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Polymer 41 (2000) 3069–3082

polymer

Reactive compatibilization of blends containing liquid crystalline polymers

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Received 21 February 1999; received in revised form 22 June 1999; accepted 26 June 1999

Abstract

This paper describes the reactive compatibilization of blends of a wholly aromatic thermotropic copolyester liquid crystalline polymer (TLCP) with random copolymers of ethylene and acrylic acid (EAA) and their salts. Two different TLCPs were used: one was a copolymer of hydroxybenzoic acid and hydroxynaphthanoic acid and the other also contained terephthalic acid and hydroquinone monomers. The EAA ionomers contained either 15 or 20 wt% acrylic acid, and the salts considered included Na^+, Zn^{2+}, Li^+ and K^+. Blends were prepared by melt-mixing in an intensive mixer, and the formation of a graft copolymer due to acidolysis between the TLCP and the acrylic acid group of the ionomer (none of the ionomers were fully neutralized) was evaluated. Chemical reaction was assessed by torque measurements during melt-mixing, thermal analysis and microscopy of the blends. The Na-salt of the EAA ionomers was especially effective at inducing a grafting reaction. The free-acid derivative and other salts either did not react or were much less effective at promoting an interpolymer reaction. The extent of reaction depended not only on the cation, but also on the composition of the ionomer, the reaction temperature and time. The reaction between the ionomer and the TLCP during mixing, effectively compatibilized the blend. Also, the addition of a minor amount of the Na-salt of EAA compatibilized a TLCP–high density polyethylene blend. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline polymer; Ethylene–acrylic acid; Ionomers

1. Introduction

During the past two decades, there have been numerous attempts to exploit the superior mechanical properties of thermotropic liquid crystalline polymers (TLCP) in polymer blends. A number of reviews summarize the published literature on this subject [1–4]. For most blends studied, the TLCP is added as the minor constituent, either to function as a processing aid or as a reinforcing phase. In the latter case, the TLCP dispersed-phase is usually deformed and oriented during processing to form a reinforcing, microfibrillar TLCP phase.

The major limitation to the use of TLCP–polymer blends is that the interfacial adhesion between the TLCP and matrix polymer is generally poor [5,6], and in recent years the research has been focussed on developing methods for improving compatibility of TLCPs and other thermoplastics. The interfacial adhesion between immiscible polymers may be improved either by adding a third, interfacially active polymer, called a *compatibilizer*, or by promoting a chemical reaction between the two polymers that effectively forms graft copolymer in situ that serves as the compatibilizer, an approach termed as *reactive compatibilization.* The literature concerned with compatibilization of TLCP–polymer blends has grown exponentially in the past several years. An exhaustive review of the subject may be found elsewhere [7].

An example of a physical compatibilizer, i.e. non-reactive compatibilization, for TLCP blends is the zinc salt of lightly sulfonated polystyrene ionomer (Zn-SPS) that was reported to compatibilize blends of a hydroxybenzoate–hydroxynaphthonate liquid crystalline copolyester and nylon 66 (PA66), or bisphenol A polycarbonate (PC) [8]. Non-reactive block and graft copolymers have also been used to promote compatibility between TLCPs and various thermoplastics [9–15].

There have been numerous reports of reactive compatibilization of blends containing TLCPs. For example, transesterification reactions have been used to improve the compatibility of a TLCP with polyesters or polycarbonates [16–22], and maleated polypropylene has been used to

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PII: S0032-3861(99)00469-3

Table 1
Materials

Designation	Polymer	Source	Acrylic acid (wt%)	Cation	Neutralized (%)	MI (g/10 min)
Liquid crystalline polymers						
Vectra A	Vectra A	Ticona				
RD501	RD501	Ticona				
Poly(ethylene-co-acrylic acid) copolymers						
EAA_{20}	Primacor 5981	Dow chemical	20	Acid		300
EAA_{15}	Escor 5200	Exxon chemical	15	Acid		37
EAA_3	Primacor 3150	Dow chemical	3	Acid		11
Ionomers						
$EAA_{15}Zn_{35}$	Iotek 7010	Exxon chemical	15	Zn	35	0.8
$EAA_{15}Na_{45}$	Iotek 8000	Exxon chemical	15	Na	45	0.8
$EAA_{15}Na_{30}$	NaOH neutralized EAA_{15}		15	Na	30	
$EAA_{15}Na_{20}$	NaOH neutralized EAA_{15}		15	Na	20	
$EAA_{15}Na_{10}$	NaOH neutralized EAA_{15}		15	Na	10	
EAA_9Na_{45}	Iotek 3110	Exxon Chemical	9	Na	45	1.3
EAA_3Na_{45}	NaOH neutralized EAA_3		3	Na	45	

improve the interfacial adhesion and mechanical properties of blends of a TLCP with polyolefins or polyamides [5,23–28]. A variety of other reactive functional groups, including epoxy [29–33], ethers [34] and thiols [35] have also been used.

In this paper, we describe the in situ formation of graft copolymers of a wholly aromatic TLCP and ethylene-*co*-acrylic acid (EAA) ionomers using reactive processing. EAA and ethylene-*co*-methacrylic acid (EMA) ionomers have been previously used to compatibilize polymer blends [36], e.g. poly(ethylene terephthalate) (PET)–PE [37], but to our knowledge, neither has been used with TLCP-containing polyblends. A key aspect of our work is the demonstration of the importance of the choice of cation used to form the ionomer on the reactivity of the ionomer with the TLCP. Most of this paper focuses on binary blends of the TLCPs and the ionomers, but some initial results of ternary blends in which the ionomer is used as a compatibilizer are also included. A subsequent paper will consider the ternary blends in more detail.

2. Experimental details

2.1. Materials

The TLCPs used were Vectra™ A and RD501, both products of the then Hoechst–Celanese Corp. which is now Ticona. Vectra A is a wholly aromatic copolyester of 73% hydroxybenzoate (HBA) and 27% hydroxynaphthanoate (HNA) that has a $T_g = 100°C$ and melts to a nematic liquid transition at $T_m = 277°C$. RD501 is also a wholly aromatic polyester, but the synthesis includes terephthalic acid and hydroquinone as comonomers in addition to HBA and HNA, and has a $T_g = 112°C$ and a $T_m = 222°C$.

The poly(ethylene-*co*-*r*-acrylic acid) copolymers (EAA) and EAA ionomers used are summarized in Table 1. Hereafter, the polymers are designated as EAA_xM_y, where x denotes the wt% acrylic acid in the EAA copolymer, M is the cation used and y is the percent neutralization of the acid groups (M and y are not used in the case of the acid copolymers). Commercial materials were obtained from Dow Chemical Co. (Primacor™ 5981 and Primacor™ 3150) and Exxon Chemical Co. (Escor™ 5200, Iotek™ 7010, Iotek™ 8000 and Iotek™ 3110). The Na-EAA ionomers designated as $EAA_{15}Na_{30}$, $EAA_{15}Na_{20}$, $EAA_{15}Na_{10}$ and EAA_3Na_{45} were prepared by partial neturalization of the melts of EAA_{15} or EAA_3 with NaOH at 200°C. High-density polyethylene (HDPE), EHM6007, was obtained from Phillips Petroleum Co. It had a density of $0.964\ g\ ml^{-1}$ and an MI of 0.75.

Blends of the ionomers with Vectra A were prepared by melt-mixing in a Brabender Plasti-Corder EPL-5501 mixer at 300°C, using a $30\ cm^3$ mixing head with two counter-rotating rotors and a rotor speed of either 30 or 50 rpm. Prior to blending, the TLCPs were dried at 100°C under vacuum for 24 h and the EAA and EAA ionomers were dried at 50–60°C under vacuum for 24 h. During melt-mixing, the mixing chamber was blanketed with nitrogen gas in order to minimize any oxidative degradation. The EAA or the ionomer was first added to the mixer and fluxed for 6–8 min before adding the TLCP. The torque was monitored as a function of mixing time. In one set of experiments, the mixing time was fixed at 10 min; in a second set of experiments, the mixing time was varied from 1 to 10 min. Blends of the ionomers with RD501were prepared at 230°C using mixing times of 5, 10 and 15 min and the same mixer and rotor speed as described above.

3. Materials characterization

The blend morphology was viewed with an AMRAY model 1000A scanning electron microscope (SEM) using fracture surfaces from samples broken in liquid nitrogen.

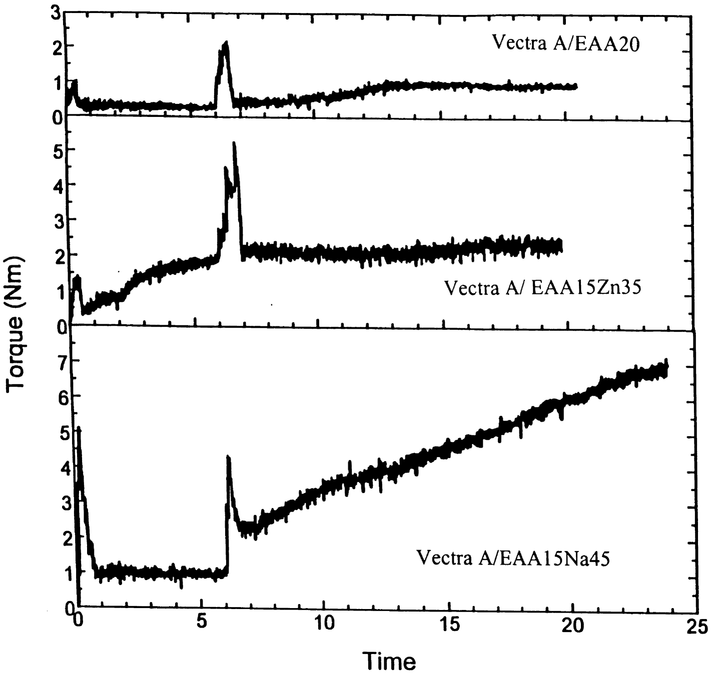


Fig. 1. Torque versus time for blends of (50/50) Vectra A–EAA_{20}, (50/50) Vectra A–$EAA_{15}Zn_{35}$ and (50/50) Vectra A–$EAA_{15}Na_{45}$ during mixing in a Brabender mixer at 300°C with rotor speed of 30 rpm.

Dynamic mechanical behavior was measured with a Polymer Laboratories model MKII dynamic mechanical thermal analyzer (DMTA) using a bending fixture and a heating rate of 2°C min^{-1}. Transition temperatures were defined as the maxima in tan δ at a frequency of 1 Hz.

Thermal analysis was carried out with a Perkin–Elmer model DSC-7 differential scanning calorimeter (DSC). Blends containing Vectra A were pre-heated to 300°C and held there for 3 min to remove the previous thermal history. The sample was then cooled to −63°C at a nominal cooling rate of 100°C min^{-1} and held at −63°C for 5 min before beginning a heating scan to 300°C at a heating rate of 20°C min^{-1}. The sample was then held at 300°C for 3 min before cooling again to −60°C at 20°C min^{-1}. Thermograms were obtained for both the heating and the cooling experiments. A similar experimental protocol was used for the blends containing RD501, except that the upper temperature limit was 230°C.

In order to assess the melt reaction that occurred in Vectra A–$EAA_{15}Na_{45}$ blends, a 50/50 sample was subjected to repetitive heating–cooling cycles in DSC. The sample was first pre-heated to 300°C at a heating rate of 20°C min^{-1}, held at 300°C for 3 min, cooled to 0°C at 20°C min^{-1}, held at 0°C for 3 min, and then reheated to 300°C at 20°C min^{-1}. This procedure was repeated nine times, and all the heating and cooling thermograms were recorded.

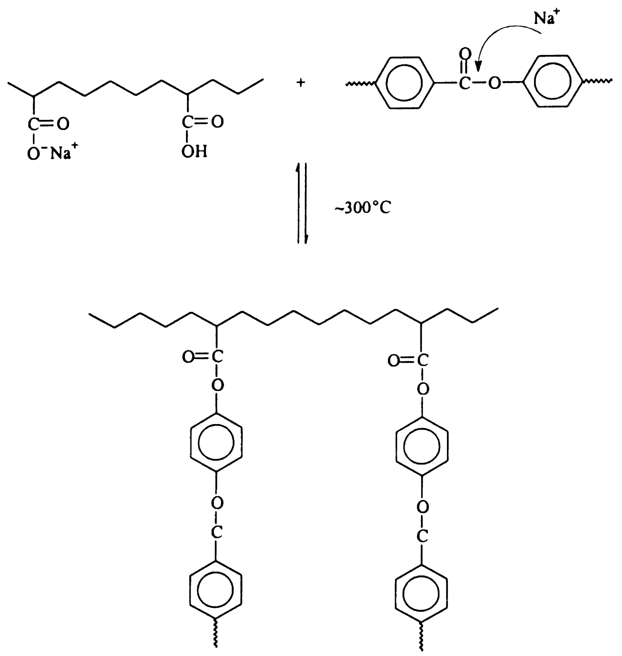
FTIR spectra were obtained on samples mixed with KBr and molded into pellets. A deconvolution analysis developed by Pariente and Griffiths [38] was used to estimate the extent of acidolysis by resolving the ester-carbonyl absorptions between 1660 and 1820 cm^{-1} into contributions for Ar–C(O)O–Ar and Ar–C(O)O–R.

4. Results and discussion

4.1. Vectra A–EAA ionomer blends

4.1.1. Rheological evidence for melt reaction

The torque of the Brabender mixer was monitored during the melt-mixing operation to assess whether a chemical reaction took place between the TLCP and EAA (and its salts). Fig. 1 shows data for TLCP–EAA_{20}, TLCP–$EAA_{15}Zn_{35}$ and TLCP–$EAA_{15}Na_{45}$ blends for mixing at 300°C and 30 rpm. The initial 6 min of each curve in Fig. 1 represents the torque for the neat EAA or ionomer melt. (Note that EAA_{15}, not EAA_{20}, was the precursor for the ionomer samples, so that some of the variation in the torques of the EAA and ionomers may be due to different molecular weight and functionality of those materials. However, neutralized ionomers usually have much higher viscosities than do their parent free-acid derivatives, so an increase in torque due to partial neutralization of the acrylic acid is expected.) The spike in the torque at ca 6 min is due to the addition of the TLCP, and the data for times greater than ca. 7 min represent the blend melt. In case of the TLCP–EAA_{20} and the TLCP–$EAA_{15}Zn_{35}$ melts, the torque attains a relatively low steady-state value which indicates that little, if any, reaction occurred in these blends. In contrast, the torque of the TLCP–$EAA_{15}Na_{45}$ melt does not reach steady-state, but rather displays a steady increase



Scheme 1.

with time that is due to a reaction between the two polymers. The torque necessary to maintain a constant rotor speed is directly related to the viscosity of the blend, and increasing torque during reactive mixing is indicative of the formation of graft copolymers or cross-linking [39,40]. Degradation of either or both polymers should lower the viscosity and the torque, so degradation does not appear to play an important role here.

The influence of the Na^+-ionomer on the interpolymer reaction contrasts sharply with that of the free-acid derivative and the Zn^{2+}-ionomer, which indicates that the sodium ion is more effective at catalyzing a reaction between the two polymers than the free carboxylic acid or zinc ion. The increase of the torque during the mixing of TLCP and Na^+-ionomer is due to the formation of graft copolymer by an acidolysis reaction between $-COO^-Na^+$ or –COOH groups of the ionomer and the ester-linkages of the TLCP. Although the exact role of the Na^+ in the grafting reaction is not clear from these data, it has been previously recognized that alkali metal salts attack and cleave the chain at the ester groups in polyesters such as polyethylene terephthalate (PET) [41]. It has also been reported that the Na^+-salt of a poly(ethylene-*co*-methacrylic acid) ionomer can compatibilize blends of PET and linear low-density polyethylene (LLDPE) as a result of acidolysis occurring at the interface [42]. In that later paper, the authors remark that “the Zn^{2+}-ionomer is less effective” at compatibilization, though no supporting data or explanation were presented.

Without additional information, we can only speculate the nature of the reaction as indicated by the torque increase during melt-mixing. However, it is most likely due to an acidolysis reaction as indicated in Scheme 1 (Acidolysis reaction between Na-EAA ionomer and TLCP). It is important to note that although all three EAA-based polymers used in the experiments shown in Fig. 1 contain a substantial amount of free carboxylic acid groups, but only those in the Na-neutralized ionomer reacted with the TLCP. This suggests that only the sodium ion is effective at cleaving the ester chain linkages in the TLCP chain.

The effect of the amount of Na^+-salt on the torque during melt-mixing of the Vectra A–ionomer blends was evaluated by varying the measurements of the mixing torque for 50/50 Vectra A–$EAA_{15}Na$ ionomers with neutralization levels varying from 10 to 30%. For each blend, the torque increased monotonically with mixing time after the addition of the TLCP to the ionomer melt. The rate of torque growth increased with increasing neutralization of the ionomer, which is expected if the Na^+ ion catalyzes the reaction. Although the results were only qualitative, they do appear to indicate that the amount of graft copolymer formed may be controlled not only by the choice of the cation used to neutralize the ionomer but also by the degree of neutralization of the ionomer, i.e. the Na^+-salt concentration.

Fig. 2 shows the effect of other alkali metal salts, the zinc salt and the free acid on the torque during melt-mixing at 300°C and a rotor speed of 30 rpm for blends of Vectra A and EAA_{20} and its ionomers prepared with different cations, but all neutralized to ca 30%. Again, the torque spike at ca.

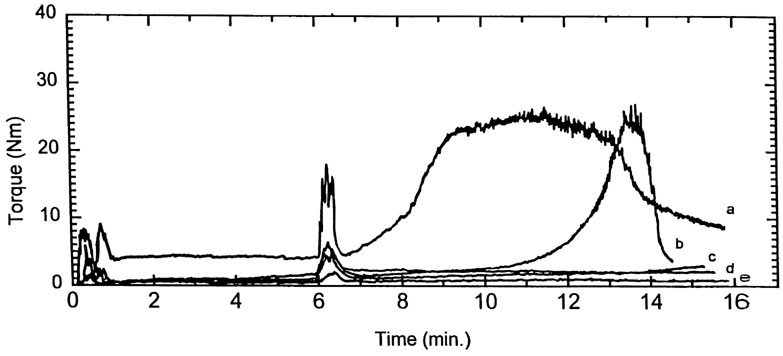


Fig. 2. Torque of blends of Vectra A–EAA-M during mixing in a Brabender mixer at 300°C with rotor speed of 30 rpm: Vectra A with (a) $EAA_{20}Na_{30}$; (b) $EAA_{20}K_{30}$; (c) $EAA_{20}Li_{30}$; (d) $EAA_{20}Zn_{30}$; (e) EAA_{20}.

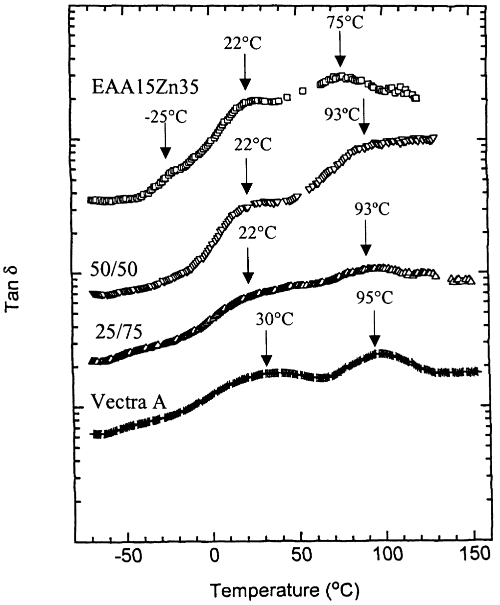


Fig. 3. Tan δ versus temperature at $f = 1$ Hz for $EAA_{15}Zn_{35}$, Vectra A and their blends: (□) $EAA_{15}Zn_{35}$; (+) Vectra A; (▽) 50/50 $EAA_{15}Zn_{35}$–Vectra A blend; (△) 25/75 $EAA_{15}Zn_{35}$–Vectra A blend. Curves are shifted for better clarity.

6 min represents the addition of the TLCP to the ionomer melt. Very little change in the viscosity (i.e. torque) of the melt occurs with time when the free acid or Zn^{2+} or Li^+ cations were used. However, as with the experiments described above, the torque immediately began to increase when the TLCP was added to the Na-neutralized ionomer, though in the experiment shown in Fig. 2, the torque leveled off at about 25 N m after about 10 min (i.e. 4 min after the addition of the TLCP) and decreased at longer times. The decrease was due to the fact that the material became a powder at the longer times so that the torque was not indicative of the viscosity of a melt. In that case, it appears that so much grafting occurred that the material became a brittle, solid-like mass.

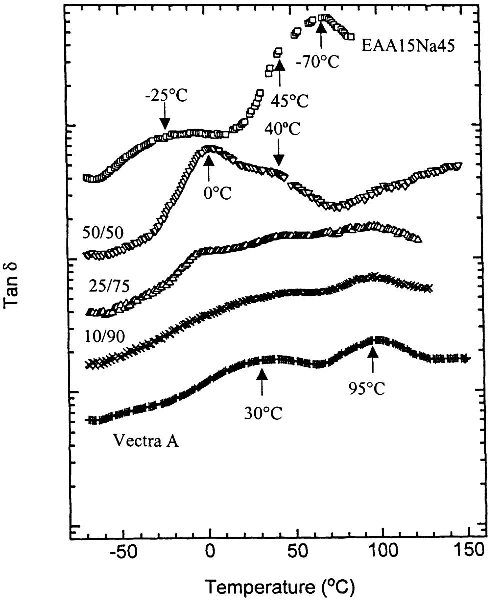


Fig. 4. Tan δ versus temperature at $f = 1$ Hz for $EAA_{15}Na_{45}$, Vectra A and their blends: (□) $EAA_{15}Na45$; (+) Vectra A; (▽) 50/50 $EAA_{15}Na_{45}$–Vectra A blend; (△) 25/75 $EAA_{15}Na_{45}$–Vectra A blend; (×) 10/90 $EAA_{15}Na_{45}$–Vectra A blend. Curves are shifted for better clarity.

The data for the K^+-salt were different from the other ionomers in that a retarded melt reaction was observed. The torque did not change much for about 5–6 min following the addition of the TLCP, but then it increased rapidly to a value comparable to that for the Vectra A–$EAA_{20}Na_{30}$ blend, and then decreased. It is not clear why the K^+ data were so much different from the Li^+ and Na^+ data. However, there were some concerns regarding the homogeneity of the K-neutralized ionomer because of the difficulties encountered in mixing KOH into the melt, and the retardation time shown in Fig. 2 may involve homogenization of the mixture, and may not accurately reflect the effectiveness of the K^+-salt at catalyzing the acidolysis reaction.

It is clear from the data in Fig. 2 that the Li^+-salt was not as reactive as the other two alkali metal salts. The Na^+-salt was the most reactive species evaluated, even though its ionic strength (charge-ionic radius) is intermediate between Li^+ and K^+. However, one must avoid placing too much confidence in a comparison of the data for the Na^+- and K^+-salts for the reasons stated above.

4.1.2. *DMTA of melt-mixed blends of Vectra A and EAA ionomers*

Tan δ versus temperature data for two different compositions of Vectra A–$EAA_{15}Zn_{35}$ blends, as well as for the pure components, are shown in Fig. 3. These data indicate that the blends are phase-separated into essentially a pure ionomer phase and a pure TLCP phase. The neat ionomer exhibited a tan δ peak at 75°C which corresponds to melting of a crystalline phase and a lower temperature-relaxation at ca. 22°C that is probably due to pre-melting relaxation of the crystalline phase. The DMTA data for the ionomer also showed a tan δ shoulder at ca. −25°C, which is either a T_g or the β-relaxation similar to that for polyethylene. The latter is usually observed for low-density polyethylene and is due to molecular motion of chain segments containing a branch point. For the neat Vectra A, the T_g occurs at 95°C and there is a sub-T_g relaxation at ca. 30°C. The Vectra A–$EAA_{15}Zn_{35}$ blends exhibited loss peak at 22 and 93°C, which correspond to the pure ionomer and TLCP phases, respectively. The absence of any changes in the temperatures of these relaxations upon melt-blending indicates that an acidolysis reaction did not occur in this system. Similar results (not shown) were observed for the blends containing EAA_{20} that were also consistent with the lack of any grafting reaction between the free-acid derivative of EAA and the TLCP.

The DMTA data for $EAA_{15}Na_{45}$ and several compositions of blends with Vectra A are shown in Fig. 4. The main

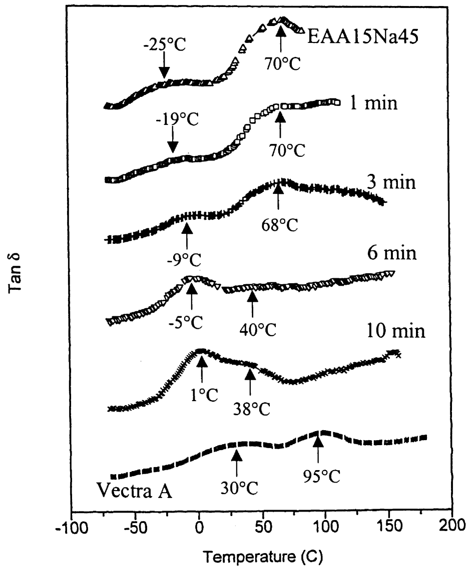


Fig. 5. Tan δ versus temperature at $f = 1$ Hz as a function of mixing time for (50/50) Vectra A–EAA$_{15}$Na$_{45}$ blends: (△) neat EAA$_{15}$Na$_{45}$; (|) neat Vectra A; (□) mixing time = 1 min; (+) 3 min; (▽) 6 min; (×) 10 min.

features of the tan δ data for the neat ionomer were a peak at ca. 70°C, a shoulder at ca 45°C and a shallow peak at ca. −25°C, which, as with the zinc-ionomer, we attribute to the melting point, a pre-melting transition and either T_g or the β-relaxation of polyethylene. In this case, however, the temperatures of the relaxations in the melt-mixed blends were much different than that in the pure component polymers. For the 50/50 blend, an intense tan δ peak occurred at ca. 0°C and a smaller peak or shoulder near 40°C. The 0°C also occurred in the other blends, though the area and intensity of the tan δ peak decreased with decreasing ionomer concentration. The latter observations lead us to assign the 0°C peak to the ionomer phase. One explanation is that it is due to the β-relaxation, and the increase in intensity and area of the relaxation compared with the neat ionomer can be explained by the increase in the concentration of branch points due to a grafting reaction of the TLCP during mixing. The 40°C relaxation is consistent with the depressed melting point of the ionomer. A weak, higher temperature tan δ peak is also observed near 90–100°C in the blends which should be the T_g of the TLCP.

Although the tan δ relaxation assignments at this point

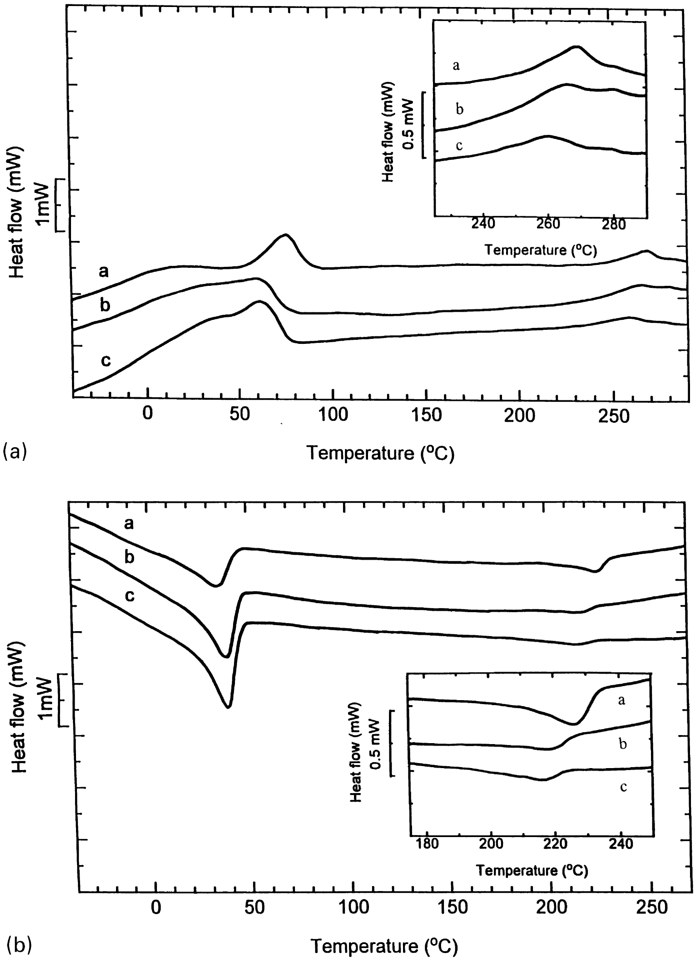


Fig. 6. (a) DSC heating thermograms (heating rate = 20°C min^{-1}) and (b) DSC cooling thermograms (cooling rate = 20°C min^{-1}) for (50/50) Vectra A–EAA$_{15}$Na$_{45}$ blends for different mixing times at 300°C: (a) 3 min; (b) 6 min; (c) 10 min.

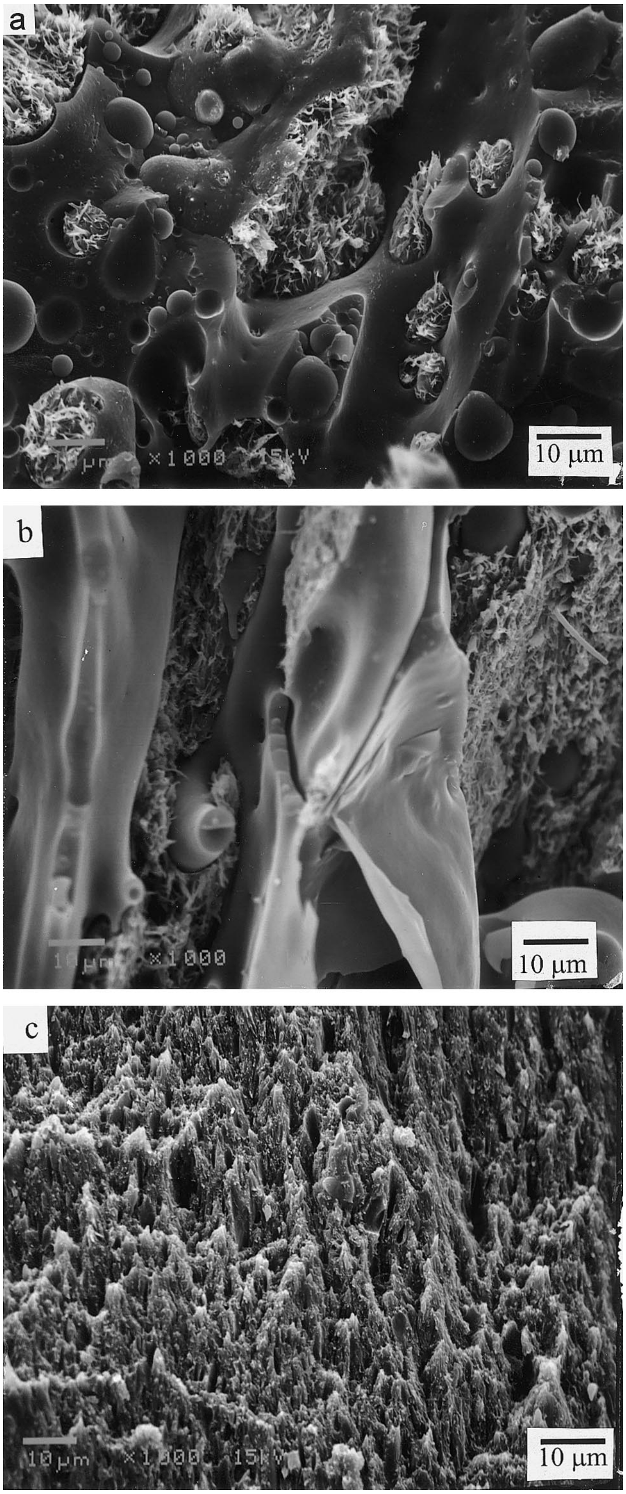


Fig. 7. SEM micrographs of fracture surfaces of (a) (75/25)Vectra A–EAA_{20}; (b) (75/25)Vectra A–$EAA_{15}Zn_{35}$; (c) (75/25)Vectra A–$EAA_{15}Na_{45}$ blends.

are somewhat tentative, it is probably safe to conclude that the changes in the viscoelastic behavior of the blends compared with that of the pure component materials are due to the melt reaction detected with the torque measurements, and the most probable explanation is the formation of a graft copolymer due to acidolysis between the TLCP and the ionomer. Further evidence of this is given in Fig. 5, which shows tan δ data for 50/50 Vectra A–$EAA_{15}Na_{45}$ blends as a function of mixing time at 300°C and a 30 rpm rotor speed. Two tan δ peaks were observed for each of the blends. The lower temperature tan δ peak increased in temperature and intensity as the mixing time increased. The peak temperatures were at −19, −9, −5 and 1°C for mixing times of 1, 3, 6 and 10 min, respectively. The increase in intensity, or area under the peak, is consistent with the assignment of the peak to a β-relaxation involving chain segments with branch points in that the grafting reaction increases the number of branches. The increase in the temperature and breadth of the relaxation can be explained by the introduction of relatively more rigid branched chains by grafting the TLCP to the ionomer and increased grafting with longer mixing time. The decrease in the mobility of the branches should increase the relaxation temperature.

The higher temperature tan δ peak occurs in the blend at 70, 68, 40 and 38°C for mixing times of 1, 3, 6 and 10 min, respectively. The decrease in temperature of that peak with mixing time is consistent with the decrease in the melting point of the ionomer with increasing mixing time. The T_g of the TLCP was not resolved in the tan δ data shown for the blends in Fig. 7, which is probably a consequence of the poor signal to noise of the DMTA measurements for the 50/50 blend above the melting point of the ionomer.

4.1.3. DSC of melt-mixed blends of Vectra A and EAA ionomers

Little or no change in either the melting points or the heats of fusion (ΔH_m) of the component polymers as a function of melt-mixing time were observed by DSC for 50/50 blends of Vectra A–EAA_{20} and Vectra A–$EAA_{15}Zn_{35}$. These results agree well with the conclusion that no melt reaction occurred between the TLCP, the free acid and Zn^{2+}-salt derivatives of the EAA ionomers.

Fig. 6 shows the DSC heating and cooling thermograms for 50/50 Vectra A–$EAA_{15}Na_{45}$ blends as a function of melt-mixing time. The melting temperature of the ionomer decreased from 75 to 60°C and the melting point of the TLCP decreased from 268 to 260°C as the mixing time increased from 3 to 10 min. The ΔH_m of the TLCP also decreased with increasing mixing time, which indicates that the grafting reaction decreases the ability of the TLCP to crystallize. Surprisingly, the ΔH_m associated with melting of the ionomer increased significantly (nearly a factor of two) as the mixing time was increased from 3 to 10 min. That the crystallinity of the ionomer should increase as a result of graft copolymer formation is unexpected, and the reason for this is not yet known.

A comparison of the DSC heating thermograms in Fig. 6(a) with the DMTA results in Fig. 5 confirms that the higher temperature tan δ peak between 40 and 60°C in the DMTA data is due to the melting of the crystalline regions in the ionomer phase. Both the melting endotherm and the

Table 2
DSC data for the cooling thermograms in an experiment in which a (50/50) Vectra A–$EAA_{15}Na_{45}$ blends initially mixed in the Brabender for 3 min was then cycled in the DSC from 0 to 300°C at 20°C min^{-1}

Cycle times	$EAA_{15}Na_{45}$		Vectra A	
	T_c (°C)	ΔH_c (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
1	33.85	11.36	225.39	2.540
2	33.15	12.26	224.78	2.494
3	33.41	13.08	224.72	2.394
4	33.24	14.34	224.77	2.276
5	33.37	15.20	222.33	2.138
6	33.51	15.88	221.23	1.784
7	33.42	16.20	220.64	1.728
8	33.75	16.92	220.08	1.502
9	33.81	17.36	219.90	1.470

tan δ dispersion decrease in temperature and increase in breadth are as a result of graft copolymer formation. The cooling thermograms in Fig. 6(b) indicate that the crystallization temperature of the ionomer was unchanged by the grafting reaction, though the amount of material that crystallized increased substantially with increasing mixing time. For the TLCP phase, both the crystallization temperature and the heat of crystallization, ΔH_c, decreased with increasing melt-mixing.

The changes in the 50/50 Vectra A–$EAA_{15}Na_{45}$ blend as a consequence of intermolecular acidolysis reaction is summarized in Table 2 for an experiment in which a blend was prepared by melt-mixing for 3 min at 300°C and then cycled between 0 and 300°C in the DSC. For each subsequent heating cycle, the crystallization temperature and ΔH_c of the TLCP decreased (i.e. lower TLCP crystallinity), and although the crystallization temperature of the ionomer did not change, the ΔH_c of the ionomer increased (i.e. higher ionomer crystallinity).

4.1.4. Morphology of melt-mixed blends of Vectra A and EAA ionomers

SEM micrographs of fracture surfaces of 75/25 blends of the Vectra A with EAA, $EAA_{15}Zn_{35}$ and $EAA_{15}Na_{145}$ are given in Fig. 7. The micrographs for the Vectra A–EAA blend and the Vectra A–$EAA_{15}Zn_{35}$ blend, Figs. 7(a) and (b), clearly show a biphasic morphology typical of a highly immiscible blend. The dispersed-phase size is very large (>10 μm) and the interfacial adhesion between phases is poor. In contrast, the micrograph for the Vectra A $EAA_{15}Na_{45}$ blend, Fig. 7(c), does not clearly show two phases which indicates a finer dispersion and a relatively good interfacial adhesion, characteristics of a well-compatibilized blend. The improved compatibility is due to the in situ formation of a TLCP-ionomer graft copolymer during melt-mixing. The graft copolymer is expected to be the ideal compatibilizing agent for a TLCP–EAA-ionomer blend. Moreover, the graft copolymer is also expected to be a good compatibilizer for blends of TLCP and polyethylene, and perhaps with other polyolefins.

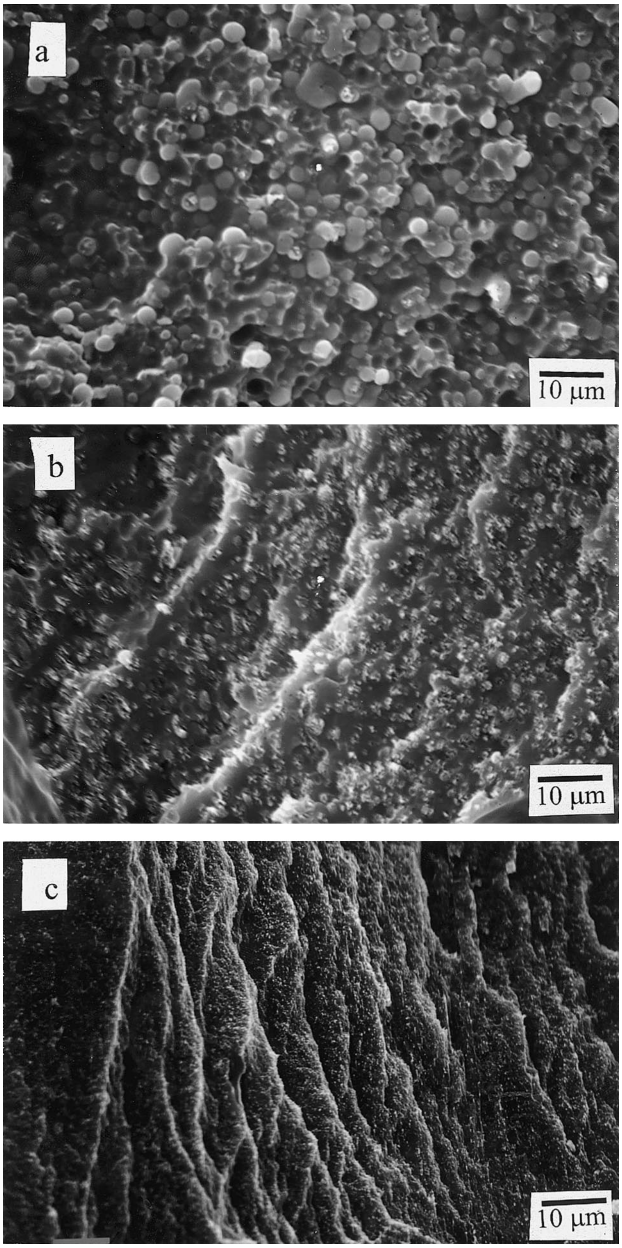


Fig. 8. SEM micrographs of fracture surfaces for (50/50) Vectra A–$EAA_{15}Na_{45}$ blends for different Brabender mixing times at 300°C and a rotor speed of 30 rpm: (a) 3 min; (b) 6 min; (c) 10 min.

The micrographs for the 50/50 Vectra A–$EAA_{15}Na_{45}$ blends in Fig. 8 show the effect of mixing time on the morphology. After 3 min mixing, Fig. 8(a), the dispersed-phase size in the blend is ~5 μm, and on the basis absence of empty holes from where a dispersed phase delaminated, the adhesion between the phases appears to be fairly good. The dispersed-phase size becomes much finer with increasing melt-mixing time. After 6 min, Fig. 8(b), the dispersed domains are ~1 μm, and after 10 min, Fig. 8(c), the domains are submicron in size ~0.1 μm. These results clearly show that as the melt-grafting reaction takes place, the compatibility between the two polymers improves.

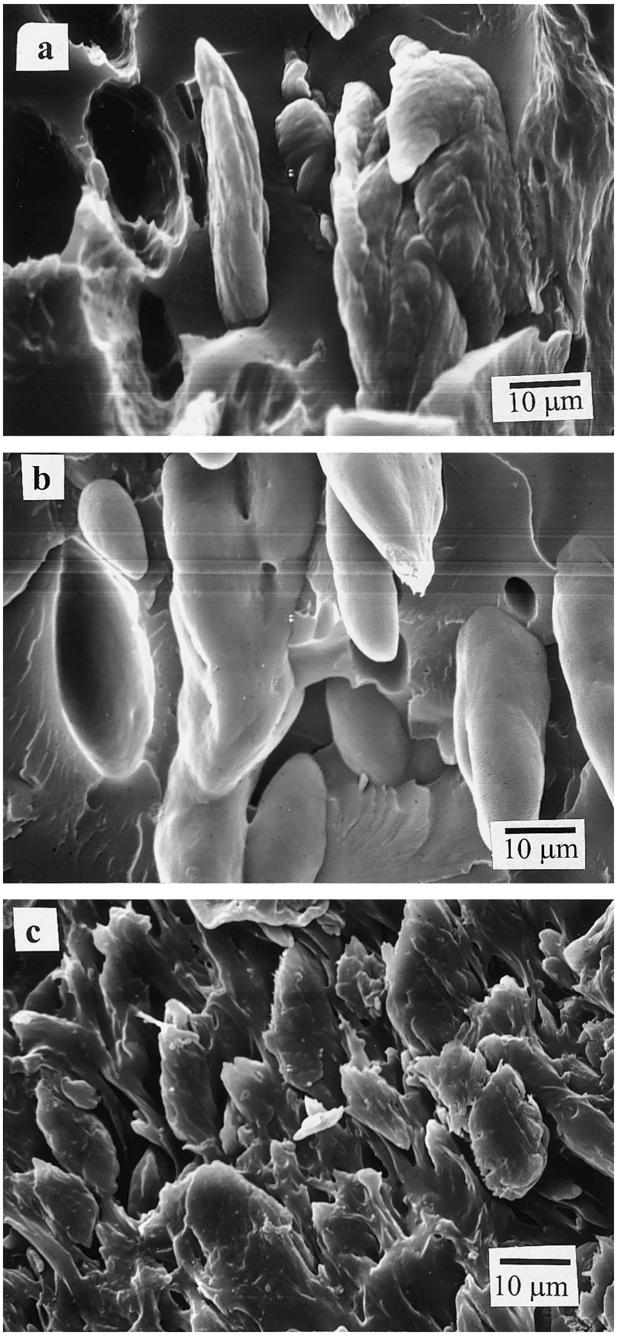


Fig. 9. SEM micrographs of fracture surfaces of (a) Vectra A–$EAA_{15}Na_{10}$ blend; (b) (50/50) Vectra A–$EAA_{15}Na_{20}$ blend; (c) (50/50) Vectra A–$EAA_{15}Na_{30}$ blend.

The influence of the Na^+-concentration on the morphology of the 50/50 Vectra A–$EAA_{15}Na$ blend melt reaction products was evaluated by varying the neutralization level of the ionomer from 10 to 30%, and the results are shown by the micrographs in Fig. 9. (Also, compare the micrographs in Fig. 9 with Fig. 8(c), in which the $EAA_{15}Na$ ionomer is 45% neutralized.) The concentrations of Na^+ for the ionomers in Figs. 8 and 9 range from 0.99 mmol g^{-1} for $EAA_{15}Na_{45}$ to 0.29 mmol g^{-1} for $EAA_{15}Na_{10}$. Although excellent compatibilization was obtained when $EAA_{15}Na_{45}$ or $EAA_{15}Na_{30}$ were used to prepare the blend, Figs. 8(c) and 9(a), the dispersion in the blend prepared with $EAA_{15}Na_{20}$ and $EAA_{15}Na_{10}$ was much grosser, Fig. 9(b) and (c). The domains, which presumably were the TLCP because of its lower viscosity, were anisotropic with diameters of the smaller dimension ~10 µm and the interfacial adhesion was relatively weak compared with that of the ionomers with higher Na^+-concentrations. These micrographs support the conclusion that Na^+ is responsible for catalyzing the acidolysis reaction and that the efficiency of compatibilization, i.e. the extent of formation of graft copolymer, may be controlled by the concentration of Na^+.

4.1.5. Effect of temperature on the acidolysis reaction between Vectra A and $EAA_{15}Na_{45}$

The effect of temperature on the kinetics of the grafting reaction between Vectra A and $EAA_{15}Na_{45}$ was assessed by measuring the crystallization temperature of the TLCP component in a 50/50 blend after annealing it at elevated temperature. The crystallization rate is expected to be perturbed by the chain branching that results from the grafting reaction, and this should manifest by a decrease in the crystallization temperature (T_c) measured in a DSC cooling experiment. The blends were first mixed for 1 min in a Brabender at 300°C. The samples were then heated in the DSC from room temperature to the desired reaction temperature, held at that temperature for times ranging from 1 to 9 min, and then cooled at 20°C min^{-1}.

The DSC-cooling scan data for reaction temperatures of 290, 310, 330 and 350°C are plotted against reaction time in Fig. 10. The crystallization temperature of the ionomer component was unaffected by annealing at 290°C, but it increased slightly when annealed for longer times at 310 and 330°C. For the last two reaction temperatures, the degree of crystallinity of the ionomer phase, as deduced from ΔH_c, increased significantly which perhaps was a consequence of degradation of the ionomer, that is, lowering the molecular weight may increase the rate of crystallization which is manifested in a dynamic DSC scan by the higher values of ΔH_c. An alternative argument is that the graft copolymer nucleates the crystallization of the ionomer, but we have no evidence to support this conclusion. When the reaction temperature was increased to 350°C, the crystallization temperature declined a little, though it was still higher than that of the sample annealed at 290°C, and the degree of crystallinity was still relatively high. Holding the blend at elevated temperature had a greater effect on the crystallization temperature of the TLCP component, which is probably a better indication of the melt reaction. In general, higher temperature and longer reaction time decreased T_c. The amount of crystallinity of the TLCP (i.e. ΔH_c) increased with increasing reaction time at 290°C, but generally decreased with increasing reaction time at the higher temperatures. The increase of ΔH_c with increasing time at 290°C is probably a consequence of more complete melting of the TLCP. Although the melting point

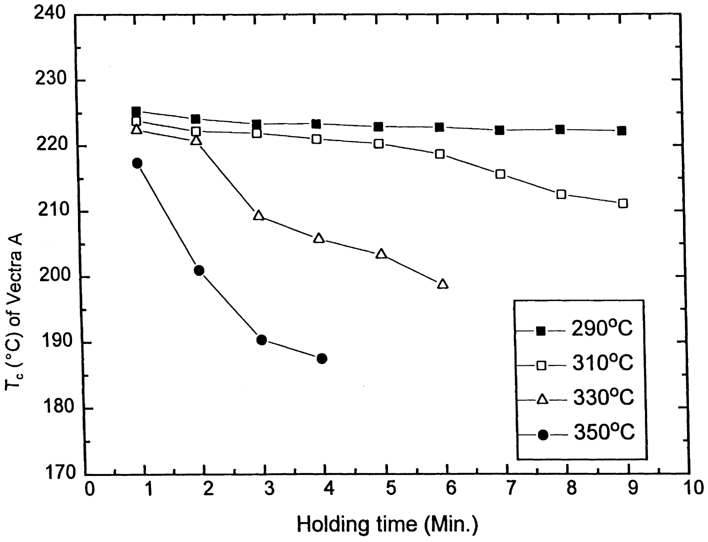


Fig. 10. Crystallization temperature versus reaction time at various temperatures for (50/50) Vectra A–EAA$_{15}$Na$_{45}$ blends. The initial blends were mixed for 1 min in the Brabender at 300°C.

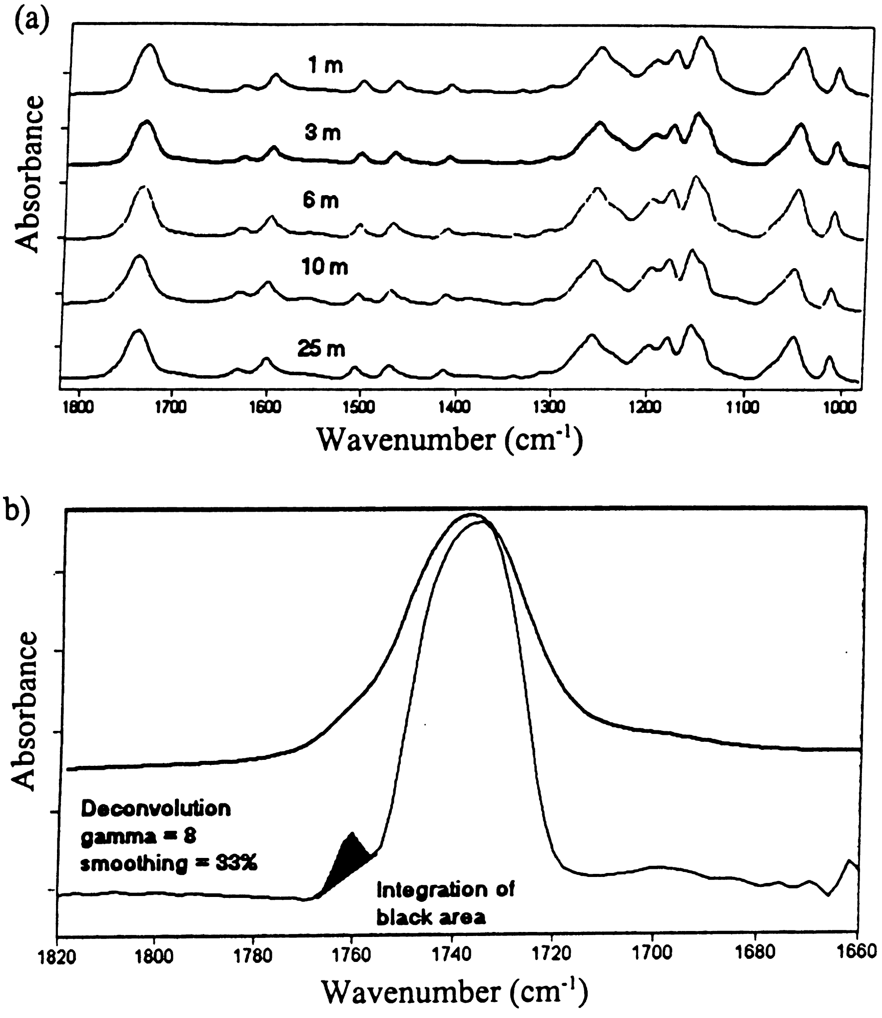


Fig. 11. (a) FTIR spectra for 50/50 Vectra A–EAA$_{15}$Na$_{45}$ blends as a function of Brabender mixing time (1–25 min) at 300°C and a rotor speed of 30 rpm; (b) example of deconvolution of the spectral region between 1820 and 1660 cm^{-1} for the sample with 6 min mixing time.

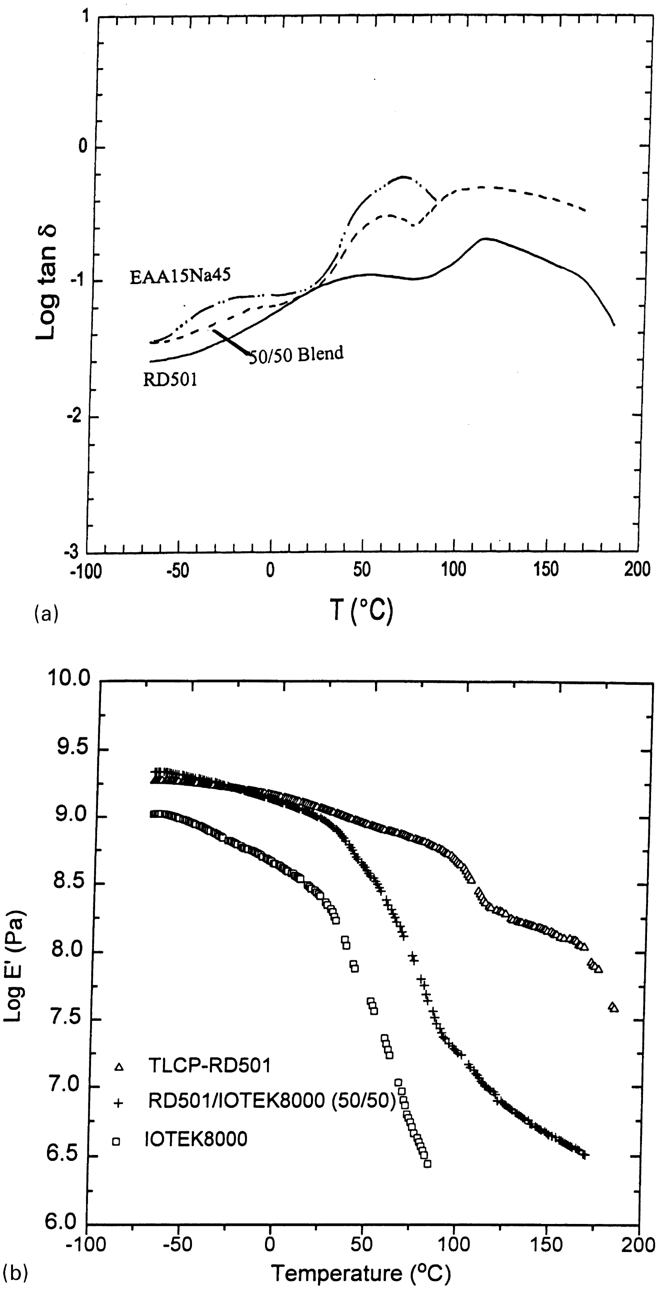


Fig. 12. Dynamic mechanical properties at $f = 1$ Hz versus temperature for RD501, $EAA_{15}Na_{45}$ and a (50/50) RD501–$EAA_{15}Na_{45}$ blend: (a) tan δ (b) E'.

of the neat TLCP measured by DSC was 277°C, other researchers have reported that a high melting fraction may persist up to ca 300°C [43,44].

4.1.6. Infrared evidence for acidolysis

The FTIR spectra of 50/50 Vectra A–$EAA_{15}Na_{45}$ samples mixed at 300°C in the Brabender for times up 25 min are shown in Fig. 11(a). The result of acidolysis is a shoulder at ca. 1761 cm^{-1}, which is due to an ester group with aromatic and aliphatic substituents, i.e. Ar–OC(O)–R, as opposed to the ester groups in the TLCP that have two aromatic substituents, Ar–OC(O)–Ar. The new absorption is more readily seen in the derivative (not shown) and deconvoluted spectra shown in Fig. 11(b). The deconvolution technique is explained in Ref. [38]. The blackened region in the insert shows the integrated area of the deconvoluted peak at 1761 cm^{-1}.

In order to estimate the extent of the acidolysis reaction, the area of the new ester-peak was normalized by the band areas characteristic of the $EAA_{15}Na_{45}$ (3025–2750 cm^{-1}) and Vectra A (1025–987 cm^{-1}). Unfortunately, the ratio of ionomer/TLCP calculated from the IR peak integrations, which should be a constant for each of the samples at a fixed composition, varied by as much as 25%. Some of the errors may be due to the heterogeneity of composition in a

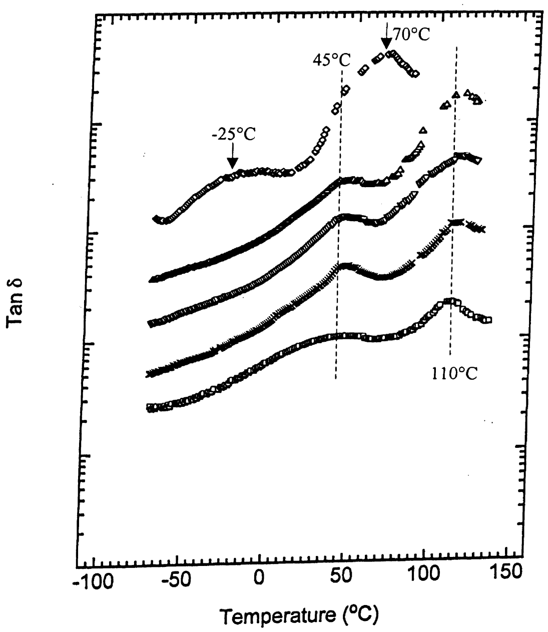


Fig. 13. DMTA tan δ at $f = 1$ Hz versus temperature for (75/25) RD501–$EAA_{15}Na_{45}$ blend as a function of Brabender mixing time at 230°C and 30 rpm: (◇) neat RD501; (△) mixing time = 5 min; (▽) 10 min; (×) 15 min.

phase-separated blend, but for whatever reason, the uncertainty in the normalizing factor prevented quantitative determination of the amount of acidolysis at each mixing time to a better than a factor of ten. A rough estimate is that the initial rate of acidolysis was 0.15–1.5 mol% min^{-1} and the extent of acidolysis for the mixing times of 6–25 min was in the range of 1–10%. Clearly, the quantification of the reaction kinetics was not very satisfying, but it does demonstrate that the extent of reaction need not be substantial to achieve satisfactory compatibilization.

4.2. RD501–EAA ionomer blends

The melting point of RD501 was about 50°C lower than that of Vectra A, and its lower processing temperature may be advantageous when preparing TLCP–EAA or TLCP–polyethylene blends. Similar mixing studies as described in the discussion above for Vectra A were also carried out for RD501 blends with the EAA and its Na^+ and Zn^{2+} salts, but using a much lower mixing temperature, ~230°C.

4.2.1. DMTA results

In general, the DMTA results for blends of RD501 with $EAA_{15}Zn_{35}$ or EAA were similar to those for blends of the ionomers with Vectra A. For all the blends, tan δ peaks or shoulders were observed that corresponded closely to relaxations observed in the pure component polymers, which indicate that little, if any, grafting reaction occurred. These results are consistent with the observations for the Vectra A blends that neither the Zn^{2+}-salt nor the free-acid derivative of the ionomers promote the acidolysis reactions or compatibility.

DMTA tan δ and E' data for RD501, $EAA_{15}Na_{45}$ and a 50/50 RD501-EAA_{45} blend are given in Fig. 12. In this case, the relaxations for the ionomer and the TLCP are perturbed by blending which is consistent with a reaction between the polymers, though the effect is not as pronounced as it was when Vectra A was used as the TLCP. The E' data in Fig. 12(b) show that the modulus behavior of the blend is intermediate between that of the two polymers, which again is consistent with the formation of graft-copolymer. The modulus of the material at the lower temperatures was dominated by the TLCP; while at the higher temperatures, above the T_g of the TLCP, the modulus was more like the ionomer melt. The latter observation suggests that the reaction with the ionomer reduced or completely suppressed the crystallization of the TLCP, which is consistent with DSC data that indicated no crystallinity in a 75/25 RD501–$EAA_{15}Na_{45}$ blend that was melt-mixed at 230°C.

Fig. 13 shows the effect of mixing time on tan δ of 75/25 RD501–$EAA_{15}Na_{45}$ blends. The blends exhibited two major tan δ peaks, at ca 45 and 110°C. The latter relaxation is the T_g of the RD501. The tan δ peak at 45°C is probably a premelting relaxation of the crystalline regions in the ionomer. There appears to be a lower temperature shoulder on the broad, higher temperature tan δ peak for the pure ionomer which may correspond to the 45°C peak in the blends. An alternative explanation is that the 45°C peak in the blends is an elevated β-relaxation of the ionomer which occurred at −25°C for the neat ionomer. For the sample prepared with a mixing time of 15 min, a weak tan δ(dispersion occurs at ca. 4°C which may have a similar origin as the tan δ(peak that was observed in the melt-mixed Vectra A–$EAA_{15}Na_{45}$ blends at ca. 0°C; that is, graft copolymer formation due to acidolysis. What is clear, however, is that the changes that occur in the DMTA results for the RD501–$EAA_{15}Na_{45}$ blends are much less than that occurred in the Vectra A–$EAA_{15}Na_{45}$ blends, c.f. Figs. 5 and 13. Although this may be a consequence of the different comonomers that are in RD501, it is more likely that the reduced graft copolymer formation was due to the lower mixing temperature used.

4.2.2. DSC results

In general, either no or very small changes were observed in the transition temperatures and heats of transition of 75/25 RD501–EAA_{15} and 75/25 RD501–$EAA_{15}Zn_{35}$ blends as a result of the melt mixing process. The crystallinity of the TLCP and the ionomer, as measured by ΔH_m from the heating thermogram, decreased about 20 and 10%, respectively. The amount of ionomer that crystallized during the cooling scan was comparable to that of the pure ionomer. Also, the crystallization temperature of the ionomer phase was higher for the RD501–EAA blend than for the neat EAA. Most of the changes can be explained without invoking compatibilization or reaction, though the increase in the T_c of the RD501–EAA is surprising.

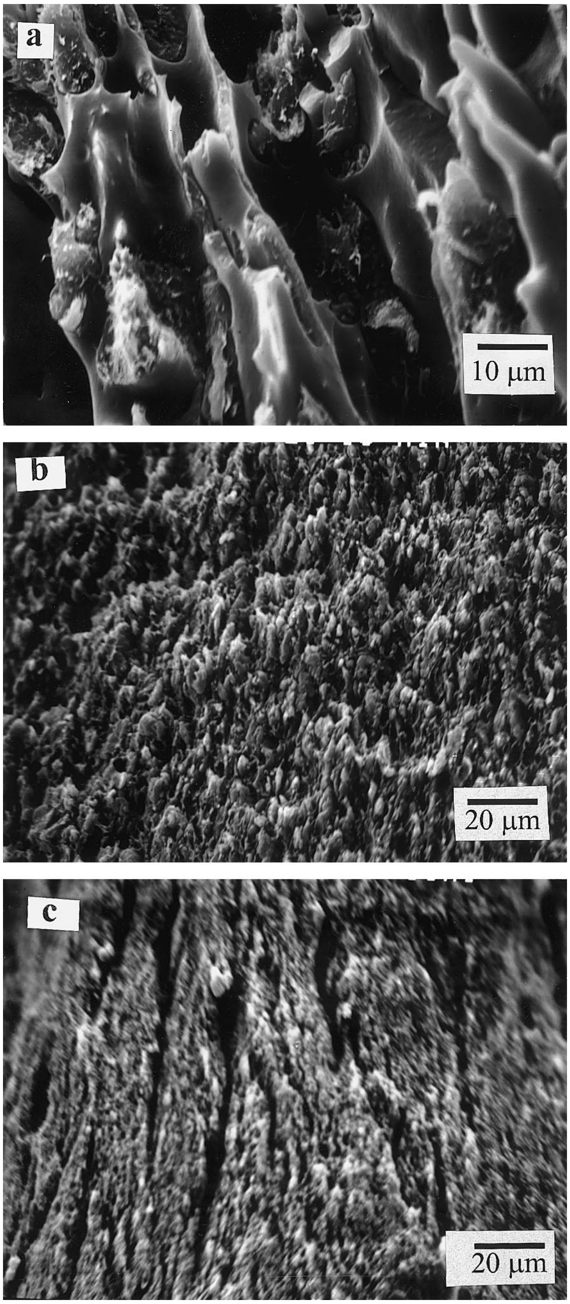


Fig. 14. SEM micrographs of fracture surface of (75/25) RD501–EAA_xNa_{45} blends after 15 min mixing in the Brabender at 230°C and 30 rpm: (a) $x = 3$; (b) $x = 9$; (c) $x = 15$.

Melting and crystallization of the TLCP were not observed for the 75/25 RD501–$EAA_{15}Na_{45}$ blends. As for the Vectra–$EAA_{15}Na_{45}$ blends, ΔH_m and ΔH_c of the ionomer increased compared with the values for the neat ionomer. Again, the reason for this is not known, but it may be due to degradation of the ionomer. Although the melting point of the ionomer did not change much upon melt-mixing, the crystallization temperature increased by about 15–17°C.

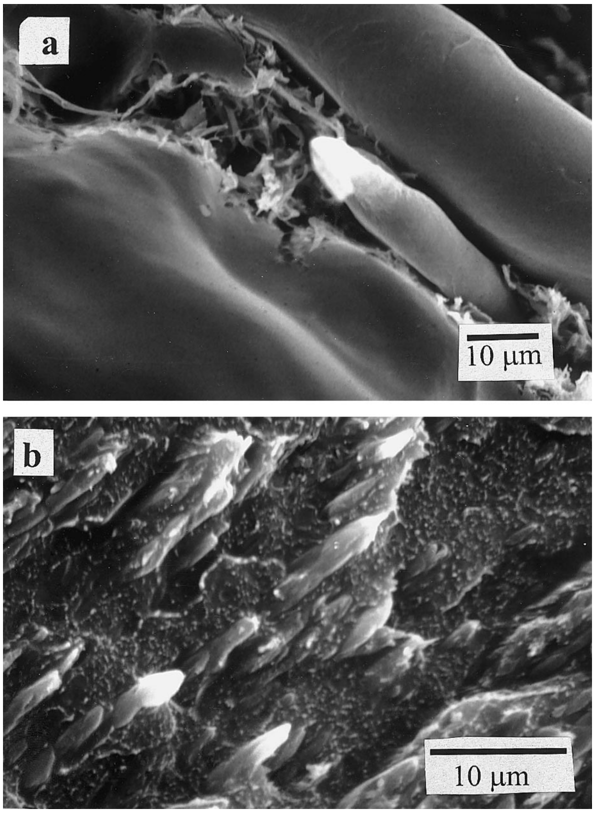


Fig. 15. SEM micrographs of fracture surface of (a) (50/50) RD501–HDPE; (b) (45.5/45.5/9) RD501–HDPE–$EAA_{15}Na_{45}$.

4.2.3. Effect of functionality of the ionomer on compatibilization

Earlier in this paper, we showed that for a constant functionality of the starting EAA precursor, e.g. EAA_{15}, the effectiveness of the melt reaction on compatibilization by Na^+-ionomers was dependent on the neutralization level. The compatibilization effectiveness increased with increasing Na^+. The micrographs in Fig. 14 demonstrate a similar result when the degree of neutralization is held constant at 45%, but the acrylic acid content of the precursor EAA copolymer was varied from 3 to 15 wt%. Whereas, (75/25) RD501–$EAA_{15}Na_{45}$ and (75:25) RD501–EAA_9Na_{45} appeared fairly homogenous upon melt-mixing at 230°C for 10–15 min, Fig. 14(a) and (b), the (75/25) RD501–EAA_3Na_{45} blend remained grossly phase-separated even after 15 min of mixing in the intensive mixer, Fig. 14(c).

4.3. Ternary blends with $EAA_{15}Na_{45}$ as a compatibilizer

The effect of processing a 50/50 mixture of RD501 and HDPE with the addition of 9 wt% of $EAA_{15}Na_{45}$ is shown by Fig. 15. Fig. 15(a) shows that a 50/50 RD501 HDPE blend exhibits gross phase separation with little, if any, adhesion between the phases. In contrast, although the blend containing the ionomer, Fig. 15(b) is also phase-separated, there is no visible delamination of the phases, which indicates good interfacial adhesion. Although the results are limited, they do suggest that the EAANa-ionomers will function effectively as a compatibilizer for blends of TLCP and polyethylene. Additional studies of the morphology and mechanical properties of similar ternary blends are underway and will be reported in a future communication.

5. Conclusions

Blends of TLCP and the sodium salt of ethylene–acrylic acid copolymers are compatibilized by a melt reaction that involves an acidolysis between acrylic acid and the ester linkages of the TLCP. The reaction is catalyzed by the presence of sodium carboxylate groups and the rate of reaction increases as the concentration of Na^+-ions increase. The free carboxylic acid and the zinc-salt derivative of EAA are ineffective at catalyzing the reaction. The extent of graft copolymer formation depends on the Na^+ concentration, the mixing time and probably the mixing temperature and the intensity of mixing.

Preliminary experiments on ternary blends suggest that the reaction graft copolymers of TLCP and Na-EAA may be suitable compatibilizers for blends of TLCP and polyethylene (PE) or other polyolefins.

Acknowledgements

This research was supported by grants from the National Science Foundation (DMR 97-12194) and from the Hoechst-Celanese Corp. We are grateful to Dr J. Rafalko for providing the infrared spectrum and analyses.

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