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The effects of interactions on the properties of acrylic polymers/silica hybrid materials prepared by the *in situ* sol–gel process

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Hybrid inorganic–organic materials based on trialkoxysilyl-functionalized, hydroxyl-functionalized and unfunctionalized methyl acrylic polymers have been prepared by the *in situ* sol–gel process in the presence of tetraethoxysilane. Especially, the trialkoxysilyl-functionalized PMMA/SiO_2 hybrid has been successfully prepared without the use of the trialkoxysilyl-functionalized polymer as a precursor which is hydrolytically unstable in the air. The interactions between the silica networks and these polymers were observed, and their influences on phase behaviour of hybrids were also investigated using differential scanning calorimetry and scanning electron microscopy. It was found that the trialkoxysilyl-functionalized polymer is best suited for preparation of hybrid materials with improved properties. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The sol–gel process, with its associated mild conditions, offers a new approach to the synthesis of composite materials with domain sizes approaching the molecular level[1,2]. For example, metal alkoxides can be mixed with monomers to be polymerized or polymers, which have functional groups that react with the hydroxyl groups generated by the hydrolysis of metal alkoxides, resulting in a homogenous polymer/metal oxide hybrid material. The bonding between the organic polymer phase and inorganic phase retards gross phase separation, thus frequently producing homogeneous hybrid materials. A number of papers have reported the preparation and characterization of hybrid materials by hydrolysis of metal alkoxides and its polycondensation with organic polymers. Various polymers, such as poly(dimethylsiloxane) (PDMS)[3], poly(tetramethylene oxide) (PTMO)[4], polyimides[5], poly(oxyethylene)[6], poly(ether ketone)[7], poly(ether sulfone)[8], etc., have been successfully incorporated into SiO_2 or TiO_2 inorganic networks by the sol–gel process, and these molecular composites can exhibit excellent mechanical properties and optical transparency.

We and others[9–11] have synthesized the poly(methyl methacrylate) (PMMA)/SiO_2 and other acrylic polymers/SiO_2 hybrid materials via the *in situ* sol–gel process because of the commercial importance of the acrylic polymers. Two methods are widely used to synthesize these hybrid materials. One requires that the homogeneous, transparent hybrids of organic polymers without trialkoxysilyl functional group with highly dispersed inorganic oxide phases be produced under certain environmental conditions. But only those polymers which can form the extensive hydrogen bonding between the silanols of the silicate network and the carbonyl groups on the polymers can produce homogeneous products with metal alkoxides. This interaction between the polymer and the silicate network can inhibit macroscopic phase separation[12].

The other method involves the coupling of polymeric species terminated with such functional groups as trialkoxysilyl or hydroxyl groups with the metal hydroxide generated by the hydrolysis of metal alkoxides, i.e. the organic polymer phase can be covalently bonded to the inorganic phase by the condensation of the functional groups and the metal hydroxide, resulting in homogeneous, transparent hybrid materials. However, the trialkoxysilyl functional groups are hydrolytically unstable, thus the trialkoxysilyl-functionalized polymers are subject to crosslinking upon exposure to moisture in the air[13], and the insolubility of polymers in tetrahydrofuran (THF) or other organic solvents would make it difficult to combine with metal alkoxides. We previously described the method of synthesizing the PMMA/SiO_2 hybrid materials by the *in situ* sol–gel process in which the polymerization of monomers, the hydrolysis and the condensation of tetraethoxysilane (TEOS) took place simultaneously, and the resulting materials showed good properties compared to the pure PMMA and the hybrids produced by the polymer precursor without the trialkoxysilyl functional group[9].

In this paper we describe the synthesis, characterization and investigation of the morphological features of the hybrids produced from trialkoxysilyl-functionalized, hydroxyl-functionalized [poly(2-hydroxyethyl methacrylate)] and unfunctionalized methyl acrylic polymers via the *in situ* sol–gel process. These hybrids are capable of having different interactions between silica networks and

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organic polymer chains through the covalent bonds and hydrogen bond. Although each of them will be dealt with, our focus will be on the trialkoxysilyl-functionalized PMMA/SiO_2 hybrid material, which shows better transparency and little phase separation.

EXPERIMENTAL

Materials

High-purity tetraethoxysilane (TEOS) was used as received, methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and 3-(trimethoxysilyl)propyl methacrylate (MSMA) were purified by distillation under vacuum, the solvents THF and DMF (*N,N*-dimethylformamide) were used after distillation, and the initiator 2,2′-azobisisobutyronitrile (AIBN) was purified by recrystallization.

In general, the samples of PMMA/SiO_2 hybrids were prepared as previously described[9] by the *in situ* sol–gel process in THF solvent, and the trialkoxysilyl-functional group was introduced into the side-chain of PMMA polymer via copolymerization of MMA and MSMA. An appropriate amount of MMA, MSMA and AIBN were dissolved in THF, and the homogeneous mixture of deionized water, hydrochloric acid and TEOS with THF was added, followed by vigorous stirring for 10 min, resulting in a homogeneous solution. The solution was polymerized and gelled at 60°C. After 6 h, the mixture was allowed to stand at ambient temperature. Upon slowly drying over 20 days, the monolithic samples of PMMA/SiO_2 and P(MMA–MSMA)/SiO_2 were obtained. They were dried at 60°C for 24 h under vacuum.

The samples of PHEMA/SiO_2 hybrids were prepared by dissolution of poly(2-hydroxyethyl methacrylate) ($\bar{M}_\eta = 8.04 \times 10^4$) in DMF. At a certain concentration, TEOS was added directly to the solution under continuous agitation. Then, the mixture of water and HCl in DMF was added, and the solution was stirred for 30 min at ambient temperature. The homogeneous solution obtained was allowed to stand at 60°C for 24 h for gelation. Finally, the gelled samples were dried slowly at room temperature for more than 20 days. All samples are listed in *Table 1*.

Measurements

Differential scanning calorimetry (d.s.c.) was performed on a Shimadzu DSC-50 thermal analyser under N_2 flow in a range from room temperature to 300°C, and the heating rate was 20°C min^{-1}. The thermogravimetry (t.g.) was performed on a Shimadzu DT-30 thermal analyser under nitrogen flow in a range from room temperature to 700°C at a heating rate of 20°C min^{-1}.

Fourier transform infra-red (*FT*i.r.) spectra were obtained using a Nicolet Magna-IR 750 instrument. Samples for *FT*i.r. were prepared in the form of KBr pellets.

The fracture surfaces of the hybrids were examined on an AMRAY 1910FE field emission scanning electron microscope (FESEM).

RESULTS AND DISCUSSION

When the organic polymer and the inorganic SiO_2 networks in hybrid materials produce minimal phase separation, the obtained hybrids can have good optical transparency and mechanical properties. Hence, the interaction between two phases plays a major role in controlling the properties of hybrid materials. It has previously been demonstrated[14] that the strong interaction of hydrogen bonding between the PMMA and the hydroxylated SiO_2 can prevent macroscopic phase separation in the PMMA/SiO_2 hybrid system. However, the covalent bond is a stronger interaction between the two phases. By introducing the 'coupling groups' into the hybrid system, the materials can be made to show little macroscopic phase separation[15]. As a result, a type of material with better properties will be obtained.

Table 1 Sample preparation and composition[a]

Sample	f[b]	TEOS (wt%)[c]	Product appearance
PMMA/SiO_2	0	33	Opaque
P(MMA–MSMA)/SiO_2	0.1	33	Transparent
P(MMA–MSMA)/SiO_2	0.25	33	Transparent
P(MMA–MSMA)/SiO_2	0.5	33	Transparent
P(MMA–MSMA)/SiO_2	0.25	43	Transparent
PHEMA/SiO_2	/	33	Transparent
PHEMA/SiO_2	/	44	Translucent
PHEMA/SiO_2	/	50	Opaque
PHEMA/SiO_2	/	67	Opaque

[a] Preparation conditions: $[H_2O]/[TEOS] = 2$ (mol ratio), $[HCl]/[TEOS] = 0.06$ (mol ratio)

[b] $f = [MSMA]/\{[MMA] + [MSMA]\}$ (mol ratio)

[c] For PMMA/SiO_2 and P(MMA–MSMA)/SiO_2 hybrids, TEOS wt% = TEOS(g)/[TEOS(g) + monomers(g)]; for PHEMA/SiO_2 hybrids, TEOS wt% = TEOS(g)/[TEOS(g) + PHEMA(g)]

FT i.r. studies and extraction analysis of the hybrids: a chemical survey of the products

The appearances of polymers obtained are listed in *Table 1*. The optical transparency can be used as an initial criterion for the formation of a homogeneous phase of both inorganic and organic constituents. When the macroscopic phase separation in the system occurs, the products look opaque because the large domain size of the inorganic oxide will cause light scattering in the system. The sample of PMMA/SiO_2 is opaque, because no covalent interaction exists to retard the phase separation and the hydrogen bonding between the PMMA and the hydroxylated SiO_2 network is too weak to prevent the phase separation. On the other hand, all the samples of P(MMA–MSMA)/SiO_2 and the PHEMA/SiO_2 samples which have lower SiO_2 content are transparent monolithic glasses, because the strong interaction of covalent bonds between the two phases inhibits the macroscopic phase separation. However, with increasing the content of silica, the appearances of PHEMA/SiO_2 samples become opaque, as a result of the phase separation in the system.

*FT*i.r. spectra of PMMA/SiO_2, P(MMA–MSMA)/SiO_2 and PHEMA/SiO_2 samples are shown in *Figures 1* and *2*, respectively, along with spectra of the pure organic polymer. The *FT*i.r. bands around 1100 cm^{-1} which are associated with Si–O–Si linkages can be observed in all hybrid materials, and the presence of residual silanols on the silica networks, which are capable of hydrogen bond formation, is evidenced in the hybrids by the appearance of the hydroxyl peaks at the 3100–3600 cm^{-1} region. In addition, the differences between the spectra of hybrids are shown more clearly by subtracting the spectrum of the organic polymer, and these differences are shown in *Figure 3*, along with the spectrum of SiO_2 generated by the hydrolysis of pure

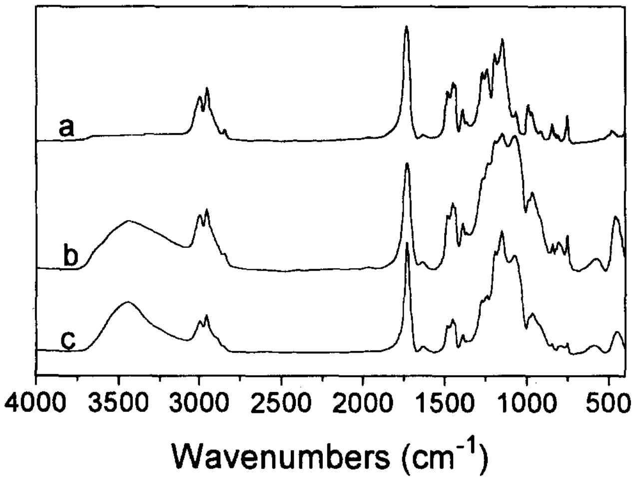

Figure 1 *FT*i.r. spectra of (a) PMMA, (b) PMMA/SiO_2 (33 wt% TEOS) and (c) P(MMA–MSMA)/SiO_2 ($f = 0.25$, 33 wt% TEOS)

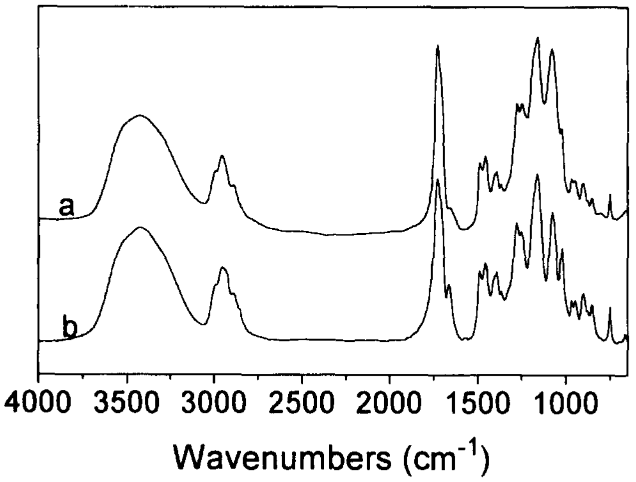

Figure 2 *FT*i.r. spectra of (a) PHEMA/SiO_2 (33 wt% TEOS) and (b) PHEMA

TEOS under the same conditions as in the preparation of hybrids.

The *FT*i.r. difference spectra of PMMA/SiO_2 and P(MMA–MSMA)/SiO_2 minus pure PMMA (*Figure 3b* and *Figure 3c*) are more complex than the *FT*i.r. spectrum of SiO_2 (*Figure 3a*), although the major bands around 1000–1100 cm^{-1} associated with Si–O–Si linkages are present. A derivative band which indicates a partial shift in the C=O stretch of hybrid from 1731 cm^{-1} to 1701 cm^{-1} also appears in the difference spectra, this being due to the presence of hydrogen bonds in the system[16]. In the difference spectrum of the P(MMA–MSMA)/SiO_2 sample minus pure PMMA (*Figure 3c*), a band of medium intensity at 1244, 1273 cm^{-1}, arising from the CH_2–Si group[17], can also be observed. The difference spectrum of the PHEMA/SiO_2 sample minus pure PHEMA is shown in *Figure 3d*. It is very similar to the spectrum of SiO_2, except for the partial shift of the C=O band from 1731 cm^{-1} to 1703 cm^{-1} resulted from the hydrogen bonds.

Solvent extractions of these three kinds of acrylic polymer/SiO_2 hybrid samples were performed for 2 days. Since there are three kinds of interactions between the two phases, a good solvent for the organic polymer should dissolve the unreacted polymer and leave the 'silica phase' as particles or gel.

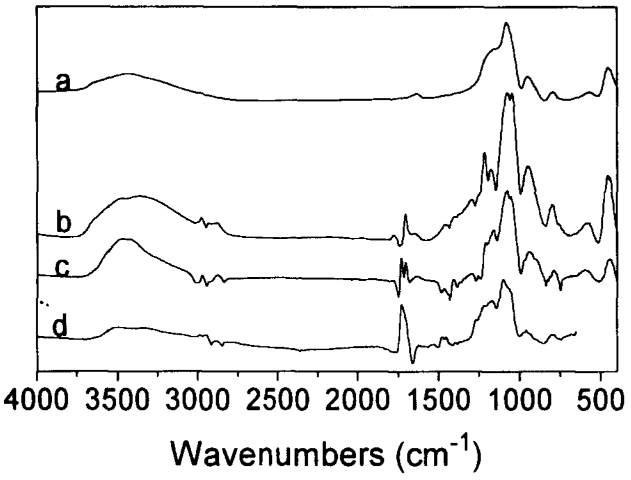

Figure 3 *FT*i.r. spectra of (a) SiO_2 prepared by hydrolysis of TEOS under conditions of [HCl]/[TEOS] = 0.06 (mol ratio) and [H_2O]/[TEOS] = 2 (mol ratio), (b) difference spectrum of *Figure 1b* (PMMA/SiO_2) minus *Figure 1a* (PMMA), (c) difference spectrum of *Figure 1c* (P(MMA–MSMA)/SiO_2) minus *Figure 1a*, and (d) difference spectrum of *Figure 2a* (PHEMA/SiO_2) minus *Figure 2b* (PHEMA)

If there are strong interactions or covalent bonds between the two phases, the part of the 'silica phase' will exceed the content of SiO_2, which can be tested through t.g.a. since essentially all the polymer components will have evolved from the sample before reaching 700°C in air or nitrogen atmosphere, and the remaining residue can reflect the silicone oxide content. The measured sol and gel fractions are summarized in *Table 2*. After solvent extraction for 2 days the PMMA/SiO_2 and PHEMA/SiO_2 samples broke into small opaque flakes, while the P(MMA–MSMA)/SiO_2 samples were intact and transparent. The percent of gel content of the PMMA/SiO_2 sample is 26.2 wt%, which is approximately comparable to the t.g. residue, while the percents of gel content of the P(MMA–MSMA)/SiO_2 samples are more than 90 wt%. The obvious difference of two systems is due to the effect of chemical bonding between silica and organic polymer, although the hydrogen bonds, which can be observed in the *FT* i.r. spectrum, exist between the C=O of PMMA and the silanols of the inorganic networks. The percent of gel content of PHEMA/SiO_2 is 34.7 wt%, which is a little more than that of the t.g. residue, but much less than that of P(MMA–MSMA)/SiO_2 samples. This may be due to the fact that the condensation between –OH of PHEMA and the silanols generated by hydrolysis of TEOS is much less effective than the condensation between the group –Si$(OH)_3$ generated by the hydrolysis of the trialkoxysilyl-functionalized PMMA and the silanols.

D.s.c. analysis of the hybrids: a determination of phase behaviour

All the hybrid materials were studied by d.s.c. analysis. The d.s.c. results of PMMA/SiO_2 and P(MMA–MSMA)/SiO_2 samples, shown in *Figure 4*, reveal an increase in the onset of the glass transition of PMMA in the composite, and a substantial increase in the breadth of the endothermic transition is also observed. Apparently, the PMMA/SiO_2 sample has similar d.s.c. behaviour to pure PMMA, but for the hybrid samples in the presence of MSMA (P(MMA–MSMA)/SiO_2), glass transition temperatures (T_gs) progressively shift to higher values with increasing silicon oxide content, and

Table 2 Extraction results of hybrids

Sample	Extraction solvent	Film appearance after extraction for 2 days	Wt% sol	Wt% gel	T.g. residue at 700°C (wt%)
PMMA/SiO_2 ($f = 0$. 33 wt% TEOS)	THF	Broken into fine particles	73.8	26.2	25.6
P(MMA-MSMA)/SiO_2 ($f = 0.1$, 33 wt% TEOS)	THF	Intact and transparent	6.3	93.7	29.8
P(MMA-MSMA)/SiO_2 ($f = 0.25$, 33 wt% TEOS)	THF	Intact and transparent	9.1	90.9	30.2
P(MMA-MSMA)/SiO_2 ($f = 0.5$, 33 wt% TEOS)	THF	Intact and transparent	4.8	95.2	32.8
PHEMA/SiO_2 (33 wt% TEOS)	DMF	Broken into fine particles	65.3	34.7	14.8

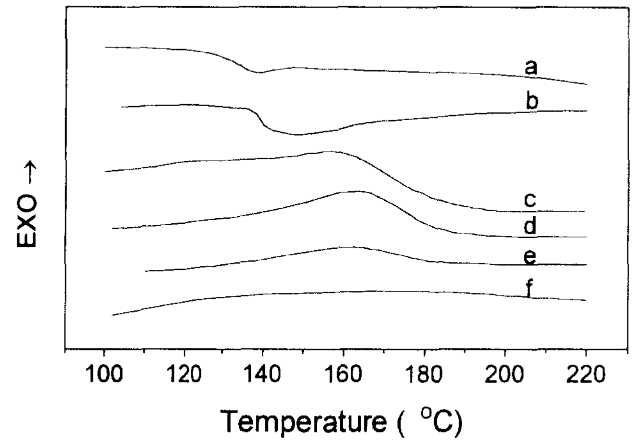

Figure 4 D.s.c. results for (a) PMMA, (b) PMMA/SiO_2 (33 wt% TEOS), (c) (MMA-MSMA)/SiO_2 ($f = 0.1$, 33 wt% TEOS), (d) P(MMA-PMSMA)/SiO_2 ($f = 0.25$, 33 wt% TEOS), (e) P(MMA-MSMA)/SiO_2 ($f = 0.5$, 33 wt% TEOS), (f) P(MMA-MSMA)/SiO_2 ($f = 0.25$, 43 wt% TEOS)

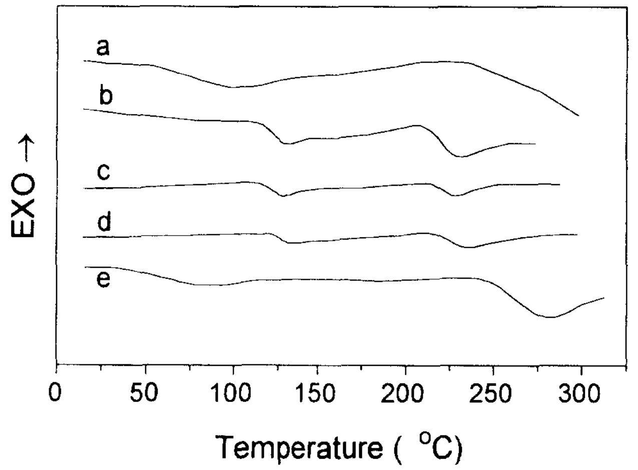

Figure 5 D.s.c. results for (a) PHEMA, (b) PHEMA/SiO_2 (33 wt% TEOS), (c) PHEMA/SiO_2 (44 wt% TEOS), (d) PHEMA/SiO_2 (50 wt% TEOS), (e) PHEMA/SiO_2 (67 wt% TEOS)

the T_g of the sample with 43 wt% silicon oxide content disappears. It is reasonable to surmise that the upward shift in, and the disappearance of, T_g reflect an increasing interaction between the silicon oxide phase and the polymer chains in terms of the formation of the P(MMA-MSMA)-Si-O-Si crosslinks. It is also noted that the breadth of the transition and the difference in heat capacity, ΔC_p, are different for all the samples and the T_g transition becomes unclear with increasing the content of 'coupling agent' MSMA. On the basis of established concepts in the field of composites[18], the T_g is expected to shift to the intermediate between the values of the homopolymers while ΔC_p is expected to decrease with increasing filler content. The breadth of transition and the decreasing ΔC_p of hybrid materials reflect less phase separation with increasing MSMA content.

The d.s.c. results of PHEMA/SiO_2 samples, shown in *Figure 5*, are much more complicated. Two transitions are observed in all hybrid samples. The T_g of PHEMA/SiO_2 samples is higher than that of the pure polymer, when the silicon oxide content is much lower. The first transition temperature decreases and the second one increases with continuously increasing silicon oxide content, and the difference of the two transition temperatures becomes larger in the samples with higher silicon oxide content (above 50 wt%). All of these show that the content of silicon oxide is a key factor influencing the compatibility of the polymer chains and the inorganic SiO_2 networks, with increasing the silicon oxide content, the more obvious phase separation will be observed. It is perhaps because the self-condensation of silanols generated by the hydrolysis of silicon alkoxide, especially in the system with higher silicon oxide content, is faster than the condensation of hydroxyl groups of PHEMA and the silanols, then, the silicon oxide networks with large size are easier to form in this system, finally resulting in phase separation.

Morphology of hybrids

The fracture surfaces of the hybrid samples were observed using SEM, which can give important information about the morphology of these materials. The SEM micrographs in *Figure 6* clearly show the miscibilization of P(MMA-MSMA)/SiO_2 hybrids, which bring about a morphological transformation from a dispersed particle microstructure of PMMA/SiO_2 hybrid (*Figure 6a*) to co-continuous phase (*Figure 6b* and *Figure 6c*). On the other hand, higher content of SiO_2 in the P(MMA-MSMA)/SiO_2 sample promotes a reversion of the morphology to disconnected particles (*Figure 7*). In this case, however, the dimensions of the particles are much smaller than in the hybrid without MSMA. The micrograph in *Figure 6d* illustrates also that the compatibilization results from the chemical reactions between the -OH groups of PHEMA and the silanols generated by hydrolysis of TEOS, and the PHEMA/SiO_2 hybrid, however, has a

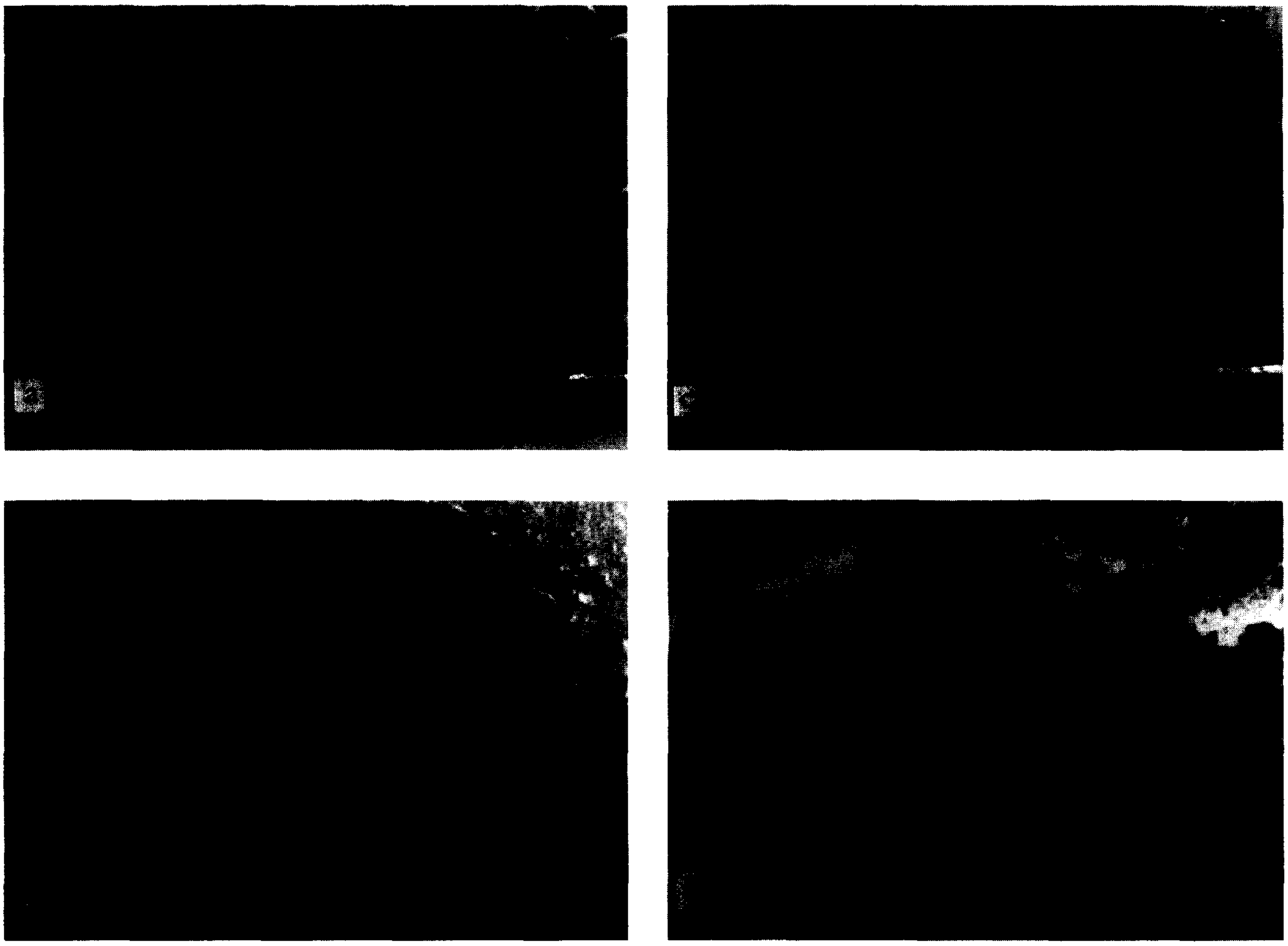

Figure 6 SEMs of fractured surfaces of the hybrids: (a) PMMA/SiO_2 (33 wt% TEOS), (b) P(MMA-MSMA)/SiO_2 ($f = 0.1$, 33 wt% TEOS), (c) P(MMA–MSMA)/SiO_2 ($f = 0.5$, 33 wt% TEOS), (d) PHEMA/SiO_2 (33 wt% TEOS)

rougher fracture surface than the P(MMA–MSMA)/SiO_2 hybrid.

In the above discussion, although the hydrogen bonds exist in the PMMA/SiO_2 system, the macroscopic phase separation still takes place. This phenomenon can be observed clearly by the SEM. A separate interface between the silica particles and PMMA matrix can be seen in *Figure 8*, which shows a magnified micrograph of *Figure 6a*. However, no phase separation is observed in the P(MMA–MSMA)/SiO_2 hybrids and the hybrid has a smoother fracture surface with increasing MSMA content (*Figure 6b* and *Figure 6c*). So it is more advantageous to use such a trialkoxysilyl functional group in the preparation of hybrids because of the formation of covalent interactions which prevent the phase separation between the organic polymer chains and the inorganic silica networks.

Figure 7 SEM of fractured surfaces of the P(MMA–MSMA)/SiO_2 hybrid ($f = 0.25$, 43 wt% TEOS)

Figure 8 SEM of fractured surfaces of the PMMA/SiO_2 hybrid, which shows a magnified micrograph of *Figure 6a*. The interface between silica particles and the polymer matrix can be observed clearly in this micrograph

CONCLUSION

Hybrid materials have been prepared by the *in situ* sol–gel process of TEOS in the presence of trialkoxysilyl-functionalized, hydroxyl-functionalized and unfunctionalized methyl acrylic polymers, and the effects of interactions between the silica networks and the polymer phase on phase behaviour and morphology of the resulting hybrids have been investigated. The trialkoxysilyl-functionalized P(MMA–MSMA)/SiO_2 hybrids, especially, have been successfully prepared without the trialkoxysilyl-functionalized polymer precursor, which can lead to cross-linking with moisture while exposed to air, and these hybrids are found to have better optical transparency.

In the PMMA/SiO_2 hybrid, the formation of hydrogen bond between the silica and the carbonyl of PMMA were observed by *FT*i.r., and the solvent extraction result shows that almost all the PMMA chains are physically entrapped within the SiO_2 network, the gel content being approximately equal to the actual SiO_2 content, which can be determined by t.g. However, the solvent extraction results of P(MMA–MSMA)/SiO_2 hybrids and PHEMA/SiO_2 hybrid, which have covalent bonds between the two phases, show that a significant fraction of polymer chains are covalently bonded to the silica networks, resulting in little phase separation. On the other hand, the percent of gel content in the P(MMA–MSMA)/SiO_2 hybrid is much higher than that in the PHEMA/SiO_2 hybrid.

The d.s.c. behaviour of the PMMA/SiO_2 hybrid is similar to that of pure PMMA, but the d.s.c. results of P(MMA–MSMA)/SiO_2 samples reveal an increase in T_g of PMMA and the breadth of transition, which show the compatibility between the two phases due to the formation of covalent interactions. The d.s.c. results of PHEMA/SiO_2 hybrids are more complicated, showing two T_g transitions, and it is shown that the SiO_2 content is an important factor in influencing the shift of the T_g transition.

The microstructure morphologies of hybrids are observed by SEM. An obvious interface between SiO_2 particles and polymer matrix can be seen in the PMMA/SiO_2 hybrid. However, the introduction of the 'coupling agent' MSMA, such as P(MMA–MSMA)/SiO_2 hybrid, prevents the formation of silica particles, thus resulting in a homogeneous material. On the other hand, the PHEMA/SiO_2 sample has a rougher fracture surface than the P(MMA–MSMA)/SiO_2 hybrids, with no dispersed SiO_2 particles formed.

By comparison of the effects of different interactions on the properties of hybrids, it can be concluded that the interfacial interaction between silica networks and polymers can be improved by use of trialkoxysilyl-functionalized polymer, and that the hydrogen bonds and the chemical bonds formed by condensation between the hydroxyl groups and the silanols and two important sources of interactions in the hybrids.

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REFERENCES

1 Hench, L. L. and West, J. K. *Chem. Rev.* 1990, **90,** 33
2 Novak, B. M. *Adv. Mater.* 1993, **5,** 422
3 Huang, H. H. and Wilkes, G. L. *Macromolecules* 1987, **20,** 1322
4 Huang, H. H. and Wilkes, G. L. *Polym. Bull.* 1987, **18,** 455
5 Mascia, L. and Kioul, A. *Polymer* 1995, **36,** 3649
6 Fujita, M. and Honda, K. *Polym. Commun.* 1989, **30,** 200
7 Noell, J. L. W., Wilkes, G. L., Mohanty, D. K. and MacGrath, J. E. *J. Appl. Polym. Sci.* 1990, **40,** 177
8 Mauritz, K. A. and Ju, R. *Chem. Mater.* 1994, **6,** 2269
9 Huang, Z. H. and Qiu, K. Y. *Polym. Bull.* 1995, **35,** 607
10 Wei, Y., Bakthavatchalam, R. and Whitecar, C. K. *Chem. Mater.* 1990, **2,** 337
11 Coltrain, B. K., Landry, C. J. T., O'Reilly, J. M., Chamberlain, A. M., Rakes, G. A., Sedita, J. S., Kelts, L. W., Landry, M. R. and Long, V. K. *Chem. Mater.* 1993, **5,** 1445
12 Landry, C. J. T., Coltrain, B. K., Wesson, J. A., Zumbulyadis, N. and Lippert, J. L. *Polymer* 1992, **33,** 1496
13 Varma, I. K., Tomar A. K. and Anand, R. C. *J. Appl. Polym. Sci.* 1987, **33,** 1377
14 Landry, C. J. T., Coltrain, B. K., Landry, M. R., Fitzgerald, J. J. and Long, V. K. *Macromolecules* 1993, **26,** 3702
15 Wei, Y., Bakthavatchalam, R., Yang, D. and Whitecar, C. K. *Polym. Prep.* 1991, **32,** 503
16 Sakai, H. and Imamura, Y. *Bull. Chem. Soc. Jpn.* 1980, **53,** 1749
17 Smith, A. L. *Spectrochim. Acta* 1960, **16,** 87
18 Lipatov, Y. S. 'Physical Chemistry of Filled Polymers, International Polymer Science and Technology (Monography No. 2)', Rubber and Plastics Research Association, Shrewsbury, England, 1977, ch. 3