

High-Resolution Solid-State ^{13}C NMR Study of Polymer Blends: Miscibility, Molecular Motion, and Interaction

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Introduction

I introduce how the miscibility, molecular motion, and interaction of polymer blends are characterized by the high-resolution solid-state ^{13}C NMR method. Firstly, intermolecular reaction between poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(methacrylic acid) (PMAA) in the PHEMA/PMAA blends is reviewed.[1] The heat-treatment at 300 °C for 10 min promotes the intermolecular dehydration between the component polymers in the solid states, but the reaction is not occurred for pure PHEMA. Next, how the local hydrogen bonding in the PMAA/poly(vinyl acetate) (PVAc) blends works for maintaining the good homogeneity. It was found that the hydrogen bond is created at 3:2=[MMA]:[VAc] unit molar ratio and the fraction of 30% is necessary to be miscible on a molecular level.[2] This characteristic interaction enabled us to observe a cross peak between PMAA and PVAc C=O carbons on a natural abundant ^{13}C 2D exchange NMR. Finally, the relation ship between the crystalline phase thickness and the melting point of poly(ϵ -L-lysine) (ϵ -PL) in the poly(vinyl isobutyl ether) (PVIBE)/ ϵ -PL blends and PVIBE/ ϵ -PL/saponite nanocomposites is discussed.[3] The lower temperature shift of the melting point with increase of PVIBE is explained by decrease of the crystalline phase thickness of ϵ -PL estimated by the ^1H spin-lattice relaxation curve simulation. The simulation was achieved by employing the insufficient ^1H cross-relaxation (spin-diffusion) rate.

Results and Discussion

Figure 1 shows the observed and expanded ^{13}C CP/MAS (cross-polarization/magic-angle spinning) NMR spectra (left-hand side) and the decomposed spectra (center) with four Gaussian curves of the CH_2 regions for PHEMA/PMAA blends after heat-treatment at 573 K for 10min. Schematic illustration of inter-molecular dehydration reaction is depicted at the right-hand side. A new peak appeared at 63.3ppm is attributed the ester methylene carbons of $\text{COOCH}_2\text{CH}_2\text{OCO}$ side chain formed after heat-treatment between PHEMA and PMAA. The ^{13}C peak area intensity of the ester CH_2 carbons is consistent with the results of the thermo-gravimetric analysis (TGA).

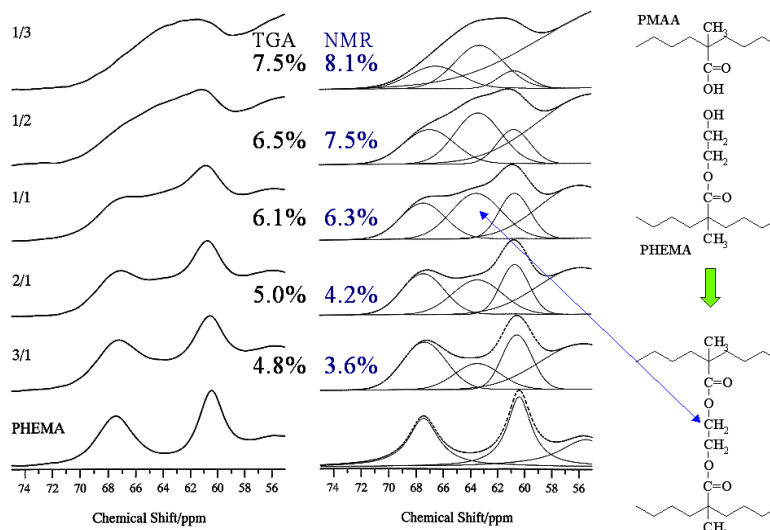


Figure 1. Observed (left) and simulated (right) ^{13}C CP/MAS NMR spectra of the side-chain CH_2 region of PHEMA for the PHEMA/PMAA blends after heating at 300°C for 10min.

Figure 2 shows the observed (A) and the decomposed (B) ^{13}C CP/MAS spectra for the

carboxyl/carbonyl (CO) regions of PMAA/PVAc blends. The pure PMAA and PVAc signals are also depicted together with that of PMAA/PVAc=2/1 blend as blue and red lines in (A), respectively. Apparently, the five peaks are observed at this region for the blends. The peaks at 179 and 175 ppm are clearly observed. The composition dependence of T_1^C values of those peaks is quite different from those of the other peaks: T_1^C is affected by molecular motion. Those are, hence, ascribed by the interacted carboxyl and carbonyl carbons via a hydrogen bond between PMAA and PVAc, respectively. Furthermore, both ^1H spin-lattice relaxation times in the laboratory and rotating frames (T_1^H and $T_{1\rho}^H$) and the spectral decomposition reveal that it is necessary for the blends to be miscible on a 2-5 nm scale that the relative ratio of those interacted peaks against the whole CO amount in the blends is over 30%.

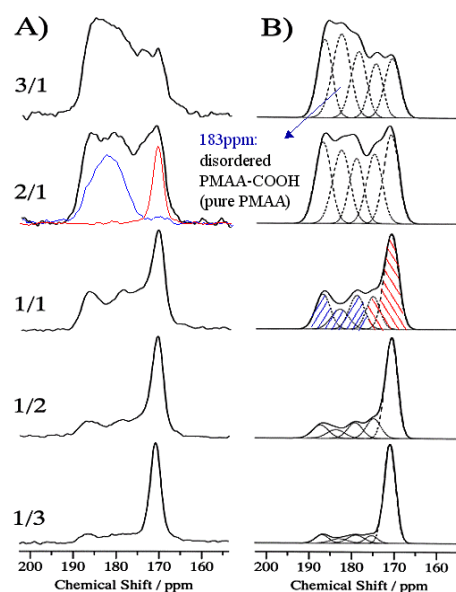


Figure 2. Observed (A) and simulated (B) ^{13}C CPMAS NMR spectra of COOH and CO regions for the PMAA/PVAc blends.

Figure 3 shows the observed and expanded DSC curves of pure PVIBE, PVIBE/ ϵ -PL/saponite=10/1/0.03, 10/2/0.06, 10/3/0.09, 10/4/0.12, 10/5/0.15 nanocomposites, and ϵ -PL/saponite=1/0.03 at the temperature range of 393 to 473 K in the left-hand side. In the right-hand side, observed T_1^H curves for the PVIBE/ ϵ -PL/saponite=10/1/0.03 nanocomposite is represented. The endothermic peaks show the melting point (T_m) of the crystalline phase of ϵ -PL. While the T_m of pure ϵ -PL is ca. 445 K, that of blends and nanocomposites decreases. T_m values of blends depend on the composition. For the nanocomposites, while the T_m values from 10/3/0.09 to 10/1/0.03 show the similar dependence, those values from 10/5/0.15 to 10/3/0.09 shows the same value of 439 K. This interesting phenomenon is discussed by the crystalline thickness estimated by T_1^H curve simulation as depicted in Fig. 3 (right).

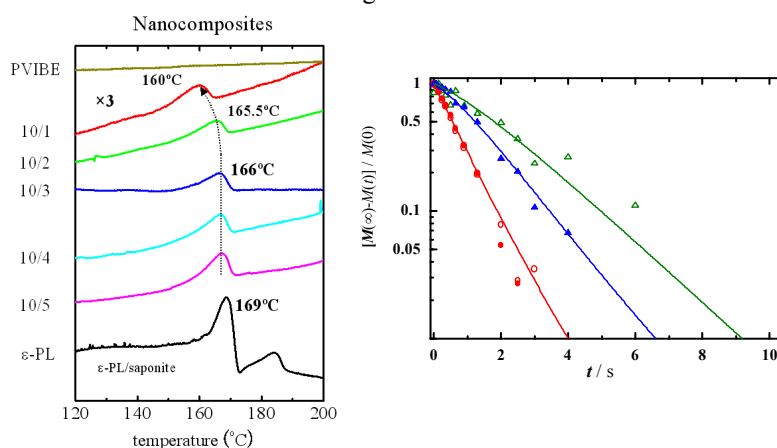


Figure 3. DSC curves (left) and ^1H spin-lattice relaxation curves (right) for PVIBE/ ϵ -PL/saponite nanocomposites: ● and ○ represents the non-crystalline (NC) and the crystalline (CR) phases of PVIBE, respectively. Similarly ▲ and △ are the observed curves of NC and CR for ϵ -PL. DSC curves show the region of the melting point of ϵ -PL.

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References

1. (a) *J. Therm. Anal. Cal.*, **56**, 1059-1063 (1999). (b) *Polym. Deg. Stab.*, **78**, 137-141 (2002).
2. (a) *Macromolecules*, **35**, 8819-8824 (2002). (b) *Polym. J.*, **36**, 23-27 (2004).
3. For (PVIBE)/ ϵ -PL blends, it is published in *e-Journal of Soft Materials*, **3**, (2007). For its nanocomposites, the paper is prepared for submitting.