Solid-state ^{19}F MAS and $^{1}H \rightarrow {}^{19}F$ CP/MAS NMR Study on Poly(chlorotrifluoroethylene) / Poly(vinylidene fluoride) Blend

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Abstract

Novel fluoropolymer blends composed of poly(chlorotrifluoroethylene) (PCTFE) and poly(vinylidene fluoride) (PVDF) have been prepared from the melt. The molecular mobility and molecular structure of each component in the blends were investigated using solid-state ^{19}F magic angle spinning (MAS) NMR spectroscopy, and they were compared with those of the parent polymers. Although the weight of PVDF in the blends is at most one-ninth of PCTFE, structural information on PVDF was selectively obtained from $^{1}H \rightarrow {}^{19}F$ cross polarization (CP) / MAS techniques. The degrees of crystallinity of both polymers in the blends are remarkably lower than that of the homopolymers, and the crystalline morphology of the PVDF component is predominantly α-form. The values of magnetic relaxation time $T_{1\rho}{}^{F}$, which are associated with the segmental motions around several tens of kHz, suggest that the amorphous domains of both PCTFE and PVDF in the blends are more mobile than those in the bulk, and they are not miscible in nanometer-scale size. In addition, the dynamics of the magnetization transfer from ^{1}H to ^{19}F also indicates that both amorphous and crystalline regions of PVDF in the blends are more mobile than those of the bulk PVDF.

Introduction

Poly(chlorotrifluoroethylene) (PCTFE) is a semicrystalline fluoropolymer which exhibits excellent mechanical properties even at cryogenic temperatures or under ultraviolet radiation.[1] Meanwhile, it is recognized that the processing of PCTFE is difficult because of its high melt viscosity and the proximity of the melting temperature (212ºC) to that of the thermal decomposition (ca 300ºC). Thus some copolymers have been commercialized such as Kel-F and the blends or alloys are being studied in order to improve the workability of PCTFE.

^{19}F MAS NMR is a powerful tool for detailed analyses of chemical structures, conformations, and molecular mobility of fluoropolymers. In addition, $^{1}H \rightarrow {}^{19}F$ CP/MAS NMR has a potential advantage for the analysis of phase structures and molecular dynamics of fluoropolymers which contain both hydrogen and fluorine atoms in their systems.[2,3] Based on this perspective, binary blends consisting of a perfluoropolymer and a partially fluorinated polymer are attractive because the molecular dynamics of the latter can be selectively observed. In this work, novel PCTFE/PVDF blends were prepared, and the dynamics and conformational information were investigated from solid-state ^{19}F MAS and $^{1}H \rightarrow {}^{19}F$ CP/MAS NMR experiments.

Experimental

PCTFE powder was purchased from Aldrich. The PVDF (KF-1100) was supplied by Kureha Chem. Industry Co. A 90/10 blend of PCTFE and PVDF was prepared by mechanical mixing for 5 minutes at 300ºC using a homemade molder, followed by quenching in ice bath. No degradation occurred under these conditions. As a reference sample, a 95/5 blend film of PCTFE/PVDF was provided by Daikin Industries, Ltd. The film was also prepared by mixing and quenching, but it could be annealed to some extent during hot-press for film forming. The melting temperatures of the samples determined by DSC were as follows: PCTFE homopolymer, 211.9ºC; PVDF homopolymer, 172.9ºC; PCTFE in 90/10 blend, 210.8ºC; PVDF in 90/10 blend, 173.9ºC; PCTFE in 95/5 blend, 211.8ºC; PVDF in 95/5 blend, 174.1ºC.

Solid-state ^{19}F MAS MMR experiments were carried out on a JEOL EX spectrometer operating at resonance frequencies of 282.65 MHz for fluorine and 300.40 MHz for proton with Chemagnetics APEX $^{19}F/^{1}H$ dual-tune probe. Samples were spun at the magic angle at a rate of $\omega_r = 16$ kHz. The fluorine and proton r.f. fields were adjusted to fulfill the Hartmann–Hahn sideband matching condition, $\omega_{1H} = \omega_{1F} - \omega_r = 83$ kHz. All the spectra were obtained at the ambient probe temperature which

was estimated as 68ºC at this spinning rate. The spin–lattice relaxation times in the rotating frame for ^{19}F ($T_{1\rho}^{F}$) were measured by variable spin-lock time (t_{SL}) experiments with t_{SL} varying from 0.1 to 20 ms under a ^{19}F spin-lock field of ca 100 kHz. The variable contact time (t_{CP}) $^{1}H \rightarrow {}^{19}F$ CP experiments were measured with t_{CP} varying from 0.1 to 10 ms.

Results

Fig. 1(a) shows a ^{19}F direct polarization (DP) MAS NMR spectrum of PVDF. The sharp peak at –89 ppm was assigned to the fluorine of vinylidene fluoride (VDF) sequence in the amorphous domain. The broad signals at –79 ppm and –93 ppm are assigned to the fluorines in the α-form crystalline.[2] Fig. 1(d) shows ^{19}F DP spectrum of PCTFE. The broad signals in the downfield (A: –100 ppm, B: –110 ppm) and upfield (C: –130 ppm) regions were assigned to the fluorines of CF_2 and CFCl in the crystalline domain, respectively.[4] Spin-lock experiments revealed that the signals ascribed to the fluorines of CF_2 and the CFCl in the amorphous domain should exist behind the crystalline signals, which were named as α and β, respectively. Fig. 1(b) and (c) show DP spectra of quenched and annealed PCTFE/PVDF blends, respectively. The featureless CF_2 signal in (b) suggests that the crystallinity of PCTFE in the quenched blend is lower than that of the homopolymer. The values of $T_{1\rho}^{F}$ for PCTFE signals changed remarkably by blending, suggesting that PCTFE domains in the blends are more mobile than in the homopolymer.

Fig. 2 shows $^{1}H \rightarrow {}^{19}F$ CP/MAS NMR spectra of PVDF homopolymer and PCTFE/PVDF blends. All of the signals ascribed to PVDF are selectively and exclusively observed even in the blends in spite of their small contents. The lineshape of the crystalline signals in the blends indicates that the dominant polymorph can be α-form, which was also confirmed by IR and DSC. The slower build-up of $^{1}H \rightarrow {}^{19}F$ CP curves (not shown) and the shorter $T_{1\rho}^{F}$ for the signals of PVDF in the blends than those for the homopolymer suggest that the PVDF chains in both crystalline and amorphous domains of blends are more mobile than that of the homopolymer. The $T_{1\rho}^{F}$ values of PVDF are not identical to those of PCTFE in the blends, indicating little spin diffusion occurs between the chains of PVDF and PCTFE. This demonstrates that both chains are not miscible in nanometer-scale size.

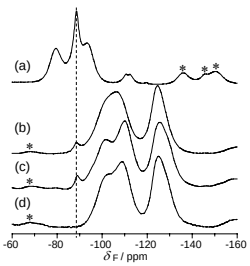

Fig. 1. ^{19}F DP spectra of PVDF homopolymer (a), 90/10 PCTFE/PVDF blend (b), 95/5 PCTFE/PVDF blend (c), and PCTFE homopolymer (d). Peaks shown with asterisks are spinning sidebands.

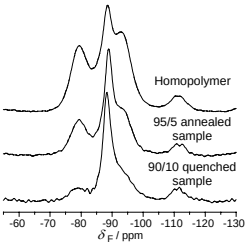

Fig. 2. $^{1}H \rightarrow {}^{19}F$ CP/MAS spectra of PVDF in blend samples and that of homopolymer. The contact time = 0.5 ms.

Table 1. $T_{1\rho}^{F}$ values of PCTFE. (units: ms)

	A	α	B	C	β
Homopolymer	8.2	0.9	12	18	3.4
In 90/10 blend	9.6	1.3	6.1	5.3	2.1

Table 2. $T_{1\rho}^{F}$ values of PVDF. (units: ms)

δ_F / ppm	–79	–89	–93	–110	–112
Homopolymer	43	8.4	61	14	16
In 90/10 blend	20	5.9	39	7.0	7.0

Conclusions

The molecular conformation and dynamics of each component in the PCTFE/PVDF blend were independently analyzed using solid-state ^{19}F MAS and $^{1}H \rightarrow {}^{19}F$ CP/MAS NMR. Both PCTFE and PVDF in the blends are more mobile than the homopolymers, and the crystalline morphology of the PVDF component predominantly develops in the α-form.

References

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