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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Landry, Christine J. T. and Coltrain, Bradley K.(1994) 'On the Effect of Organic Substitution of Silicon Alkoxides in Poly(Vinyl Acetate) Organic-Inorganic Composites', *Journal of Macromolecular Science, Part A*, 31: 12, 1965 – 1973

To link to this Article: DOI: 10.1080/10601329409350111

URL: <http://dx.doi.org/10.1080/10601329409350111>

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ON THE EFFECT OF ORGANIC SUBSTITUTION OF SILICON ALKOXIDES IN POLY(VINYL ACETATE) ORGANIC–INORGANIC COMPOSITES

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ABSTRACT

Organic–inorganic composites (OICs) were prepared via the in-situ polymerization of an organically (phenyl) substituted trialkoxysilane, phenyltriethoxysilane (PhTEOS), in the presence of poly(vinyl acetate) (PVAc). The mechanical reinforcement above T_g previously observed in OICs of unfunctionalized organic polymers such as PVAc with acid catalyzed in-situ polymerized tetraalkoxysilane was not observed when the tetraalkoxysilane was replaced with PhTEOS. Although both systems are optically transparent and both exhibit a high degree of hydrogen bonding between the carbonyl of PVAc and the residual hydroxyls of the silicate, the polymerization of the alkoxide is different. The tetrafunctional alkoxide polymerizes to form a load-supporting silicate network, leading to a high plateau in the tensile modulus above T_g , whereas the trifunctional alkoxide reacts to form primarily low molecular weight oligomers. These increase the T_g of the PVAc but do not provide mechanical reinforcement.

INTRODUCTION

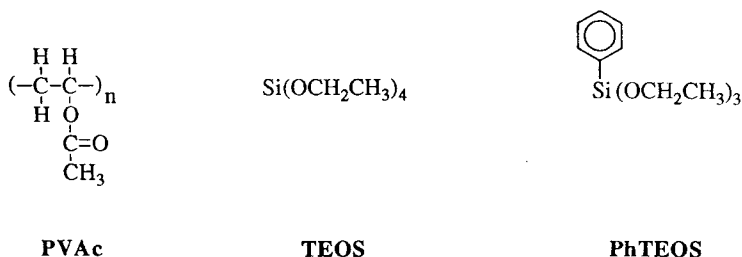
There has been much recent work in the area of organic-inorganic composites (OIC) prepared by in-situ polymerization of metal alkoxides in organic polymers [1-19]. One common important criterion is that the resulting composites be macroscopically homogeneous. Constraining phase separation between the inorganic and the organic components to less than a few hundred angstroms provides optically transparent materials with improved properties. Generally, the modulus, both below and above the glass transition temperature (T_g), is increased [11, 12, 14, 19], better abrasion resistance is achieved [9], and the index of refraction can be modified [9]. On the other hand, brittleness is also increased. The ability to retard or prevent phase separation during the preparation of OICs is very important and can be achieved by increasing the compatibility of the inorganic alkoxide or oxide with the organic polymer. Several methods have been successful and have been discussed previously [1-19].

The addition of organic substituents on silicate networks has been shown to substantially modify the final glass properties. Schmidt and coworkers [1] extensively studied the properties of organic-modified silicates. Additionally, the use of organic-modified silane monomers, $\text{RSi}(\text{OR}')_3$, has been shown to produce homogeneous OIC materials with good physical properties [3, 10]. Mark and coworkers showed that poly(dimethylsiloxane) (PDMS) composites with in-situ polymerized methyl, vinyl, or phenyl-substituted trialkoxysilane monomers had better reinforcement in some cases than did tetraethoxysilane (TEOS) composites of the same polymer [3]. This was suggested as possibly due to the deformability of the particles formed from the organic-substituted monomers. It has also been shown that the use of phenyltriethoxysilane (PhTEOS) produced highly homogeneous composites with a trialkoxysilane-encapped epoxy resin [10]. These composites possessed higher moduli and homogeneity than did TEOS-filled analogs. The improved homogeneity was suggested as due to better compatibility between the silicate network and the organic polymer, possibly via interactions between aromatic rings on the polymer and the phenyl groups on the silicate. It should be noted that the two systems just described utilized polymers having silane functionality capable of crosslinking with the growing inorganic network. It was of interest to determine whether organic substituents on the silicate network could act as homogenizers in composites with polymers without alkoxy silane functionalization to better disperse the inorganic fillers, analogous to the use of silane coupling agents on the surface of oxide filler particles. It should also be noted that the PDMS composites were produced using a tin catalyst, whereas the epoxy composites were generated under high pH conditions. Thus neither composite was prepared under acid-catalyzed conditions that have been shown to provide the most homogeneous composites with unfunctionalized polymers [12, 13].

In this work, OICs prepared by the acid-catalyzed in-situ polymerization of PhTEOS in poly(vinyl acetate) (PVAc) are examined and compared with previously reported composites of PVAc with in-situ polymerized TEOS. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and size exclusion chromatography (SEC) are utilized to characterize the composites.

EXPERIMENTAL

High molecular weight phenyl silsesquioxane (Ph-sils) was prepared by the method of Katchman [20]. The polymer was obtained as a white powder and had an absolute $M_w = 80$ K and a polydispersity $M_w/M_n = 2.11$, as determined by SEC. PVAc was purchased from Polysciences, Inc. The absolute weight- and number-average molecular weights, as determined by SEC, were 218 K and 63 K, respectively. Tetraethoxysilane (Fluka) and phenyltriethoxysilane (Aldrich) were used without further purification. The chemical structures of these are shown below.



The composite solutions were prepared by direct addition, under continuous mixing, of either TEOS, PhTEOS, or a mixture of TEOS and PhTEOS, to a 20 wt% solution of PVAc in tetrahydrofuran (THF), followed by the addition of a stoichiometric amount of water (based on the number of hydrolyzable alkoxide substituents) in the form of 0.15 M HCl. Thus, 4 moles of water were added per mole of TEOS and 3 were added per mole of PhTEOS. The solutions were mixed for 48 hours at ambient temperature, knife-coated onto Kapton at 30°C, and dried at 100°C for 20 hours under vacuum. All samples were stored under nitrogen prior to determining their physical properties. Samples for FT-IR were prepared by spin-coating the solution onto a KBr pellet, followed by drying as above. The composition of the composites are given in Table 1. The wt% Si was determined by neutron activation analysis (NAA). The amount of silicon dioxide (SiO_2) was also determined for most samples by thermal gravimetric analysis (TGA) as the residue at 1000°C in air.

Size exclusion chromatography was performed in THF on the extracted solutions from fully cured PVAc/PhTEOS composites. The results are presented in polystyrene equivalents.

Dynamic mechanical properties were determined using a Rheometrics Solids Analyzer (RSA-II). The heating rate was 2–3°C/min, and the driving frequency was 10 Hz. DSC was performed on a Perkin-Elmer DSC7 at a heating rate of 20°C/min. FT-IR spectra were obtained using a Bio-Rad (Digilab Division) FTS-7 spectrometer (3240-SPC) at a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

The temperature dependencies of the storage tensile moduli (E') and the loss tangents ($\tan \delta$) for the various composites are shown in Fig. 1. At the glass transi-

TABLE 1. Composition of PVAc/PhTEOS Samples

Sample ^a	PhTEOS, mol%	TEOS, mol%	Wt% Si, theoretical/NAA	Wt% SiO ₂ , TGA	DSC T _g (°C), onset/midpoint	ΔC _p (DSC), J/g·C
PVAc	—	—	—	—	39.1/42.6	0.50
PVAc/TEOS-26	—	26.4	9.4/9.8	20.9 (NAA)	41.2/52.4	0.25
PVAc/PhTEOS-26	26.4	—	7.6/8.3	16.5	41.3/45.6	0.41
PVAc/PhTEOS-38	38.1	—	10.5/11.0	22.4	43.4/47.1	0.39
PVAc/PhTEOS-49	48.9	—	12.8/12.4	26.4	48.5/52.5	0.37
PVAc/PhTEOS-59	58.9	—	14.8/14.0	30.8	47.8/51.9	0.35
PVAc/PhTEOS-68	68.3	—	16.6/15.4	34.7	49.1/53.0	0.27
PVAc/TP-26	13.2	13.2	8.4/—	—	—	—
PVAc/Ph-sils-26	—	—	7.6/—	17.0	41.4/43.8	—

^aThe numerical suffix indicates the mol% silicon monomer relative to PVAc.

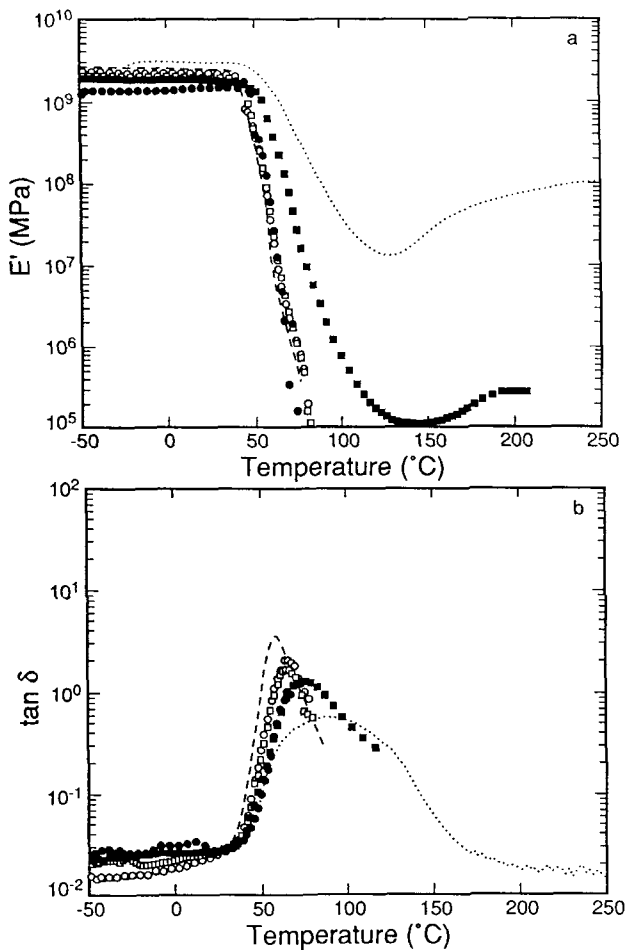


FIG. 1. Temperature dependence of (a) the storage modulus and (b) the loss tangent for (- -) PVAc, (O) PVAc/PhTEOS-26, (□) PVAc/PhTEOS-38, (●) PVAc/PhTEOS-68, (···) PVAc/TEOS-26, and (■) PVAc/TP-26.

tion temperature, pure PVAc exhibits a narrow peak in $\tan \delta$, and a sharp decrease in E' , followed by polymer flow. In contrast, as previously reported [11], a composite prepared from PVAc and acid-catalyzed TEOS shows a very different DMA spectrum. The composite does not flow above T_g , as evidenced by the high plateau in E' that extends to about 300°C. This is shown in Fig. 1 for a sample prepared from 26 mol% TEOS. It is thought that an interpenetrating network of PVAc and the silicate network is formed, with the latter supporting the load above T_g . This has been discussed extensively in previous reports [11, 19]. In these composites the distribution of relaxation times of the PVAc chains was also shown to be affected [11], as reflected by the broadening of the loss peak. The dip in the E' data just above T_g has been previously explained as being due to further curing of the silicate network [11, 12]. Further curing will result in suppression of this dip in E' ; how-

ever, it will not affect the magnitude of E' at higher temperatures (for example, above 200°C).

The results for the composites prepared with PhTEOS (up to a very high loading of 68 mol% PhTEOS) show no evidence of a plateau in E' above T_g . Their DMA spectra are very similar to that for pure PVAc, with a few notable differences. As the amount of PhTEOS increases, there is a slight decrease in the glassy modulus. This is in contrast to PVAc/TEOS composites, which show a slight increase in E' below T_g with increasing silicate [11, 19]. There is also an increase in the onset and midpoint of T_g with increasing addition of PhTEOS. This is shown by the temperature dependence of the loss peak and the DSC data (Table 1). No broadening of the T_g is observed, however, in contrast to results obtained for PVAc/TEOS composites, where broadening of the T_g was accompanied by a substantial decrease in the magnitude of ΔC_p at T_g . There is a substantially larger decrease in the magnitude of ΔC_p for the 26 mol% TEOS versus 26 mol% PhTEOS composites.

When a mixture of TEOS and PhTEOS is used in the preparation of the composite, a reinforcement in the mechanical properties above T_g is observed. This is shown for a PVAc composite prepared from a 50/50 mixture of TEOS and PhTEOS (the total amount of silicon monomers is 26 mol%) (PVAc/TP-26 in Table 1) in Fig. 1. A plateau in E' above T_g is evident, although it is much lower than that observed for the PVAc/TEOS (26 mol%) composite. A sample prepared from a 20/80 mixture of TEOS and PhTEOS (26 mol% total alkoxide) did not show reinforcement above T_g .

A THF extraction was performed on the fully cured PVAc composite containing 38 mol% PhTEOS. The sample fully dissolved and was eluted down a SEC column. The results are shown in Fig. 2. The peak at $\log M$ of about 5.3 corresponds to the PVAc chains. The low molecular weight peak is evidence of the presence of low molecular weight silicate species, consisting of mixtures of cyclic and branched oligomers of the inorganic alkoxide. The presence of cyclic species is not surprising. Silsesquioxanes are polymeric silicate materials, $\text{RSiO}_{1.5}$, which are the expected

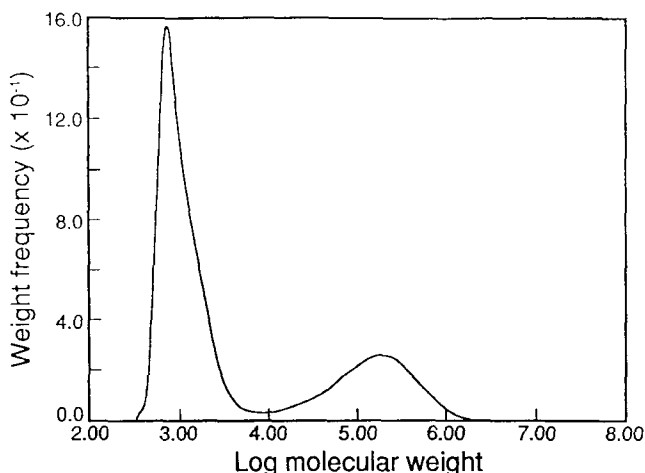


FIG. 2. Molecular weight distribution for PVAc/PhTEOS-38.

products in the present case. The polymers have been extensively studied and a comprehensive review is available [21]. The most widely studied of these is phenylsilsesquioxane, which is thought to adopt a ladder structure in its high polymer form [20, 22–24]. The catalyst, solvent, and monomer concentrations were found to have a profound effect on the reaction pathways. Generally, low pH favors cyclization and high pH favors reorganization to high polymer [21]. Brown [22, 23] and Katchman [20] showed that the acid-catalyzed hydrolysis and condensation of phenylsilane monomers leads predominantly to a variety of cyclic materials (with some higher molecular weight species present), such as the 4-membered cyclotetrasiloxanetetrol and the insoluble cubic $(C_6H_5SiO_{1.5})_8$ species. It should be noted that a variety of low molecular weight species are present, resulting in a complex mixture of components. Higher molecular weight polymer can be obtained by concentrating the cyclic species in an aprotic high boiling solvent and heating with excess base to reequilibrate the cyclics [20–22, 25].

In the present system the use of acid-catalyzed conditions likely leads predominantly to cyclic and low molecular weight phenylsilsesquioxane formation. This would preclude the generation of a second load-bearing phase or interpenetrating network, as was seen for the TEOS composites. The previously reported composites with phenyltrialkoxysilane [3, 10] were prepared with polymers capable of cross-linking with the added monomer and, at least in the case of the epoxy resin [10], were synthesized under high pH conditions that could yield high polymer.

Blends of PVAc and high molecular weight phenylsilsesquioxane (Ph-sils) were prepared. However, macroscopic phase separation of the polymer and the inorganic occurred, demonstrating the intrinsic immiscibility of the components. The T_g for this composite was essentially unshifted from that of PVAc.

The carbonyl region of the infrared spectrum is shown for the composites in Fig. 3. The presence of extensive hydrogen bonding between residual silanols on the

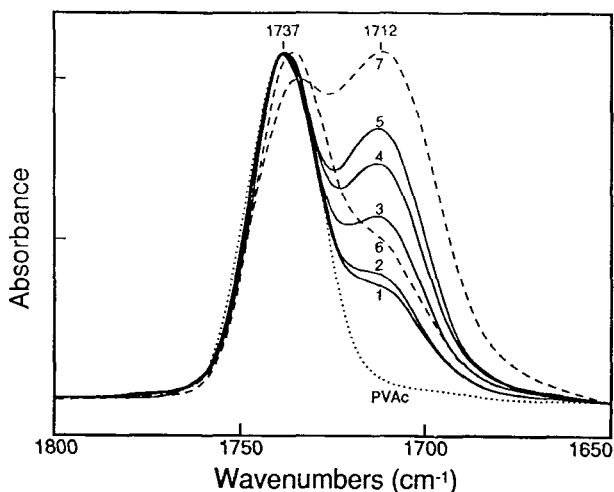


FIG. 3. FTIR spectra of the carbonyl regions for (1) PVAc/PhTEOS-26, (2) PVAc/PhTEOS-38, (3) PVAc/PhTEOS-49, (4) PVAc/PhTEOS-59, (5) PVAc/PhTEOS-68, (6) PVAc/TEOS-26, and (7) PVAc/TEOS-59.

silicate network and the carbonyl of PVAc is characteristic of in-situ prepared composites with TEOS, and has been reported previously [11]. This is evidenced by the shift to lower wavenumbers (1712 cm^{-1}) of a portion of the carbonyl stretching band. The spectra for two PVAc/TEOS samples are shown as the dashed curves for comparison. The composites prepared with PhTEOS also show substantial amounts of hydrogen bonding to the carbonyl of PVAc, which increases with increasing silicate content. The slightly higher proportion of hydrogen-bound carbonyls in the PVAc/TEOS samples relative to the PVAc/PhTEOS samples is attributed to TEOS having four hydrolyzable groups rather than three, thus increasing the probability for interaction. The primary conclusion from these data is that the presence of hydrogen bonding between the silicate and the PVAc is irrelevant in determining whether a plateau in E' above T_g will be observed. The amount of hydrogen-bound carbonyls for the PVAc with 68 mol% PhTEOS sample is much greater than for the PVAc with 26 mol% TEOS sample. The latter shows a high plateau in E' above T_g , whereas the former does not.

The presence of extensive hydrogen bonding suggests that the cyclic octamer is not the dominant species, as this has no residual silanols. The results suggest the presence of low molecular weight species with substantial silanol groups present.

CONCLUSIONS

The mechanical reinforcement above T_g previously demonstrated in composites of unfunctionalized organic polymers (PVAc, PMMA) with acid-catalyzed in-situ polymerized tetraalkoxysilane was not observed when the tetraalkoxysilane was replaced with an organically (phenyl) substituted trialkoxysilane. Although both systems are optically transparent and both exhibit a high degree of hydrogen bonding between the carbonyl of PVAc and the residual hydroxyls of the silicate, the polymerization of the alkoxide is different. The tetra-functional alkoxide polymerizes to form a load-supporting silicate network, leading to a high plateau in the tensile modulus above T_g , whereas the tri-functional alkoxide reacts to form primarily low molecular weight oligomers. These raise the T_g of the PVAc but do not provide mechanical reinforcement.

ACKNOWLEDGMENT

The authors are grateful for the technical assistance of Carolyn Parmigiani.

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Received December 30, 1993

Revision received February 14, 1994