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Morphological, thermal and solid-state NMR study on a novel PMMA/crosslinked silicone semi-IPN

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Abstract

A novel PMMA/silicone semi-IPN, in which linear PMMA and silicone network were the guest and host polymers, respectively, was synthesized in this study. The silicone network formed by the self-condensation reaction among the pendent reactive methoxysilane groups on the polymethylphenylsiloxane (DC3074). Before curing, PMMA and DC3074 were miscible at any blended ratio, but phase separation occurred when the silicone network formed. The morphology of this semi-IPN was investigated by SEM and DSC, an inward-shift T_g for the pure components in the blends and a particular broad T_g were observed in the 50/50 blend. The phase structure for the blends was further investigated by the dynamic relaxation experiments of ^{13}C-CP/MAS NMR spectroscopy. A multi-exponential relaxation rate of T_1(H) at 50/50 ratio shows that this semi-IPN is not homogeneous at the interfacial on the length scale of 21 nm. The decrease of T_{CH} and the change of $T_{1\rho}$(H) for this semi-IPN, comparing to the pure materials, imply that intermolecular polarization transfer between PMMA molecules and silicone network is possible.

Keywords: Semi-IPN; Silicone; Solid-state NMR

1. Introduction

Interpenetrating polymer networks (IPNs) consist of two or more polymers where these components form two or more than interpenetrated networks by crosslinkage in the presence of others, even though these polymers have rather low miscibility [1]. While in the semi-IPN, at least one of the component polymers does not form network but interpenetrating in the network. Due to the immisibility of polymer components, phase separation is expected in IPNs. It is thus of great interest to study the phase-separated microstructures and morphology of phase-separated IPNs.

Among many varieties of polymeric blends, addition of silicone or silicon containing polymers can greatly improve the material performance that has become an interesting subject of both scientific and industrial research [2–10]. Moreover, crosslinked silicone polymers have many advantages, including flexibility, low surface tension, low dielectricity, ultraviolet resistance, non-flammability, as well as high thermal and chemical stability. Although some of IPNs based on crosslinked polysiloxanes have been reported in the literature [3,11,12], and yet the crosslinked silicone network through self-condensation of the reactive methoxysilane groups ($\equiv$Si–OCH$_3$), has been seldom studied. In this work, we have synthesized a novel PMMA/silicone semi-IPN in which linear PMMA and silicone network treated as the guest and host polymers, respectively. It is shown that the mixture of linear thermoplastic PMMA with the reactive methoxy-functional silicone (DC3074) formed a homogeneous blend at any ratio of the two before the self-condensation crosslinking; however, it turned into a phase-separated system after the reaction. Based on SEM and DSC analysis, the polymer blend revealed a variety of phase-separated morphology depending on the compositions.

Solid-state NMR has been proven a fruitful technique to investigate microstructure and molecular dynamics of polymer blends [13–15]. Detail information about morphology, miscibility, microstructure and mobility can be directly accessed [16–29]. In this study, we have performed ^{29}Si and ^{13}C-CP/MAS solid-state NMR spectroscopy to characterize the chemical structure in the synthesized PMMA/silicone semi-IPN. The microstructure of the system was analyzed and the spatial dimension of the domains was estimated via proton relaxation approaches.

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2. Experimental section

2.1. Material

Poly(methyl methacrylate) (PMMA, $M_w = 90000$) was a commercial product from Chi-Mei Chemical Engineering, a reactive methoxy-functional silicone resin (DC3074) ($M_w = 1400$; methoxy content = 18 wt%) was purchased from Dow Corning Co., tin catalyst (M & T FASCAT*4200) was purchased from M and T Chemicals Inc. Reagents and solvents was used without further purification in this study.

2.2. Sample preparation of PMMA/silicone semi-IPN

PMMA (solid grains) was dissolved in THF, then DC3074 (liquid) was added at the desired weight ratios; 100/0, 75/25, 50/50, 25/75 and 0/100, together with 0.1 wt% of tin catalyst based on the weight of DC3074. The blend was first kept in circulation oven at 40°C for evaporating the most part of solvent, and subsequently processed in vacuum oven at 60°C for 24 h to ensure the complete removal of the solvent. The resulting solvent casting films were then heated in a circulation oven at 120°C for 72 h in order to allow the self-condensation crosslinking reaction completed among the methoxysilane groups. It was noticed that the crosslinking reaction rate might be very slow at the temperature below 80°C.

2.3. Measurements

Different scanning calorimetry (DSC) was applied to determine the glass transition temperatures at a heating rate of 10°C/min using DuPont DSC 2010. Scanning electron micrographs were taken from a JEOL JSM-25 scanning electron microscopy (SEM).

High-resolution solid-state NMR experiments were carried out on Bruker AVANCE 400 spectrometer operating at 100.6 and 400.2 MHz for ^{13}C and ^{1}H, respectively. The samples was packed in 4 mm o.d. zicronia rotors and spun at 6 kHz under MAS condition. All experiments were performed at 25°C.

Variable contact time technique was conducted to determine $T_{1\rho}(\mathrm{H})$ and T_{CH}, where the contact times varied in the range of 50 μs to 25 ms. $T_1(\mathrm{H})$ was measured by the inversion-recovery method. The ^{1}H 90° pulse width 3.5 μs and the recycle delay time was set in 6–12 s. Single-pulse ^{29}Si NMR spectra were acquired at 79.5 MHz with 90°pulse width of 4.6 μs and a 200 s recycle delay.

In $T_1(\mathrm{H})$ experiment the resonance intensity decays exponentially as the following equation [15]:

$$M(\tau) = M_\infty[1 - 2\exp(-\tau/T_1(\mathrm{H}))]$$

where $T_1(\mathrm{H})$ is the proton spin-lattice relaxation time in the laboratory frame, τ is the delay time for the measurement of $T_1(\mathrm{H})$ and $M(\tau)$ is the corresponding resonance intensity, and M_∞ is the intensity of the signal at $\tau \geq 5T_1(\mathrm{H})$. Taking the natural logarithm of both sides of equation obtains:

$$\ln[(M_\infty - M(\tau))/2M_\infty] = -\tau/T_1(\mathrm{H})$$

Thus, plotting $\ln[(M_\infty - M(\tau))/2M_\infty]$ against delay time τ yields $T_1(\mathrm{H})$. The $T_1(\mathrm{H})$ values for the carbonyl carbon of PMMA and phenyl carbons of DC3704 (at 128 and 135 ppm) in the semi-IPN and the pure components were listed in Table 2.

The T_{CH} and $T_{1\rho}(\mathrm{H})$ were obtained by performing CPVC experiment which the contact period itself is varied with time. The $T_{1\rho}(\mathrm{H})$ was obtained by a semilog method by plotting $\ln((M(t)/M_{\max})$ vs. contact time after the signals have reached their maximum intensity. The $T_{1\rho}(\mathrm{H})$ can thus be found as −1/slope using the longer contact times. The T_{CH} may be calculated after the $T_{1\rho}(\mathrm{H})$ was determined from the following equation [13,15]:

$$M(t) = M_1 \exp\left(\frac{-t}{T_{1\rho}(\mathrm{H})}\right)\left(1 - \exp\left(\frac{-t}{T_{\mathrm{CH}}}\right)\right)$$

where $M(t)$ is the peak intensity as function of contact time t, M_1 is the normalization constant, $T_{1\rho}(\mathrm{H})$ is the proton spin-lattice relaxation time in the rotating frame, and T_{CH} is the cross-polarization transfer time constant. The $T_{1\rho}(\mathrm{H})$ and T_{CH} values were also listed in Table 2.

3. Results and discussion

3.1. SEM and DSC analysis

Fig. 1 shows the synthetic route for the PMMA/silicone semi-IPN, in which the linear PMMA was interpenetrated in the silicone network that was formed after the crosslinking reaction among the methoxysilane groups on the side chains of DC3074. It should be noted that before the crosslinking reaction proceeded the solvent casting film was transparent and colorless at room temperature, indicating a highly miscible mixture system of the PMMA and unreactive DC3074. After the curing reaction was completed, the resulting film was opaque and white, an evidence of forming a phase-separated blend of PMMA and the crosslinked silicone network.

The SEM micrographs of cold-fracture surface of the PMMA/silicone semi-IPN are shown in Fig. 2(a)–(e). The crosslinked DC3074 was transparent and shown to be a uniform morphology, see Fig. 2(e), revealing a rather smooth surface. In Fig. 2(b) and (c), the PMMA/silicone (75/25) and (50/50) blends both exhibited a heterogeneous morphology consisting of dispersed spherical particles, which are comprised of PMMA, and the silicone network matrix. In comparison of these two, the former one showed a two-size particles feature with diameter of 0.6 and 1.6 μm for each, whilst the latter appeared an one-size particles character with diameter of 2 μm. Notice that, in contrast to the well-defined domain boundary in the 75/25 blend, the boundary of the two domains, seen in the 50/50 blend,

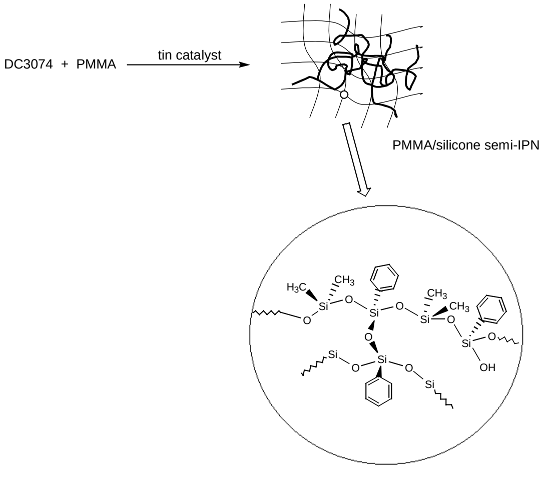


Fig. 1. Synthetic route for PMMA/silicone semi-IPN.

Table 2
Results of T_1(H) (s), T_{CH} (ms) and $T_{1\rho}$(H) (ms) of PMMA/silicone semi-IPN

PMMA/DC3074	Carbon (ppm)	T_1(H)	T_{CH}	$T_{1\rho}$(H)
100/0	177	0.75	1.10	21.3
75/25	177	0.89	0.94	20.5
	128	1.38	0.32	18.8
	135	1.26	0.30	20.2
50/50	177	–[a]	0.92	18.5
	128	1.28	0.71	16.1
	135	1.25	0.64	17.1
25/75	177	0.77	0.87	21.5
	128	1.41	0.74	18.3
	135	1.37	0.62	18.2
0/100	128	1.41	0.83	29.8
	135	1.45	0.69	29.7

[a] A multi-exponential T_1(H) was present, see discussion in text.

is less distinguishable. The evidences obtained from SEM for the 50/50 blend, an increase in the diameter and the less defined domain boundary, implied the compatibility between the PMMA and the crosslinked silicone network is better than that of the other ratios, which consisted with the observation from the DSC measurement described below. However, as the PMMA content decreases to 25 wt% (see Fig. 2(d)), no distinct separated spherical domain is observed, but showing a network-grain type morphology.

The thermal transition behavior of PMMA/silicone semi-IPN was investigated by DSC analysis; the DSC curves, 100/0, 75/25, 50/50, 25/75 and 0/100, are shown in Fig. 3 (their T_g are listed in Table 1). Polymer blend like IPNs are usually phase-separated, and the glass transition temperatures of the substituents are tend to shift inward depending on miscibility and the ratio of the substituents [1,30]. In this study, the PMMA/silicone semi-IPN showed the same behavior, an indication of phase separation and the existence of two domains. The inward shift of the T_g of 75/25, 50/50 and 25/75 blends reflected for a degree of compatibility of PMMA in the silicone network. It is noteworthy that the inward shift and broadening of high T_g component ($T_{g,1}$, attributed to the PMMA-rich domain) in 50/50 blend is more pronouncing than the others. This broadening of T_g arises from different regions of space that have different compositions, each yielding its own T_g and resulting a distribution [1]. Therefore, it can deduce that the PMMA-rich domain gave a gradient concentration distribution across the interface region, especially in 50/50 blend.

Table 1
Glass transition temperatures ns of the PMMA/silicone semi IPN measured from DSC

PMMA/DC3074	T_{g1} (K)[a]	T_{g2} (K)
100/0	382.1	–
75/25	372.9	329.2
50/50	368.8	327.8
25/75	377.6	326.9
0/100	–	321.9

[a] T_{g1} is the glass transition temperature for the PMMA-rich domain, and T_{g2} for silicone-rich domain.

3.2. NMR characterization

^{29}Si solid-state NMR spectrum of the PMMA/silicone semi-IPN (50/50 blend) revealed three resonances at −18, −71, and −79 ppm, respectively, shown in Fig. 4. The signals were denoted as D^1, T^1 and T^2 with respect to different silicon sites [4,31], as shown below:

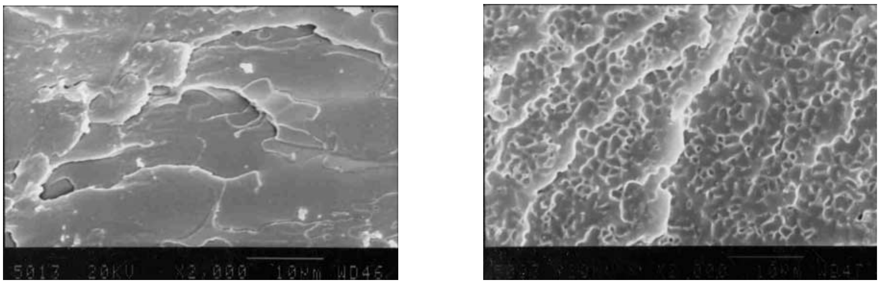
$$\mathrm{D}^1 = (\mathrm{SiO})\mathrm{Si}^*(\mathrm{OSi})(\mathrm{CH}_3)_2$$

$$\mathrm{T}^1 = (\mathrm{SiO})\mathrm{Si}^*(\mathrm{OSi})\mathrm{Ph}(\mathrm{OH})$$

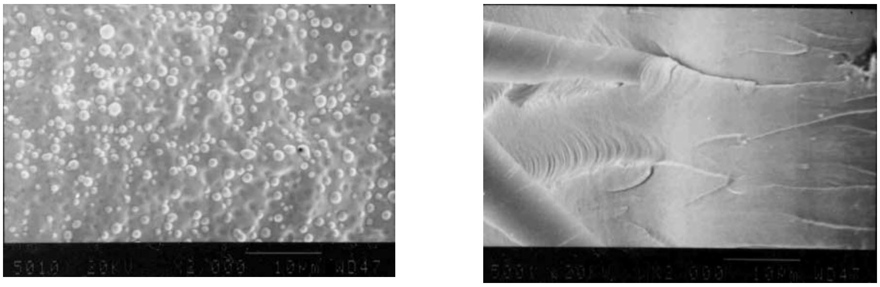
$$\mathrm{T}^2 = (\mathrm{SiO})_3\mathrm{Si}^*\mathrm{Ph}$$

where T^2 corresponds the silicon site which is associated the crosslinking reaction between two methoxysilane groups, T^1 is the one due to the hydrolysis reaction on the side chain, D^1 refers to the dimethyl silicon sites. The conversion of the reaction of methoxysilane groups can be directly determined by the T^2 and T^1 peak integrals available from the ^{29}Si single-pulse NMR measurements; T^2/T^1 + T^2. It was found that the conversions around 52 ± 3% for all the blends.

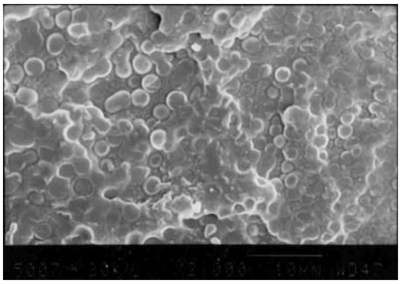
Fig. 5 shows the ^{13}C-CP/MAS spectra of (a) crosslinked DC3074, (b) PMMA/silicone (50/50) semi-IPN and (c) PMMA. In Fig. 4(c) the resonance peaks at 17, 45, 57, 177 ppm were assigned to CH_3, backbone quaternary carbon, CH_3–O– (shown as low field shoulder) and backbone –CH_2–, and carbonyl carbon of PMMA, respectively. For crosslinked DC3074 (Fig. 5(a)), the resonance peaks at 128 and 135 ppm are attributed to the ortho- and para-position and the meta-position carbons on phenyl



(a) pure PMMA (d) 25/75



(b) 75/25 (e) pure crosslinked DC3074



(c) 50/50

Fig. 2. SEM micrographs of the fracture surfaces of PMMA/silicone semi-IPN.

ring, respectively, and the small peak at 130 ppm corresponds to the quaternary carbon attached directly to silicon.[1] As seen in Fig. 5(a), the disappearance of resonance peak for methoxysilane ($Si-OCH_3$) is taken a proof that all the methoxysilane groups were reacted, either for crosslinking reaction or hydrolysis reaction as showing in Fig. 1. Although there is no change for the ^{13}C chemical shifts of PMMA and DC3074 in their blend, the lineshapes of phenyl carbons in 50/50 blend become broader than that of pure crosslinked DC3074. This might suggest that the microenvironment for the phenyl rings of the crosslinked DC3074 is affected in the presence of the PMMA.

3.3. T_1(H) *and* $T_{1\rho}$(H) *measurements*

To further investigate the detail of the microstructure of PMMA/silicone semi-IPN, the T_1(H) and $T_{1\rho}$(H) relaxation experiments were conducted via the ^{13}C-CP/MAS spectroscopy. From such relaxation time measurements, one can investigate the scale of miscibility of a polymer blend. In those cases where the length scale of mixing is longer than the spin diffusion length scale, the measured rate will be identical to that for pure polymer, and in cases where there is heterogeneous mixing the relaxation behavior may be more complex, and multiexponential relaxation may be observed. As mentioned, the microstructure of the semi-IPNs depends on the interpenetrating capability as well as the compatibility of the substituent polymers. From the T_1(H) and $T_{1\rho}$(H) relaxation studies, it can be verified the degree of heterogeneity of the PMMA/silicone semi-IPN.

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[1] The assignment is on the basis of the 2D $^{13}C\{^1H\}$ HETCOR NMR spectrum, which was obtained under fast MAS (25 kHz), of our new PEO/silicone semi-IPN system that is prepared for publication.

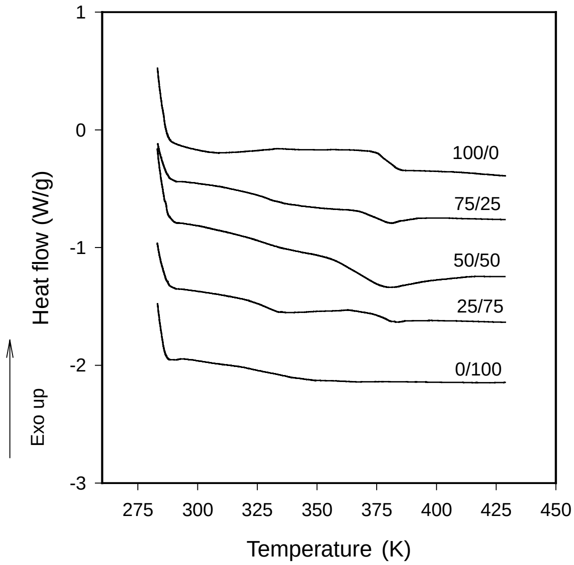

Fig. 3. DSC thermograms for PMMA/silicone semi-IPN.

The T_1(H) relaxation data are summarized in Table 2. It should note that in 50/50 blend at the delay time smaller than 2 s the relaxation behavior (see Fig. 6) is similar as the pure PMMA and the slope corresponds to a relaxation rate identical to that of pure PMMA (0.75 s), whereas at the delay time longer than 2 s a multi-exponential relaxation decay was observed for the carbonyl carbon of PMMA. It can be concluded that the 50/50 blend is not homogeneous on the length scale measured by T_1(H). Therefore, the multi-exponential T_1(H) relaxation behavior and the broad transition in DSC analysis for the 50/50 blend is again a clear evidence that there exists a interfacial region with heterogeneous concentration between PMMA-rich domain and silicone-rich domain as shown in Fig. 2(c).

The relaxation time measurements are also commonly used to determine the length scale of polymer mixing. An approximate estimation of the length scale of spin diffusion L measured by such experiments depends on the relaxation time and the diffusion coefficient D, as follows [15,32–34]:

$$L = \sqrt{6DT}$$

The D is the spin diffusion coefficient determined by the average proton–proton distance and the strength of the dipolar interaction, and it has typically a value of about 100 nm^2 s^{-1}. T (T_1(H) or $T_{1\rho}$(H)) is the characteristic time over which the spin diffusion proceeds. The above equation is possible to estimate the maximum length of microheterogeneous domains with single component decay and the minimum domain sizes with double-component decay. Therefore, the minimum length of the microheterogeneous phase is estimate from the fast-component T_1(H) (0.75 s) of 50/50 blend to be 21 nm, and the local concentration fluctuations would be expected to be rife in the phase boundary region rather than that of distinct domains.

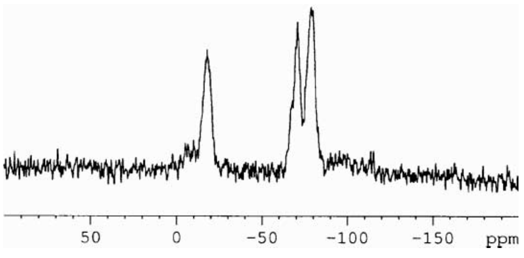

Fig. 4. ^{29}Si single-pulse spectrum for PMMA/silicone (50/50) seim-IPN.

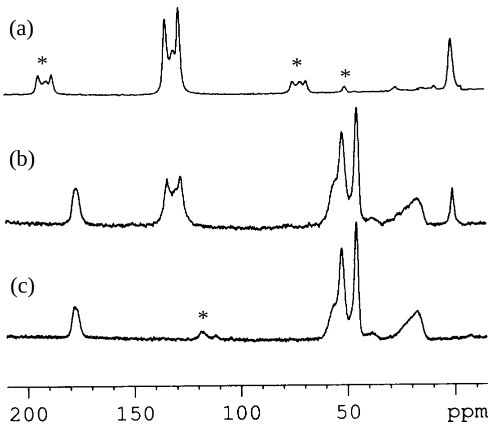

Fig. 5. ^{13}C CPMAS spectra for (a) pure crosslinked DC3074 (b) PMMA/silicone (50/50) seim-IPN and (c) pure PMMA.

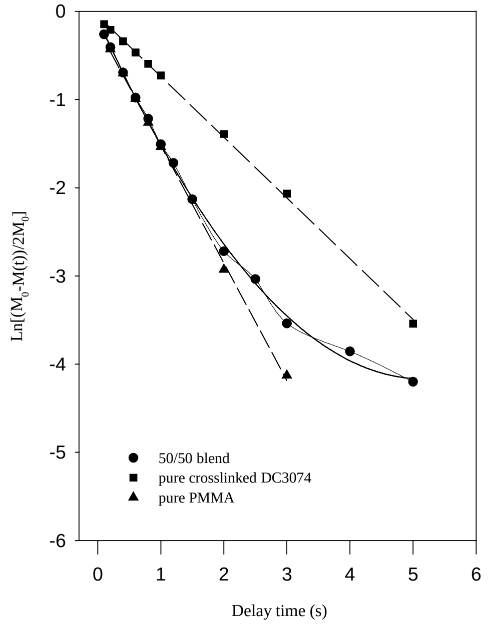

Fig. 6. TI(H) relaxation curves vs delay times; carbonyl carbon of pure PMMA (▲), carbonyl carbon PMMA/silicone (50/50) seim-IPN (●), and quaternary phenyl carbon of pure crosslinked DC3074 (■).

In 75/25 blend a single T_1(H) value (0.89 s) was found for carbonyl carbon resonance (see Table 2), and the value was greater than that of pure PMMA carbon (0.75 s). On the other hand, the phenyl carbons of DC3074 (silicone-rich phase) in 75/25 blend also showed a single T_1(H) values (1.38 and 1.26 s). This result is expected since spin diffusion averages all in intrinsic T_1(H) values within a homogeneous phase. Therefore, in 75/25 blend the length scale of concentration fluctuation at interfacial region is presumably much less 21 nm. The phenomena explain the distinct domain interface observed in SEM photography and two inward distinguished transition temperature rather a broad one in DSC analysis in 75/25 blend. The similar phenomena were also observed at the 25/75 ratio.

The T_{CH} represent the rate of polarization transferred from proton the carbon nuclei, and carbons that are not protonated or have less close neighbor protons need long T_{CH} to have their resonance intensities to maximum. In Table 2, it can be found that the T_{CH} of the carbonyl carbon of PMMA decreases from 1.08 to 0.87 ms with increasing wt% silicone. At the same time, the T_{CH} of the phenyl carbons of DC3704 also decrease from 0.83 to 0.30 ms with increasing amount of PMMA. This indicates that intermolecular polarization transfer between the carbonyl carbon and the proton of silicone network is possible. The great reduction of T_{CH} observed from the silicone-rich phase also indicates that some of PMMA molecules were not expelled after crosslinking reaction, but retained in the silicone network.

$T_{1\rho}$(H) is very sensitive to the short-range spatial proximity of interacting dipole moments of protons and can be used in determining the homogeneity and dynamics of the polymer blends. It can be seen in Table 2 that single $T_{1\rho}$(H) values were obtained for the carbonyl and phenyl carbons in both pure component and their blends, implying that interdomain spin diffusion occurred fast enough among all the protons within the timescale of $T_{1\rho}$(H) ($\sim$20 ms) that corresponds to a length scale of 3.5 nm. In addition, the $T_{1\rho}$(H) value for the carbonyl carbon of PMMA of the blends are smaller than that of pure PMMA, especially at 50/50 ratio it decrease from 21.3 to 18.5 ms. Besides, it is worthy to note that the $T_{1\rho}$(H) values of the phenyl carbons of DC3074 in the semi-IPNs is much smaller than that of pure crosslinked DC3074 (29.8 ms decreases to 18–20 ms), and is close to that of PMMA-rich domain. This indicates again that in silicone-rich phase contains not only pure 3074 but also some PMMA and the relaxation behavior in the silicone-rich domain is similar as PMMA-rich domain.

4. Conclusions

A phase separated PMMA/silicone semi-IPN was synthesized by the self-condensation reaction of polysiloxane containing reactive methoxysilane groups. The SEM micrographs show that PMMA formed distinct spherical island morphology a 75/25 ratio; however, the domain interface became ambiguous at 50/50 ratio. The combined results obtained by DSC analysis and CP/MAS ^{13}C NMR analyses with T_1(H) and $T_{1\rho}$(H) Measurements provided a clear insight into the microstructure and the scale of miscibility this PMMA/silicone semi-IPN. These results indicated that there existed an interfacial concentration fluctuation in 50/50 blend, and its length scale was estimated to be 21 nm. However, the concentration fluctuation at interfacial region was not observed in 75/25 and 25/75 blends. The change of lineshape for the phenyl carbons of DC3074, reduction of T_{CH} for the carbons of PMMA and DC3074, and the smaller $T_{1\rho}$(H) for the carbons of PMMA and DC3074 confirmed the existence of dispersed PMMA molecules in the silicone network.

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References

[1] Sperling L. Interpenetrating networks and related materials. New York: Plenum Press, 1981.
[2] Clarson SJ, Semlyem JA, editors. Siloxane polymers. New Jersey: Prentice-Hall, 1993.
[3] Zeigler JM, Fearon FW, editors. Silicon-based polymer science. Washington: American Chemical Society, 1990.
[4] Joseph B, Zhang S, Ford WT. Macromolecules 1996;29:1305.
[5] Lee SS, Kim SC. J Appl Polym Sci 1997;64:941.
[6] Derouet D, Forgeard S, Brosse J-C, Emery J, Buzare J-Y. J Polym Sci A: Polym Chem 1998;36:437.
[7] Xie XQ, Ranade SV, DiBenedetto AT. Polymer 1999;40:6297.
[8] Hou SS, Kuo PL. Macromol Chem Phys 1999;200:2501.
[9] Hou SS, Chung YP, Chan CK, Kuo PL. Polymer 2000;41:3263.
[10] Kuo PL, Chen CL, Hou SS. Macromol Chem Phys 2000;201:1451.
[11] He XW, Widmaier JM, Herz JE, Meyer GC. Polymer 1989;30:364.
[12] Golmer TC, Hall PK, Ehernfeld H, Wilson K, Biven T, Clay D, Endreszl C. J Polym Sci A: Polym Chem 1996;34:1025.
[13] Mathias LJ, editor. Solid state NMR of polymers. New York: Plenum Press, 1991.
[14] Ibbett RN, editor. NMR spectroscopy of polymers. London: Chapman & Hall, 1993.
[15] Bovey FA, Mirau PA. NMR of polymers. San Diego: Academic Press, 1996.
[16] Stejskal EO, Schaefer J, Sefcik MD, McKay RA. Macromolecules 1981;14:275.
[17] Dickincon LC, Yang H, Chu CW, Stein RS, Chien JCW. Macromolecules 1987;20:1757.
[18] Zhang X, Takegoshi K, Hikichi K. Macromolecules 1991;24:5756.
[19] Okamoto DT, Cooper SL, Root TW. Macromolecules 1992;25:1068.
[20] Tang P, Reimer JA, Denn MM. Macromolecules 1993;26:4269.
[21] Dong L, Hill DJT, Whittaker AK, Ghiggino KP. Macromolecules 1994;27:5912.
[22] Kwak SY, Kim JJ, Kim UY. Macromolecules 1996;29:3560.
[23] Schantz S. Macromolecules 1997;30:1419.
[24] Geppi MG, Forte CF, Passaglia E, Mendez B. Macromol Chem Phys 1998;199:1957.
[25] White JL, Dias AJ, Ashbaugh JR. Macromolecules 1998;31:1880.

[26] Garbow JR, Geotz J, Asrar J. Macromolecules 1998;31:3925.
[27] Perera MCS. Polymer 1999;40:1667.
[28] Grobelny J. Polymer 1999;40:2939.
[29] Cheung MK, Wang J, Zheng S, Mi Y. Polymer 2000;41:1469.
[30] Klempner D, Frisch KC, editors. Advances in interpenetrating polymer networks. Pennsylvania: Technomic Publishing Company, 1989.
[31] Bourgeat-Lami E, Espiard P, Guyot A. Polymer 1995;36:4385.
[32] Abragam A. The principles of nuclear magnetism. New York: Oxford University Press, 1961.
[33] McBrierty VJ, Dougalass DC, Kwei TK. Macromolecules 1978;11:1265.
[34] McBrierty VJ, Packer KJ. Nuclear magnetic resonance in solid polymers. Cambridge, UK: Cambridge University Press, 1993.