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Effects of sodium concentration on the morphology and rheological behaviour of alkoxide-carboxylate co-ionomeric mixtures of phenoxy and ethylene terpolymers

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Abstract: Mixtures at various weight ratios of phenoxy (PH) and a terpolymer of ethylene tert. butyl acrylate-acrylic acid (EAA) were prepared in a Brabender Plasticorder in the presence of different amounts of sodium ethoxide (NaOEt). The mixtures were examined by SEM, DSC, and dynamic rheometry.

While the crystallisation characteristics of EAA were affected only to a small extent by the addition of NAOEt, the corresponding mixtures with phenoxy acquired an increasingly more pronounced amorphous nature by increasing the concentration of NaOEt.

SEM examinations revealed that the morphology of the mixtures became more homogeneous when NaOEt was present. This was manifested also by a change from dual relaxations to single relaxations in the Cole-Cole plots of the rheological data.

Key words: Ionomeric mixtures – phenoxy – alkoxide – carboxylate

Introduction

Previous work has revealed the formation of co-ionomeric species in mixtures of sodium ionomers of ethylene carboxylic acid copolymers and phenoxy, enhanced by the addition of a sodium cation donor, such as sodium ethoxide (NaOEt) [1–4]. The occurrence of strong interactions between the two polymeric components of the mixture in the form of ionic associations between carboxylate and alkoxide anions through common sodium cations was confirmed by a series of observations, varying from solubility tests to thermal analysis.

When an A-B-A block oligomer, bisphenol epoxyl dimontanate (C_{26-32}), was added to the mixture the reduction in degree of crystallinity was found to be counteracted by the nucleation effects brought about by the dimontanate oligomer. It was shown also that the addition of both the A-B-A oligomer and NaOEt, individually or in combination, always enhanced the compatibility of the two polymers with a tendency to produce a co-continuous lamellar morphology. The use of NaOEt was found, however, to be much more effective in reducing the domain dimensions of the two phases or the size of the dispersed particles [2]. This provided clear evidence that ionic interaction is, by far, a more efficient mechanism for the compatibilisation of polymeric mixtures than by means of surfactants even when used above their critical micelle concentration (CMC) [5].

Enhancing the miscibility of polymer pairs by the formation of ionic aggregates is an approach that has been used by many authors [6–9]. Sullivan and Weiss [10] and Lu and Weiss [11] have reported the formation of strong associations between sulphonated polystyrene ionomers and polyamides by the addition of sodium, zinc, and manganese cations. Agarwal et al. [12], on the other hand, have revealed an increase in miscibility by the addition of sodium, magnesium and zinc cations to mixtures of styrene 4-vinyl pyridine copolymers and sulphonated ethylene propylene copolymers.

Similar findings have been reported by Clark et al. [13] with the incorporation of zinc cations from neutron scattering experiments. Molnár and Eisenberg [14] have subsequently established that the miscibility of sulphonated polystyrene ionomers with polycaprolactone is greatest with cations having a small atomic radius, e.g., lithium.

Although a considerable number of publications have appeared on the effects of different types of cations on the rheological properties of ionomers from single polymer systems [15–18], very little is known about the behaviour of ionically associated mixtures in the melt state.

The present study was carried out, therefore, primarily to elucidate the relationship between the morphology and rheological behaviour of coionomeric mixtures of phenoxy and ethylene acrylic acid copolymers and, in particular, to illustrate the effects of increasing the sodium ions concentration. Another objective of this work was to examine the use of low acid content ethylene copolymers as a means of enhancing the ionic contribution from the alkoxide anions of the phenoxy component. To this end, it was postulated that if an excess of free acid groups within the polyolefin component were to be present, the sodium cations would find a thermodynamically more favourable environment within the carboxylate ionomeric clusters than in the less ionisable alkoxide groups of the phenoxy component.

Experimental

Blends composition and preparation

The polymers used for the preparation of coionomeric mixtures were respectively:

a) Lupolen 7210M (BSAF): An ethylene-tert.butyl acrylate-acrylic acid terpolymer, containing approximately 19% w/w tert.butyl acrylate and 4% w/w acrylic acid (i.e., ca 1.4% molar).
b) Phenoxy UCAR PKHH (Union Carbide): A polyhydroxy ether obtained by reacting bisphenol A with epichlorohydrin using sodium ethoxide as catalyst, having a degree of polymerisation around 80, i.e. Mn $\simeq$ 30000.

Blends of the two polymers at 25/75, 50/50 and 75/25 weight ratios and the respective controls (i.e. single polymer compositions) were produced in a Brabender Plasticorder at 170 °C using a 25 cc mixing chamber, fitted with Z-rotors, and with a rotor speed of 100 rpm. The two polymers were first predried in vacuum oven at 70 °C for 3 h and then fed and melted sequentially at low speed to allow them to be dried completely, Sodium ethoxide (NaOEt) was then added slowly in amounts varying from 0.5 to 6.0%, the speed was increased to the specified value and mixing was continued for 30 min to ensure that ionomerisation took place to the fullest extent possible.

Plaques $70 \times 70 \times 0.5$ mm were compression moulded at 170 °C after pre-drying the mixes for about 60 h at 65–70 °C in a vacuum oven. Care was taken to control the cooling rate in the press to about 6 °C/min to about 40 °C before removing the plaques.

Characterisation and evaluation of the blends

The mixtures were examined using the following techniques:

a) Thermal analysis by means of a Perkin Elmer (DSC 4) Instrument at heating and cooling rates of 20 °C/min under a constant flow of nitrogen and with a 10 min isothermal interval at 250 °C. The thermograms were analysed from both the cooling scan and the second heating cycle.
b) Stereoscan electron microscopy (Cambridge 600 Instrument) on samples fractured after cooling for 3 min in liquid nitrogen and subsequently allowed to stand for 30 s at room temperature.
c) Rheological measurements using a Rheometrics RDA II Dynamic Analyser fitted with 25 mm diameter cone-and-plate fixture. Measurements were made over a wide range of frequencies at 220 °C using the compression moulded plaques and ensuring that the compression force developed was within 10% of the maximum recorded value.
d) Intrinsic viscosity measurements were carried out for the pure phenoxy containing various amounts of NaOEt at 100 °C in DMF solutions at various polymer concentrations up to 4 g/L using a Ubbelohde capillary viscometer. The intrinsic viscosity was calculated from a linear extrapolation of the solution viscosity to zero concentration.

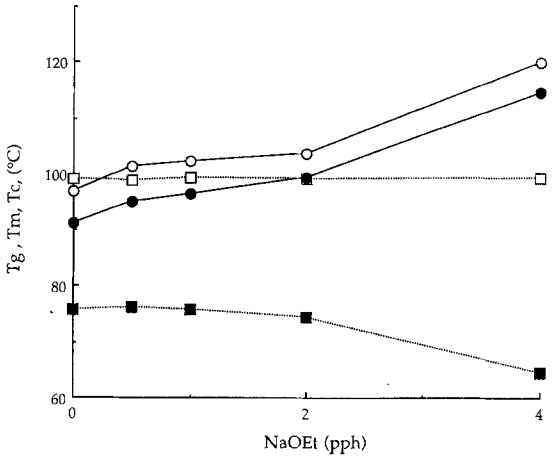


Fig. 1. Variation of main transition temperatures of single polymer systems with NaOEt concentration, measured by DSC from cooling and second heating scans —○— PH (T_g) heating; —●— PH (T_g) cooling; ··· ■ ··· EAA (T_c); ··· □ ··· EAA (T_m)

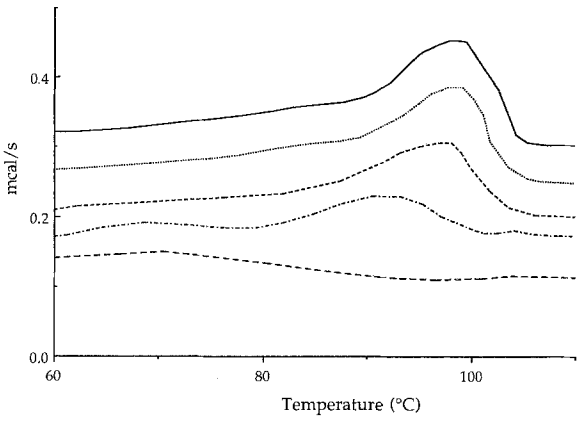


Fig. 3. Effect of NaOEt concentration on crystallisation exotherm for EAA/PH mixtures at 50/50 weight ratio. —— 0 pph NaOEt; .....0.5 pph NaOEt; ------ 2.0 pph NaOEt; ·-·-·- 4.0 pph NaOEt; – – – 6.0 pph NaOEt

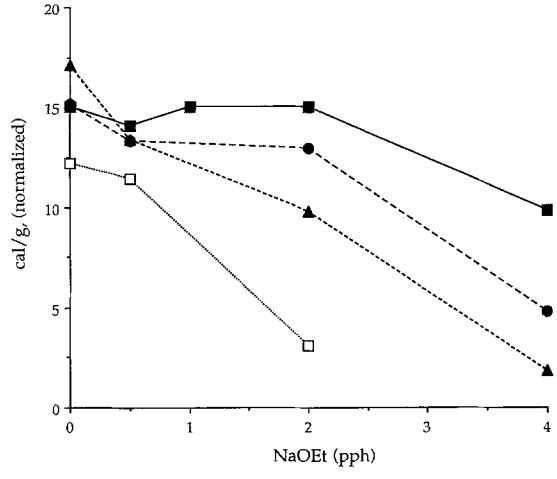


Fig. 2. Variation of heat of fusion (normalised) of the EAA component with NaOEt concentration for different PH/EAA mixtures —■— 0/100; – –●– – 25/75; – – –▲– – – 50/50; ··· □ ··· 75/25

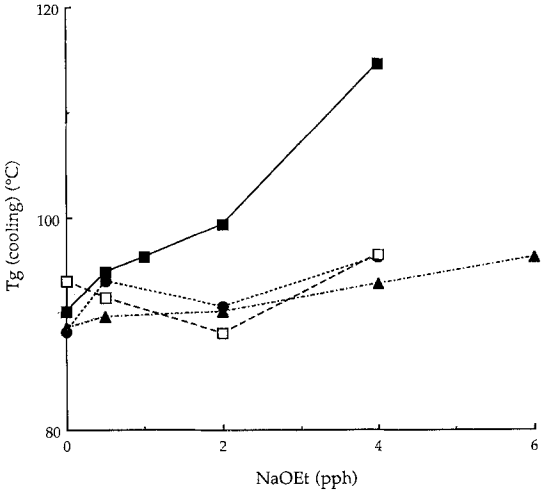


Fig. 4. T_g of phenoxy component (cooling scan) of EAA/PH mixtures at different weight ratios. —■— PH 100%; – – –●– – – PH 75% – ·-▲-· – PH 50%;– –□– – PH 25%

Results and discussion

In Fig. 1 is shown the variation of the main transition temperatures with increasing amounts of NaOEt, in parts per hundred (pph) for the two polymer components in isolation, i.e., respectively ethylene-tert.butyl acrylate-acrylic acid terpolymer (EAA) and phenoxy (PH), which were recorded during the cooling scan and in the second heating cycle. It was observed that the melting transition (T_m) of EAA is not affected by the addition of NaOEt, while the peak crystallisation temperature (T_c) decreases by a few degrees above 2 pph NaOEt. The glass transition temperature (T_g) of phenoxy, on the other hand, increases gradually, producing

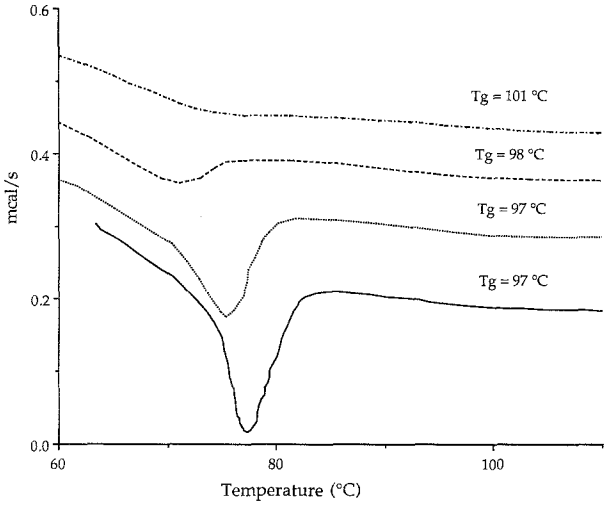
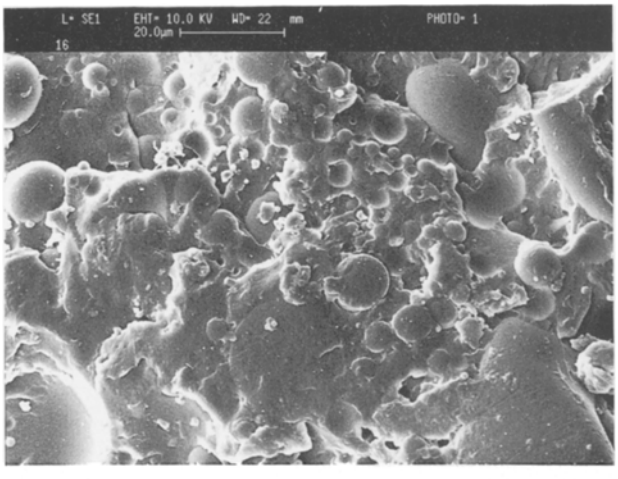


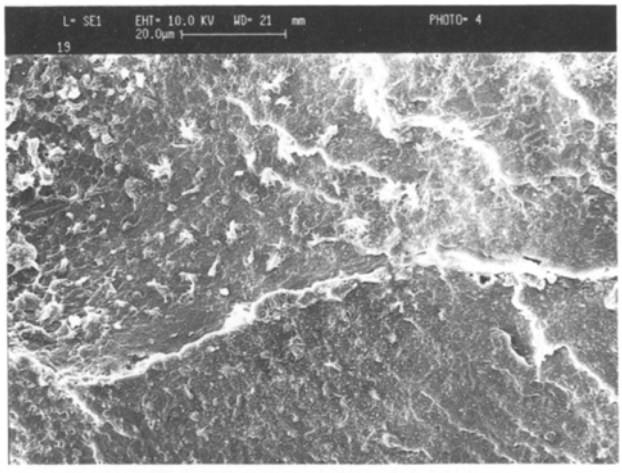
Fig. 5. Glass transition of phenoxy component and crystallisation exotherm of EAA from DSC cooling scans on 75/25 EAA/PH mixtures. —— pph NaOEt; ..... 0.5 pph NaOEt; - - - - 2.0 pph NaOEt; ·---· 4.0 pph NaOEt;

an overall rise of more than 20 °C at 4 pph NaOEt.

In Fig. 2 is shown the effect of the NaOEt addition on the normalised heat of fusion (ΔH_f) of the EAA component in blends at various weight ratios of the two polymer components. An inspection of these curves reveals that while EAA by itself begins to show an appreciable reduction in heat of fusion only above 2 pph NaOEt, the blends with phenoxy show a rapid decrease in ΔH_f from very low concentrations, at a rate which



A



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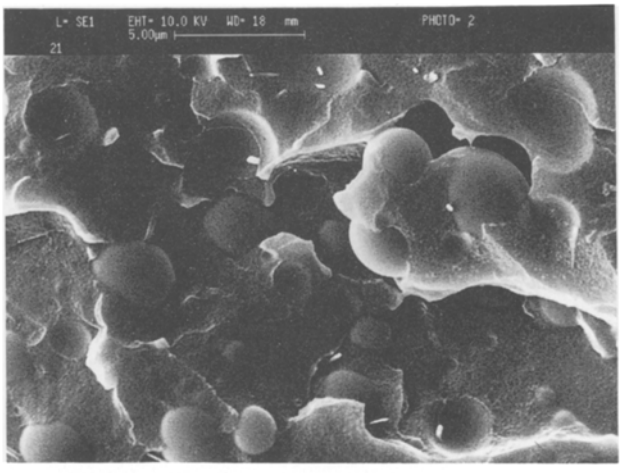

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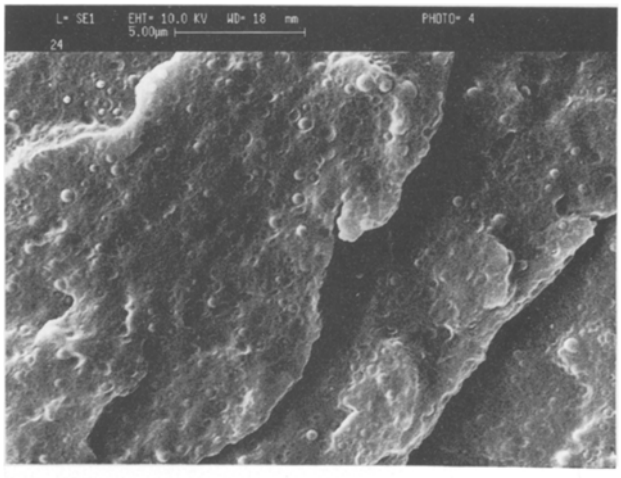

D

Fig. 6. Micrographs of EAA/PH mixtures, showing the miscibilisation resulting from the addition of NaOEt. A = 50/50 mixture; B = 50/50 mixture + 4 pph NaOEt; C = 75/25 mixture; D = 75/25 mixture + 4 pph NaOEt

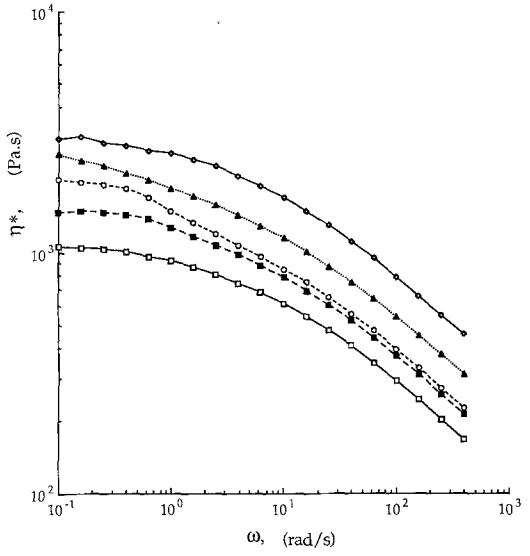

Fig. 7. Complex viscosity at 220 °C as a function of frequency for phenoxy, EAA and EAA/PH mixtures at different weight ratios. —□— 100/0; --■-- 75/25; ··· ○ ··· 50/50; --▲--25/75; —◇— 0/100

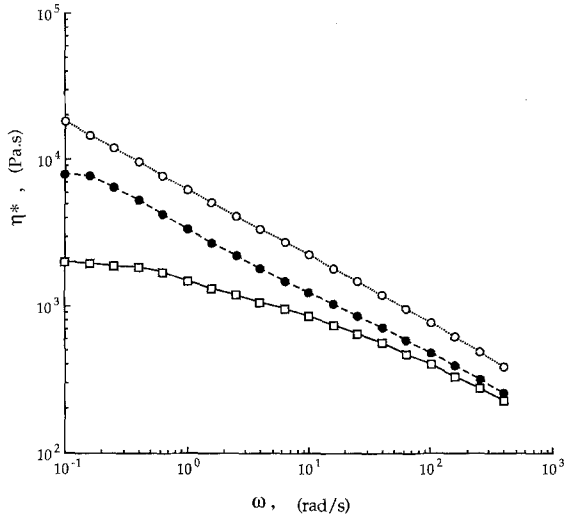

Fig. 9. Complex viscosity at 220 °C as a function of frequency for EAA/PH mixtures at 50/50 weight ratio and different concentrations of NaOEt —□— 0 pph NaOEt; --●-- 0.5 pph NaOEt; ··· ○ ··· 2.0 pph NaOEt

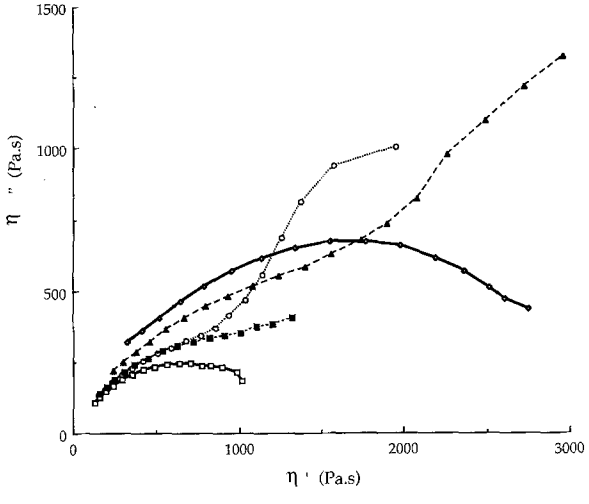

Fig. 8. Cole-Cole plots from rheological data at 220 °C for phenoxy, EAA and EAA/PH mixtures at different weight ratios —□— 100/0; --■-- 75/25; ··· ○ ··· 50/50; --▲--25/75; —◇— 0/100

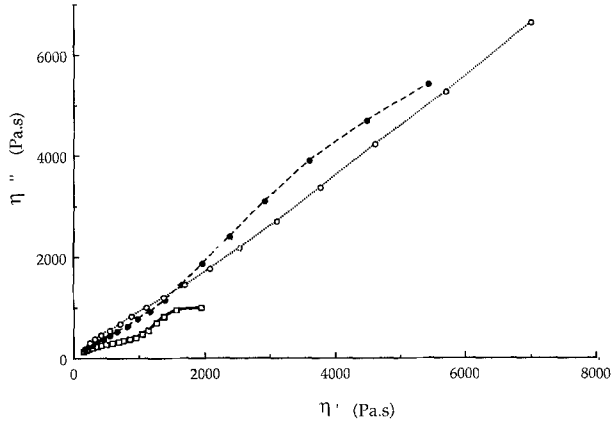

Fig. 10. Cole-Cole plots from rheological data at 220 °C for EAA/PH mixtures at 50/50 weight ratio and different concentrations of NaOEt. —□— 0 pph NaOEt; --●-- 0.5 pph NaOEt; ··· ○ ··· 2.0 pph NaOEt

increases with increasing amounts of phenoxy present (see also Fig. 3).

It has to be noted that at 4 pphr NaOEt full neutralisation of the acid groups in EAA is expected for the polymer in isolation. According to some early work reported by Rees and Vaughan [19], at levels of acid present in the EAA terpolymer used in this study even after complete ionomerisation of the acid groups there are sufficiently long sequences of polyolefin chains capable of participating in the formation of crystals by chain folding and subsequent growth of lamellae. This suggests that the solubilisation of the phenoxy component into the polyolefin, through

the formation of ionic aggregates, may hinder the motion of crystallisable segments, preventing the nucleation and subsequent growth of crystals from the EAA component.

This is supported by the observation that the T_g of the phenoxy component in the blend changes only slightly with increasing amounts of NaOEt present (Fig. 4), and that the enthalpy change at the glass transition of the phenoxy occurs over a broad range of temperatures and is not very pronounced (Fig. 5).

The extensive miscibilisation of the two polymer components in the blend has also been revealed by the SEM studies. The micrographs in Fig. 6 show, in fact, that the amount of non-miscibilised polymer is clearly much smaller than the total amount of the polymer present and that it forms very small dispersed particles within a matrix of solubilised polymer mixture.

The rheological curves for the blends at various weight ratios of the two polymer components are shown in Fig. 7 in the form of plots of complex viscosity (η^*) against angular velocity of the rotating cone-and-plate fixture (ω). From an inspection of these curves it is interesting to note that the curves for the two single polymer components are practically superimposable through a vertical shift, while this is not the case for the blends and a clear deviation is apparent for the 50/50 blend. The viscosity of the blends is always intermediate between that exhibited by the individual polymer components.

The lack of a superposition of the rheological behaviour of the blends at the lower frequency range is clearly revealed from Cole-Cole plots in Fig. 8, i.e. plots of the melt elasticity component (η'') of the complex viscosity (η^*) against the Newtonian viscosity component (η'). The rheological curves for the 50/50 blends in Fig. 9 show, on the other hand, that the addition of NaOEt increases considerably the viscosity of the blends, particularly in the low frequency range, while the corresponding Cole-Cole plot (Fig. 10) reveals a gradual change in relaxation behaviour with the addition of NaOEt.

From this plot it is noted also that, whereas two distinct distributions of relaxation times are exhibited by the simple blend (0 pph NaOEt), evidenced by the occurrence of two semi-circular curves merging into each other, the blend containing 2 pphr. NaOEt shows only one continuous

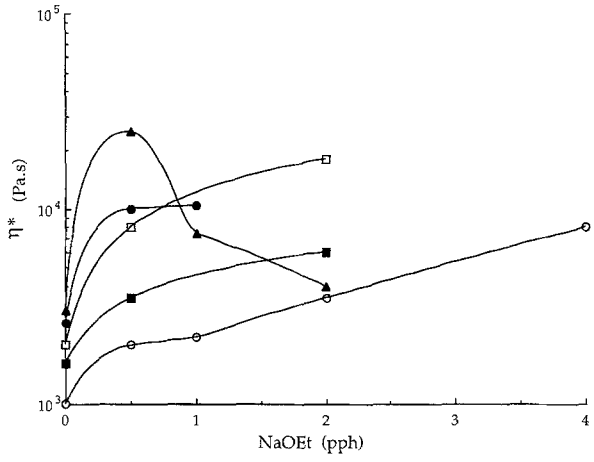

Fig. 11. Complex viscosity at 220 °C and 10^{-1} rad/s as a function of NaOEt concentration for EAA/PH mixtures at different weight ratios. ○ 100/0; ■ 75/25; □ 50/50; ● 25/75; ▲ 0/100

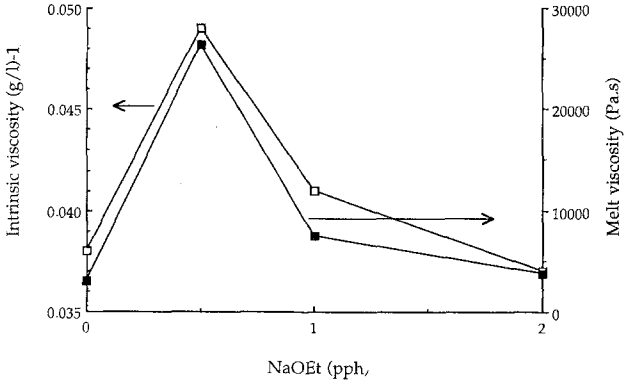

Fig. 12. Correlation between melt viscosity and solution viscosity data for phenoxy mixed with different amounts of NaOEt —□— Intrinsic viscosity; —■— Melt viscosity

distribution of relaxation times, i.e. it behaves as if it was a homogeneous mixture.

The complex viscosity at 10^{-1} rad/s for the various blends as a function of the NaOEt concentration is shown in Fig. 11. It is observed that at phenoxy content greater than 50% the viscosity begins to decrease, after an initial rapid increase, at NaOEt concentrations greater than 1 pph and that for the pure phenoxy the viscosity reaches a maximum at 0.5 pph NaOEt. The changes in melt viscosity for the phenoxy with increasing NaOEt concentration was found to correlate with the intrinsic viscosity data

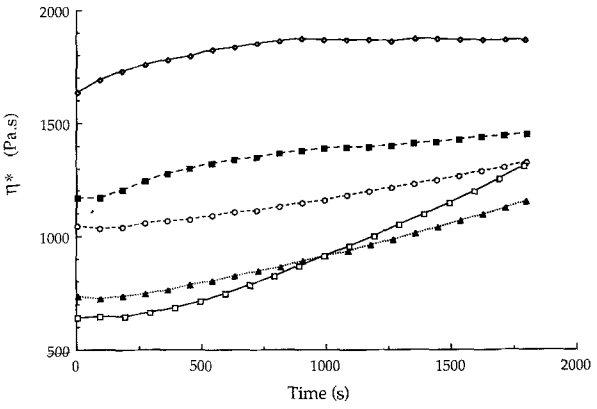

Fig. 13. Complex viscosity at 220 °C and 10 rad/s as a function of residence time in the gap of the cone-and-plate rheometer, for EAA/PH mixtures not containing NaOEt. —□— 100/0; --■-- 75/25; --○-- 50/50; ··· ▲ ··· 25/75; —◇— 0/100

obtained from solution viscosity measurements (Fig. 12).

This indicates that the maxima in the viscosity curves are the resultant of two competing phenomena, i.e. ionomerisation of the hydroxyl groups to produce alkoxide anions and chain scissions within the polymer chains, through hydrolysis at the ether linkages. Although the possibility of thermoxidative reactions involving the tertiary hydrogen of the $CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2$ groups cannot be excluded there are strong indications that these are of secondary importance since the viscosity of both phenoxy and the mixtures not containing NaOEt did not change very much (i.e. ca 20%) over a period of 30 min at 220 °C when left in the cone-and-plate gap of the rheometer at 10 rad/s frequency and in air atmosphere (Fig. 13).

Conclusion

The results of this have confirmed that the formation of the co-ionomeric species in blends of carboxylic acid containing polyethylenes with phenoxy is an effective mechanism to enhance their miscibility. This is accompanied by a reduction in the crystallinity level of the polyolefin component of the mixture and an increase in melt viscosity.

For mixtures where the phenoxy component predominates care has to be exercised, however, to ensure that this does not undergo excessive degradation during mixing through chain scission reactions.

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