In situ polymerization of tetraethoxysilane in polymers: chemical nature of the interactions

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The formation of molecular composites by the *in situ* polymerization of tetraethoxysilane in various organic polymers has been studied. The results show that highly homogeneous, transparent composites can be formed for polymers such as poly(methyl methacrylate), poly(vinyl acetate), poly(vinyl pyrrolidone), and poly(*N*,*N*-dimethylacrylamide). These composites have improved mechanical properties and increased solvent resistance. Strong interactions between the SiO_2 networks and these polymers were observed, and the data suggest hydrogen bonding between residual hydroxyls on the SiO_2 and carbonyl groups on the polymer chains as the major source of these interactions.

(Keywords: interactions; composites; polymerization; tetraethoxysilane)

INTRODUCTION

It has been previously reported[1] that transparent, free-standing films can be obtained when tetraethoxysilane (TEOS) is polymerized *in situ* in a poly(methyl methacrylate) (PMMA) binder under certain conditions. These molecular composites exhibit excellent mechanical properties at temperatures extending far above the glass transition temperature (T_g) of PMMA, consistent with a reinforcing, interacting inorganic network that has not phase separated from the organic polymer. The morphology, observed by transmission electron microscopy (TEM), and the mechanical properties, obtained from dynamic mechanical spectroscopy (d.m.s.), were discussed as a function of sample preparation conditions. It was shown that the morphology and degree of phase separation between the SiO_2 and the PMMA are extremely important in determining the ultimate material properties. The critical factors influencing the morphology are the pH at which polymerization of the TEOS proceeds and the temperature at which the solution is coated.

These results suggest that strong interactions exist between the SiO_2 and the PMMA when prepared from TEOS under acidic conditions. It is the objective of this work to elucidate the origin of these interactions in view of designing new molecular composites and controlling their morphology.

In this study, several organic polymers, none of which was capable of covalently bonding with the polymerizing alkoxide, were used as the binder in which TEOS was polymerized. Although aspects of each are discussed, the focus will be primarily on the PMMA composites. Raman, *FT*i.r., d.m.s., and ^{29}Si n.m.r. were utilized to characterize the origin of these interactions. Further insight was gained from extraction of the soluble, organic component from several samples and subsequent chemical composition analysis of the soluble (sol) and insoluble (gel) fractions.

EXPERIMENTAL

Materials

The organic polymers are presented in *Figure 1*; their sources and some molecular weight data are listed in *Table 1*. TEOS was obtained from Fluka. All reagents and solvents were reagent grade and were used as received unless otherwise noted.

In general, the samples were prepared as previously described[1] by dissolution of the organic polymer in THF, or other appropriate solvent, at a concentration of *ca.* 20 wt%. TEOS was added directly to the solution under continuous agitation. Then a stoichiometric amount of water per alkoxide (4 moles based on Si), either as 0.15 M HCl or 1 M NH_4OH, was added, and the solution was stirred for 16 h at ambient temperature. The free-standing films were prepared by knife-coating the solutions onto sheets of Kapton-H mounted on a temperature-controlled coating block. These were then dried and cured at elevated temperatures under vacuum. All samples are listed in *Table 2*.

The extractions were performed by immersing the composite, which had been dried and cured under vacuum at 160°C for at least 15 h, in an excess (> 100 ml solvent per g composite) of an appropriate good solvent. This process required several days at ambient temperature

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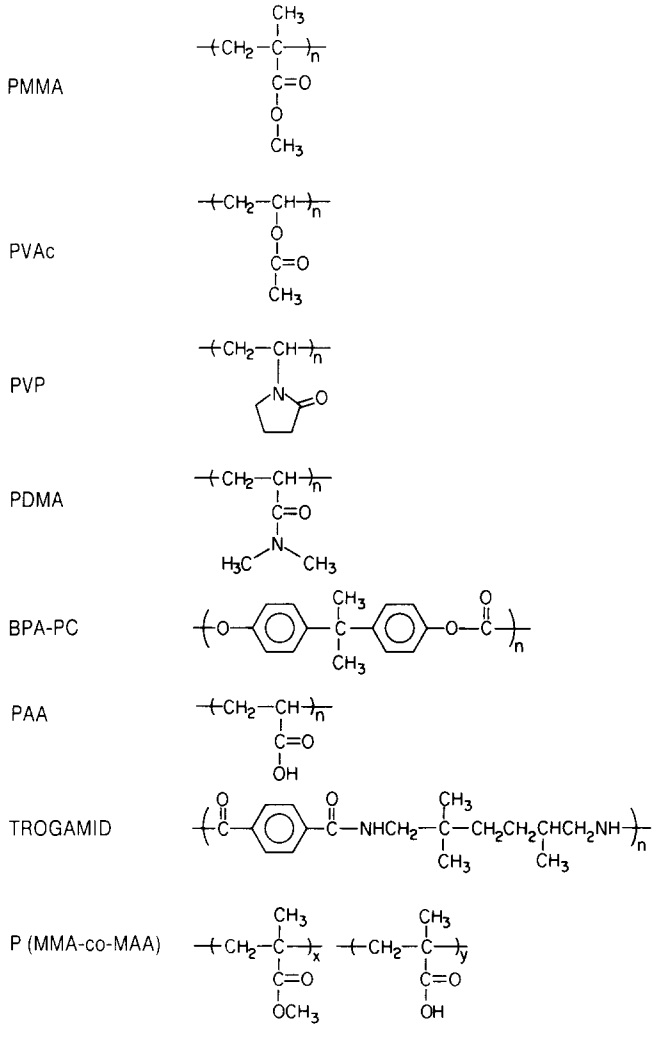

Figure 1 Molecular structures of the organic polymers used in the composites

Table 1 Organic polymers used

Polymer	Abbreviation	Source	Molecular weight
Poly(methyl methacrylate)	PMMA	Plexiglass V(811)-100 Rohm & Haas Co.	$\bar{M}_w = 73k^a$ $\bar{M}_n = 41k^a$
Bisphenol-A polycarbonate	BPA-PC	Lexan General Electric	$\bar{M}_w = 49k^a$ $\bar{M}_n = 23k^a$
Poly(vinyl acetate)	PVAc	Polysciences	
Poly(vinyl pyrrolidone)	PVP	Polysciences	$40k^b$
Poly(acrylic acid)	PAA	Aldrich (37 wt% in water)	
Poly(*N*,*N*-dimethyl acrylamide)	PDMA	Polysciences	
Poly(methyl methacrylate-co-methacrylic acid) (10 mol% MAA)	P(MMA-co-MAA)	Eastman Kodak Company	
Nylon-Trogamid-T	Trogamid	Scientific Polymer Products	

[a] As determined by s.e.c. in THF, given in polystyrene equivalents
[b] Manufacturer's specification

and was followed by vigorous boiling in the solvent for 2 h. The sol and gel fractions were separated by filtration. Each fraction was dried under vacuum at progressively higher temperatures, the highest being 120°C for 8 h.

One sample of 50/50 wt% TEOS/PMMA in THF, with a stoichiometric amount of 0.15 M HCl, was 'gelled in solution' in a closed container at 60°C; the gel time was on the order of 200 h. The sol and gel fractions were then extracted by immersing the sample in THF at ambient temperature, followed by filtration and drying as described above.

Measurements

Differential scanning calorimetry (d.s.c.) was performed with a DuPont 990 thermal analyser, equipped with a data analysis program from Laboratory Micro Systems, Inc. The heating rate was 20°C min^{-1}. The glass transition temperature, T_g, is taken as the onset of the change in heat capacity.

Dynamic mechanical measurements (d.m.s.) were obtained using a Rheovibron DDV-II dynamic tensile tester (Toyo Measuring Instruments Ltd, Japan) automated by IMASS Inc. The data were obtained at frequencies of 1.1, 11.0 and 110.0 Hz, using a heating rate of 1.5°C min^{-1}.

*FT*i.r. spectra were obtained using a Nicolet 5DXB spectrometer with 4 cm^{-1} resolution. Samples for *FT*i.r. were prepared by casting the solutions directly onto KBr discs at room temperature and heating for 2–3 min under heat lamps to drive off the solvent. Samples for *FT*i.r. of the gel fractions from the solvent extractions were prepared in the form of KBr pellets. Raman spectra were obtained from knife coatings of the THF solutions forming free-standing films; all Raman samples were dried at 90°C for 3–5 days. Raman spectra were excited with 568.1 nm excitation from a SP Kr^+ laser (0.15 W) and detected with a SPEX 1877 Triple-Mate spectrograph and an EG&G PARC model 1420 Reticon intensified diode array detector at 4 cm^{-1} resolution.

^{29}Si n.m.r. spectra were obtained at 39.7 MHz on a 4.7 T home-built n.m.r. spectrometer, designed specifically for multinuclear solid state studies. The samples were either punched into discs or ground. Magic angle spinning (MAS) at 4 kHz was used to acquire all data. Cross-polarization techniques, normally employed for sensitivity enhancement were not used, in order to obtain reliable data on the intensities of the various spectral components. This limited the S/N of the spectra. Several days of signal averaging were required for the *FT*/MAS spectra.

Elemental analyses were performed by combustion analysis (for N, C and H), inductively coupled plasma (for Si), and neutron activation analysis (for Si and O)

Table 2 Sample preparation and compositions

Sample	Coating conditions		Film appearance
	T(°C)	Solvent	
PMMA/TEOS 50/50 acid	≳30	THF	Transparent
PMMA/TEOS 50/50 acid	≈11	THF	Opaque
PMMA/TEOS 50/50 base	≳30	THF	Opaque
PMMA/TEOS 25/75 base	≳30	THF	Opaque
PVAc/TEOS 50/50 acid	≳30	THF	Transparent
BPA-PC/TEOS 50/50 acid	≳30	THF	Opaque
PVP/TEOS 50/50 acid	≳30	EtOH	Transparent
PAA/TEOS 50/50 acid	≳30	EtOH	Opaque
P(MMA-co-MAA) 50/50 acid	≳30	THF	Transparent
P(MMA-co-MAA) 50/50 base	≳30	THF	Opaque
PDMA/TEOS 50/50 acid	≳30	DMF	Transparent
Trogamid/TEOS 50/50 acid	≳30	DMF	Opaque

on the sol and gel fractions obtained by extraction. Additional information on the composition of the gel fractions was provided by *FT*i.r. The fractions, as well as some composites, were also studied by thermal gravimetric analysis (t.g.a.), using a heating rate of 10°C min^{-1} under both nitrogen and air atmospheres. Size exclusion chromatography (s.e.c.) was performed on the sol fractions in THF.

Quasi-elastic light scattering (q.l.s.) was performed with a Brookhaven Instruments Corp. BI 240 goniometer and BI 2030 correlated (128 channel). An Innova 90-4 argon ion laser (Coherent Radiation Corp.) at 514.5 nm was used as a light source. The sample cell was thermostated at 20°C during the measurements. The autocorrelation functions were recorded at several scattering angles between 45° and 135°. The first cumulant, Γ, of the correlation function obtained by cumulant analysis was used to calculate the apparent diffusion coefficient, $D = \Gamma/q^2$, where q is the scattering wave vector

$$q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}$$

and n is the refractive index of the scattering medium. The apparent particle diameter, d, was then calculated from the Stokes-Einstein relation

$$d = kT/6\pi\eta D$$

where η is the solvent viscosity and kT has the usual meaning.

RESULTS AND DISCUSSION

It has previously been demonstrated[1] that optimal mechanical properties are obtained when the organic polymers and inorganic SiO_2 networks show minimal phase separation. Inherently, these two polymers are immiscible. It was postulated that a strong interaction between the PMMA and the hydroxylated SiO_2 is necessary in order to prevent macroscopic phase separation. The question posed herein is what chemical properties of the two polymers and what processing conditions are critical in minimizing phase separation of an organic polymer and a growing SiO_2 network.

In the first section, preliminary results on the optical transparency of composites prepared from other organic polymers and TEOS are discussed. The mechanical properties for one of these composites, which is optically transparent, are also shown. In the second section, an attempt is made to understand the underlying chemistry resulting in homogeneous composites by utilizing several spectroscopic and analytical techniques, primarily on the PMMA/TEOS and PVAc/TEOS composites.

Polymer composites showing optical transparency and a high modulus above T_g: a preliminary survey

Various organic polymers, none having functional groups capable of forming covalent bonds with the polymerizing TEOS, have been blended with TEOS and solution-coated under conditions similar to those utilized to obtain the transparent PMMA/TEOS films. These organic polymers are listed in *Table 1*. The coating conditions and film appearances are listed in *Table 2*. Optical transparency is used as an initial criterion for the formation of a homogeneous phase composition of the inorganic and organic constituents; when the domain size of the inorganic oxide is substantially smaller than *ca.* 1000 Å scattering will not occur. Under the conditions specified herein, clear films were obtained for blends of TEOS with PMMA, PVAc, PVP, P(MMA-co-MAA) (10 mol% MAA) and PDMA.

For the limited number of organic polymers surveyed, it is suggested that the polymers which result in optically transparent composites with polymerized TEOS are those capable of hydrogen bond formation with residual hydroxyls present on the surface of the SiO_2 formed under acidic conditions. Hydrogen bonding often occurs between polymers and hydroxylated silica at low pH. In basic media, the silica surface retains a sufficient concentration of ionic charges to inhibit hydrogen bond formation[2]. Examination of the molecular structures presented in *Figure 1* reveals that each organic polymer which formed a clear composite with TEOS has a functional group which is a hydrogen bond acceptor, such as a carbonyl. Many of these have shown some degree of miscibility with other hydrogen bond donating polymers such as poly(vinyl phenol)[3,4]. Although the other polymers also contain carbonyl groups, the situation seems to be more complex. Both the PAA and the Trogamid contain a hydrogen donating moiety adjacent to the carbonyl. This may increase the amount of self-association present within the polymer itself, thus decreasing the amount of possible interactions with the polymerizing TEOS. Other factors, such as the role of solvent in the gelation kinetics of the inorganic and solvent induced phase separation, may also be significant in some of these systems. These results are far from complete and further work is currently under way in this area.

The PVAc/TEOS composite, prepared with 50 wt% TEOS under acidic conditions and solution-coated above 30°C, was studied by d.s.c. and d.m.s. The films were cured at 150°C for 14 h under vacuum. The d.s.c. results, shown in *Figure 2*, reveal only a slight increase in the onset of the glass transition of PVAc in the composite. However, a substantial increase in the breadth of the endothermic transition is observed. The same phenomenon was previously noted for the PMMA/TEOS, acid catalysed samples[1]. The d.m.s. results, shown in *Figure 3*, are reminiscent of the properties of the transparent

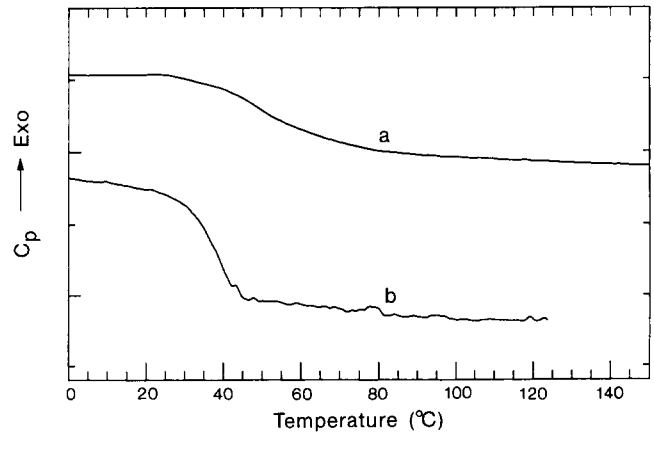

Figure 2 D.s.c. results for (a) a PVAc/TEOS 50/50 composite prepared under acidic conditions and coated at 30°C and (b) PVAc. Cured at 150°C for 14 h under vacuum

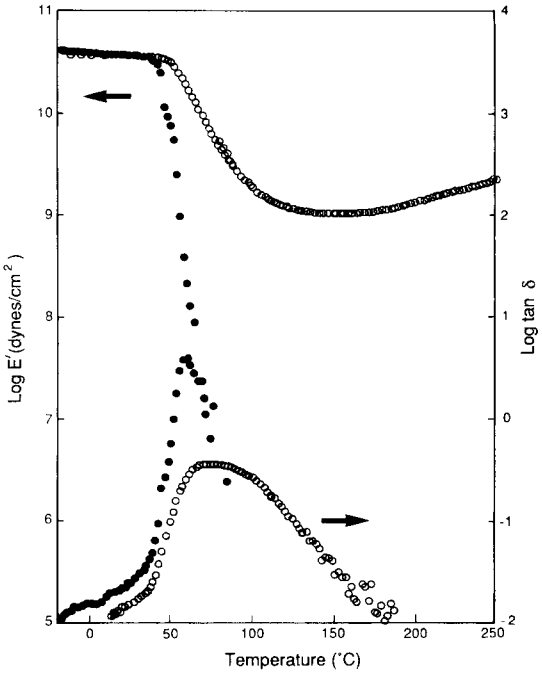

Figure 3 D.m.s. (11 Hz) results for (●) PVAc and for (○) PVAc/TEOS 50/50 composite prepared under acidic conditions and coated at 30°C. Cured at 150°C for 14 h under vacuum

PMMA/TEOS material: a slight increase in the T_g, a lowering and broadening of the tan δ peak, and the presence of a rubbery plateau having a modulus greater than 10^9 dynes cm^{-2} are observed.

Determination of the origin of the apparent miscibility in these composites

FT*i.r. and Raman results.* Raman spectra of the PMMA/TEOS 50/50 wt% composites, prepared under various conditions are shown in *Figure 4*. Few differences from PMMA are apparent except for the loss of the 914 cm^{-1} solvent band and an increase in intensity at 970 cm^{-1} in the base catalysed sample. A general decrease in intensity of the 1733 cm^{-1} C=O bands is observed in all the composites relative to PMMA. More subtle differences are observed by subtracting the PMMA spectrum from those of the composites, as shown in *Figure 5*. These spectra will be discussed in further detail below, in context with the *FT*i.r. difference spectra of the same materials.

*FT*i.r. spectra of the 50/50 wt% composites of TEOS with BPA-PC, PMMA (acid catalysis) and PMMA (base catalysis) are shown in *Figures 6–8* along with spectra of the organic polymer alone. *FT*i.r. bands around 1100 cm^{-1} associated with Si–O–Si linkages can be observed in all composites. *Figure 7a* shows the presence of considerable OH, as indicated by a broad band around 3400 cm^{-1}. Additionally, a shoulder on the low frequency side of the C=O band at 1733 cm^{-1} is observed for the clear, acid catalysed PMMA/TEOS composite. This feature is not observed in the other samples. Finally, the 1100–1300 cm^{-1} Si–O region of *Figure 7a* is broader and more ill-defined than in the other spectra. Again, the differences between the spectra of the composites are shown more clearly by subtracting the spectrum of the organic polymer. These differences are shown in *Figure 9b–d*, along with spectra of hydrolysed and neat TEOS.

Polycarbonate/TEOS: a phase separated composite. The first difference spectrum in *Figure 9b*, for the acid catalysed 50/50 wt% mixture of BPA-PC and TEOS, clearly shows that the polycarbonate spectrum subtracts

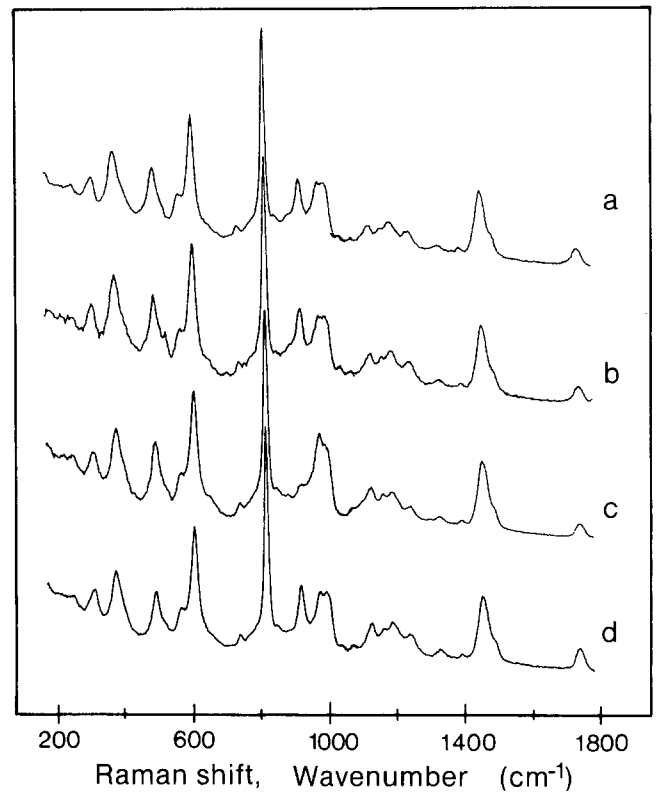

Figure 4 Raman spectra of (a) 50/50 wt% PMMA/TEOS acid catalysed composite, coated at 30°C and dried at 90°C for 63 h; (b) same as (a) except coated at 11°C; (c) same as (a) except base catalysed; and (d) PMMA

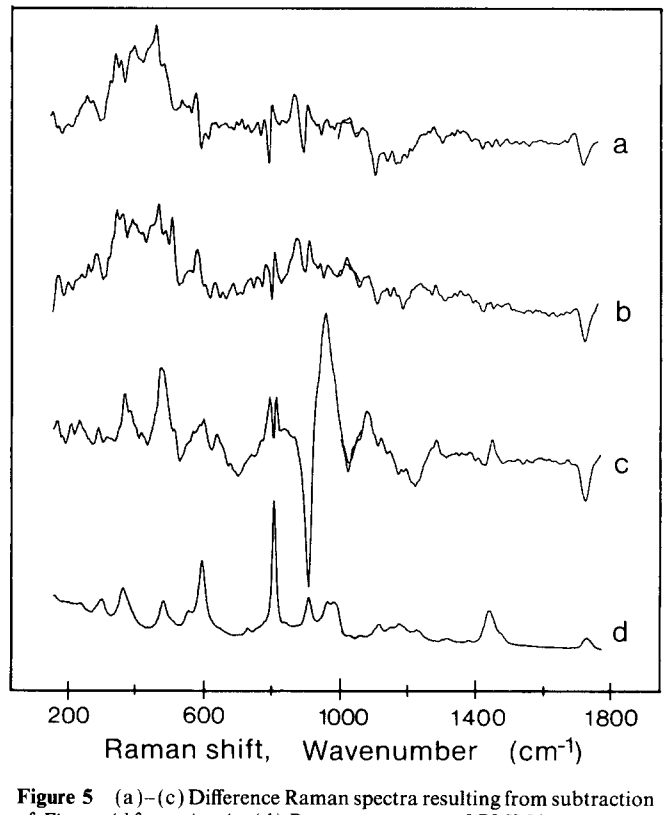

Figure 5 (a)–(c) Difference Raman spectra resulting from subtraction of *Figure 4d* from *4a–4c*. (d) Raman spectrum of PMMA

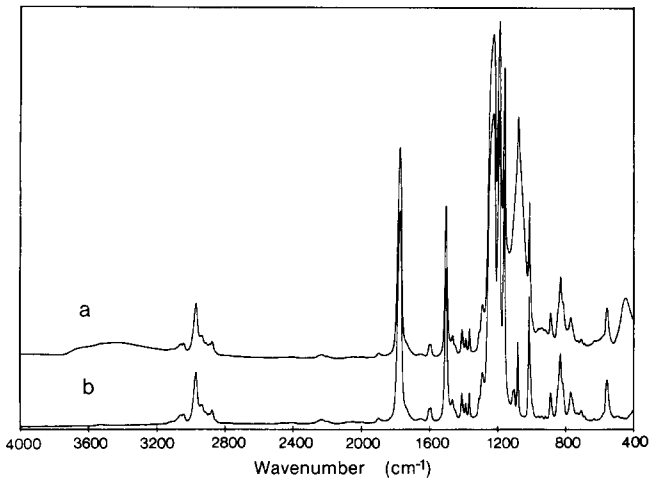

Figure 6 *FT*i.r. spectra of (a) 50/50 wt% BPA-PC/TEOS acid catalysed composite and (b) BPA-PC

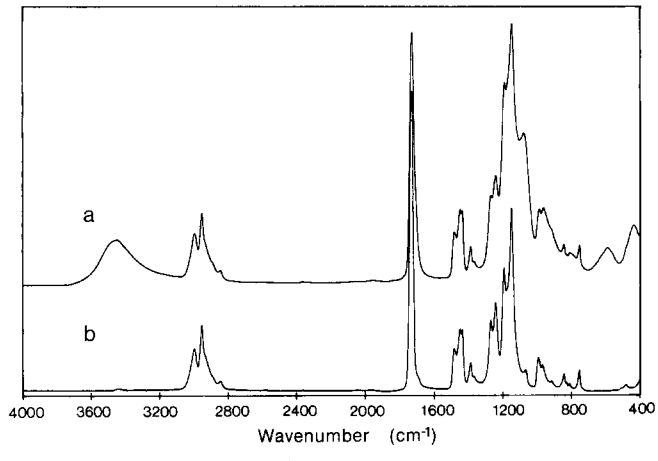

Figure 7 *FT*i.r. spectra of (a) 50/50 wt% PMMA/TEOS acid catalysed composite and (b) PMMA

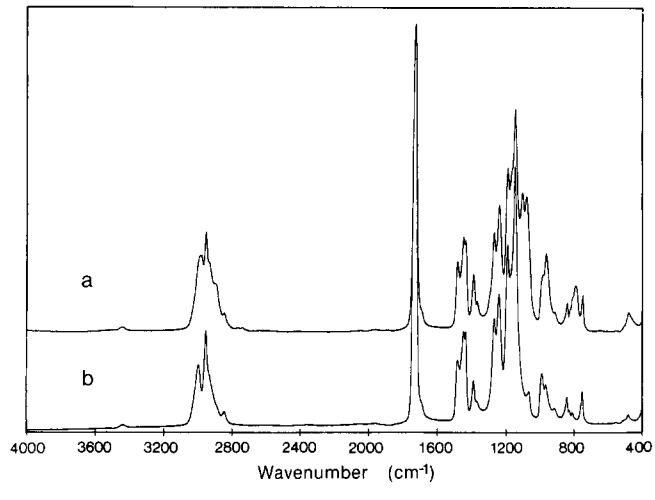

Figure 8 *FT*i.r. spectra of (a) 50/50 wt% PMMA/TEOS base catalysed composite and (b) PMMA

completely from the composite. The resultant spectrum is that of hydrolysed TEOS (essentially that of SiO_2), although some residual OH is observed in the composite. This suggests that (1) there is no interaction between hydrolysed TEOS and polycarbonate and (2) the resultant film is an incompatible mixture of domains of polycarbonate and partially hydrated SiO_2.

Poly(methyl methacrylate)/TEOS, acid catalysed: a homogeneous composite. The *FT*i.r. difference spectrum (*Figure 9c*) of acid catalysed PMMA/TEOS minus PMMA is clearly different from either hydrolysed TEOS (*Figure 9a*) or unhydrolysed TEOS (*Figure 9e*), although the major bands associated with SiO_2 (*Figure 9a*) are present. Other major features include a partial shift in the C=O stretch of the composite from 1733 cm^{-1} to 1710 cm^{-1}, which is shown by a derivative band in the difference spectrum, the indication of substantial hydration in the 3465 cm^{-1} band, and a band at 1170–1200 cm^{-1} which is not observed in any other sample. These results, coupled with the inability to obtain complete subtraction of PMMA even though all bands are less than 0.5 absorbance units, indicate interactions between the components of the composite.

Although not shown here, the *FT*i.r. spectrum of a composite of 50/50 wt% PVAc/TEOS prepared under acid conditions was obtained. Similar to the results obtained for the compatible PMMA/TEOS composite, the difference spectrum obtained after subtraction of PVAc shows a partial shift of the C=O band from 1733 to 1710 cm^{-1}, an intense, broad band at 1170–1190 cm^{-1} which is more intense than the 1080 cm^{-1} Si–O–Si absorption, a large OH absorption at 3450 cm^{-1}, and shifts in the OAc vibrations in the composite relative to pure PVAc.

The Raman difference spectrum of the acid catalysed

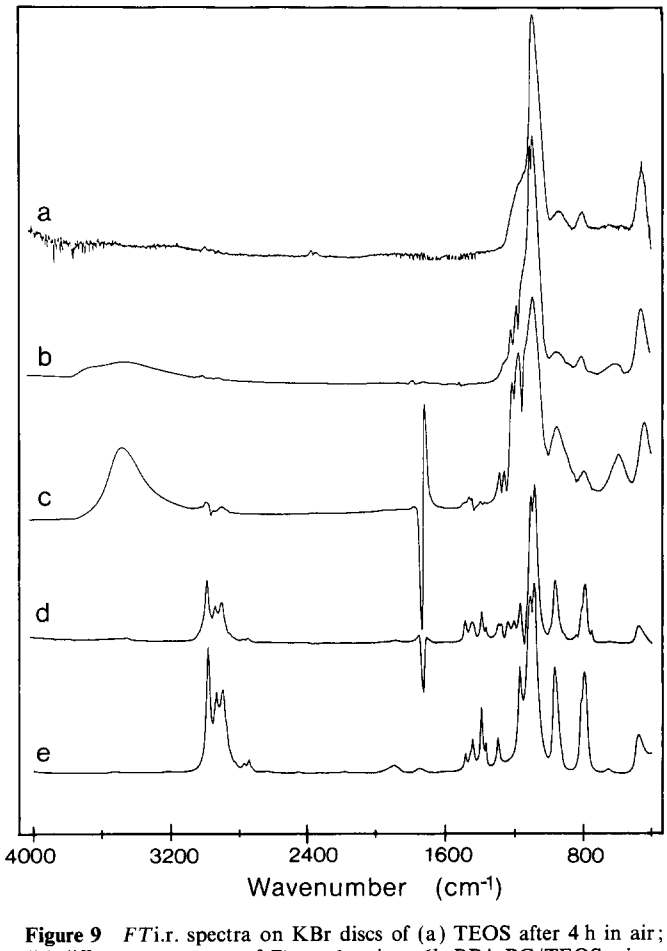

Figure 9 *FT*i.r. spectra on KBr discs of (a) TEOS after 4 h in air; (b) difference spectrum of *Figure 6a* minus *6b*, BPA-PC/TEOS minus BPA-PC; (c) *Figure 7a* minus *7b* PMMA/TEOS (acid) minus PMMA; (d) *Figure 8a* minus *8b* PMMA/TEOS (base) minus PMMA; (e) neat TEOS

PMMA/TEOS composite coated from THF at 30°C (clear film) also shows a partial shift of the C=O from that of PMMA, as shown by the derivative difference band at 1710–1733 cm^{-1} (*Figure 5a*). Taken together, these *FT*i.r. and Raman spectra of the clear composite films suggest a strong interaction between the ester C=O and hydrolysed TEOS. Similar shifts have been observed from a non-hydrogen-bonded C=O at 1733 cm^{-1} to a hydrogen-bonded carbonyl at 1710 cm^{-1} for compatible blends of acrylates and acetates with poly(vinyl phenol)[5–8]. Additionally, Sakai and Imamura have studied the adsorption of PMMA on silica particles and observed a frequency shift from 1736 to 1712 cm^{-1} and line broadening which they associated with hydrogen bonding[9]. It therefore seems reasonable to suggest a relatively strong hydrogen bonding interaction of the ester group with residual OH groups on the heavily hydrated SiO_2 formed when the polymerization of TEOS is carried out in acidic media.

An alternative explanation is partial hydrolysis of the PMMA ester to methacrylic acid. This is suggested because a copolymer of methyl methacrylate and methacrylic acid shows the same C=O features, i.e., an ester peak at 1733 cm^{-1} with a shoulder at 1710 cm^{-1}, as does the PMMA/TEOS composite. However, the fact that the same shift occurs in PVAc/TEOS where hydrolysis would produce acetic acid which would be removed during drying, argues against this explanation. It has been suggested[10] that the C=O envelope in P(MMA-co-MAA) also results from an H-bonding interaction, i.e., that the 1733 cm^{-1} band results from the C=O of free ester and acid, while the 1710 cm^{-1} results from H-bonded ester and acid. If this is an appropriate interpretation, then a comparison of the relative intensities of the 1733 and 1710 cm^{-1} bands in the PMMA/TEOS compatible system predicts that 15–20% of the ester groups are H-bonded.

The presence of the intense, broad band around 1170 cm^{-1} in the *FT*i.r. of compatible PMMA/TEOS and PVAc/TEOS composites is somewhat puzzling. It is not consistent with a Si–C linkage (for which a sharp band is observed at 1255–1260 cm^{-1} as, for example, in the case of methyltriethoxysilane and its hydrolysis products) or with a Si–O–C bond (typically observed at 1080–1120 cm^{-1})[11]. We tentatively suggest that the band may be associated with an H-bonded Si–OH group.

The Raman difference spectrum (*Figure 5a*) provides no evidence regarding such an H-bonded silicate structure but does give information about the extent of reaction of the TEOS. Previous work[12] has shown that the bands associated with partially condensed intermediates in the polymerization of tetramethoxysilane (TMOS) can be isolated and identified. Raman bands at 673–730 cm^{-1} are associated with monomeric and partially hydrolysed TMOS monomers (Q^0 species; the superscript refers to the number of silicon substituted oxygens attached to the silicon of interest), 608 and 586 cm^{-1} with end-group Si–O–Si species (Q^1), 525 cm^{-1} with Si–$(O–Si)_2$ species (Q^2), 484 cm^{-1} with Si–$(O–Si)_3$ species (Q^3), and 432 cm^{-1} with the fully formed SiO_2 network (Q^4). *Figure 5a* shows mostly Q^3 and Q^4. It is given that, quantitatively, the relative amounts of Q^1 through Q^4 present in the samples will vary with cure conditions as will be studied with ^{29}Si n.m.r. and discussed later.

Interestingly, the Raman difference spectrum (*Figure 5b*) of the same composite coated at 11°C, which results in an opalescent film, is essentially identical to that in *Figure 5a* within the noise of the spectral subtraction. There is a hint of less of a derivative shape to the C=O region (1710–1740 cm^{-1}) difference spectrum (suggesting less H-bonding), but the change between *Figure 5a* and *Figure 5b* is less than the noise.

Poly(methyl methacrylate)/TEOS, base catalysed: incomplete hydrolysis. A comparison of the *FT*i.r. spectra shown in *Figure 9d* (PMMA/TEOS, base catalysed) and *Figure 9e* (unhydrolysed TEOS) suggests that a major component of the composite is unreacted TEOS. However, some hydrolysis has taken place, as evidenced by the fact that the ratio of the intensity of the $-OC_2H_5$ absorptions to the 1080 cm^{-1} Si–O band is less in the composite than in neat TEOS. Also, because the C=O band must be over-subtracted to remove other PMMA bands, it appears that there is some interaction between the components of the composite. However, this interaction does not appear to result from hydrogen bonding as in the case of acid hydrolysis.

The Raman difference spectrum (*Figure 5c*) of this composite shows a decrease in retained solvent compared to the acid catalysed samples and pure PMMA; a negative THF peak is observed at 914 cm^{-1}. Unfortunately, polarization scrambling in the opaque, base-catalysed sample results in changes in relative band intensities. Therefore, no conclusions regarding the degree of condensation of the SiO_2 network can be drawn at this time. Once again ^{29}Si n.m.r. will shed light on this question.

The vibrational spectroscopy results taken together suggest that polymerization of the TEOS with basic water generates only a weakly hydrolysed silicate intermediate with a large amount of TEOS remaining, and that the film formed from a mixture of this material and PMMA phase separates into TEOS-rich and PMMA-rich domains with only weak interaction. However, acidic catalysis of TEOS in the presence of PMMA or PVAc results in a homogeneous, interpenetrating network of hydrated silica hydrogen bonded to the ester groups.

^{29}Si n.m.r. results. Three composites were examined. Two are PMMA/TEOS (50/50 by wt) acid catalysed and cast from THF at 30°C or 9°C. The third is base catalysed, cast from THF at 30°C. The base catalysed sample was prepared in such a way as to ensure a Si content of at least 10 wt% in the final composite. All samples were cured at 150°C for 18 h under vacuum. The *FT*/MAS spectra are shown in *Figures 10–12*.

The peaks for pure acid and base catalysed TEOS gels have been previously assigned by Maciel and Sindorf[13] in terms of Q^2, Q^3 and Q^4 species as defined above. Lineshape analysis of the *FT*/MAS spectra, where line intensities are directly related to composition, indicates that acid catalysed TEOS gels contain approximately equal amounts of Q^3 and Q^4 species. The more highly condensed base catalysed gels, on the other hand, contain a somewhat larger proportion of Q^4 species.

As for the PMMA/TEOS composites (*Figures 10–12*), the differences in silanol content of the material are similar to those seen for the pure inorganic gels. The acid catalysed material shows a slight preponderance of Q^3 over Q^4 groups and the base catalysed material shows an overwhelming content of Q^4 groups. It is also

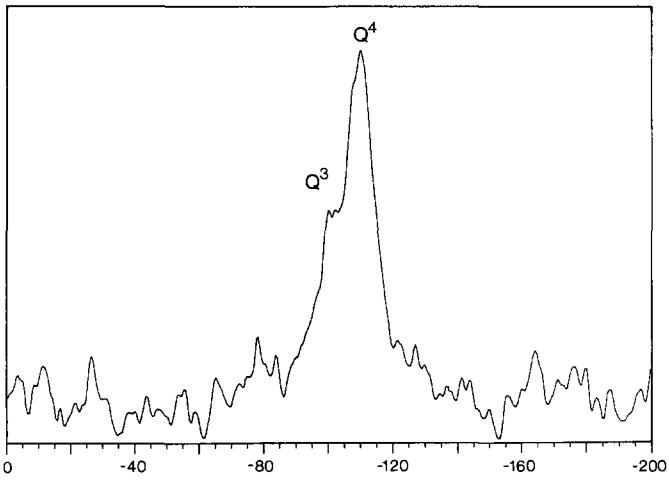

Figure 10 *FT*/MAS ^{29}Si n.m.r. spectra of a PMMA/TEOS 1/5 composite prepared under basic conditions. Cured at 150°C for 18 h under vacuum

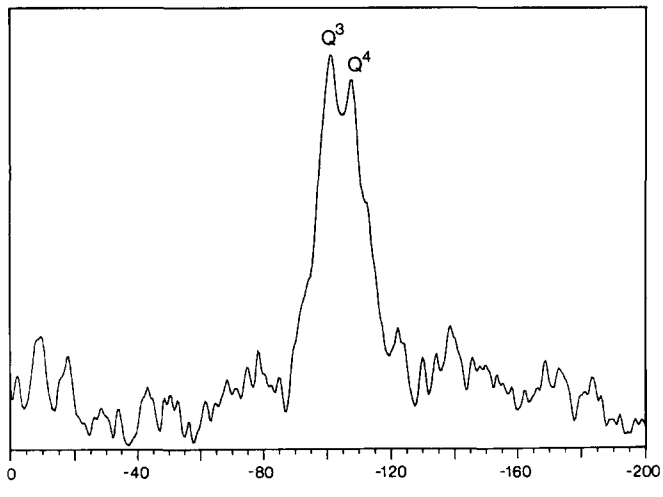

Figure 11 *FT*/MAS ^{29}Si n.m.r. spectra of a PMMA/TEOS 50/50 composite prepared under acid conditions and coated at 30°C. Cured at 150°C for 18 h under vacuum

interesting to note that the degree of reaction for the acid catalysed composite cast at 9°C is identical to that of the acid catalysed composite cast at 30°C, although these two composites showed extremely different morphologies and mechanical properties. *Figure 12* shows the effect of post-cure on the degree of condensation of the silica phase. The spectra shown are for the 50/50 PMMA/TEOS acid catalysed composite cast at 9°C, but identical results are observed for the film cast at 30°C. The n.m.r. spectra are shown for the composite after curing for 5 days at 90°C under vacuum (*Figure 12a*) and after curing for 18 h at 150°C under vacuum (*Figure 12b*). Although the morphology of the composite does not change with post-cure (as observed by electron microscopy)[1], the n.m.r. spectra do show evidence of further condensation.

It seems, therefore, that the course of acid or base catalysed polymerization of TEOS is not profoundly altered by the presence of the polymer (PMMA). This is consistent with electron microscopy results, reported earlier[1]. Nevertheless the presence of the polymer may influence the kinetics of the condensation process.

Chemical characterization. Further information about the nature of the interaction between the organic polymer phase and the inorganic (silicate) phase can be obtained from chemical composition and solubility data. Since there is no obvious chemistry that would lead to the formation of covalent bonds between the two phases, a good solvent for the organic polymer should dissolve the polymer and leave the silica phase as particles or gel. Since hydrogen bonding is suspected, the nature of the solvent can be varied to test for this effect. More specifically, since the focus here is on the PMMA/TEOS composites, the per cent soluble material from extractions obtained with a strongly hydrogen bonding solvent (acetonitrile) can be compared with those obtained with one that is not (THF); both solvents are good solvents for PMMA. The chemical compositions of the separate phases can be measured to determine if polymer is contained in the gel phase and if the sol phase contains soluble components derived from the silica chemistry. One convenient way to test for SiO_2 is through t.g.a. since essentially all the polymer components will be evolved from the sample before reaching 700°C in air or nitrogen atmospheres, and the remaining residue then reflects the SiO_2 content. However, it must be recognized that the silicate phase in the composite consists of partially condensed $SiO_x(OH)_y$ species which will be consolidated to SiO_2 by the thermal treatment in t.g.a. and contribute to the weight loss.

The SiO_2 contents from t.g.a. for several PMMA/TEOS films are listed in *Table 3*, along with the theoretical loadings based on complete reaction to SiO_2.

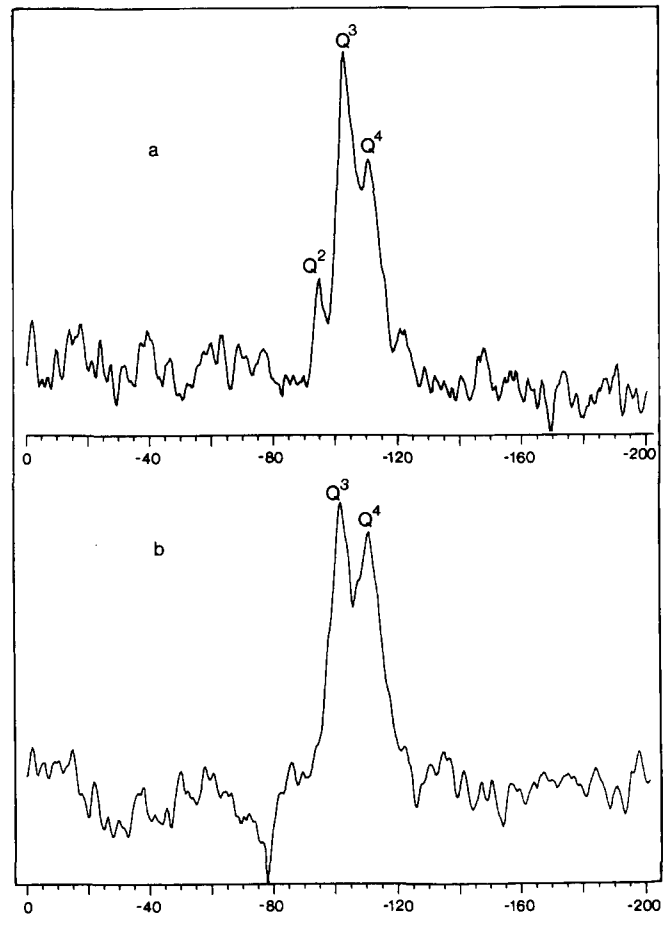

Figure 12 *FT*/MAS ^{29}Si n.m.r. spectra of a PMMA/TEOS 50/50 composite prepared under acid conditions and coated at 9°C and (a) cured at 90°C for 5 days or (b) cured at 150°C for 18 h (both under vacuum)

Data from a pure TEOS sample are also included for comparison, as well as PVAc and PVP composite results. Note that the residue level for the acid catalysed TEOS sample is only 81% due to the consolidation process mentioned above. The theoretical SiO_2 loading of the 50/50 polymer/TEOS composites is 22.4 wt%, and the observed levels for acid catalysed films range from 21 to 23 wt% – essentially complete incorporation. On the other hand, the base catalysed films are all depleted in SiO_2 compared to theory. Data from the 50/50 PMMA/TEOS films with different solution hold times indicate that the fractional incorporation of silica under base catalysed conditions increases as the reaction time in solution increases. The monomer–cluster growth mechanism expected for base catalysed conditions[2,14] would suggest that these solutions contain substantial amounts of unreacted TEOS when the films are cast, and this was observed in *FT*i.r. and Raman studies of these materials. TEOS could very likely evaporate from the film during drying. Longer reaction times before casting should lead to greater amounts of TEOS reacting, and therefore, greater incorporation of SiO_2 in the composite, consistent with the t.g.a. data.

Table 3 T.g.a. data on composite films

Sample	Residue at 700°C	
	Experimental	Theory
TEOS acid, gelled at 100°C	81	100
PMMA/TEOS 50/50; acid, cast 30°C	21	22
PMMA/TEOS 50/50 base, cast 30°C;		
cast after 16 h	9	22
cast after 1.5 h	3	22
PMMA/TEOS 33/66; base,		
cast 30°C; cast after 16 h	19	37
PMMA/TEOS 25/75; base,		
cast 30°C; cast after 16 h	29	46
PMMA/TEOS 50/50; acid, cast 13°C	22	22
PVP/TEOS 50/50; acid, cast 30°C	23	22
PVAc/TEOS 50/50; acid, cast 30°C	23	22

Solvent extractions of several PMMA/TEOS composite films were performed in either THF or acetonitrile. Acetonitrile is known to inhibit adsorption of PMMA to silica particles, presumably by competing for hydrogen bonding sites[15], while THF is expected to be much less active in that regard. The measured sol and gel fractions are reported in *Table 4*, and the chemical compositions, determined by elemental analysis, *FT*i.r., and t.g.a. are reported in *Table 5*. Frequently, the sample size did not allow for testing by all the chemical characterization techniques, so there are absences in *Table 5*. After 3 h in THF the clear PMMA/TEOS film (acid catalysed, coated at $T \gtrsim 30$°C) was still intact and transparent. The film remained intact for several days until the THF was brought to a vigorous boil. At this point, the film broke

Table 4 Extraction results: sol/gel fractions

Sample	Extraction solvent	Film appearance after 3 h (moderate stirring)	wt% sol	wt% gel
PMMA/TEOS 50/50 (gelled in solution)	THF	–	78	22
PMMA/TEOS 50/50 (acid, cast > ~30°C)	THF	Intact	69	31
(acid, cast > ~30°C)	Acetonitrile	Broken into opaque flakes	71	29
PMMA/TEOS 50/50 (acid, cast 11°C)	THF	Broken into opaque flakes	75	25
PMMA/TEOS 50/50 (acid, cast 13°C)	Acetonitrile	Broken into opaque flakes	74	26
PMMA/TEOS 25/75 (base, cast > ~30°C)	THF	Dissolved completely into fine particles	69	31

Table 5 Extraction results: chemical compositions

Sample	wt% C(EA) sol/gel	wt% C(*FT*i.r.)[a] gel	wt% Si sol/gel	wt% O sol/gel	T.g.a. res at 700°C sol/gel
TEOS acid, gelled at 100°C; no extraction	<1	nd	37	nd	81
PMMA/TEOS 50/50 acid, cast 30°C; no extraction	41	nd	10	38	21
PMMA/TEOS 50/50 (gelled in solution)	62/<1	0	<1/37	nd	–/80
PMMA/TEOS 50/50 acid, cast 30°C extraction in THF	61/24	23	<1/25	nd	0/57
PMMA/TEOS 50/50 acid, cast 30°C extraction in acetonitrile	59/12	14	<1/30	nd[b]	0/71
PMMA/TEOS 50/50 acid, cast 11°C extraction in THF	61/11	10	<1/32	nd	–/72
PMMA/TEOS 50/50 acid, cast 13°C extraction in acetonitrile	61/11	nd	<1/32	nd[b]	0/75
PMMA/TEOS 25/75 base, cast 30°C extraction in THF	63/6	1	<1/36	nd	0/86

[a] Present in the form of PMMA
[b] Less than 1% nitrogen was observed in these samples indicating that the acetonitrile was removed on drying
nd = not determined

into small opaque flakes. On the other hand, the acid catalysed composite coated at 11°C broke into small flakes within a few hours. The base catalysed composites (50/50 and 25/75 compositions) broke up immediately and appeared to dissolve completely within a few hours. However, small dust-like particles could be seen when the solution was agitated. In each of the acid catalysed cases, the isolated gel fraction was greater than the measured SiO_2 content from *Table 3*, except for the sample which was gelled in solution (the t.g.a. of the initial sample gelled in solution sample was not obtained). This could be due to either PMMA in the gel fraction or incomplete condensation of the silica.

The extraction of the sol and gel from base catalysed films deserves further discussion. Initially, attempts were made to isolate the gel from a 50/50 wt% PMMA/TEOS film, but the particles were so fine that they were not trapped quantitatively by the filter. The particle size by q.l.s. was found to be approximately 0.2 μm, with some dispersity in size. Therefore, a sample which was more concentrated in SiO_2 was prepared and extracted in THF (a composition of 25/75 wt% PMMA/TEOS as listed in *Tables 3*, *4* and *5*). The silica particles or aggregates in this sample were much larger (>1 μm by q.l.s.) and readily isolated from the sol.

All the results from chemical characterization of the extracted materials are listed in *Table 5*. The chemical compositions are expected to be consistent only within a few per cent because of the usual experimental uncertainties and possible residual volatiles in the samples. Data from unextracted samples of a pure TEOS sample and a PMMA/TEOS composite (acid catalysed) are included as well. For the pure TEOS sample where no extraction was done, elemental analysis found 37% Si and almost no carbon, and the t.g.a. results indicated that the sample was only 81% SiO_2. Having no carbon is consistent with the removal of all the ethoxy groups from Si, as expected under acid catalysed conditions. The expected composition of Si in pure SiO_2 is 47 wt%, but if the observed Si content is corrected for the actual SiO_2 level based on t.g.a. results (37%/81%), a value of 46% Si is obtained. So it would appear that the t.g.a. residue was pure SiO_2 and the original material was completely hydrolysed, but only partially condensed. In fact, Si n.m.r. studies have shown that acid catalysed TEOS is completely hydrolysed but only about 75% condensed (Si–O–Si bonds) at the gel point[15].

Turning to the composite film, the theoretical composition at complete conversion to SiO_2 would be 10.5 wt% Si, 36.7 wt% O, 45.8 wt% C, and 7 wt% H, where the actual data (*Table 5*) show somewhat less carbon and slightly more oxygen. This can be accounted for by incomplete condensation of the silica phase, which contributes additional oxygen (from OH groups) while reducing the weight fraction of PMMA (and therefore carbon) by a few per cent.

If the solvent extraction successfully separates the two phases, then the sol should be approximately 59 wt% carbon (pure PMMA) with no Si, and the gel should have no carbon and about 37 wt% Si (incompletely condensed SiO_2). The t.g.a. residues should be about 0 and 80% for the sol and gel respectively, at least for the acid catalysed films. A quick scan of *Table 5* reveals that the sol phases appear to be essentially pure PMMA in every case, with essentially no Si by elemental analysis and no t.g.a. residue. The carbon contents of the sol fractions are systematically high, but probably within the expected error on this measurement. The molecular weights and molecular weight distributions, as measured by s.e.c., were essentially identical to those of the initial PMMA material, indicating that no gelation or degradation of the PMMA occurred during sample preparation or extraction.

The data for the gel fractions, however, are somewhat more complex. The gel fraction from the 'gelled in solution' PMMA/TEOS composite appears to be free of organic polymer, showing no carbon and the appropriate amounts of Si and t.g.a. residue for an acid catalysed TEOS material. Conversely, the acid catalysed composite gels all show substantial carbon (and hydrogen; not shown) contents and reduced Si and t.g.a. residue values, indicating that the PMMA was incompletely removed from the silica phase. The organic content of the gel phase was confirmed quantitatively as PMMA by *FT*i.r. analysis. The ratio of the 1733 cm^{-1} (PMMA carbonyl) and 1160 cm^{-1} (silicon oxide) bands was obtained and a wt% carbon calculated from that data. Taking the carbon content from elemental analysis and *FT*i.r., the weight percentage of PMMA in the gel can be calculated to be about 40 wt% for the 30°C film extracted in THF. About 21 wt% of the gel was found to be PMMA for the acetonitrile extraction of the same sample, and about 19 wt% of the gels isolated from the 11°C film were found to be PMMA, independent of the solvent used. Therefore, the residues observed in t.g.a. are reduced from the expected value of about 80% for pure TEOS by amounts roughly proportional to the measured PMMA contents, and the weight fractions of sol and gel reported in *Table 4* for the acid catalysed films are brought close to the theoretical values of 0.78 and 0.22 respectively after correcting for the amount of PMMA in the gel fraction.

The gel fraction from the base catalysed film differs in two ways from the other samples. First, although the gel fraction contained a significant amount of carbon, very little of that carbon derived from PMMA, as determined by *FT*i.r. A plausible source for carbon in this sample is unreacted TEOS or perhaps some residual ethoxy groups on the silica phase, since alcoholysis can occur under basic conditions leading to a redistribution of siloxane bonds and accounting for the presence of unhydrolysed monomers even past the gel point[16]. Second, the t.g.a. residue for

$$\mathrm{ROH} + (\mathrm{RO})_3\mathrm{Si{-}O{-}Si}(\mathrm{OR})_3 \overset{\mathrm{OH}^-}{\rightleftharpoons} \mathrm{Si}(\mathrm{OR})_4 + \mathrm{HOSi}(\mathrm{OR})_3$$

the gel fraction was significantly larger than the others. Under base catalysed conditions, solution n.m.r. data show that the reacted silicons are nearly completely condensed[15], leaving fewer possibilities for further condensation during the t.g.a. heating cycle.

There are at least three factors that will likely affect the interaction between the organic polymer, in particular PMMA, and the silica phase. The most obvious is the nature of the surface, especially in the sense that PMMA might be expected to hydrogen bond to the Si–OH moieties on the surface of silica particles. The relative surface area of the silica phase will certainly matter, and it will be inversely related to the particle size. Finally, the silicate structures developed through the inorganic polymerization may lead to physical entrapment of

polymer chains, either during the particle formation process in solution or during collapse of the early stage structure on dry down of the composite layer.

The coupling of limited surface interaction between PMMA and base catalysed SiO_2, the large particle size observed in these samples, and the expectation of a relatively dense internal structure of the silica phase is consistent with very little PMMA carried along with the gel phase. The low temperature acid catalysed film also contained relatively large silica domains, but the disc shape of these domains, described in the earlier report[1], was taken as an indication of collapse of a fragile, spherically symmetric structure, which one would normally expect from a random growth mechanism. Such a collapse could lead to entrapment of chains. Although hydrogen bonding between Si–OH surface groups and PMMA is expected, the large particle size (1 to 2 μm) would limit the surface area and therefore the amount of surface adsorption. The high temperature film, with silica structures on a size scale of < 100 Å, should present the same surface chemistry, but more than 100 times the surface area when compared to the low temperature film. While the high temperature gel carried along twice as much PMMA, roughly half of that amount of polymer was removed by extracting with acetonitrile, and presumably was only adsorbed to the silica surface. The remainder is assumed to have been trapped in the collapse of the structure on dry down, and the quantity trapped was about the same for the two acid derived films.

It is most likely that, in the high molecular weight limits, PMMA and SiO_2 would not be inherently miscible, and it would be expected that, given sufficient time and mobility, the system would tend towards complete phase separation. This idea was probed by gelling a PMMA/TEOS sample in a closed container under acid catalysis conditions. It took about 200 h for gelation to occur in this sample. As the SiO_2 chains increase in molecular weight, phase separation between the inorganic and the PMMA is favoured. All this takes place in solution where mobility is high and the PMMA chains can escape the growing SiO_2 rich regions. For this gelled sample, total separation of the PMMA and SiO_2 phases was possible through extraction in THF, indicating that no organic polymer chains were entrapped within the inorganic network. The sample, however, did not undergo the dry down step before extraction, and there are no data on the size scale of the silicate structure, so it is somewhat difficult to compare with the other composites. Therefore, when the solution is coated in the early stages of TEOS polymerization, the rate of vitrification of the system counterbalances the rate of phase separation. If the former is more rapid, then a homogeneous composition of organic and inorganic polymers can be achieved.

CONCLUSIONS

This work, together with the results reported in ref. 1, proffer that hydrogen bonding is one of the principal factors which determine whether a homogeneous composite may be prepared through the *in situ* polymerization of TEOS within an organic polymeric binder which has no functionality capable of forming covalent bonds with the polymerizing TEOS. Homogeneous blends have enhanced mechanical properties above T_g, and are optically transparent in the absence of crystallinity in the organic polymer.

Hydrogen bond formation necessitates the presence of functional groups which are hydrogen bond acceptors on the polymer chains. Additionally, acidic hydrolysis conditions are necessary during the polymerization of TEOS to ensure that the growing SiO_2 chains are highly hydrated.

Under basic conditions the inorganic phase consists of highly densified SiO_2 particles (predominantly Q^4 species). No strong adhesion between the PMMA and SiO_2 phases is observed when the composite is submerged in THF. The composite dissolves readily and total separation of the PMMA from the SiO_2 phase is possible. The particle size of the gel, about 0.2 μm observed by q.l.s. for the 50/50 wt% composite, is consistent with the size of the SiO_2 particles observed by TEM on a cross-section of the composite[1].

On the other hand, when the polymerization of the TEOS is performed at low pH, hydrogen bond formation between the silica, which contains a significant amount of Q^2 and Q^3 species, and the carbonyl of PMMA or PVAc is observed by *FT*i.r. Solvent extraction results show that a significant amount of PMMA chains are physically entrapped within the SiO_2 network. Additionally, when the surface area of the SiO_2 is large (corresponding to small silica domains, as is the case for the samples formed at 30°C) a considerable amount of PMMA is found to be adsorbed to the silica surface. The adsorbed PMMA could not be removed by extraction in THF but could be removed by acetonitrile, which itself is capable of hydrogen bond formation with the silica. The increase in T_g, the presence of a plateau in the modulus above T_g, and the broadening of the tan δ peak and the d.s.c. transition at T_g are features manifested by the PMMA/TEOS and PVAc/TEOS acid catalysed composites (coated at 30°C) which suggest that the organic polymer chains are in close proximity, on the molecular scale, with the SiO_2 network. The occurrence of phase homogeneity in these systems, however, is a kinetically driven, not a thermodynamically driven, process. When coated at sub-ambient temperatures, hydrogen bonding is nonetheless present as observed by *FT*i.r.; however, the kinetics of vitrification and the resulting morphology are different. The formation of flattened disc shaped SiO_2 domains lying parallel to the coating direction was previously observed[1]. In ref. 1 it was proposed that TEOS polymerizes to form extended ramified structures and these chains form spheres similar to those observed for the base catalysed systems. However, in the acid catalysed case the individual spheres would be much less densely crosslinked and will collapse, during the drying process, in the direction perpendicular to the coating substrate resulting in the disc shaped particles observed by electron microscopy. Many PMMA chains may be entrapped within the SiO_2 network as it collapses, and therefore not removed by extraction. The extraction results for this sample support this 'collapse' theory; 11 wt% carbon still remained in the gel fraction (both for the THF and acetonitrile extractions) even though the PMMA and SiO_2 phases appeared to be considerably phase separated.

The importance of these results is that by judicious selection of the organic polymer and advantageous use of the vitrification of the system, a morphology can be locked in, in which phase separation occurs only on a

microscopic size range, and enhancement of physical properties is attained. This can be achieved without the necessity of synthetically functionalizing the organic polymer with groups capable of forming covalent bonds with the TEOS.

A preliminary survey revealed that poly(vinyl acetate), poly(vinyl pyrrolidone) and poly(*N*,*N*-dimethyl acrylamide) are all capable of forming homogeneous composites with polymerized TEOS. In future work, we are extending the ideas put forth herein to investigate other possible polymers which may meet these criteria.

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