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THERMAL DEHYDRATION AND MISCIBILITY OF PHEMA/PMAA BLENDS

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Abstract

Miscibility and dehydration of poly(2-hydroxyethyl methacrylate) and poly(methacrylic acid) (PHEMA/PMAA) blends were investigated by temperature modulated DSC (TMDSC), TG and solid state ^{13}C NMR methods. TMDSC spectra and ^{1}H spin-relaxation times showed that the blends are homogeneous on a scale of 5–10 nm for all compositions. From TG and ^{13}C NMR, we elucidated that the mass loss of the blends at 300°C is ascribed to the dehydration between the hydroxyl group of PHEMA and the carboxyl group of PMAA.

Keywords: dehydration, miscibility, NMR, polymer blend, poly(2-hydroxyethyl methacrylate) (PHEMA), poly(methacrylic acid) (PMAA), TG, TMDSC

Introduction

Poly(2-hydroxyethyl methacrylate) (PHEMA) is one of the polymers used for biomedical purposes. It has a hydroxyl group (OH). Poly(methacrylic acid) (PMAA) has a carboxyl group (COOH) and is known to form intramolecular six-membered cyclic anhydrides around 250–300°C [1]. It is interesting to study to what extent the homogeneous phase of the PHEMA/PMAA blends exists and how the thermal dehydration of PMAA is affected by blending with PHEMA.

In this study, we examine the miscibility and the blending effects on thermal dehydration of PMAA for the PHEMA/PMAA blends using temperature modulated differential scanning calorimetry (TMDSC) [2], thermogravimetry (TG) and solid-state high-resolution ^{13}C nuclear magnetic resonance (NMR) techniques.

Experimental

PHEMA (M_w=300000) was obtained by ALDRICH Chemical Co., Inc. and PMAA (M_w=150000) by Scientific Polymer Products, Inc. The PHEMA/PMAA blend films (unit molar ratios of 1/3, 1/2, 1/1, 2/1 and 3/1) were obtained by casting the methanol solutions of 10 w/v% on a Teflon plate. All the heat-treated films were prepared in nitrogen atmosphere.

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TMDSC and TG measurements were made by using a Perkin Elmer DSC 7 and TGA 7, respectively. The heating and cooling rates for TMDSC measurements [2] are 20°C min^{-1} (T to T+4°C) and 10°C min^{-1} (T+4°C down to T+2°C), respectively. The heating rate for TG measurements is 20°C min^{-1}.

Solid-state high-resolution ^{13}C NMR measurements were made by using a Bruker DMX 500 spectrometer with the cross-polarization/magic-angle-spinning (CP/MAS) technique. ^{13}C chemical shifts were measured relative to tetramethylsilane by using solid adamantane as an external standard.

Results and discussion

TMDSC detects sensitively the small heat capacity change due to the glass transition for PHEMA and the PHEMA/PMAA blends (Fig. 1). The observed glass transitions are depicted by arrows in the figure. For all the blends, a single glass transition is clearly observed, and the each observed glass-transition temperature (T_g) depends on the composition. This suggests that the blends consist of a homogeneous phase on a few 10 nm scale for all compositions [3].

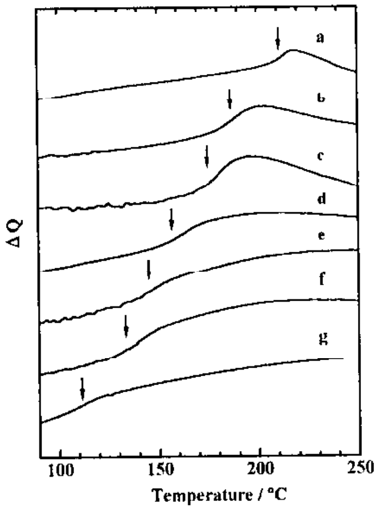

Fig. 1 Real parts of the complex heat capacities observed by TMDSC for (a) PMAA, PHEMA/PMAA= (b) 1/3, (c) 1/2, (d) 1/1, (e) 2/1, (f) 3/1 blends and (g) PHEMA. Arrows show grass transitions

Figure 2 shows the ^{1}H spin-lattice relaxation times in the laboratory frame (^{1}H-T_1) of PHEMA in the blends obtained through ^{13}C CP/MAS NMR. Theoretically estimated ^{1}H-T_1 values based on the ^{1}H molar ratios are also given in the figure as a solid curve. The observed ^{1}H-T_1 values show a compositional dependence, although the values do not agree with the theoretical curves completely. This disagreement is due to the change of molecular motion by blending [4, 5]. This observation also suggests

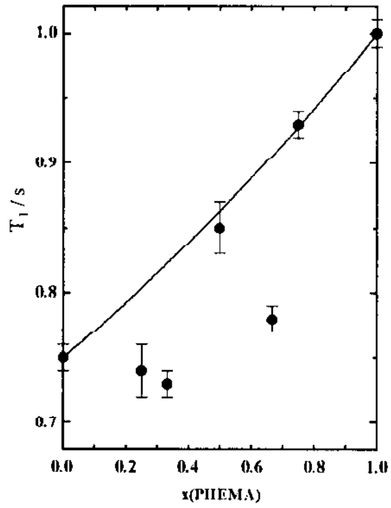

Fig. 2 Observed and calculated ^{1}H-T_1 values of PHEMA, PMAA and PHEMA in the PHEMA/PMAA blends *vs.* composition (●). The calculated values are depicted by a solid line and obtained by as follows:

$$T_{1\text{calc}}=\frac{N_{\text{PMAA}}}{N_{\text{PHEMA}}+N_{\text{PMAA}}}T_{1\text{PMAA}}+\frac{N_{\text{PHEMA}}}{N_{\text{PHEMA}}+N_{\text{PMAA}}}T_{1\text{PHEMA}}$$

where N_i is ^{1}H mol number of *i*-component in the blends and T_{1i} ^{1}H–T_1 values of *i*-component

that the blends are homogeneous on a few 10 nm scale [4]. Furthermore, we observed the ^{1}H-$T_{1\rho}$ values in the rotating frame of PHEMA in the blends. The observation suggested that the PHEMA/PMAA blends are miscible on a few nm scale [5].

To examine the blending effect on the thermal dehydration of PMAA in the PHEMA/PMAA blends, we measured TG-curves for all the samples from 30 to 800°C. Figure 3 shows the expanded TG-curves for PHEMA, PMAA and the blends. The mass loss of PMAA begins at ~250°C and reaches to ~15% at 350°C. The mass hardly decreases until 420°C, indicating PMAA becomes anhydrides [1]. The mass loss of PHEMA at 300°C is 6% and the large loss begins at over 300°C. The mass loss due to dehydration of PMAA reaches to 10.5% theoretically. The excess loss of ~5% is due to sorbed water or monomer [1]. Therefore, the mass loss of 6% for PHEMA is not due to degradation or dehydration but due to sorbed water or monomer. In fact, the ^{13}C CP/MAS NMR spectrum of PHEMA after heat-treatment at 300°C for 10 min coincided with that before heat-treatment, while that of PMAA exhibited the spectrum of anhydrides.

The mass losses at 300°C for the 1/3, 1/2, 1/1, 2/1 and 3/1 blends are 12, 11, 11, 10 and 8%, respectively, which are larger than that of PMAA except for the 3/1 blend. This indicates that the intermolecular dehydration between PHEMA and PMAA occurs. The mass losses for those blends are already observed at 200°C and

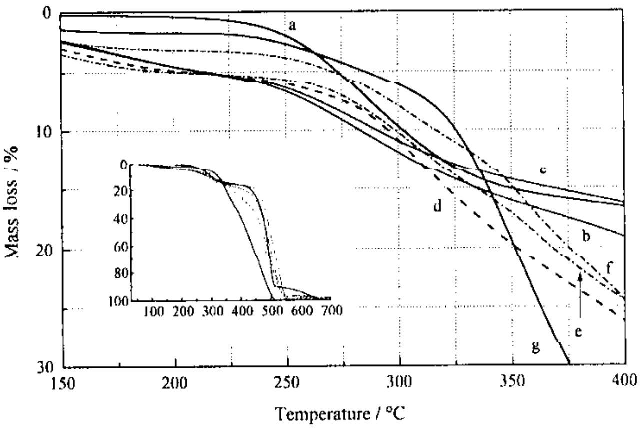

Fig. 3 Expanded TG curves for (a) PMAA, PEHMA/PMAA= (b) 1/3, (c) 1/2, (d) 1/1, (e) 2/1, (f) 3/1 blends and (g) PHEMA at 150–400°C

the values are in the range of 3.2–5.0%. This loss is probably caused by evaporation of sorbed water. Therefore, the net mass losses due to intermolecular dehydration for the 1/3, 1/2, 1/1, 2/1 and 3/1 blends are 7.5, 6.5, 6.1, 5.0 and 4.8%, respectively. The dehydration occurs more often for the PMAA-rich blends (include the 1/1 blend) than that for the PHEMA-rich blends. Furthermore, the mass loss at 400°C for the blends is 16–26%, while that for PHEMA reaches to 40%. This suggests that the blends become thermally more stable than PHEMA by the produced anhydride; PHEMA-PMAA ester consists of a $-COOCH_2CH_2OOC-$ bond.

Figure 4 shows the observed ^{13}C CP/MAS NMR (A: left column) and simulated spectra (B: right column) in the side-chain CH_2 region for PHEMA, the 3/1, 1/1 and 1/3 blends after heat-treatment at 300°C for 10 min. Both the ^{13}C spectra of PHEMA and the blends before heat-treatment are successfully fitted to a sum of three Lorentzian curves: side-chain OCH_2 (67.5), CH_2OH (60.4) and main-chain CH_2 (55.5 ppm). For the heat-treated blends, the ^{13}C spectra are fitted completely to a sum of four Gaussian curves (Fig. 4B): the side-chain OCH_2, a new peak at 63.3 ppm, CH_2OH and the main-chain CH_2. We could not fit those spectra to a sum of several Lorentzian curves. The change from Lorentzian to Gaussian line shape is due to reduction of mobility of molecular motion for PHEMA by dehydration with PMAA. The new peak at 63.3 ppm is ascribed to the CH_2 carbons of the PHEMA-PMAA ester bond. The ^{13}C peak intensity of the PHEMA-PMAA ester at 63.3 ppm increases with increasing the ratio of PMAA in the blends. This is consistent with the results of TG measurements.

We can estimate the amount of the PHEMA-PMAA ester against PHEMA from the ^{13}C peak areas at the two side-chain CH_2 (OCH_2 and CH_2OH) and the ester CH_2 resonances. The amount of dehydrated PHEMA for the PHEMA-rich blends is estimated as 25–35% (~30%) and that for the PMAA-rich blends 45–55% (~50%). From the rough estimation using the amount of PHEMA-PMAA ester, we can calcu-

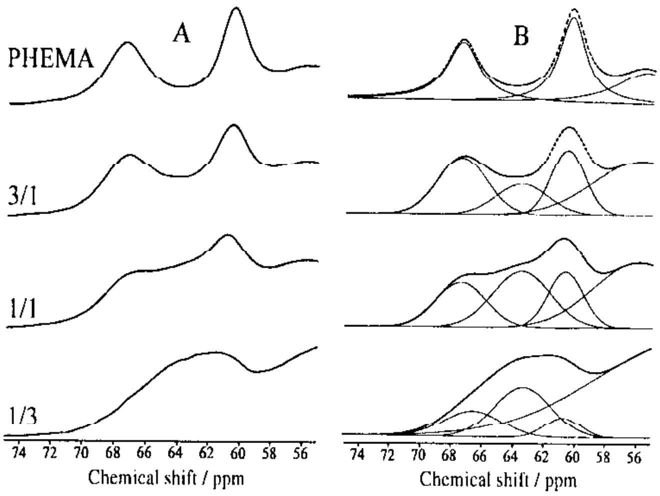

Fig. 4 125.75 MHz ^{13}C CP/MAS NMR spectra (A: left column) and the curve fittings (B: right column) of PHEMA, PHEMA/PMAA=3/1, 1/1 and 1/3 blends in the side chain CH$_2$ region after heat-treatment at 300°C for 10 min. The broken lines in simulated spectra B are sum of each Lorentzian or Gaussian curves. The spectrum of PHEMA is fitted to a sum of three Lorentzian curves and that of the blends a sum of four Gaussian curves

late the values of the mass loss caused by dehydration in the blends. The values are 8.1, 7.5, 6.3, 4.2 and 3.6% for the 1/3, 1/2, 1/1, 2/1 and 3/1 blends, respectively. Here, we assumed that all remained PMAA is dehydrated to form intramolecular anhydrides. The mass loss values estimated from ^{13}C NMR are in good agreement with the results from the TG measurements at 300°C within an experimental error. This proves that the intermolecular dehydration between PHEMA and PMAA occurs in the miscible PHEMA/PMAA blends.

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