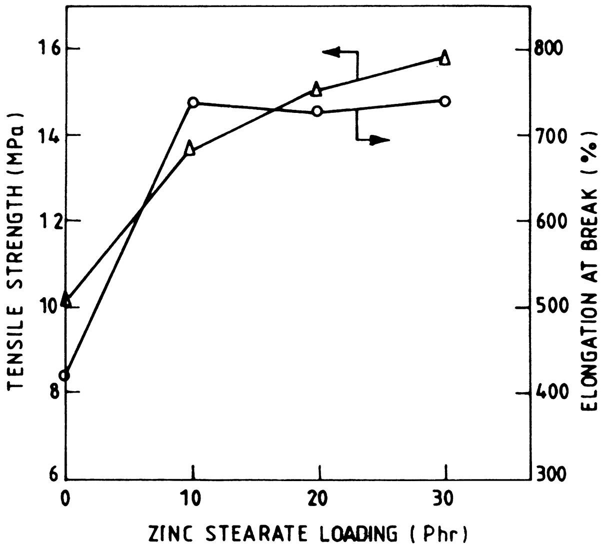

Fig. 5. Plots of tensile strength (– △ –) and elongation at break (– ∘ –) of the mixes versus zinc stearate loading.

Fig. 8 shows a schematic representation of the interaction between zinc stearate and the ionic aggregates in the blend by exchange reaction in the melt.

3.4. Reprocessability studies

Fig. 9 shows the variation of apparent viscosity and

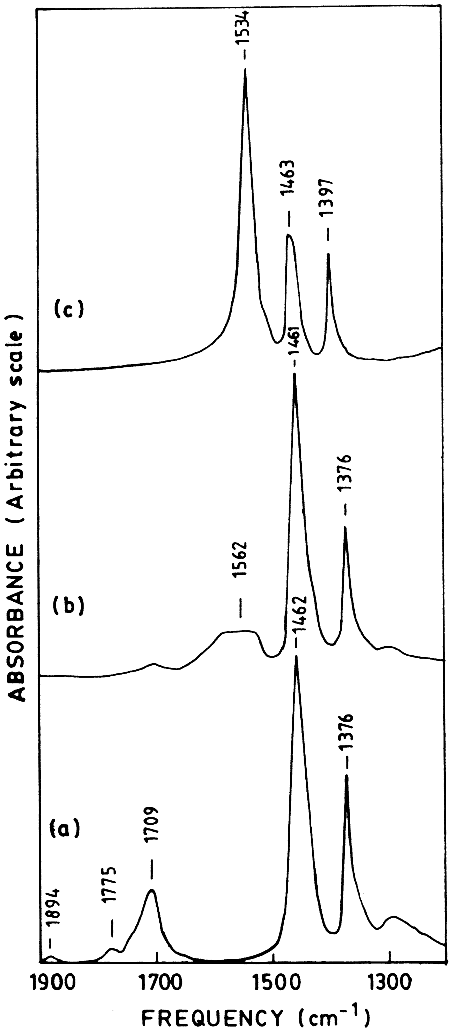

Fig. 6. Infra-red spectra of (a) mix PM4, (b) mix PM0 and (c) zinc stearate in the range of 1900–1200 cm^{-1}.

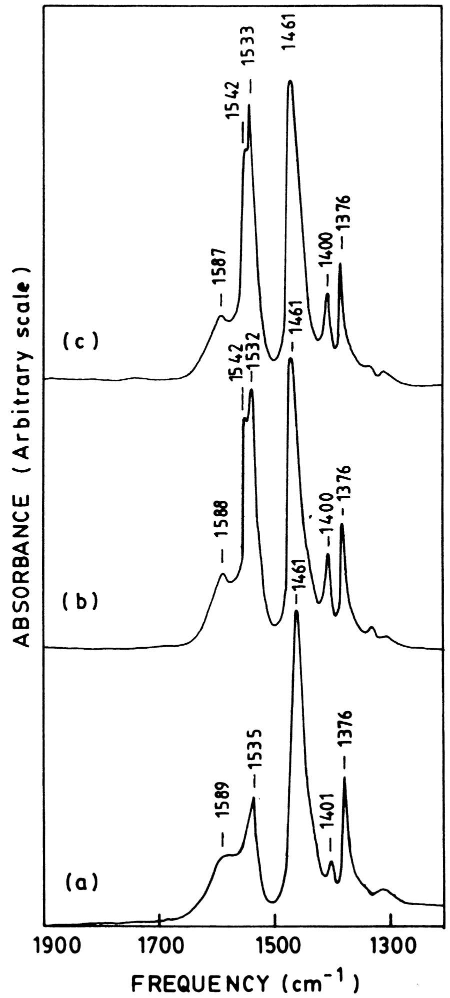

Fig. 7. Infra-red spectra of (a) mix PM1, (b) mix PM2 and (c) mix PM3 in the range of 1900–1200 cm^{-1}.

tensile strength of the extrudate of mix PM2 with number of cycles of extrusion. It is observed that the apparent viscosity of the blend and the tensile strength of the extrudate remain almost constant even after three cycles of extrusion, indicating the thermoplastic elastomeric nature of the blend.

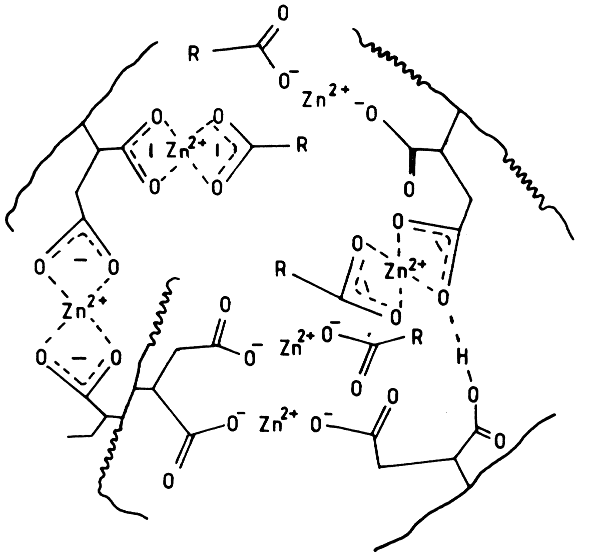

Fig. 8. Probable mechanism of interaction of zinc stearate, $(RCOO)_2Zn$, with ionic aggregates in the blend. 〰 mEPDM, mEPDM; 〰 mHDPE, mHDPE.

4. Conclusions

Processability studies in the MPT show that the ionomeric polyblend exhibits higher melt viscosity than the corresponding non-ionomeric polyblend. The addition of zinc stearate causes a dramatic reduction in the melt viscosity of the ionomeric polyblend and makes it melt-processable particularly at high shear rate. The ionomeric polyblend shows higher tensile strength, tear strength, hardness and lower tension set than the corresponding non-ionomeric polyblend. The addition of zinc stearate to the ionomeric polyblend increases the tensile strength, elongation at break, hardness and tension set, but there is a marginal decreases in modulus and a marginal increase in tear strength. Infra-red spectroscopic studies reveal that ionic interactions occur between zinc stearate and the ionomeric polyblend. Reprocessability studies show that

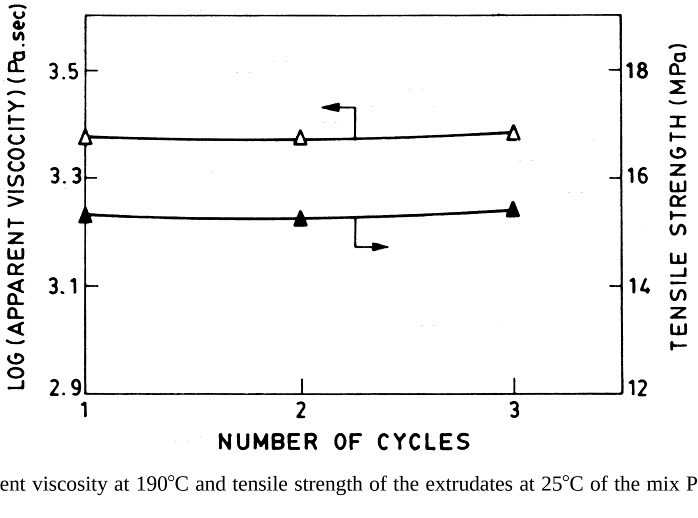

Fig. 9. Variation of apparent viscosity at 190°C and tensile strength of the extrudates at 25°C of the mix PM2 with extrusion cycle.

the blend could be reprocessed without deterioration in strength, signifying its thermoplastic elastomeric nature.

References

[1] Holliday L, editor. Ionic polymers. London: Applied Science, 1975.

[2] Bazuin CG, Eisenberg A. Ind Eng Chem Prod Res Dev 1981;20:271.

[3] Eisenberg A, Bailey FE, editors. Coulombic interactions in macromolecular systems, ACS Symposium Series No. 302. Washington, DC: American Chemical Society, 1986.

[4] Macknight WJ, Lundberg RD. Rubber Chem Technol 1984;57:652.

[5] Eisenberg A, King M. Ion-containing polymers: physical properties and structure. New York: Academic Press, 1977.

[6] MacKnight WJ, Earnest TR. J Polym Sci, Macromol Rev 1981;16:41.

[7] Fitzgerald JJ, Weiss RA. J Macromol Sci, Rev Macromol Chem Phys 1988;C28:99.

[8] Greener J, Gillmor JR, Daly RC. Macromolecules 1993;26:6416.

[9] Lundberg RD, Makowski HS. In: Eisenberg A, editor. Ions in polymers, Advances in Chemistry Series No. 187. Washington, DC: American Chemical Society, 1980:Ch. 3.

[10] Makowski HS, Lundberg RD, Westerman L, Bock J. In: Eisenberg A, editor. Ions in polymers, Advances in Chemistry Series No. 187. Washington, DC: American Chemical Society, 1980:Ch. 1.

[11] Weiss RA, Agarwal PK. J Appl Polym Sci 1981;26:449.

[12] Weiss RA, Fitzgerald JJ, Kim D. Macromolecules 1991;24:1071.

[13] Duvdevani I, Lundberg RD, Wood-Lordova C, Wilkes GL. In: Eisenberg A, Bailey FE, editors. Coulombic interactions in macromolecular systems, ACS Symposium Series No. 302. Washington, DC: American Chemical Society, 1986.

[14] Makowski HS, Lundberg RD. In: Eisenberg A, editor. Ions in polymers, Advances in Chemistry Series No. 187. Washington, DC: American Chemical Society, 1980.

[15] Datta S, De SK, Kontos EG, Wefer JM. J Appl Polym Sci 1996;61:177.

[16] Lundberg RD, Duvdevani I, Peiffer DG, Agarwal PK. In: Kohudic MA, editor. Advances in polymer blends and alloys technology, vol. 1. Lancaster: Technomic Publishing Co., Inc., 1988.

[17] Bagrodia S, Pisipati R, Wilkes GL, Storey RF, Kennedy JP. J Appl Polym Sci 1984;29:3065.

[18] Bagrodia S, Wilkes GL, Kennedy JP. Polym Eng Sci 1986;26:662.

[19] Tong X, Bazuin CG. J Polym Sci, Part B: Polym Phys 1992;30:389.

[20] Lundberg RD, Makowski HS, Westerman L. Am Chem Soc Polym Prepr 1978;19:310.

[21] Antony P, Datta S, De SK. Paper presented at a Meeting of the Rubber Division, ACS, Anaheim, CA, 6–9 May 1997.

[22] Smith AL. Applied infrared spectroscopy. New York: Wiley Interscience, 1979:287.

[23] Socrates G. Infrared characteristic group frequencies. Chichester: Wiley Interscience, 1980:31.

[24] Williams DH, Fleming I. Spectroscopic methods in organic chemistry. London: McGraw-Hill, 1987:29.