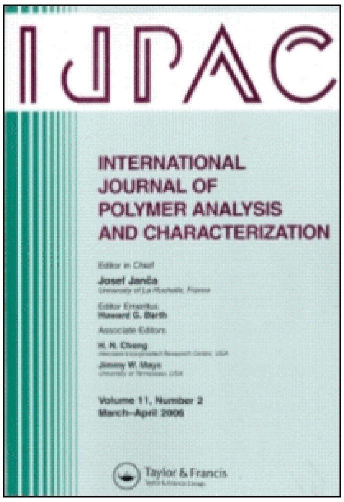


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Effect of the Interfacial Structure on the Local Dynamics of Poly(methyl methacrylate)-Silica Hybrids

Y. T. Wang[a]; T. C. Chang[a]; Y. S. Hong[a]; H. B. Chen[b]
[a] Department of Applied Chemistry, Chung Cheng Institute of Technology, NDU, Tahsi, Taoyuan, Taiwan [b] Chemical Systems Research Division, Chung Shan Institute of Science and Technology, Lungtan, Taoyuan, Taiwan

To cite this Article Wang, Y. T. , Chang, T. C. , Hong, Y. S. and Chen, H. B.(2003) 'Effect of the Interfacial Structure on the Local Dynamics of Poly(methyl methacrylate)-Silica Hybrids', International Journal of Polymer Analysis and Characterization, 8: 3, 209 — 224

To link to this Article: DOI: 10.1080/10236660304876

URL: http://dx.doi.org/10.1080/10236660304876

International Journal of Polymer Anal. Charact., 8: 209–224, 2003
Copyright © 2003 Taylor & Francis
1023-666X/03 $12.00 + .00
DOI: 10.1080/10236660390128373

Effect of the Interfacial Structure on the Local Dynamics of Poly(methyl methacrylate)-Silica Hybrids

Y. T. Wang, T. C. Chang, and Y. S. Hong
Department of Applied Chemistry,
Chung Cheng Institute of Technology,
NDU, Tahsi, Taoyuan, Taiwan

H. B. Chen
Chemical Systems Research Division,
Chung Shan Institute of Science and Technology,
Lungtan, Taoyuan, Taiwan

Poly(methyl methacrylate-maleic anhydride)-silica hybrid materials, P(MMA-MA5)-SiO_2, were synthesized from the in situ reaction of methyl methacrylate (MMA) with 5 mol % maleic anhydride (MA), then hydrolyzed with 3-amino-propyl methyl diethoxysilane (APrMDEOS) coupling agent and tetraethoxysilane (TEOS) by a sol-gel process. By the same method, the poly(methyl methacrylate-glycidyl methacrylate)-silica hybrids (P[MMA-GMA5]-SiO_2), reacted with 5 mol % glycidyl methacrylate (GMA), were obtained. The structure and relaxation of the hybrids were characterized by IR, and ^{29}*Si- and* ^{13}*C-NMR spectroscopy. The effect of the interfacial structure on the local dynamics of the hybrids was investigated using the* ^{29}*Si-*^{1}*H cross-polarization and proton spin-lattice relaxation time in the rotation frame.*

Keywords: Poly(methyl methacrylate); Silica; Hybrid; Relaxation

Received 7 September 2001; accepted 17 December 2001.

The authors thank the National Science Council of the Republic of China (Grant NSC 89-2113-M-014-009). We would also like to thank Miss S. Y. Fang for her expert technical assistance.

Address correspondence to Te-Chuan Chang, Department of Applied Chemistry, Chung Cheng Institute of Technology, NDU, Tahsi, Taoyuan, Taiwan 335, R.O.C. E-mail: techuan@ccit.edu.tw

INTRODUCTION

Organic-inorganic hybrids are attractive materials with heat resistance, useful mechanical and electrical properties, and radiation resistance[1]. Two main procedures are used to prepare poly(methyl methacrylate)-silica hybrid materials through variations of the sol-gel method. The first uses a mixture of a tetrafunctional silicon alkoxide and PMMA to produce composite materials[2–8]. The second creates stable chemical bonds between PMMA and silica with a functional coupling agent, resulting in homogeneous, transparent hybrid materials[9–15]. The components in the latter can be linked by the 3-(trimethoxysilyl)propyl methacrylate (MSMA) coupling agent. The P(MMA-MSMA)-SiO_2 hybrids have been investigated focusing on the microstructure[9], morphology[10], mechanical properties[11], optical properties[12,13], and thermal stability[14,15]. Recently, the copolymer of MMA and maleic anhydride (MA) was condensed with 3-aminopropyl trimethoxy-silane (APTMS) coupling agent, which was then hydrolyzed with tetraethoxysilane (TEOS). Transparent poly(methyl methacrylate-maleic anhydride)-silica hybrids, P(MMA-MA)-SiO_2, with amide bonds are then prepared by this two-step process[16].

In our previous work, P(MMA-MSMA)-SiO_2 hybrids were prepared by in situ polycondensation of alkoxysilane in the presence of trialkoxysilane-functional PMMA. We found that the polarization transfer relaxation time (T_{SiH}) and rotating frame spin-lattice relaxation times ($T^{H}{}_{1\rho}$) values of silica moieties decreased with increasing silica content[15]. To understand the effect of the interfacial structure between PMMA and silica on the local dynamics of the hybrids, we further modified the interfacial structures of the PMMA-SiO_2 hybrid materials in this work. The diethoxysilyl functionalized copolymers of poly-(methyl methacrylate-maleic anhydride) P(MMA-MA5), with imide groups and poly(methyl methacrylate-glycidyl methacrylate) P(MMA-GMA5) with amine groups were prepared by in situ additional copolymerization of 95 mol % MMA with 5 mol % MA and GMA, respectively, and condensation with 3-aminopropyl methyl diethoxysilane (APrMDEOS) coupling agent. Thereafter, the P(MMA-MA5)-SiO_2 and P(MMA-GMA5)-SiO_2 hybrids were obtained by co-hydrolysis of P(MMA-MA5) and P(MMA-GMA5) copolymers with TEOS via the sol-gel technique.

EXPERIMENTAL

Materials

The monomer methyl methacrylate (MMA, Janssen) was purified by distillation before use. Maleic anhydride (MA, Showa Chemical Inc.), glycidyl methacrylate (GMA, TCI), tetraethoxysilane (TEOS, TCI), and 3-aminopropyl methyl diethoxy-silane (APrMDEOS, Gelest Inc.) were used without purification. Azoisobutyronitrile (AIBN, BDH) was recrystallized from ethanol just before use. Tetrahydrofuran (THF, Aldrich) was fractionally distilled in the presence of metallic sodium and benzophenone under a nitrogen atmosphere. Deionized water (18 MΩ) was used during hydrolysis.

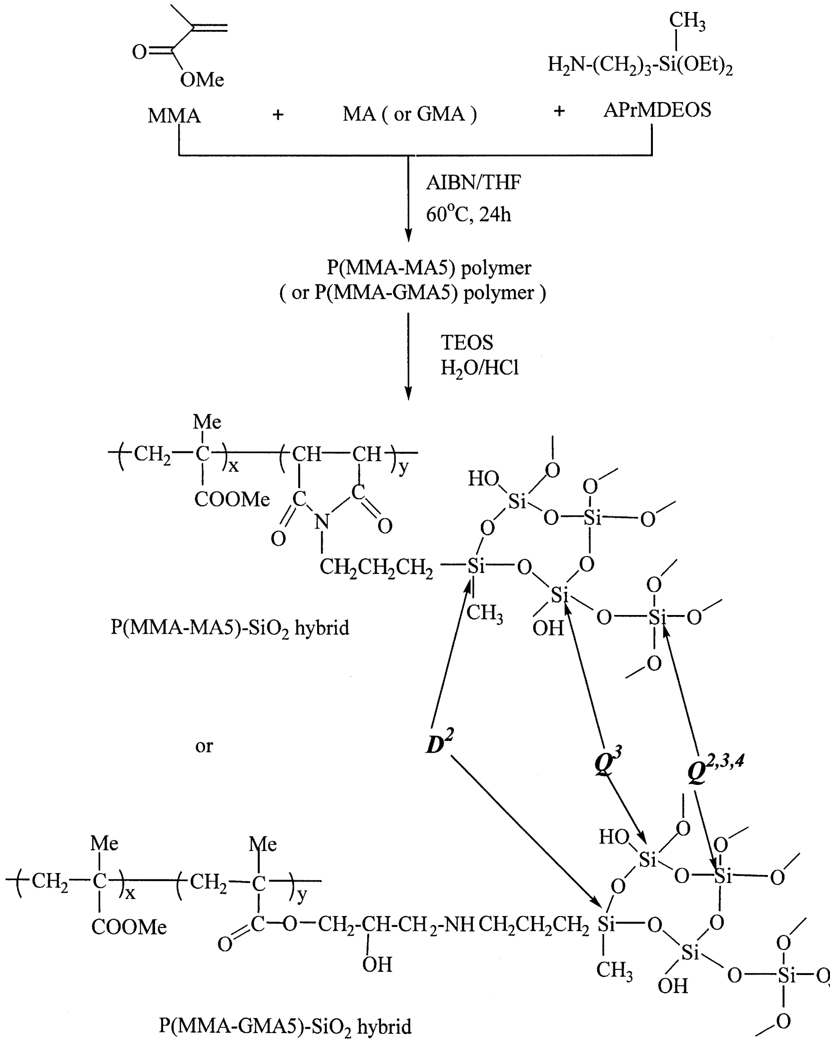
Preparation of the Hybrids

P(MMA-MA5)-SiO_2 and P(MMA-MA5)-SiO_2 hybrids were prepared by in situ sequential synthesis, as shown in Scheme 1. In a typical example, a mixture of MMA (2.0 g), MA (0.1 g), APrMDEOS (0.2 g), AIBN (3.63×10^{-3} g), and THF (14 mL) was poured into a 250 mL round-bottom flask under nitrogen, and the solution was stirred at 60°C (24 h) to initiate the copolymerization of the methacrylic monomers. Thereafter, a desired amount of water (0.43 g), TEOS (1.24 g), and HCl with THF was added, and then vigorously stirred for 10 min at room temperature. The resulting homogeneous mixture was poured onto a Teflon dish. After drying at room temperature for 24 h under atmospheric pressure, the film was heated 3 h at 60°C, 3 h at 100°C, and finally 24 h at 150°C under vacuum. Hybrid MA5-70 was obtained, where 70 denotes that 70 wt % of 95 mol % MMA with 5 mol % diethoxysilyl functional group condenses with 30 wt % of TEOS based on the weight of monomer (MMA, MA, and APrMDEOS). The formulation of the other hybrids is listed in Table I.

Characterization of the Hybrids

Imide-containing P(MMA-MA5)-SiO_2 and amine-containing P(MMA-GMA5)-SiO_2 hybrids were confirmed by IR spectrum (Bomem DA 3.002) of a sample prepared with the KBr-pellet technique. The ^{13}C- and ^{29}Si-NMR spectra of the solid-state hybrids were determined (Bruker MSL-400) with cross-polarization combined with magic-angle spinning (CP/MAS). The nomenclatures of D^i and Q^i are taken from Glaser et al.[17], where i refers to the number of -O-Si groups bounded to the silicon atom of interest. D^i and Q^i denote species that have two and no organic side groups, respectively. The relative proportions of the D^i species and Q^i species were calculated on the basis of the experimental spectra.

CP contact time studies can produce the Si-H polarization transfer constant (T_{SiH}). The ^{1}H-^{29}Si spin contact time with the Hartmann-Hahn condition fulfilled in the rotating frame was typically about 5 ms but was optimized in a range of 0.5–20 ms. The spin-lattice relaxation times in



SCHEME 1 Scheme abbreviations: MMA = methyl methacrylate; MA = maleic anhydride; GMA = glycidyl methacrylate; APrMDEOS = 3-aminopropyl methyl diethoxysilane; TEOS = tetraethoxysilane; AIBN = azoisobutyronitrile; D^2 = two O-Si groups and two organic side groups bonded to the silicon atom of interest; $Q^{2\text{-}4}$ = two–four -O-Si groups, but compound does not have any one organic side group bonded to the silicon atom of interest; P(MMA-MA5) = copolymer contains 95 mol % MMA and 5 mol % MA; P(MMA-GMA5) = copolymer contains 95 mol % MMA and 5 mol % GMA.

TABLE I Experimental conditions for hybrids

Hybrids	MMA[a] (mmol %)	MA[b] (mmol%)	GMA[c] (mmol%)	APrMDEOS[d] (mmol%)	TEOS[e] (wt %)
A: MA5	95	5	0	5	0
B: MA5-90	95	5	0	5	10
C: MA5-85	95	5	0	5	15
D: MA5-80	95	5	0	5	20
E: MA5-75	95	5	0	5	25
F: MA5-70	95	5	0	5	30
G: GMA5	95	0	5	5	0
H: GMA5-90	95	0	5	5	10
I: GMA5-85	95	0	5	5	15
J: GMA5-80	95	0	5	5	20
K: GMA5-75	95	0	5	5	25
L: GMA5-70	95	0	5	5	30

[a] Methyl methacrylate.
[b] Maleic anhydride.
[c] Glycidyl methacrylate.
[d] 3-Aminopropyl methyl diethoxysilane.
[e] Tetraethoxysilane; $[H_2O]/[TMOS] = 4$.

the rotating frame ($T^{H}_{1\rho}$) were measured with a ^1H spin-lock τ-pulse sequence followed by CP. The ^1H 90° pulse widths were 4.5 μs, and the CP contact time was 2 ms. The length of delay time τ ranged from 0.1 to 25 ms for $T^{H}_{1\rho}$.

RESULTS AND DISCUSSION

Structural Characterization

Theoretical schematic structures of the hybrids are shown in Scheme 1. IR spectra of MA5-70 and GMA5-70 hybrids are shown in Figure 1, lines A and B, respectively. The characteristic peaks of anhydride (1733, 1786, and 1857 cm^{-1})[16] and amide (1630–1660 and 1520–1580 cm^{-1})[16] are not observed in Figure 1, line A, while that of imide C–N stretching vibration peak (1387 cm^{-1}) is displayed[18]. Moreover, a shoulder at 1718 cm^{-1} may be due to the imide C=O asymmetric stretching peak. The results suggest that the P(MMA-MA5)-SiO_2 hybrid with imide groups is obtained by an additional polymerization and condensation in situ process. It differs from the two-step process that forms amide bonds[16]. In Figure 1, line B, the characteristic peak of the epoxy (909 cm^{-1})[19] is not observed in the

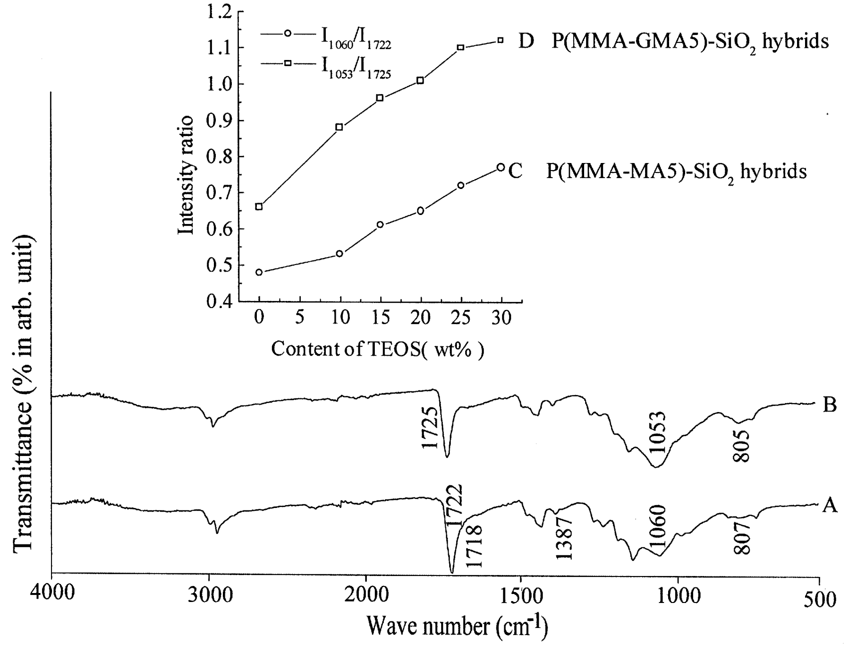


FIGURE 1 IR spectra of hybrids: (A) MA5-70; (B) GMA5-70; relative intensity ratio of (C) I_{1060}/I_{1722} in P(MMA-MA5)-SiO_2 hybrids; (D) I_{1053}/I_{1725} in P(MMA-MA5)-SiO_2 hybrids.

GMA5-70 hybrid, indicating that the epoxy group opens up after curing, while that of the ester carbonyl group (1729 cm^{-1}) and secondary amine (1387 cm^{-1}; C–N vibration) is seen. The results suggest that the structure of the P(MMA-GMA5)-SiO_2 hybrid showed in Scheme 1 has undergone an epoxy-amine reaction[20]. On the other hand, a weak band at 807 cm^{-1} (Figure 1, line A) or 805 cm^{-1} (Figure 1, line B) is the characteristic Si–OH bending vibration[16]. The more intense peak of the latter suggests that the degree of condensation in the GMA5-70 hybrid is less than in the MA5-70 hybrid. In addition, the ratio of intensity of the Si–O–Si band to the PMMA band increases, as the feed ratio of TEOS increases (Figure 1, lines C and D). This implies that the three-dimensional Si–O–Si hybrid network is formed by the cross-linking reaction of the already hydrolyzed TEOS[21]. Moreover, the greater ratios of the order I_{1053}/I_{1722} may be rationalized on the basis of the P(MMA-GMA5)-SiO_2 hybrid that has more carbonyl groups as compared to the P(MMA-MA5)-SiO_2 hybrid.

^{13}C-CP/MAS NMR spectra of the P(MMA-MA5)-SiO_2 and P(MMA-GMA5)-SiO_2 hybrids are nearly identical. A set of the same chemical shifts for the PMMA segments are observed at 178, 55, 52, 45, and 16 ppm in the ^{13}C CP/MAS NMR spectrum of MA5-70 (Figure 2) and GMA5-70 hybrids (Figure 3), which corresponds to carboxyl, methylene, methoxy, quaternary, and methyl carbons, respectively[15]. The broadening of the methyl resonance (16 ppm) is a general phenomenon for polymers with rapidly reorienting side groups or main-chain carbons subject to motion[22]. Moreover, the chemical shift at -1 ppm is due to Si–CH_3 resonance. In addition, a shoulder around 173 ppm (Figure 2) results from the imide carboxyl carbon[23], in agreement with the IR spectrum. The peak around 67 ppm (Figure 3) results from the carbon beside carboxyl group from the GMA[24].

^{29}Si–CP/MAS NMR spectrum of the MA5-70 (Figure 4) and GMA5-70 hybrids (Figure 5) show the same four peaks at about -19, -94, -101, and -110 ppm, corresponding respectively to the D^2, Q^2, Q^3, and Q^4 species, attributed to the silicon in the diethoxysilyl groups and the three-dimensional silica network. Moreover, the GMA5-70 hybrid presents a narrow peak at -82 ppm (Figure 5) designated as a Q^0 structure due to residual noncondensed $Si(OH)_4$. The relative proportion of D^2 decreases with increasing silica content (Figures 4 and 5), whereas that of Q^3 increases. It is correlated with the FT-IR spectra, in which the char-

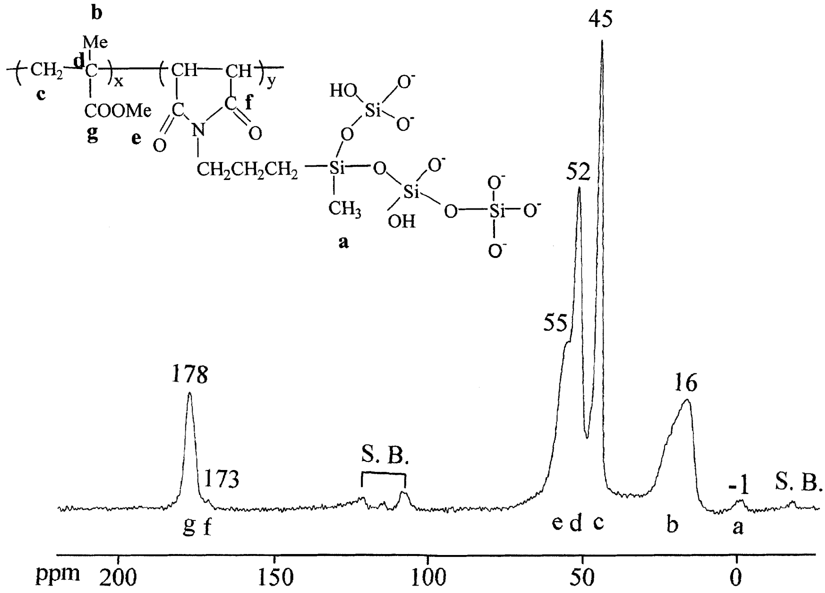


FIGURE 2 The ^{13}C–CP/MAS NMR spectrum of the MA5-70 hybrid.

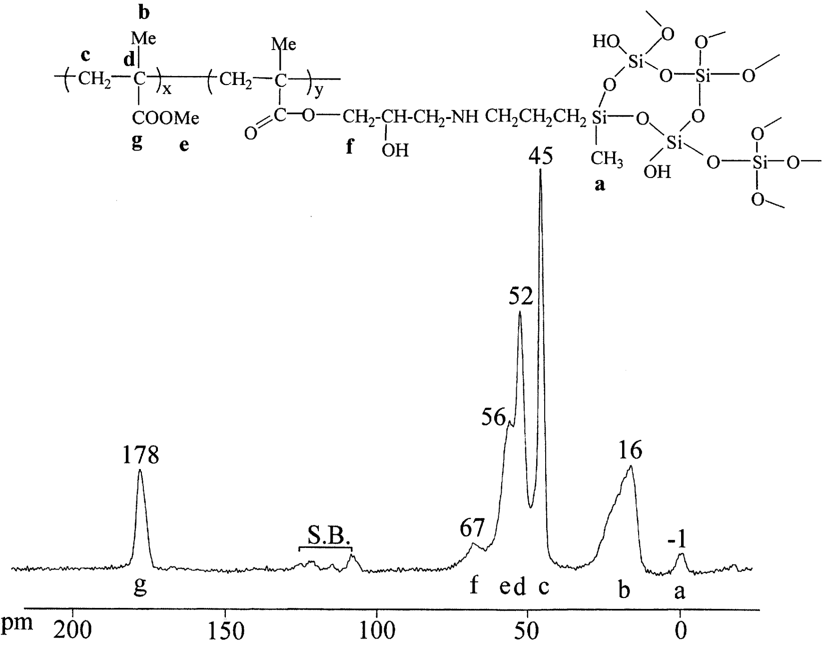


FIGURE 3 The ^{13}C–CP/MAS NMR spectrum of the GMA5-70 hybrid.

acteristic band of the Si–O–Si bond is broader with increasing silica content. This indicates that more three-dimensional silica network is developed as the TEOS proportion increases.

Table II lists the actual degree of condensation (D_c) evaluated from the proportions of D^i and Q^i species according to the following equation:

$$D_c(\%) = \left(\frac{D^1 + 2D^2}{2} + \frac{Q^1 + 2Q^2 + 3Q^3 + 4Q^4}{4}\right) \times 100 \qquad (1)$$

The D_c values of the hybrids decrease with increasing TEOS content, suggesting that the hydrogen bonding between polymer and silica network increases. Moreover, the lower D_c value in the P(MMA-GMA5)-SiO$_2$ hybrids than in the P(MMA-MA5)-SiO$_2$ hybrids may be due to the hydrophilic hydroxyl-containing amine in the former that inhibits the condensation of the silanol group.

^{29}Si Cross-Polarization Dynamics

Figure 6 is an example of the effect of contact time t on the ^{29}Si-resonance of the MA5-70 hybrid. The intensities in Figure 6 reflect local

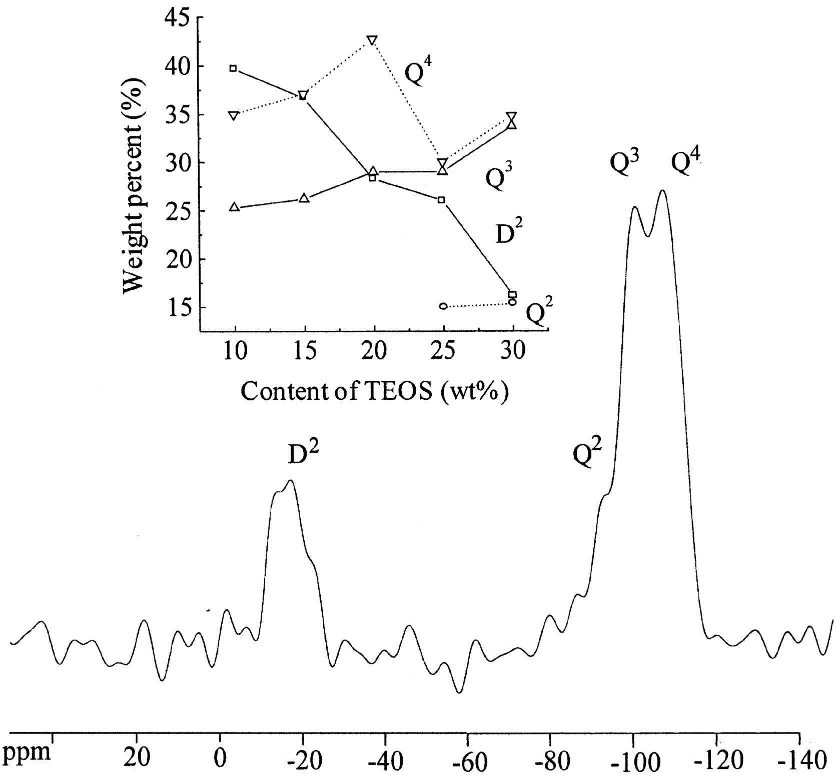


FIGURE 4 The ^{29}Si single-pulse excitation MAS spectrum of the MA5-70 hybrid as well as the relative proportions of D^2, Q^2, Q^3, and Q^4 species.

CP dynamics, which may vary from site to site. The buildup of ^{29}Si-magnetization, $M_c(t)$, is expressed as a function of the contact time as follows[25]:

$$M_c(t) = M_e\left[\exp(-t/T^H_{1\rho}) - \exp(-t/T_{SiH})\right] \qquad (2)$$

Here, M_e is the ^{29}Si-equilibrium magnetization obtained when both spin systems are fully in contact with each other without any energy exchange with the lattice. T_{SiH} is the time constant for the energy exchange between the ^{1}H and ^{29}Si spin systems, and $T^H{}_{1\rho}$ is the spin-lattice relaxation time in the rotating frame. This equation indicates that ^{29}Si-magnetization appears at the rate of the order of $(T_{SiH})^{-1}$ and disappears at the rate of $(T^H{}_{1\rho})^{-1}$.

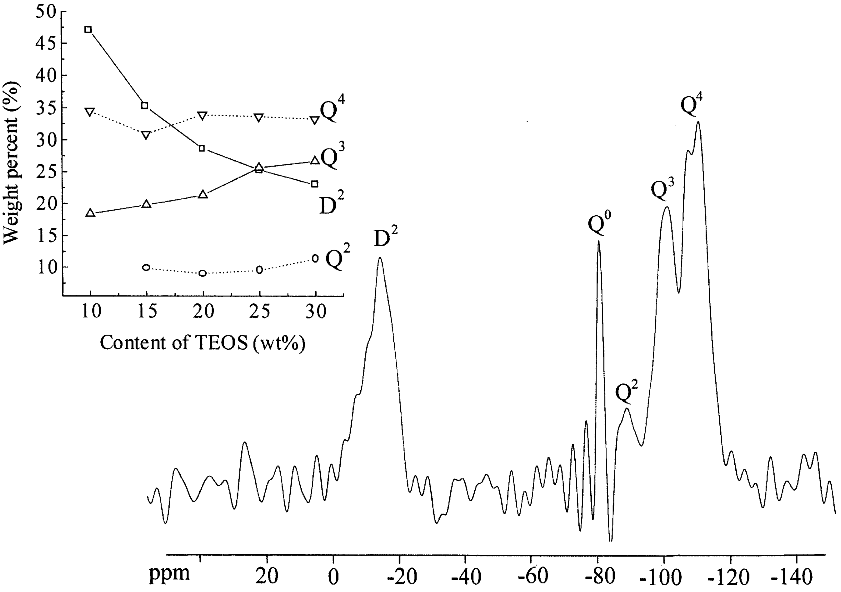


FIGURE 5 The ^{29}Si single-pulse excitation MAS spectrum of the GMA5-70 hybrid as well as the relative proportions of D^2, Q^2, Q^3, and Q^4 species.

Figures 7 and 8 show a semilogarithmic plot of the peak intensity as a function of the contact time for the silicon in MA5-70 and GMA5-70 hybrids, respectively. A steeper slope is an indication of a faster transfer of magnetization (shorter T_{SiH}) or a faster relaxation by spin-diffusion (shorter $T^{H}{}_{1\rho}$). The values of T_{SiH} and $T^{H}{}_{1\rho}$ estimated by the curve-fittings are summarized in Table II. The T_{SiH} values of the Q^3 species in the P(MMA-MA5)-SiO_2 hybrids are smaller than those of the Q^4 species, resulting from the fact that the Q^3 centers contain more protons, which can provide Si–H dipolar coupling[26]. Moreover, the T_{SiH} values of the Q^3 and Q^4 species in the P(MMA-MA5)-SiO_2 hybrids decrease with increasing silica content, while those of the D^2 species are around 0.95 ms. This data reveals that Si–H dipolar coupling in Q^3 and Q^4 species is enhanced as the silica content increases, while that of the flexible D^2 species is independent of the silica content. However, the T_{SiH} values of the D^2, Q^3, and Q^4 species in the P(MMA-GMA5)-SiO_2 hybrids are around 0.82 ms (Table II). The independence of the rate of polarization transfer in P(MMA-GMA5)-SiO_2 hybrids may be due to residual non-condensed Q^0 species that have greater motion.

The $T^{H}{}_{1\rho}$ value of hybrids, as compared with P(MMA-MSMA)-SiO_2 hybrids, is in the order of P(MMA-GMA5)-$SiO_2 <$ P(MMA-MSMA)-

TABLE II T_{SiH} and $T^{\mathrm{H}}{}_{1\rho}$ values of the respective resonance lines and L values of the hybrids

Hybrids	D_c (%)[a]	T_{SiH} (ms)[b]			$T^{\mathrm{H}}{}_{1\rho}$ (ms)/L (nm)[c]		
		D^2	Q^3	Q^4	D^2	Q^3	Q^4
B: MA5-90	93.7	0.95	1.06	1.90	14.80/3.85	35.69/5.97	30.23/5.50
C: MA5-85	93.5	1.02	0.99	0.91	13.55/3.68	19.15/4.38	28.37/5.33
D: MA5-80	92.8	0.93	0.39	0.41	13.98/3.74	25.44/5.04	36.82/6.07
E: MA5-75	85.1	0.89	0.40	0.49	14.43/3.80	25.52/5.05	38.30/6.19
F: MA5-70	83.9	1.01	0.37	0.40	16.08/4.01	25.70/5.07	44.86/6.70
L_{av} (nm)[d]					3.82	5.10	5.96
H: GMA5-90	95.4	0.91	0.80	0.86	8.64/2.94	10.75/3.28	16.56/4.07
I : GMA5-85	85.9	0.87	0.80	0.70	8.63/2.94	9.00/3.00	14.13/3.76
J : GMA5-80	83.0	0.99	0.84	0.83	8.68/2.95	11.68/3.42	17.12/4.14
K: GMA5-75	82.9	0.85	0.83	0.76	10.22/3.20	11.62/3.41	17.97/4.24
L: GMA5-70	81.7	0.97	1.05	0.84	9.00/3.00	12.87/3.59	20.21/4.50
L_{av} (nm)					3.01	3.34	4.14

[a] Degree of condensation.

[b] Polarization transfer relaxation time.

[c] $T^{\mathrm{H}}{}_{1\rho}$ = rotating frame spin-lattice relaxation times; L = spin-diffusion path length.

[d] L_{av} = Average L value of hybrid.

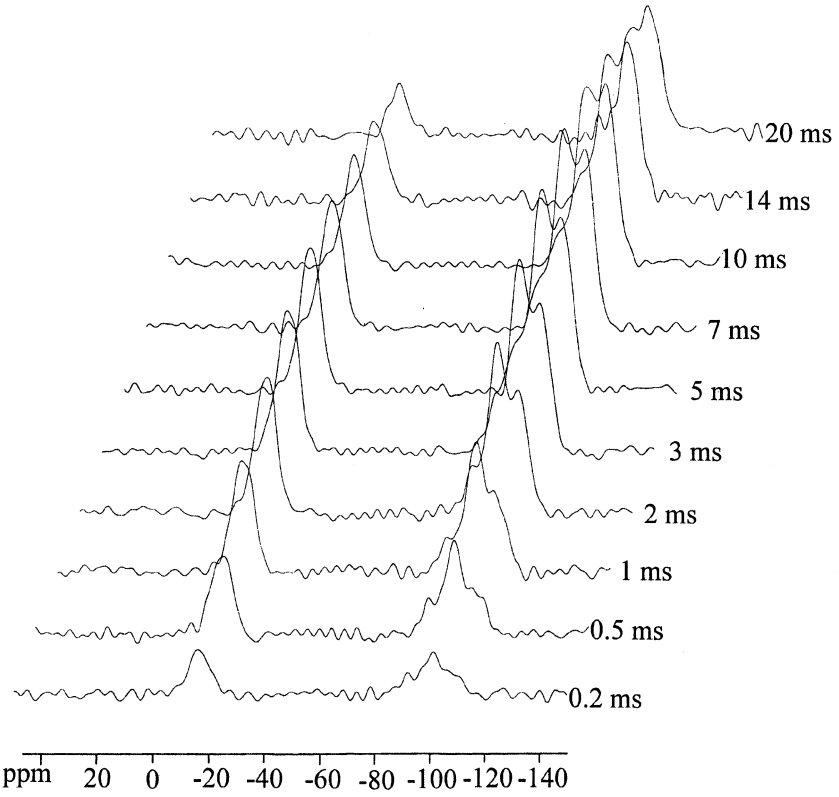


FIGURE 6 Stacked plot of the ^{29}Si–CP/MAS NMR spectra of MA5-70 hybrid as a function of contact time.

$SiO_2 <$ P(MMA-MA5)-SiO_2 hybrids. The faster relaxation in the P(MMA-GMA5)-SiO_2 hybrid may be due to more hydrogen bonding in the P(MMA-GMA5)-SiO_2 hybrids. Moreover, $T^{H}{}_{1\rho}$ values of the P(MMA-GMA5)-SiO_2 and P(MMA-MA5)-SiO_2 hybrids are in the order $D^2 < Q^3 < Q^4$ species, due to the presence of more protons of silicon centers, which increase the Si–H dipolar coupling[26]. However, the curves in Figures 7 and 8 are linear, which suggests that large-scale phase separation of D^2, Q^3, and Q^4 species does not occur in these materials[25]. The spin-diffusion path length, L, can be estimated with the following equation[25]:

$$\langle L^2 \rangle = (T^{H}_{1\rho}/T_2)\langle L_0^2 \rangle \tag{3}$$

Here, L_0 is the distance between protons, typically about 0.1 nm. T_2 is the proton spin-spin relaxation time, which, below T_g, is approximately

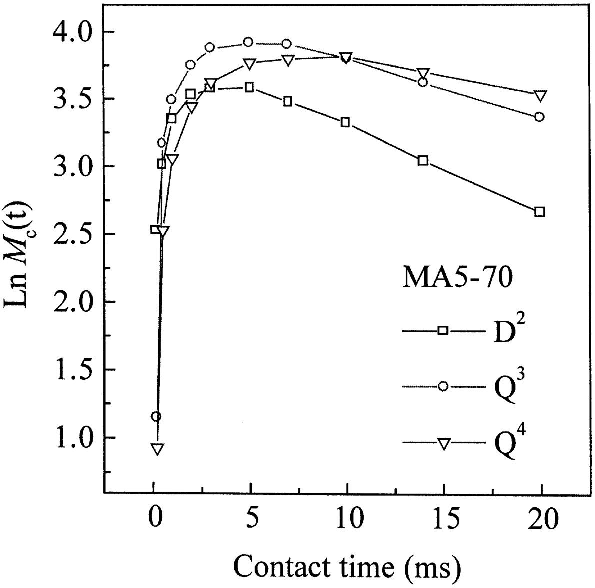


FIGURE 7 Semilogarithmic plot of the peak intensities of the D^2, Q^3, and Q^4 species as a function of the contact time in the MA5-70 hybrid.

10 μs, and $<L^2>$ is the mean square distance over which magnetization is transported. The calculated average spin-diffusion path length (L_{av}) of the P(MMA-MA5)-SiO$_2$ hybrids is in the order of D^2 (3.82 nm) < Q^3 (5.10 nm) < Q^4 (5.96 nm) species, while that of the P(MMA-GMA5)-SiO$_2$ hybrids is, respectively, about 3.01, 3.34, and 4.14 nm (Table II). However, the L_{av} value of hybrids, as compared with P(MMA-MSMA)-SiO$_2$ hybrids, is in the order of P(MMA-GMA5)-SiO$_2$ < P(MMA-MSMA)-SiO$_2$ < P(MMA-MA5)-SiO$_2$ hybrids. This trend indicates that the linear, flexible interface in the P(MMA-GMA5)-SiO$_2$ hybrids decreases the average spin-diffusion path length, whereas the rigid interface in the P(MMA-MSMA)-SiO$_2$ hybrids increases the average spin-diffusion path length.

CONCLUSIONS

Poly(methyl methacrylate)-silica hybrid materials, P(MMA-MA5)-SiO$_2$ and P(MMA-GMA5)-SiO$_2$, were prepared and characterized by solid-state NMR. ^{29}Si-NMR studies showed that the degree of condensation (D_c) may be influenced by the interfacial structure of the hybrids. The incomplete reaction of hydrolyzed TEOS appeared to be

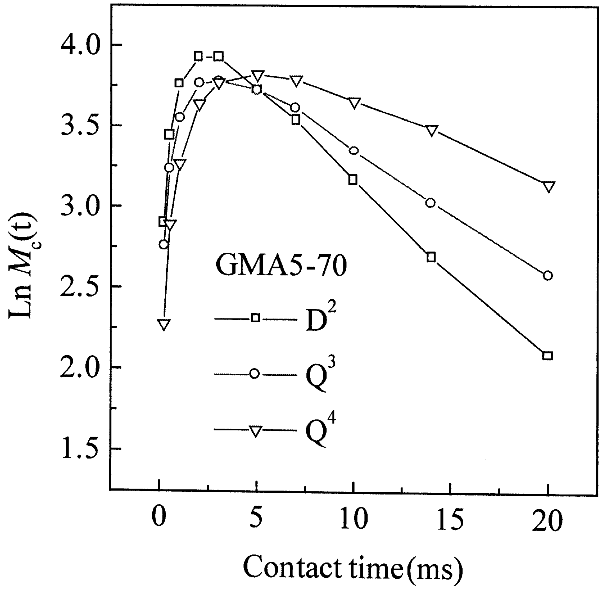


FIGURE 8 Semilogarithmic plot of the peak intensities of the D^2, Q^3, and Q^4 species as a function of the contact time in the GMA5-70 hybrid.

caused by more hydrogen bonding of the P(MMA-GMA5)-SiO_2 hybrids. The T_{SiH} values showed that Si–H dipolar coupling of the Q^3 and Q^4 species in the P(MMA-MA5)-SiO_2 hybrids was enhanced as the silica content increased, while that of the flexible D^2 species was independent of the silica content. However, the T_{SiH} ($\sim$ 0.82 ms) of the P(MMA-GMA5)-SiO_2 hybrids showed a weaker dipolar coupling for the high silica content, which resulted from increased motion of residual noncondensed Q^0 species. The $T^H{}_{1\rho}$ and L_{av} values of hybrids were in the order of P(MMA-GMA5)-SiO_2 < P(MMA-MSMA)-SiO_2 < P(MMA-MA5)-SiO_2 hybrids. This trend indicates that the linear, flexible interface in the P(MMA-GMA5)-SiO_2 hybrids reduced the average spin-diffusion path length and enhanced relaxation. However, the higher L_{av} values of the P(MMA-MA5)-SiO_2 hybrids may have resulted from the rigid interface.

REFERENCES

[1] Mark, J. E., C. Y. Lee, and P. A. Bianconi. (1995). *Hybrid Organic-Inorganic Composites*, ACS Symposium Series 585. Washington, DC: American Chemical Society.

[2] Philipp, G., and H. Schmidt. (1984). New materials for contact lenses prepared from Si- and Ti-alkoxides by the sol-gel process. *J. Non-Cryst. Solids* 63: 283–292.

[3] Pope, E. J. A., M. Asami, and J. D. Mackenzie. (1989). Transparent silica gel-PMMA composition. *J. Mater. Res.* 4: 1018–1026.

[4] Novak, B. M., and C. Davis. (1991). "Inverse" organic-inorganic composite materials. 2: Free-radical routes into nonshrinking sol-gel composites. *Macromolecules.* 24: 5481–5483.

[5] Huang, Z. H., and K. Y. Qiu. (1995). Preparation and thermal property of poly-(methyl methacrylate)/silicate hybrid materials by the in-situ sol-gel process. *Polym. Bull.* 35: 607–613.

[6] Rodrigues, D. E., B. G. Risch, and G. L. Wilkes. (1997). Phase separation behavior of silicate phases grown in poly(methyl methacrylate) by a sol-gel process. *Chem. Mater.* 9: 2709–2719.

[7] Landry, C. J. T., B. K. Coltrain, and B. K. Brady. (1992). In situ polymerization of tetraethoxy-silane in poly(methyl methacrylate): Morphology and dynamic mechanical properties. *Polymer*. 33: 1486–1495.

[8] Landry, C. J. T., B. K. Coltrain, J. A. Wesson, N. Zumbulyadis, and J. L. Lippert. (1992). In situ polymerization of tetraethoxysilane in poly(methyl methacrylate): Chemical nature of the interactions. *Polymer*. 33: 1496–1506.

[9] Coltrain, B. K., C. J. T. Landry, J. M. Oreilly, A. M. Chamberlain, G. A. Rakes, J. S. Sedita, L. W. Kelts, M. R. Landry, and V. K. Long. (1993). Role of trialkoxysilane functionalization in the preparation of organic-inorganic composites. *Chem. Mater*. 5: 1445–1455.

[10] Sunkara, H. B., J. M. Jethmalani, and W. T. Ford. (1994). Composite of colloidal crystals of silica in poly(methyl methacrylate). *Chem. Mater*. 6: 362–364.

[11] Yang, J. M., C. S. Lu, Y. G. Hsu, and C. H. Shih. (1997). Mechanical properties of acrylic bond cement containing PMMA-S_iO_2 hybrid sol-gel material. *J. Biomed. Mater. Res*. 38: 143–154.

[12] Jethmalani, J. M., and W. T. Ford. (1996). Diffraction of visible light by ordered monodisperse silica-poly(methyl acrylate) composite films. *Chem. Mater*. 8: 2138–2146.

[13] Chen, W. C., and S. J. Lee. (2000). Synthesis and characterization of poly(methyl methacrylate)-silica hybrid optical thin films. *Polym. J*. 32: 67–72.

[14] Pu, J. E., Z. Mark, J. M. Jethmalani, and W. T. Ford. (1997). Effects of dispersion and aggregation of silica in the reinforcement of poly(methyl acrylate) elastomers. *Chem. Mater*. 9: 2442–2447.

[15] Chang, T. C., Y. T. Wang, Y. S. Hong, and Y. S. Chiu. (2000). Organic-inorganic hybrid materials.V: Dynamics and degradation of poly(methyl methacrylate)-silica hybrids. *J. Polym. Sci. Part A: Polym. Chem*. 38: 1972–1980.

[16] Xie, T. X., C. G. Zhou, S. Y. Feng, and X. Q. Wang. (2000). Study of poly(methyl methacrylate-maleic anhydride)/silica hybrid materials. *J. Appl. Polym. Sci*. 75: 379–383.

[17] Glaser, R. H., and G. L. Wilkes. (1988). Structure property behavior of poly-dimethylsiloxane and poly(tetramethylene oxide) modified TEOS based sol-gel materials V: Effect of titaninmisopropoxide incorporation. *Polym. Bull*. 19: 51–57.

[18] Smaihi, M., J. C. Schrotte, C. Lesimple, I. Prevost, and C, Guizard. (1999). Gas separation properties of hybrid imide-siloxane copolymers with various silica contents. *J. Membr. Sci*. 161: 157–170.

[19] Ghosh, S., and N. Krishnamurti. (2000). Use of glycidyl methacrylate monomers for developing cross-linkable pressure sensitive adhesives. *Eur. Polym. J*. 36: 2125–2131.

[20] Chu, F., and T. F. Mckenna. (1997). A study of the preparation and mechanism of the ambient temperature curing of acrylic latex with epoxy resins. *Polymer*. 38: 6157–6165.

[21] Jang, J., and H. Kim. (1995). Copolymerization of the silane-modified polyvinylimidazole(1) as a metal corrosion inhibitor. *J. Appl. Polym. Sci.* 56: 1495–1504.

[22] Tekely, P., D. Canet, and J. J. Delpuech. (1989). Observation of ^{1}H nuclei in heterogeneous solids via cross-polarization ^{13}C N.M.R.: Preparation via the sol-gel reaction. *Mol. Phys.* 67: 81–96.

[23] Chang, T. C., and K. H. Wu. (1998). Characterization and degradation of some silicon-containing polyimides. *Polym. Degrad. Stab.* 60: 161–168.

[24] Miyashita, Y., Y. Yamada, N. Kimura, H. Suzuki, M. Iwata, and Y. Nishio. (1997). Phase structure of chitin/poly(glycidyl methacrylate) composites synthesized by a solution coagulation/bulk polymerization method. *Polymer* 38: 6181–6187.

[25] Mehring, M. (1983). *Principles of High Resolution NMR in Solids*, 2nd ed. p. 260. Berlin: Springer.

[26] Glaser, R. H., and G. L. Wilkes. (1989). Solid-state ^{29}Si NMR of TEOS-based multifunctional sol-gel materials. *J. Non-Cryst. Solids*. 113: 73–87.