Ionomeric Polyblends of Zinc Salts of Maleated EPDM Rubber and Poly(ethylene-*co*-acrylic acid). II. Effect of Zinc Stearate on Processability

PRINCE ANTONY, A. K. BHATTACHARYA, S. K. DE

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

Received 24 October 1997; accepted 4 June 1998

ABSTRACT: Rheological properties of the ionomeric polyblends of zinc salts of maleated ethylene propylene diene monomer (EPDM) rubber and poly(ethylene-*co*-acrylic acid) were studied using a Monsanto Processability Tester. The ionomeric polyblend exhibits higher melt viscosity than the corresponding nonionomeric polyblend. Besides reduction in the melt viscosity of the ionomeric polyblend, zinc stearate increases the tensile strength and elongation at break of the ionomeric polyblend. Reprocessability studies reveal the thermoplastic elastomeric nature of the blend. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1257–1265, 1999

Key words: zinc salt of maleated EPDM rubber; zinc salt of poly(ethylene-co-acrylic acid); ionomeric polyblend; zinc stearate; processability

INTRODUCTION

The introduction of a small amount of ionic groups onto a hydrocarbon polymer results in a substantial increase in melt viscosity and physical properties.^{1–3} The high melt viscosity of the ion-containing polymers is due to the influence of strong intermolecular ionic interactions. The flow behavior of ionomers is rheologically complex due to the energetic requirements needed to dissociate the ionic interactions.⁴ The ionic aggregates present in the ionomers act as thermally labile physical crosslinks, permitting adequate melt flow at processing conditions.^{4,5} The melt rheology of the ionomers depends on several factors, such as the type of ionic moiety, the counter ion type, the degree of neutralization, and the presence of plasticizers.^{4,6,7} The polar plasticizers adversely affect the ion-pair associations and thereby cause a reduction in the melt viscosity. Zinc stearate is known to behave as an ionic plasticizer above its melting point but behaves as a filler at ambient temperatures, in the case of zinc salt of sulfonated EPDM and zinc salt of maleated EPDM rubber.⁸⁻¹⁰ Makowski and coworkers studied the plasticization of the metal sulfonated EPDM with various stearic acid derivatives.¹⁰ Lundberg and coworkers have reported the effect of both polar and nonpolar plasticizers on the melt viscosity of sodium salt of sulfonated polystyrene.¹¹ Bagrodia et al. have also studied the effect of plasticizer on the rheological behavior of ionomers.^{12,13}

The present article reports the results of studies on the effect of zinc stearate on the properties of ionomeric polyblend based on zinc-oxide-neutralized maleated EPDM rubber, abbreviated as Zn-mEPDM, and zinc-oxide-neutralized poly(ethylene-*co*-acrylic acid), abbreviated as Zn-PEA, in

Correspondence to: S. K. De.

Journal of Applied Polymer Science, Vol. 71, 1257–1265 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/081257-09

Materials	Properties	Source	
Poly(ethylene-co-acrylic acid), abbreviated as PEA (trade name, Polybond 1009) Malaoted EPDM, abbreviated	Acrylic acid, 6%; $M_w = 97,000$; specific gravity, 0.95; melt flow rate at 190°C, 6 g/10 min Ethylong content 55%; specific	Uniroyal Chemical Co., Naugatuck, U.S.A.	
as mEPDM (trade name, Royaltuf 465)	gravity, 0.89 maleic acid-maleic anhydride content, 1%; ML_{1+4} at 125°C, 60 molecular weight, $M_w = 3.99 \times 10^5$, and M_n $= 1.16 \times 10^5$	do	
		E. Merck Ltd.,	
Zinc oxide	Rubber grade; specific gravity, 5.6 Rubber grade; melting point,	Mumbai, India	
Stearic acid	76°C Rubber grade; melting point,	Obtained locally	
Zinc stearate	128°C	Obtained locally	

Table I Details of Materials Used

the composition of 60/40 parts by weight. In an earlier communication, it has been observed that the 60/40 Zn-mEPDM–Zn-PEA blend behaves as an ionic thermoplastic elastomer.

EXPERIMENTAL

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

Preparation of Blends

Formulations used for the preparation of the blends are given in Table II. The masterbatch of mEPDM with zinc stearate were prepared by mixing of the 2 components in a 2-roll mill at room temperature for 4 min. The blending of PEA with the mEPDM masterbatch was done in a Brabender Plasticorder, model PLE-330, at 170°C

and at a rotor speed of 60 rpm. First, PEA 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 and produce water, which converts the anhydride groups into the acid groups.⁹ After mixing, the hot material was sheeted out in a 2-roll mill. The blends were then molded at 170°C for 20 min in an electrically heated hydraulic press. After molding was over, the blends were cooled to room temperature by circulation of cold water through the platens.

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

Table II Formulations of the Blends

			Blend Number		
Ingredients	PM0	PM1	PM2	PM3	PM4
mEPDM	60	60	60	60	60
PEA	40	40	40	40	40
Zinc oxide	20	20	20	20	0
Stearic acid	1	1	1	1	0
Zinc stearate	0	10	20	30	0



Figure 1 (a) Log-log plots of shear stress versus shear rates of the blends. (b) Plots of log (apparent viscosity) versus zinc stearate loading at different shear rates.

Processability Studies

The flow properties of the blends were measured in a Monsanto Processability Tester (MPT), which is a fully automatic high-pressure capillary viscometer, at shear rates of 61.5, 122.9, 245.8, and 491.6 s⁻¹ and at a temperature of 190°C. The barrel and capillary were electrically heated with a microprocessor-based temperature controller system. The instrument details are available from the literature.^{14,15} The capillary length (30 mm)-to-diameter (1 mm) ratio (L/D) was 30. The preheat time for each sample was 5 min.

The barrel pressure and ram rate were converted into the apparent shear stress (τ_a) and shear rate $(\dot{\gamma}_a)$, respectively, using the following equations:

$$\tau_a = B_p / (4 \times L/D) \tag{1}$$

where B_p is the barrel pressure, and L/D is the capillary length to diameter ratio.

$$\dot{\gamma}_a = 32Q/\pi d_c^3 \tag{2}$$

where Q is the volumetric flow rate, and d_c is the capillary diameter.

The apparent viscosity (η_a) was calculated by the equation,

$$\eta_a = \tau_a / \dot{\gamma}_a \tag{3}$$

Measurement of Physical Properties

The stress-strain properties of the samples were performed with dumbbell samples according to ASTM D412 (1987) in a Zwick Universal Testing Machine (UTM), model 1445, at a crosshead speed of 500 mm/min. Tear strength was also measured in a Zwick UTM, model 1445, using a 90° nick cut crescent 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).

Infrared Spectroscopic Studies

Infrared spectroscopic studies on the compression-molded thin films of the samples were carried out using a Perkin–Elmer 843 spectrophotometer with a resolution of 3.2 cm^{-1} .

Reprocessability Studies

The reprocessability studies were made by extruding the sample through MPT at 190°C, using a die of L/D ratio 30 at a shear rate of 122.9 s⁻¹. The extrudate was re-extruded under similar con-

	App	Apparent Viscosity (Pa S) at Shear Rates (S^{-1})			
Blend Number	61.5	122.9	245.8	491.6	Behavior Index (n)
PM0	4685	2903	1812	1134	0.311
PM1	2749	1791	1148	726	0.356
PM2	2356	1543	986	624	0.360
PM3	992	1300	839	534	0.367
PM4	2319	1529	1008	646	0.389

Table III Apparent Viscosity and Flow Behavior Index of the Blends

ditions, and the process was repeated for 3 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.

RESULTS AND DISCUSSION

Rheological Properties

The log-log plots of shear stress versus shear rates are shown in Figure 1(a). All blends show the same trend in their behavior, as follows: shear stress increases with an increasing shear rate. It is also seen that the ionomeric polyblend (blend PM0) exerts higher shear stress at all shear rates than the corresponding nonionomeric polyblend (blend PM4). The addition of zinc stearate causes a marked reduction in the shear stress of the blend PM0, and, with the addition of 14% of zinc stearate (blend PM2), the shear stress decreases to the level of blend PM4. The log-log plots of shear stress versus shear rate are linear. Therefore, the material obeys a power law model of flow response. The power law model of flow is described by the following equation:

$$\tau_a = \mathbf{K} \dot{\gamma}_a^{\mathrm{n}} \tag{4}$$

where K and n are constants characteristic of the material. The constant n is usually called non-Newtonian index or flow behavior index, and the values of n for the different blends can be calculated from the slope of the Figure 1(a). The n values of the blends are shown in Table III. The low values of n(<1) are indicative of pseudoplastic behavior of the blends. Blend PM0 shows a lower n value than blend PM4. It is also observed that

the value of n slightly increases with an increase in zinc stearate loading.

The plots of log (apparent viscosity) versus zinc stearate loading at different shear rates are shown in Figure 1(b). Table III also shows the apparent viscosity of the blends at different shear rates. At all shear rates, the apparent viscosity decreases with an increase in zinc stearate loading. It is also obvious that at a particular zinc stearate loading, the apparent viscosity decreases with an increasing shear rate. Zinc stearate acts as an ionic plasticizer above its melting point and, hence, reduces the melt viscosity of the ionomer either by solvation or by a shear-induced exchange reaction between the zinc stearate and the metal carboxylate groups in the ionomer during melt flow.⁸⁻¹⁰ The microphotographs of the extrudates at different shear rates are shown in Figure 2. The extrudates of the ionomeric polyblends shows no melt fracture at low shear rates; however, melt fracture occurs at high shear rates. The addition of zinc stearate minimizes the melt frac-



Figure 2 Photomicrographs of the extrudates at 190°C and at different shear rates.

Properties	Blend Number				
	PM0	PM1	PM2	PM3	PM4
Modulus at 100% elongation (MPa)	6.6	6.0	6.3	6.3	4.6
Modulus at 200% elongation (MPa)	7.7	6.8	7.0	7.0	4.7
Modulus at 300% elongation (MPa)	8.6	7.7	8.0	7.8	4.8
Tensile strength (MPa)	12.3	15.3	16.2	15.0	5.1
Elongation at break (%)	608	810	816	766	455
Tear strength (kNm ⁻¹)	83.7	79.4	78.2	78.9	53.9
Hardness (Shore A)	84	84	85	85	79
Tension set at 100% elongation (%)	20	25	27	30	50

Table IV Physical Properties at 25°C

ture and thereby improves the surface smoothness of the extrudates, especially at high shear rates. Therefore, it can be concluded that zinc stearate not only improves the melt flow properties by promoting ionic bond interchange in the ionomeric polyblend but also improves the surface smoothness of the extrudates.

properties than the corresponding nonionomeric polyblend (blend PM4). The higher physical properties of the ionomeric polyblend is attributed to the improved compatibility of the blend components, wherein the interfacial ionic crosslinks facilitate the compatibility. The lower tension set of blend PM0 results from the existence of ionic crosslinks. Figure 4 shows the variation of phys-

Physical Properties

The physical properties of the blends measured at 25°C are summarized in Table IV. The stress– strain properties are shown in Figure 3. It is apparent that blend PM0 exhibits higher physical



Figure 3 Stress-strain plots of blend PM0 (-----), blend PM2 (----), and blend PM4 (-----).



Figure 4 Variation of physical properties of blend PM0 with zinc stearate loading.

ical properties of blend PM0 with zinc stearate loading. It is interesting to note that zinc-stearate-filled ionomeric polyblends show higher elongation at break and tensile strength than blend PM0, which does not contain zinc stearate. It is known that at ambient temperature, zinc stearate acts as filler, in the case of EPDM-based ionomers.⁸⁻¹⁰ It is seen that beyond 14% of zinc stearate, both the elongation at break and tensile strength slightly decrease. It is also apparent that the incorporation of zinc stearate causes a mar-



Figure 5 Infrared spectra of (a) blend PM4, (b) blend PM0, and (c) zinc stearate in the range of 1800-1200 cm⁻¹.



Figure 6 Infrared spectra of (a) blend PM2, (b) blend PM3, and (c) addition spectrum in the range of $1800-1200 \text{ cm}^{-1}$.

ginal increase in hardness and tension set, but a marginal decrease in modulus and tear strength occurs.

Infrared Spectroscopic Studies

Figure 5 shows the infrared spectra of the 60/40 nonionomeric polyblend (blend PM4), 60/40 ionomeric polyblend (blend PM0), and zinc stearate.



(a) 2R - COOH + ZnO - (RCOO)₂ Zn + H₂O Formation of water molecule

Figure 7 Schematic model for the formation of interfacial ionic crosslinks in the Zn-mEPDM–Zn-PEA blend and the shear-induced exchange reaction of zinc stearate during melt flow.

The spectrum of blend PM4 shows an intense band at 1709 cm⁻¹, which is ascribed to the presence of hydrogen-bonded carboxylic acid pairs.¹⁶ The strong and intense band at 1464 cm⁻¹ denotes the $-CH_2$ — bending vibration, and a sharp band at 1376 cm⁻¹ is associated with $-CH_3$ symmetric deformation.^{16,17} It is seen from the spectrum of blend PM0 that neutralization of carboxylic acid groups present in blend PM4 with zinc oxide results in the disappearance of the band at 1709 cm^{-1} and causes the appearance of a broad band centered at 1560 cm^{-1} in the asymmetric carboxylate stretching region. The band at 1560 cm^{-1} is assigned to the asymmetric metal carboxylate stretching vibration.¹⁶ The spectrum of zinc stearate, taken by the KBr disk technique, shows a strong and intense band at 1534 cm^{-1} , which is attributed to the asymmetric carboxylate stretching of zinc carboxylate ions present in zinc stearate. The band at 1463 cm⁻¹ accounts for the $-CH_2$ — bending vibration.

Figure 6 shows the infrared spectra of ionomeric polyblends containing 14% (blend PM2) and 20% (blend PM3) of zinc stearate and the addition spectrum. The addition spectrum was obtained by the weighted addition of the spectra of zinc stearate and the ionomeric polyblend. It is interesting to note that the asymmetric carboxylate stretching region $(1650-1500 \text{ cm}^{-1})$ of blends PM2 and PM3 show a triplet band around 1587, 1542, and 1532 cm^{-1} . It is also seen that the intensity of the asymmetric carboxylate stretching region increases with an increase in zinc stearate loading. The appearance of 3 bands, instead of a broad band in blend PM0 and a sharp band in zinc stearate, is believed to be due to the changes in the spectral features due to the interaction of the zinc carboxylate ions present in the zinc stearate with that in the ionomeric polyblend. The interaction causes marked changes in the geometrical arrangement of carboxylate ions around zinc ions. It is also interesting to compare the asymmetric carboxylate stretching region of the spectrum of blend PM2 and the corresponding addition spectrum. A remarkable difference between the 2 spectra in the asymmetric carboxylate stretching region occurs. In contrast to the spectrum of blend PM2, the addition spectrum shows a sharp band at 1535 cm^{-1} with a shoulder at 1588 cm⁻¹. This also confirms the strong interaction of zinc stearate with the ionomeric polyblend.

Figure 7 shows the schematic model for the formation of interfacial ionic crosslinks in the Zn-mEPDM–Zn-PEA blend and the shear-induced exchange reactions of zinc stearate during melt flow.

Reprocessability Studies

Figure 8 shows the variation of apparent viscosity and tensile strength of the extrudate of blend PM2 with the number of cycles of extrusion through the MPT. It can be seen that after 3 cycles of extrusion, both the apparent viscosity of the blend and tensile strength of the extrudate almost remain unchanged, indicating the thermoplastic elastomeric nature of the blend. This also indicates the thermal and shear stability of the blend.



Figure 8 Variation of apparent viscosity at 190°C and tensile strength of the extrudates at 25°C of blend PM2 with extrusion cycle.

CONCLUSIONS

- 1. The rheological properties show that the ionomeric polyblend exhibits higher melt viscosity than the corresponding nonionomeric polyblend.
- 2. At high processing temperatures, molten zinc stearate causes a marked reduction in the melt viscosity of the ionomeric polyblend and improves the melt processability particularly at high shear rates.
- 3. At ambient temperatures, zinc stearate enhances the tensile strength, elongation at break, hardness, and tension set, but a marginal decrease in modulus and tear strength of the ionomeric polyblend occurs.
- 4. Infrared spectroscopic studies reveal that ionic interactions between zinc stearate and the ionomeric polyblend exist.
- 5. Reprocessability studies show that blend could be reprocessed without deterioration in properties.

The authors thank Uniroyal Chemical Co., U.S.A., for supplying the materials and also the University Grants Commission, New Delhi, for providing the financial support for the present work.

REFERENCES

- 1. Eisenberg, A.; King, M. Ion-containing Polymers, Physical Properties and Structure, Academic Press: New York, 1977.
- Bazuin, C. G.; Eisenberg, A. Ind Eng Chem Prod Res Dev 1981, 20, 271.

- Eisenberg, A.; Bailey, F. E., Eds., Coulombic Interactions in Macromolecular Systems, ACS Symposium Series No. 302, American Chemical Society: Washington, DC, 1986.
- 4. MacKnight, W. J.; Earnest, T. R. J Polym Sci Macromol Rev 1981, 16, 41.
- 5. MacKnight, W. J.; Lundberg, R. D. Rubber Chem Technol 1984, 57, 652.
- Fitzgerald, J. J.; Weiss, R. A. J Macromol Sci Rev Macromol Chem Phys 1988, C28, 99.
- Greener, J.; Gillmor, J. R.; Daly, R. C. Macromolecules 1993, 26, 6416.
- Duvdevani, I., Lundberg, R. D.; Wood-Lordova, C. Wilkes, G. L. in Coulombic Interactions in Macromolecular Systems, Eisenberg, A.; Bailey, F. E., Eds., ACS Symposium Series No. 302, American Chemical Society: Washington, DC, 1986, p. 184.
- Datta, S.; De, S. K.; Kontos, E. G.; Wefer, J. M. J Appl Polym Sci 1996, 61, 177.
- 10. Makowski, H. S.; Lundberg, R. D. in Ions in Poly-

mers, Eisenberg, A., Ed., Advances in Chemistry Series 187, American Chemical Society: Washington, DC, 1980, p. 37.

- 11. Lundberg, R. D.; Makowski, H. S.; Westerman, L. Am Chem Soc Polym Prep 1978, 19, 310.
- Bagrodia, S.; Pisipati, R.; Wilkes, G. L.; Storey, R. F. Kennedy, J. P. J Appl Polym Sci 1984, 29, 3065.
- Bagrodia, S.; Wilkes, G. L.; Kennedy, J. P. Polym Eng Sci 1986, 26, 662.
- Roger, E. R.; Baker, R. J.; Hanna, G. C. paper presented at the 10th Meeting of the Rubber Division, American Chemical Society: San Francisco, California, 4–8 Oct. 1976.
- 15. Monsanto Processability Tester, Operation and Service Manual, Monsanto Company.
- Smith, A. L. Applied Infrared Spectroscopy, Wiley-Interscience: New York, 1979, p. 287.
- Williams, D. H.; Fleming, I. Spectroscopic Methods in Organic Chemistry, McGraw-Hill: London, 1987, p. 29.