PII: S0032-3861(96)00607-6

Polymer Vol. 38 No. 6, pp. 1395–1402, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/\$17.00 + 0.00

Characterization of ionomers formed *in situ* from miscible blends of poly (ethylene-*co*-acrylic acid) (PEA) and epoxidized natural rubber (ENR)

Subhra Mohanty and Golok B. Nando*
Rubber Technology Centre, IIT Kharagpur-721302, India
(Received 7 November 1995; revised 27 May 1996)

Reactive processing of binary blends of poly (ethylene-*co*-acrylic acid) (PEA) and epoxidized natural rubber (ENR) in a Brabender Plasticorder at an elevated temperature led to miscibility beyond 50 wt% of PEA forming PEA-g-ENR. The blends were then neutralized with zinc oxide to form zinc ionomers which have been analysed by i.r. spectroscopy. The effect of zinc stearate on the ionomers has also been investigated. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: esterification reaction; ionomers; miscibility)

INTRODUCTION

Polymer blends have played a significant role in the last two decades in revolutionizing the polymer technology in almost every sphere of human endeavour, leading to diverse useful applications such as in footwear, automobiles, space and marine engineering. This trend has been gaining momentum because of the ease with which polymer properties can be modified to 'tailor' products within the shortest possible time and with minimum consumption of labour and energy. The latter half of the present century has witnessed the emergence of ionic polymers as a new class of materials for domestic, industrial and engineering applications; it is in this context that the present work has been undertaken to develop ionomers from useful blends. Some of the unique applications of these materials have been in golf ball covers, barrier films and in packaging industries. Moreover scientists and technologists have been fascinated by these types of materials because of their higher performance properties, such as oil resistance and dielectric strength. Considerable research is being carried out in this field in various laboratories and in research institutes all over the world and a large number of patents and publications have been brought out. The ionomers from different homopolymers and copolymers have been synthesized and have also been commercialized in recent years. However, literature on ionomers produced from blends of polymers is scarce; hence, an attempt has been made in this study to develop ionomers from interactive polymer blends of poly (ethylene-*co*-acrylic acid) (PEA) and epoxidized natural rubber (ENR) and to find suitable applications.

It may be useful at this stage to discuss some of the fundamental aspects of ionomers in general. These are polymers containing pendant acid groups to the extent of only 10 mol% in a hydrocarbon chain and may be either partially or fully neutralized to form metallic salts. These are different from 'polyelectrolytes' where the neutralized salts are present on alternate repeating units in the molecular chain. The ionic polymers range from organic water-soluble polyelectrolytes and hydrogels to ionomers derived from carboxylate rubber and plastics and at the extreme end an infusible inorganic silicate mineral. The ions, either singly or as clusters in the polymers, take part in the formation of ionic bonds and act as crosslinkers; in halatotelechelic polymers the ionic bonds form an integral part of the polymer backbone itself.

Since the introduction of zinc and sodium salts of ethylene methacrylic acid copolymer as ionomers by Dupont in 1960s, this copolymer has been considered the precursor of ionic crosslinks in the elastomers and has provided better understanding of the ionic polymers. It is evident that neutralization of the carboxylated polymers with divalent metallic cations such as Cu^{2+} and Zn^{2+} produce bridges between two carboxylate ions and the polymers behave like vulcanized rubber. However, the monovalent cations like Na^+ and K^+ show the presence of dipole–dipole interaction between the salt pairs. A schematic representation of divalent and monovalent ionomers are given below:

$$\begin{array}{cc} -\mathrm{COO}^{-1} \cdots \mathrm{M}^{2+} \cdots {}^{-1}\mathrm{OOC}- & -\,\mathrm{COO}^{-1+1}\mathrm{M} \\ & \mathrm{M}^{+1-1}\mathrm{OOC}- \\ \text{Divalent} & \text{Monovalent} \end{array}$$

A number of models have been proposed to describe the microstructure of the ionomers. The first and foremost model has been proposed by Eisenberg, based on

---

* To whom correspondence should be addressed

multiplets and clusters[1]. He defined the multiplets as a group of ion pairs with no hydrocarbon content, while a cluster is a loose association of multiplets. The association of multiplets is favoured by electrostatic interactions between multiplets and is opposed by forces arising from the elastic nature of the backbone chain. The subsequent development of models is based on two considerations: (1) steric factors which are used to calculate the largest number of ion pairs that can group together without the presence of any intervening hydrocarbon; and (2) energetic considerations which are invoked to argue for the formation of large entities[2].

The clusters, as proposed by Eisenberg, are responsible for the physical properties of these polar materials. The microstructure of the clusters can be determined by far i.r. spectroscopic study, Raman spectroscopy, small-angle X-ray scattering studies, small-angle neutron scattering, and Fluorescence probing techniques[2-5].

The present article corroborates the following parameters of the ionomers prepared from blends of ENR and PEA: (1) the miscibility of the blends of ENR and PEA; (2) characterization of the ionomers formed from ZnO by i.r. spectroscopy; (3) effect of zinc stearate on the ionomer; and (4) the degree of neutralization.

EXPERIMENTAL

Materials

The PEA containing 6 wt% of acrylic acid (specific gravity 0.93) used in the present study was supplied by Exxon Chemical Corporation, Belgium under the trade name ESCOR-5001. ENR containing 50 mol% of epoxy groups (density of 1.03) was supplied by Guthre Co., Malayasia. Zinc oxide and zinc stearate used were of Laboratory reagent grade.

Reactive processing

The reactive processing of PEA and ENR was performed by a melt-mixing technique in a Brabender Plasticorder (Model-PLE-330) fitted with a cam-type rotor at 150°C (rotor speed of 80 r.p.m.) for a total of 10 min. The reaction conditions such as temperature and time of the mixing were optimized by the authors[6]. Zinc oxide was added to the mixer in various proportions after 8 min to neutralize the acid present in the copolymer and the residual acid present in the blends. After 2 min of melt-mixing with ZnO, in the Plasticorder, zinc stearate was added to the mix in various proportions. Melt processing was carried out until a stable torque was obtained and the proportion of zinc stearate incorporated was also optimized in the Results and Discussion section. The blends have been coded as N_p Z_q St_r where the subscripts p, q and r stand for the proportion of epoxidized natural rubber, zinc oxide and zinc stearate in the blend composition respectively.

I.r. study

Thin films of the pure components, blends and ionomers were prepared (< 0.3 mm) in a hydraulic press at 150°C under a pressure of 10 MPa with a residence time of 2 min. The films were analysed in a Perkin-Elmer (Mode-843) i.r. spectrophotometer with attached computer data analyser (Software package provided by Perkin-Elmer) at room temperature, in the range from 4000 cm^{-1} to 400 cm^{-1}. The absorbance values of all the samples were corrected to the same thickness (1 mm) for convenience and comparison. The data obtained, are calculated for 1 mm thickness in all cases and are tabulated.

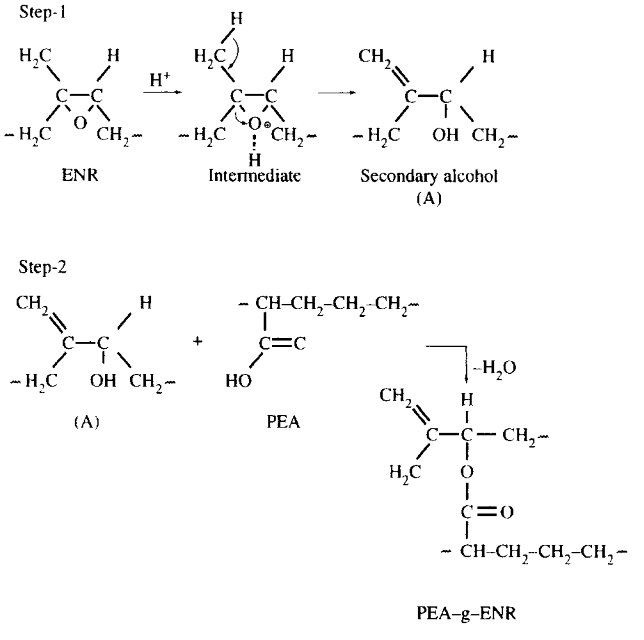
RESULTS AND DISCUSSION

Miscibility of ENR and PEA blends via esterification reaction

The authors in an earlier communication have reported that the blends of epoxidized natural rubber and poly (ethylene-*co*-acrylic acid) are miscible as the PEA proportion exceeds 50 wt% in the blends[6]. Some of the epoxy rings in ENR break down into secondary alcoholic groups and some are reported to convert into furan ring structure, aliphatic ether and carbonyl groups[7]. The secondary alcoholic groups thus generated *in situ* during melt-blending at 150°C react with the free acid groups of the PEA to form ester linkages; this has been confirmed from the i.r. spectroscopic study of the difference spectra. A plausible mechanism of the reaction between ENR and PEA forming PEA-g-ENR has been shown in *Scheme 1*. The blends N_{50} and N_{30} are found to be completely miscible to the molecular level as indicated by the occurrence of a single glass transition temperature from dynamic mechanical analysis and a negative interaction parameter[8], whereas the N_{70} blend is found to be partly miscible. Scanning electron photomicrographic studies of the N_{70} blend show a minor phase separation[6] whereas N_{50} and N_{30} blends exhibit single-phase behaviour. Further evidence of miscibility via chemical interaction has been obtained from the study of melt flow behaviour of the blends which shows maximum positive deviation of the melt viscosity for the same[9]. Thermogravimetric analysis of the blends show highest thermal stability for the N_{30} blend[10].

Effect of ZnO proportion in the blends

Figure 1 shows the i.r. spectra of pure PEA and zinc oxide neutralized PEA in the wavelength range from 1800–1400 cm^{-1} and 750–700 cm^{-1}, respectively.



Scheme 1

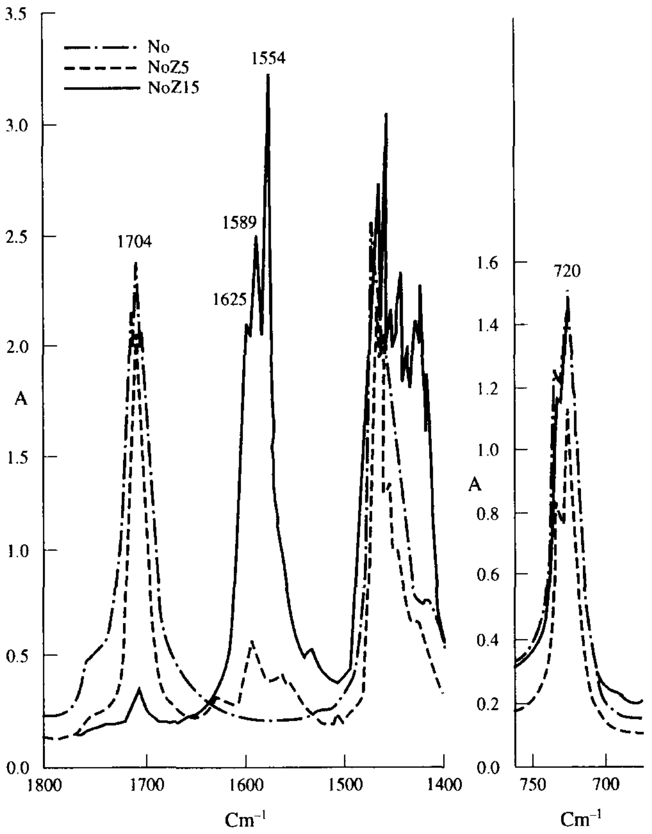


Figure 1 The i.r. spectra of N_0 (pure PEA), N_0Z_5 and N_0Z_{15} blends, respectively, in the regions 1800–1400 cm^{-1} and 750–700 cm^{-1}

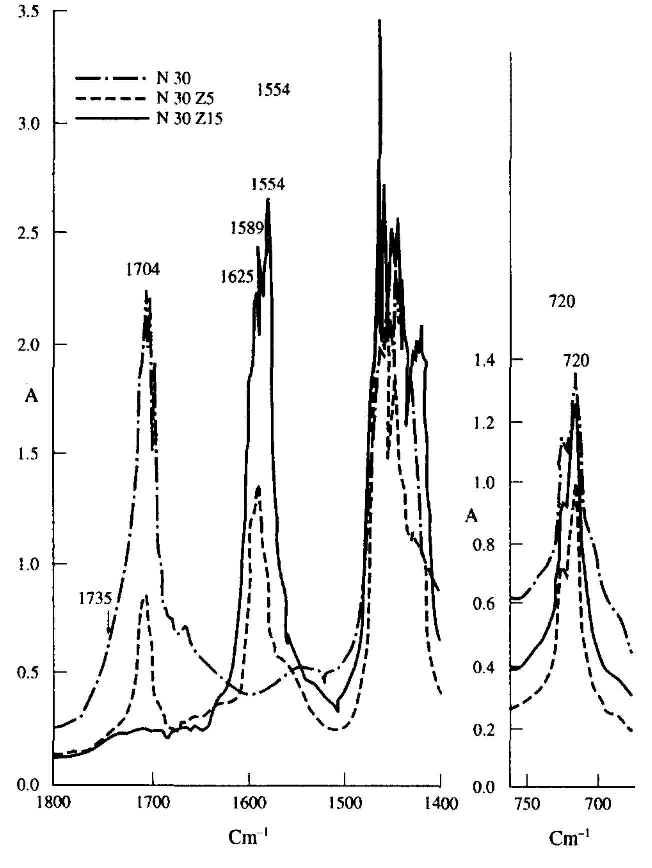


Figure 2 The i.r. spectra of N_{30}, $N_{30}Z_5$ and $N_{30}Z_{15}$ blends in the regions 1800–1400 cm^{-1} and 750–700 cm^{-1}

Figure 1 shows the i.r. spectrum of pure PEA. A prominent peak at 1704 cm^{-1} is due to carbonyl stretching of the carboxylic acid groups[11–13], but on incorporation of ZnO into PEA in different proportions the area under the 1704 cm^{-1} peak decreases, and has a reciprocal relationship with the amount of ZnO added. A new peak simultaneously appears at 1589 cm^{-1} whose area increases proportionately with ZnO concentration. In addition to this change, minor peaks also appear at 1625, 1560, 1554 cm^{-1} which may be assigned to the occurrence of different ionomeric structures as reported earlier[14–18]. The spectra of PEA with 5 and 15 parts ZnO are shown in *Figure 1*. Although i.r. spectrometry studies of all the other blends with varying proportion of ZnO have been carried out, their spectrograms are not produced here owing to lack of space. However, the areas of all these peaks at 1704, 1625, 1589, 1561 and 1554 cm^{-1} at different proportions of ZnO have been calculated with the base line correction and are listed in *Table 1*. The area of the peak at 1419 cm^{-1} has not been reported as it occurs as a small hump with respect to other ionomeric peaks in the spectrum. The peak areas have been calibrated to a uniform thickness of 1 mm. As expected, the extent of the neutralization reaction increases with an increase in the proportion of ZnO added, and a characteristic difference between the spectra of the blends containing 5 parts ZnO and 15 parts ZnO has been observed. The peaks at 1625, 1569 and 1554 cm^{-1} disappear in the blend containing 15 parts ZnO. This has been explained as being due to the presence of different ionomeric structures. In the case of the neutralized salts of PEA, the peaks which appear in the range 1645–1500 cm^{-1} have been assigned to the –COO asymmetric stretching vibration of $-COO^-Zn^{2+-}OOC-$ moiety and the peak observed at 1419 cm^{-1} is due to the symmetric stretching vibration of the ionic groups. No special importance has been given to this symmetric stretching vibration because its intensity is much weaker than the asymmetric stretching bands[14–18]. The peaks occurring at different wave numbers in the region 1645–1500 cm^{-1} are due to different types of structures present in the ionomers, as suggested by Coleman *et al.*[19].

Figure 2 shows the spectra of N_{30} blend and their zinc-neutralized salts containing 5 and 15 parts of ZnO in the wavelength region 1800–1400 cm^{-1}. For N_{50} and N_{70} blends (50 and 70 parts of ENR, respectively) similar spectra are obtained in the i.r. spectrophotometer, which have not been shown here because of limited space. The remaining acid groups which have been left out after esterification reaction in the blends subsequently react with the ZnO during processing to form ionomers.

The neutralized blends have therefore been characterized by the i.r. bands at 1625, 1585 and 1560 cm^{-1} for different isomeric structures. The absorption peak 1585 cm^{-1} in the region 1608–1570 cm^{-1} has been assigned to the –COO stretching vibration of the ionomers formed from the tetra coordinated zinc complex structure[19]. The shoulder peaks at 1625 cm^{-1} in the regions 1645–1616 cm^{-1} and that at 1561 cm^{-1} in the region 1570–1556 cm^{-1} have been attributed to the hexa-coordinated carboxylate multiplet structure and acid salt structure (with 5 pbw of ZnO) in *Figure 2*. As the proportion of ZnO is increased to 15 phr as shown in *Figure 2* in the blend both the shoulder peaks of 1585 cm^{-1} occurring at 1625 and 1561 cm^{-1}, respectively,

Table 1 Area of i.r. peaks in cm^{-1} within the given region and with respect to degree of neutralization

Blend code	699–725 720	1685–1720 1704	1645–1616 1625	1608–1570 1589/1585	1570–1558 1561	1558–1547 1554	% of neutralization
N_0	18.4	303.5		–	–		–
N_0Z_5	15.59	232.078	44.88	99.33	35.29	36.52	10.0
$N_0Z_{7.5}$	13.28	68.123	26.72	235.52		–	68.9
N_0Z_{10}	9.08	43.29		324.62	20.3	21.27	71.5
N_0Z_{15}	6.226	27.6	–	350.6	–	–	73.5
N_0St_{20}	12.5	173.5	–	90.5	33.19	–	15.8
$N_0Z_5St_{10}$	9.85	34.41	–	215.85	7.72	–	78.8
$N_0Z_5St_{15}$	9.18	21.89		270.8	21.97	7.78	90.5
$N_0Z_5St_{20}$	7.54	11.516	–	420.93	–	–	90.9
$N_0Z_5St_{40}$	6.83	9.93	–	431.54	–	–	91.1
$N_0Z_{7.5}St_{20}$	7.39	11.1	–	32.18	–	–	90.8
$N_0Z_{10}St_{20}$	6.89	9.68	–	449.74	–	–	91.5
$N_0Z_{15}St_{20}$	5.53	7.18	–	468.97	–	–	92.1
N_{30}	17.28	241.97	–	–		–	–
$N_{30}Z_5$	11.39	73.92	31.43	205.55	–	29.35	53.6
$N_{30}Z_{7.5}$	10.88	45.14	–	221.63		15.33	70.8
$N_{30}Z_{10}$	7.58	18.49	–	279.73	–	15.3	82.5
$N_{30}Z_{15}$	6.075	17.18	–	266.75	–	17.43	82.9
$N_{30}Z_5St_{20}$	6.075	7.23	–	350.5	–		91.5
N_{50}	13.19	157.28		–	–	–	–
$N_{50}Z_5$	9.39	39.53	26.53	195.87	–	25.48	64.5
$N_{50}Z_{7.5}$	8.93	25.77	–	211.36	–	14.6	75.8
$N_{50}Z_{10}$	7.68	14.64	–	241.27	32.81	31.45	84.0
$N_{50}Z_{15}$	7.14	13.32	–	234.3	–	25.9	84.3
$N_{50}Z_5St_{20}$	8.12	7.53	–	321.57	–	–	92.3
N_{70}	7.107	56.59	–	–	–	–	–
$N_{70}Z_5$	7.003	7.77	46.0	178.93	–	44.93	83.0
$N_{70}Z_{7.5}$	6.58	6.97		170.9		10.9	86.6
$N_{70}Z_{10}$	5.12	5.18	–	165.5	–	18.6	87.3
$N_{70}Z_{15}$	4.39	4.23	–	160.84	–	10.9	87.9
$N_{70}Z_5St_{20}$	6.95	2.45	–	309.68	–	–	95.5

merge to form a single peak at 1585 cm^{-1}. The area of the different ionomeric peaks for various blend ratios such as N_{30}, N_{50} and N_{70} are given in *Table 1*. The disappearance of these peaks implies that only the tetra-coordinated structures are formed at a higher proportion of ZnO. This type of rearrangement in the structure of ionomers may occur owing to availability of Zn^{2+} ions abundantly in the matrix. As the proportion of ZnO increases in the blend, the number of Zn^{2+} ions also increases; consequently, the formation of lower coordinated complex structures are more favoured than the higher coordinated complex ones. As the amount of ZnO increases from 5 to 15 pbw in the blends the degree of neutralization increases (see *Table 1*) but, conversely, the area of the ionomeric peak decreases. This reduction in peak area observed may be due to structural breakdown of ionomeric clusters in presence of excessive positive metal ions.

Effect of zinc stearate on the ionomers from ENR and PEA blends

Figure 3 shows the effect of various proportions of zinc stearate on the zinc ionomers formed from pure PEA containing 5 parts of ZnO (N_0Z_5) in the region of 1800–1400 and 750–700 cm^{-1}, respectively. For convenience, this variation was carried out only for the ionomer N_0Z_5 to study the effect of zinc stearate. The amount of zinc stearate is varied from 10 (parts by weight) pbw to 40 pbw shown in *Figure 3*. The area under the peak at 1704 cm^{-1} and those of ionomer peaks in the region 1618–1570 cm^{-1} (i.e. 1589 cm^{-1}) are depicted in *Table 1*; the degree of neutralization for all the blends are also reported. For $N_0Z_5St_{10}$ the ionomeric peak, which appeared earlier at 1625 cm^{-1} for N_0Z_5, surprisingly disappeared but the area under the 1589 cm^{-1} peak increased remarkably. At the same time, the area under the 1704 cm^{-1} peak was reduced noticeably. (The areas in all these cases are calculated keeping the film thickness constant.) It shows that more and more –COOH groups have been utilized to form the zinc ionomers with incorporation of zinc stearate into the copolymer. This may be explained as the plasticizing action of the stearate in the entangled matrix. As a result, the residual –COOH groups, which were previously caged in within the matrix, subsequently come out of the macromolecular system to react with the Zn^{2+} cations to form the ionomers; the concentration of Zn^{2+} ions increase in the system and the formation of low coordinated complexes like tetra-coordinated and di-coordinated structures are apparently formed instead of highly coordinated complexes like hexa-coordinated structures. This occurs either at higher doses of ZnO or at lower doses of ZnO

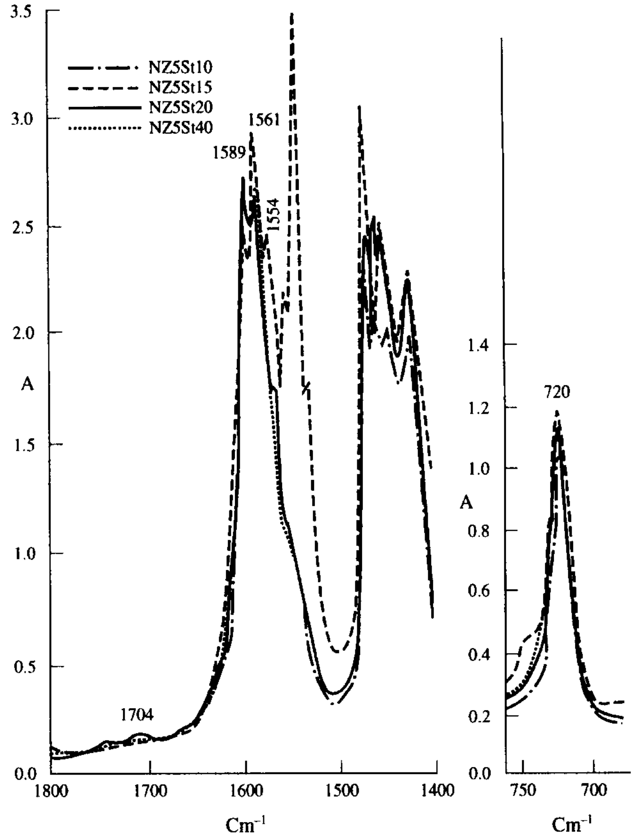


Figure 3 The effect of different proportions of zinc stearates [10, 15, 20 and 40 phr (parts per hundred of rubber), respectively] on the N_0Z_5 blend in the regions 1800–1400 cm^{-1} and 750–700 cm^{-1}

in combination with higher doses of zinc stearate. The primary objective of incorporating zinc stearate is to improve the processibility of the ionomers thus formed from PEA and the blends which otherwise are rather very tough and difficult to process. This has been confirmed from the i.r. spectroscopic study of the zinc ionomers which shows an improvement in the processing characteristics of PEA simultaneously exhibiting synergistic effect in ionomer properties. The processibility of PEA and its blend in presence of zinc stearate is beyond the scope of this paper and shall be reported separately.

On increasing the proportion of zinc stearate from 10 to 20 pbw the degree of neutralization increases but beyond 20 pbw of zinc stearate the increase is marginal. Thus 20 pbw of zinc stearate has been taken as the optimum proportion for pure PEA. Subsequently, the same proportion of zinc stearate has also been used for the blends, although it may require less amounts of zinc stearate as the blends contain lower proportion of PEA.

Figure 4 shows the i.r. spectra of ionomers of PEA containing 20 wt% of zinc stearate and various doses of ZnO. *Figure 4* gives the i.r. spectrum of N_0St_{20} which contains only 20 pbw of zinc stearate and no ZnO in the system in the range 1800–1400 cm^{-1}. It shows that even 20 pbw of zinc stearate alone is unable to neutralize all the acid groups present in PEA (i.e. only 15.8%). The i.r. spectrum shows different isomeric ionomer peaks at 1589, 1560, 1546 and 1536 cm^{-1}, respectively. Of these, the additional peaks at 1536 and 1546 cm^{-1} are attributed to the zinc trimer and hexa-coordinated zinc

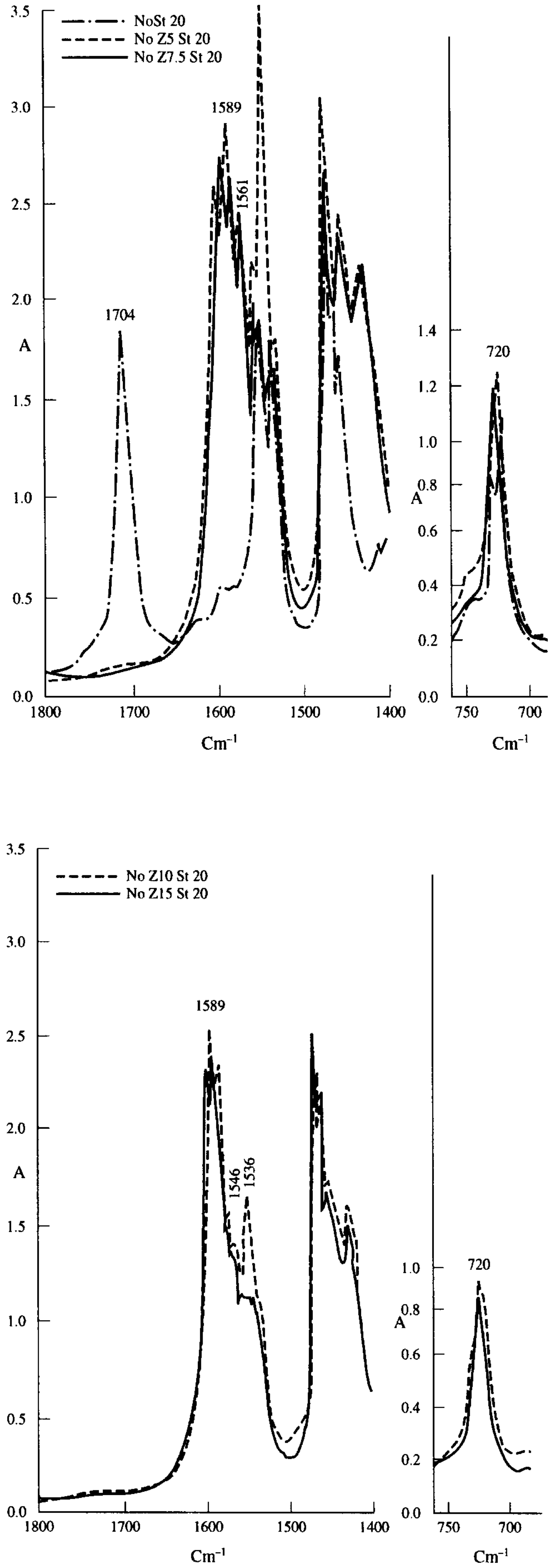


Figure 4 The effect of different proportions of ZnO with a constant proportion of zinc stearate on pure PEA (N_0) in the regions 1800–1400 cm^{-1} and 750–700 cm^{-1} (i.e. N_0St_{20}, $N_0Z_5St_{20}$, $N_0Z_{7.5}St_{20}$, $N_0Z_{10}St_{20}$, $N_0Z_{15}St_{20}$)

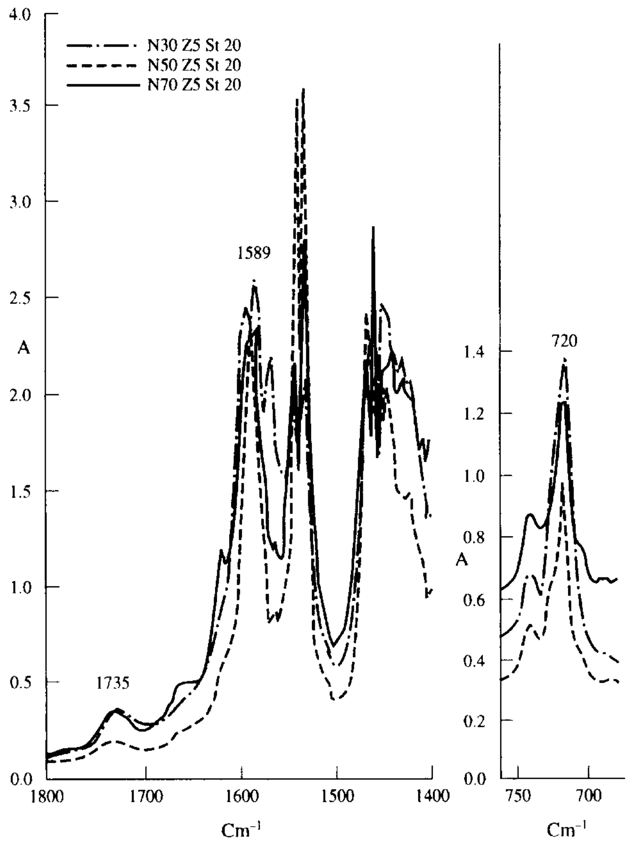
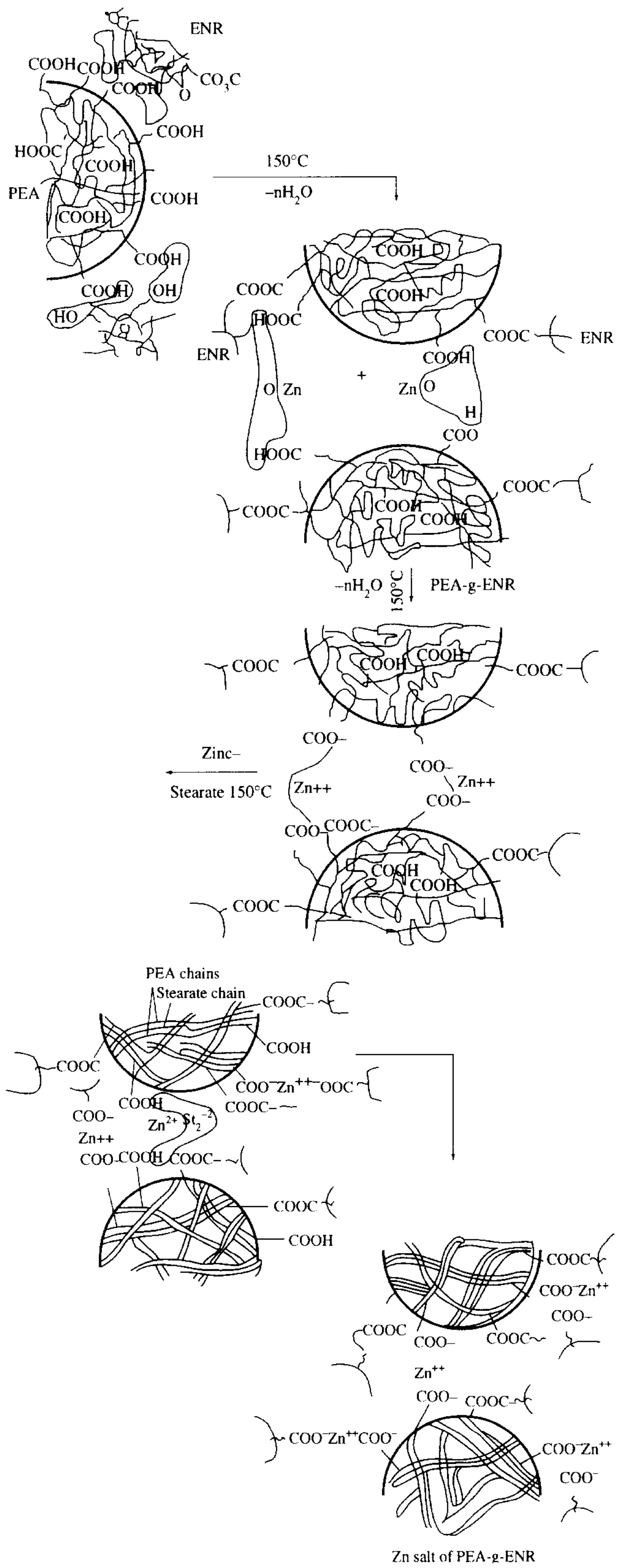


Figure 5 The spectra of $N_{30}Z_5St_{20}$, $N_{50}Z_5St_{20}$ and $N_{70}Z_5St_{20}$ in the region 1800–1400 cm^{-1} and 750–700 cm^{-1}, respectively

structure of the ionomer, as suggested by Coleman *et al.*[19]. By increasing the proportion of zinc oxide from 5 to 15 pbw the change in ionomer formation is marginal (*Figure 4*), except there is an increase in the degree of neutralization by 2% (i.e. from 90.5% to 92.1%), which will be discussed in the subsequent section. Because the change is not as significant here, 5 parts of ZnO has been taken as optimum proportion with 20 parts of zinc stearate.

Infra-red spectra of all the other blends of PEA with ENR containing 5 parts ZnO and 20 parts zinc stearate are studied and the spectrograms are depicted in *Figure 5*. In all these cases the unutilized acid remaining after the esterification reaction was neutralized with the help of zinc ions (ZnO and zinc stearate). This is shown from the absence of the acid peaks in the i.r. spectrogram at 1704 cm^{-1} and the appearance of a distinct peak at 1735 cm^{-1} due to the esterification reaction between PEA and ENR. The area under the ionomeric peaks and acid peaks in all these blends are given in *Table 1*.

To explain the mechanism of action of zinc stearate on the ionomers, *Scheme 2* has been proposed, taking into consideration the cluster aggregate model of R. Longworth and D. J. Vaughan (unpublished results)[20]. According to this model, when the acid groups are ionized, a profound structural reorganization takes place and clusters of ions are formed, approximately 100 Å diameter or more. The crystalline and ionic regions are then connected by a hydrocarbon matrix.



Scheme 2

In the present system the remaining acid groups of PEA after melt-blending with ENR are supposed to be neutralized by ZnO, but in practice this does not take place. This is explained in the reaction mechanism suggested in *Scheme 2*. It has been reported that the blends of PEA and ENR are miscible owing to chemical interaction between the two components via ester link formation, leading to grafting of ENR onto the PEA matrix, i.e. PEA-g-ENR. Therefore, the viscosity of the blends should increase, resulting in a very small number of acid groups available at the interface to react with zinc ions. On incorporation of ZnO into the blend matrix under similar conditions these acid groups are neutralized. This results in a further increase in the viscosity, as has been observed during reactive processing where the torque rises from 12 Nm to 40 Nm after 2 min of addition of ZnO. This has been attributed to two reasons: (1) formation of the grafted structures for instance PEA-g-ENR in the blends; (2) formation of clusters of ionomers in the matrix. Because of an increase in viscosity and molecular entanglement some of the acid groups get shrouded within the matrix, as explained earlier, and cannot come to the surface for the reaction. This fact has been confirmed from the i.r. spectral data which shows a peak at $1704\,\mathrm{cm}^{-1}$ in the ionomer after incorporation of ZnO, indicative of presence of $-\mathrm{COOH}$ groups.

In order to make the residual acid groups active and to bring them to the surface for the reaction, zinc stearate was added. Zinc stearate acts in two steps. During melt processing, the zinc stearate breaks into Zn^{2+} cation and $\mathrm{C}_{17}\mathrm{H}_{35}\mathrm{COO}^{-}$. These stearate anions, being long-chain hydrocarbons, are stable and act as a plasticizer to penetrate into the matrix through the interstices. Consequently, the viscosity of the matrix decreases and the encaged $-\mathrm{COOH}$ groups come out of the bulk to the surface to react with the additional Zn^{2+} ions, forming bigger ionic clusters. This is in consonance with the significant increase in the area of the ionomeric peaks as observed in the spectrograms and a subsequent increase in the degree of neutralization reaction reported in *Table 1*.

Degree of neutralization

A quantitative estimation of the degree of neutralization reaction of ionomers is given in *Table 1*. Because the ionomers possess different structures it is very difficult to calculate the percentage neutralization from the formation of ionomeric peaks. Therefore the degree of ionomer formation has been calculated from the percentage neutralization of the acid present in pure copolymer and the blends of copolymer with ENR.

For the purpose of calculation of the degree of neutralization, the characteristic polyethylene peak at $720\,\mathrm{cm}^{-1}$ (which is a doublet at 720 and $730\,\mathrm{cm}^{-1}$) of PEA in the i.r. spectrum has been chosen as the internal standard. As the degree of neutralization of both pure PEA and the blends containing PEA are to be studied, there is no other choice but to consider the peaks such as $-\mathrm{CH}_2$ scissor or $-\mathrm{CH}_2$ asymmetric bending vibrations at 1460 and $1741\,\mathrm{cm}^{-1}$ (low density polyethylene, LDPE characteristic peaks) as the reference standard. Even the peaks for C–H bending due to $-\mathrm{CH}_2$ and $-\mathrm{CH}_3$ groups at 1377, 1369 and $1352\,\mathrm{cm}^{-1}$ have been ruled out because the epoxidized natural rubber (ENR) also exhibits peaks in the same region. Thus, instead of showing a decrease in the area of these peaks in the blends compared with that of pure PEA the area increases. Therefore there was no choice other than to consider one of the polyethylene crystalline peaks such as that at 720 and $730\,\mathrm{cm}^{-1}$ (doublet) due to $-\mathrm{CH}_2$ rocking vibration, as the internal standard because it remains unaffected in presence of ENR. In the present case $720\,\mathrm{cm}^{-1}$ peak which lies in the range from 700–$725\,\mathrm{cm}^{-1}$ has been chosen for convenience as the reference peak.

The degree of neutralization of the pure acid and the blends have been calculated keeping the film thickness constant at 1 mm as per the following formula:

$$\text{Per cent neutralization} = \left[1 - \left\{\frac{\mathrm{Ad.\ Ae^{o}}}{\mathrm{Ae.\ Ad^{o}}}\right\}\right] \times 100 \quad (1)$$

where $\mathrm{Ad^{o}}$ = area of the peak $1704\,\mathrm{cm}^{-1}$ due to $>\mathrm{C=O}$ stretching vibration of $-\mathrm{COOH}$ group (in the region 1685–$1720\,\mathrm{cm}^{-1}$) in completely unionized polymer. Ad = area of the peak at $1704\,\mathrm{cm}^{-1}$ due to the acid group present in ionomer (in the region 1685–$1720\,\mathrm{cm}^{-1}$). $\mathrm{Ae^{o}}$ = area of internal standard peak at $720\,\mathrm{cm}^{-1}$ peak (in the region 699–$725\,\mathrm{cm}^{-1}$) in unionized polymer. Ae = area of internal standard peak at $720\,\mathrm{cm}^{-1}$ peak (in the region 699–$725\,\mathrm{cm}^{-1}$) in ionomers.

The percentage of neutralization of N_0, N_{30}, N_{50} and N_{70} blends were calculated using the formula given above and are presented in *Table 1*.

It is found that for the N_0 blend containing 5 pbw of ZnO, the degree of neutralization is approximately 10%. By increasing the ZnO level to 7.5, 10 and 15 parts the degree of neutralization increases sharply to 68.9, 71.5 and 73.5% respectively (*Table 1*). This is a clear indication of rapid ionomer formation under the conditions studied. Keeping the ZnO level constant at 5 parts, when zinc stearate level is increased from 10 to 40 parts (i.e. for $\mathrm{N_0Z_5St_{10}}$, $\mathrm{N_0Z_5St_{15}}$, $\mathrm{N_0Z_5St_{20}}$ and $\mathrm{N_0Z_5St_{40}}$) then the pure PEA neutralized to the extent of 78.8, 90.5, 90.0 and 91.1% respectively. However, it is observed that after 20 parts of zinc stearate, the degree of neutralization increased only marginally. Therefore 20 parts of zinc stearate has been taken as the optimum proportion.

Further, by keeping the zinc stearate level constant and changing the ZnO level in PEA, i.r. studies have been carried out. Accordingly the degree of neutralization is calculated for $\mathrm{N_0St_{20}}$, $\mathrm{N_0Z_5St_{20}}$, $\mathrm{N_0Z_{7.5}St_{20}}$, $\mathrm{N_0Z_{10}St_{20}}$ and $\mathrm{N_0Z_{15}St_{20}}$ blends and is reported in *Table 1*. The respective neutralization levels are 15.8, 90.5, 90.8, 91.5 and 92.1%. A significant increase is observed with increase in ZnO level from 0 to 5 parts. Beyond 5 parts ZnO there is little change in the degree of neutralization and the effect of zinc stearate beyond 20 parts is marginal. Therefore 5 parts ZnO and 20 parts zinc stearate has been taken as the optimum level for PEA and its blends.

For the N_{30} blend the degree of neutralization was estimated to be 53.6% at 5 pbw ZnO which increased to 82.9% at 15 parts ZnO. With 20 parts zinc stearate and 5 parts ZnO the degree of neutralization increased from 53.6 to 91.5%. As the amount of PEA is reduced from N_{30} to N_{50} in the blend 5 parts ZnO neutralized only 64.5% of acid groups and with 15 parts ZnO nearly 84.3% of acid was neutralized; however, with 5 parts ZnO and 20 parts zinc stearate the neutralization level increased to the higher level of 92.3%. In N_{70} blend only 5 parts ZnO was able to neutralize 83.0% of the acids present. This was expected because after esterification reaction only a very small number of acid groups were present in the matrix. With 15 parts ZnO, 87.9% of acid groups were neutralized. But with 20 parts zinc stearate and 5 parts ZnO the degree of neutralization increased to 95.5% for N_{70} blends.

CONCLUSIONS

The following conclusions can be drawn from the study.

1. Peaks at 1589 cm^{-1} and 1419 cm^{-1} indicate the formation of zinc ionomers in case of pure PEA and its blends with ENR.
2. Zinc oxide or zinc stearate, when used independently have less effect on the neutralization reaction. When both are used in combination, the system exhibits synergism and enhances the neutralization reaction.
3. The optimum proportion of ZnO and zinc stearate for complete ionomer formation are 5 and 20 parts, respectively.

REFERENCES

1 Eisenberg, A. *Macromolecules* 1970, **3**, 147

2 Macknight, W. J. and Earnest, T. R. Jr *J. Polym. Sci., Macromolec. Rev.* 1981, **16**, 41

3 Holliday, L., (Ed.) 'Ionic Polymers', Applied Science Publishers, London, 1975 p. 69

4 Eisenberg, A. and King, M. 'Ions Containing Polymers: Physical Properties and Structures', Academic Press, New York, 1977

5 Eisenberg, A. (Ed.) 'Ions in Polymers, Advances in Chemistry Series 187', American Chemical Society, Washington DC, 1980

6 Mohanty, S., Roy, S., Santra, R. and Nando, G. B. *J. Appl. Polym. Sci.* 1995, **58**, 1947

7 Roy, S., Gupta, B. R. and Chaki, T. K. *Kautsch. Gummi Kunstst.* 1993, **46**(9), 293

8 Mohanty, S., Vijoyan, K., Neelkanthan, N. R. and Nando, G. B. *Polymer* 1996, **37**, 5387

9 Mohanty S., Bhattacharya, A. K., Nando, G. B. and Gupta, B. R. *Int. Polym. Proc.* (communicated)

10 Mohanty, S., Mukunda, P. G. and Nando, G. B. *Polym. Degrd. Stab.* 1995, **50**, 21

11 Socrates, G. 'Infrared Characteristic Group Frequencies', John Wiley & Sons, Inc., New York, 1980

12 Silverstein, R. M. and Bassler, G. C. 'Spectrophotometric Identification of Organic Compounds', John Wiley & Sons, Inc., New York, 1967

13 Kemp, W. 'Organic Spectroscopy', The Macmillan Press Ltd, 1975

14 Otocka, E. P. and Kwei, T. K. *Macromolecules* 1968, **1**, 244

15 Lim, Jong-chul., Park, Jung-ki. and Song, Hae-young. *J. Polym. Sci. Pt B: Polym. Phys.* 1994, **32**, 29

16 Eisenberg, A. and Navratil, M. *Macromolecules* 1973, **6**, 604

17 Painter, P. C., Brozoski, B. A. and Coleman, M. M. *J. Polym. Sci. Polym. Phys.* 1982, **20**, 230

18 Brozoski, B. A., Coleman, M. M. and Painter, P. C. *Macromolecules* 1984, **17**, 23

19 Coleman, M. M., Lee, J. Y. and Painter, P. C. *Macromolecules* 1990, **23**, 2339