Miscibility of Chitosan/Poly(acrylonitrile-*co*-acrylic acid) Blends

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INTRODUCTION

Recently, more focus has been concentrated on natural polymers, because natural polymers are inexhaustible resources with biocompatible and biodegradable properties and do not cause environmental problem. Therefore, many blend systems containing natural polymers have been studied in various fields.[1-2] Chitosan, a common name for a (1 → 4) linked 2-amino-2-deoxy-β-D-glucan, is an N-deacetylated product of chitin that is the second most abundant polysaccharide in nature. Moreover, it has very useful functional groups such as hydroxyl, amine and acetamide groups, and also shows antimicrobial activity. In particular, a few interesting observations on the blends of chitosan with some synthetic polymers such as poly(vinyl alcohol),[3] poly(vinyl pyrrolidone),[4] and poly(ethylene oxide)[5] have been reported. In the present study, the miscibility of chitosan/poly(acrylonitrile-*co*-acrylic acid) blends has been investigated.

EXPERIMENTAL

Raw chitosan was purified using the reprecipitation method.[6] Chitosan was dissolved in 5% acetic acid and filtered with stainless steel mesh. It was poured into sodium hydroxide solution, and the precipitates were then washed and dried under vacuum at 60 ℃. The degree of deacetylation was measured by titration method. Poly(acrylonitrile-*co*-acrylic acid), poly(AN-*co*-9AA), 9 mol% acrylic acid content, were prepared by emulsion polymerization with a redox catalyst of sodium hydrogen sulfite and potassium peroxosulfate. The copolymer composition of poly(AN-*co*-AA) was determined by NMR. The intrinsic viscosity of poly(AN-*co*-9AA) was characterized in N,N-dimethylformamide at 25 ℃. The results of characterization are summarized in Table 1. Blend samples of chitosan/poly(AN-*co*-AA) were prepared by solution blending. The solution was cast on a polystyrene plate and solvent evaporation was carried out under reduced pressure. The thermal analysis was performed

with a Perkin Elmer DSC-7. Differential scanning calorimeter (DSC) was calibrated with indium and zinc. To determine the glass transition temperature (T_g) of the blends, blend samples were heated in a nitrogen atmosphere to 250 ℃ at a heating rate of 20 ℃/min and then quenched to room temperature. The samples were immediately reheated to 250 ℃ at a heating rate of 20 ℃/min. The dynamic mechanical properties were measured with a dynamic mechanical thermal analyzer (Rheometric Scientific DMTA MK Ⅲ) at 1Hz over the range from 30 ℃ to 250 ℃ at a heating rate of 2 ℃/min. The films about 0.1mm in thickness were used for the dynamic mechanical test.

RESULTS AND DISCUSSION

The observation of a single glass transition temperature for a blend pair, between those of the homopolymers, is regarded as decisive evidence of polymer miscibility, although different methods of measuring T_g are sensitive to different scales of homogeneity.[7] For all blends and chitosan homopolymer, however, glass transition temperature is not detected in DSC thermograms. It becomes increasingly difficult to determine exactly the location of the discontinuity in heat flow as the chitosan content in the blends increases. In many blend miscibility studies,[1,7] dynamic mechanical analysis has proven to be more sensitive than calorimetric measurements for the detection of T_g. Figure 1 shows the dynamic mechanical analysis spectra of chitosan/poly(AN-co-9AA) blends. The chitosan homopolymer shows a glass transition at 97 ℃. As mentioned above, the sensitivity of DMTA is greater than that of DSC. However, despite this higher sensitivity the glass transition monitored at 97 ℃ is still very weak considering the scale to which it is shown in Figure 1. The tanδ vs. temperature plot of poly(AN-co-9AA) shows a single glass transition centered at 137 ℃. The amplitude of this transition reflects well the high mobility at the glass transition, in contrast to chitosan which shows a weak transition due to its rigid units. The chitosan/poly(AN-co-9AA) blends show a single composition-dependent T_g which decreases with increasing the amount of chitosan in blends, indicating that chitosan and poly(AN-co-9AA) are miscible.

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Table 1. Polymer Characteristics

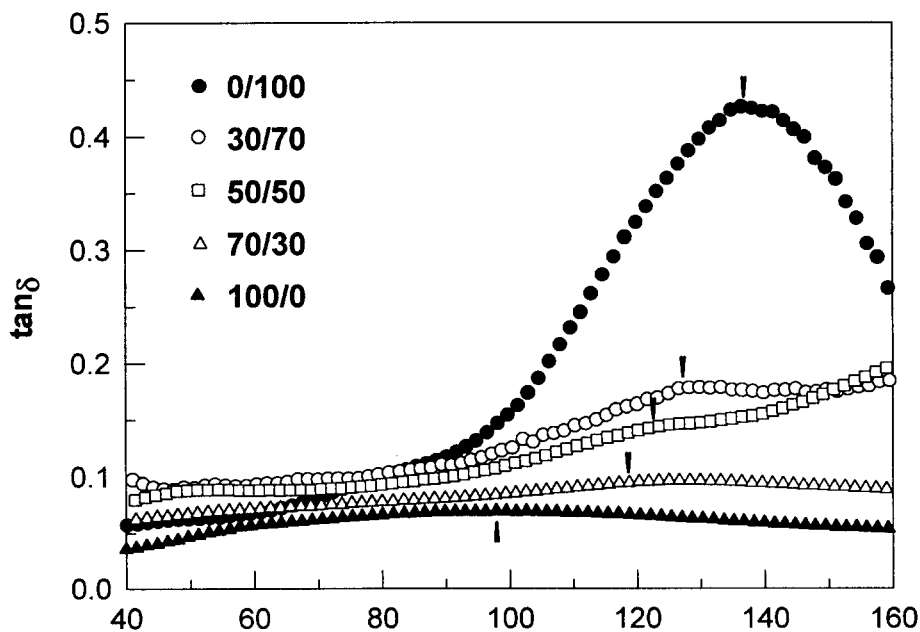|	Source	$[\eta]$(dL/g)	T_g (°C)[a]
Poly(AN-co-9AA)	Synthesized	2.76	137
Chitosan	Keumho Chemical Co., Ltd.	-	97

[a] Determined by DMTA

Figure 1. Temperature dependence of the dynamic mechanical thermal properties of chitosan/poly(AN-*co*-AA) blend. The arrows indicate the glass transition temperature of each component.