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Compatibilization in ionomer blends

1. Ionomers with identical charge

Ming Jiang, Chunlin Zhou, and Zhongquan Zhang

Institute of Materials Science, Fudan University, Shanghai 200433, China

Summary

Two kinds of copolymers, i.e. poly(styrene-co-methacrylic acid) (SMaa) and poly(butyl methacrylate-co-methacrylic acid) (BmaMaa) containing a common but minor (10-20%) component of methacrylic acid, were synthesized. The blends of the corresponding ionomers of SMaa and BmaMaa neutralized with a series of metal-ions produced by solvent casting and moulding were examined by DSC and TEM. It has been shown that introducing metal-ions to the blends of copolymers apparently improves the miscibility. This miscibility enhancement depends on the nature and amount of the counter ions. In the case of SMaa-Na^+/BmaMaa-Na^+ even a single-phase blend can be produced. The results confirm compatibilization in the blends of similar-charged ionomers.

Introduction

Introduction of polar or ion groups capable of forming specific interaction into a immiscible polymer pair can improve its miscibility[1]. The ion-ion interaction in ionomer blends has been studied intensively by Eisenberg etc.[2-6]. In these studies, it is proved that two polymers of a blend containing opposite charges show apparently miscibility improvement, and in some cases introducing a small amount of ionic groups can make immiscible blends miscible. Apparently, this miscibility enhancement can be attributed to the columbic interaction between the ions with opposite charges being carried by the two component polymers, respectively. In this communication we are interested in whether the compatibilization effect still exists in blends of ionomers with identical charge. Almost no experimental information related to this question can be found in literature except that for blends of sodium-neutralized copolymers of styrene-methacrylic acid and ethyl acrylate-acrylic acid [7,8], no apparent miscibility enhancement was reported.

Experimental

Polymerization Styrene (S), butyl methacrylate (Bma) and methacrylic acid (Maa) were distilled before use. Azobisisobutyronitrile (AIBN) was recrystallized. The copolymers of SMaa and BmaMaa were prepared by copolymerization of the corresponding monomers in toluene at 70°C initiated by AIBN under a nitrogen atmosphere. The polymerization was stopped at about 30-50% conversion of the monomers by pouring the reaction mixture into methanol/water (v/v 1/10) followed by a routine drying procedure. The compositions of the copolymers were determined by acid-base titration in methanol/toluene (v/v 1/4). In this work, SMaa with 13.7mol% of Maa and BmaMaa with 20.2mol% of Maa were used.

Blends of the copolymers The mixture of the copolymers was dissolved in methanol/THF (V/V, 1/4) to a 5% solution with stirring for an hour. For making solvent-casting films, a portion of the solution was transferred into a sample cell made of polytetrafluoroethylene(PTFE). The cell was loosely covered by a glass sheet for a slow evaporation of the solvent. The film samples formed over a week and were then completely dried under vacuum. For making melt molding blends, a portion of the solution was precipitated in methanol/water mixture. The dried blend powder was then moulded at about 180°C under a pressure of 6 MN/M^2.

Blends of ionomers The copolymers or their mixtures were partially neutralized with different metal acetates in methanol/THF (v/v 1/4) at 45°C for 24 hours. The reaction mixture was precipitated in methanol/water. The amount of the counter-ion was calculated based on the total molar number of Maa units. After repeating washing with methanol/water, the precipitate was press-moulded or redissolved in methanol/THF for making mould films and solvent casting films, respectively. The preparation conditions of the blend films were the same as those for the copolymer blends described above.

Characterization Differential Scanning Calorimetry (DSC) measurements were performed using a Dupont 1090B thermal Analyzer with a heating rate of 20°C/min under nitrogen atmosphere. The glass transition temperature (Tg) was taken as the midpoint of the abrupt heat-capacity jump between the liquid and glassy states. For transmission electron microscope (TEM) observations, the films were ultratomed first. The ultra-thin sections were then stained with vapor of 1% ruthenium tetroxide (RuO_4) solution in water for three hours and then was observed using a Hitachi H500H transmission electron microscope. Since there are no carbon-carbon double bonds in any of the components of the blends, the routine staining agent (OsO_4) was not effective. Ruthenium tetroxide (RuO_4), which had been proved powerful to selectively stain phenyl ring-containing component, was successfully used in this work to stain copolymers of styrene and methacrylic acid.

Results and Discussion

The Glass transition behavior of the solvent-cast films of the ionomer blends with a composition of SMaa/BmaMaa 50/50 but different sodium-ion contents covering a range from 0mol% to 52.7mol%, calculated based on the total molar content of methacrylic acid in the blends, was examined by DSC and the related results are shown in Fig.1. For the blend of copolymers SMaa and BmaMaa, without neutralization, the DSC curve clearly shows two glass transitions around 55°C and 85°C, associated with BmaMaa-rich and SMaa-rich phases, respectively. This two-phase structure does not change when a small amount (5.3mol%) of methacrylic acid was neutralized by sodium acetate. However, an apparent change of the phase behavior is observed when the sodium-ion content reaches 10.6mol%, i.e. the low-Tg almost disappears (curve 3). This indicates that introduction of the metal ions greatly increases the miscibility. This miscibility enhancement is further confirmed by the presence of only one relatively sharp glass transition between the low-Tg of BmaMaa-Na^+ and high-Tg of SMaa-Na^+ in the blends with higher sodium ions, i.e. 31.6, 52.7mol% (curve 5,6). Since in this system, both the components carry groups of $-COO^-$ with negative charge, this result can be regarded as an evidence of compatibilization of the ionomer blends via introducing the same ion groups into blend components.

It is interesting to notice that different results were obtained when Zn^{2+} was used as the counter ion. For all the blends of this series, in which the Zn^{2+} content varies from 0 to 26.4mol%, two glass transition regions can be detected (Fig.2). In the blends, the high Tg becomes broad and there is no clear variation tendency of Tg as the ion content increases. This two phase structure is clearly confirmed by TEM observation shown in Fig.3. In the microphotograph, SMaa phase being ellipsoidal in a size of a few micrometers which appears dark due to staining by RuO_4, is randomly dispersed in BmaMaa matrix. The phase boundary is sharp which indicates relatively complete phase separation.

Since the counter ions of Na^+ and Zn^{2+} lead to quite different results as regard to compatibilization of the ionomer blend, it is worthwhile exploring the behavior of the more counter ions. Some preliminary results for ions of Cu^{2+}, Mg^{2+} and Mn^{2+} are shown in Fig.4, with the curves for Na^+ and Zn^{2+} for comparison. The concentration of the metal ions is the same , i.e. 26.4%. The results show that the behavior of Cu^{2+} is quite similar with Zn^{2+}, i.e. showing two glass transitions indicating phase separation, however, Mn^{2+} or Mg^{2+} present only one Tg of 60°C and 75°C, respectively, showing apparent compatibilization effect just as Na^+ does. It is noticed that in the cases showing apparent miscibility enhancement, the introduced ion content needed is still at a relatively low level, i.e. only about 4-5mol% of the repeating units in the blend components are connected with the metal-ions. Although at present we are not able to relate compatibilization to the counter-ion structure based on the existing data, we believe that compatibilization in the blends composed of similarly-charged ionomers is a rather common phenomenon. In the present case because of the two kinds of the polymer chains carrying the same, negative charge, there is definitely no favorable columbic interaction for mixing. Although in the literature there is a suspicion against the possibility of rendering two polymer miscible through introducing identical ionic units onto the component polymers[3], the results presented here make us believe that in certain cases, the repulsive interaction between the ion groups and hydrocarbon chains may be strong enough for forming ion-aggregates through not only intra-component but also inter-component mixing.

While all the results described above were for the solvent-cast films, for comparison, the melt blends of Zinc-neutralized

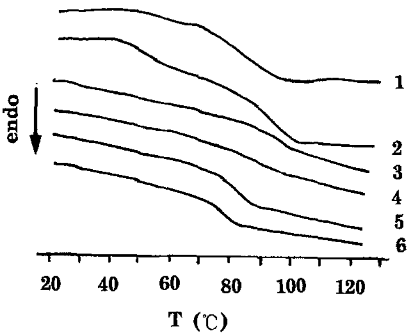

Fig.1 DSC curves of blends of SMaa and BmaMaa (w/w 50/50) with different contents of Na^+ (film formed in methanol/THF). Na^+ mol% (calculated based on Maa units, the Same below): 1, 0; 2, 5.3; 3, 10.6; 4, 21.1; 5, 31.7; 6, 52.7.

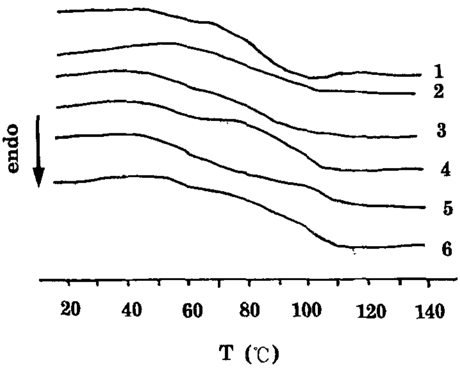

Fig.2 DSC curves of blends of SMaa and BmaMaa (w/w 50/50) with different contents of Zn^{2+} (film formed in methanol/THF). Zn^{2+}mol%: 1, 0; 2, 2.6; 3, 5.3; 4, 10.6; 5, 15.8; 6, 26.4.

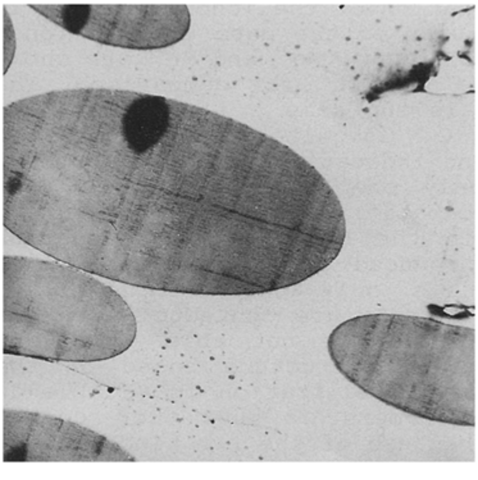

Fig.3 Electron micrograph of SMaa-Zn^{2+}/BmaMaa-Zn^{2+} (w/w 50/50) system (the film formed in methanol/THF and stained by RuO_4)

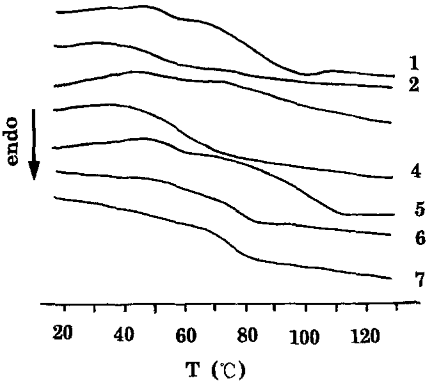

Fig.4 DSC curves of SMaa/BmaMaa (w/w 50/50) system with different metal-ions (film formed in methanol/THF). Metal ion mol%: 1, 0; 2, Co2+ 26.4; 3, Cu^{2+} 26.4; 4, Mn^{2+} 26.4%; 5, Zn^{2+} 26.4; 6, Mg^{2+} 26.4; 7, Na^+ 52.7.

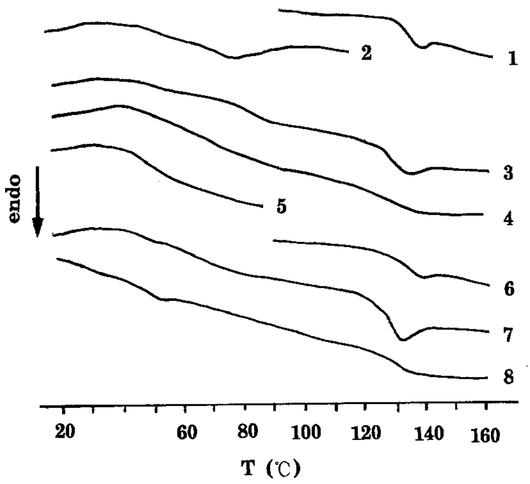

Fig.5 DSC curves of samples prepared at different moulding conditions. Preheated at 180~200°C for 4 minutes and then moulded at $60kg/cm^2$ for 1 minutes:
1, SMaa-0.283Zn^{2+};
2, BmaMaa-0.247Zn^{2+};
3, SMaa/BmaMaa;
4, SMaa/BmaMaa-0.264Zn^{2+}.
Preheated at 180~200°C for 10 minutes and then moulded at $60kg/cm^2$ for 1 minutes:
5, BmaMaa-0.247Zn^{2+};
6, SMaa-0.283Zn^{2+};
7, SMaa/BmaMaa;
8, SMaa/BmaMaa-0.264Zn^{2+}.

ionomers formed at 180°C under pressure were examined with DSC and the related results are shown in Fig.5. From the data, it may be concluded as follows:(1) In all the melt blends of either copolymers of SMaa and BmaMaa or their zinc salts, there is a two-phase structure, as indicated by the presence of two glass transitions. The two Tgs in the ionomer blends are almost the same as the corresponding pure ionomers. (2) At a high temperature of 180°C, moulding caused a relatively stable phase structure since a heating-period change from four to ten minutes does not cause any Tg variation of the separated phases.

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