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Use of Organic Copolymers as Compatibilizers for Organic−Inorganic Composites

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ABSTRACT: Random, block, and graft copolymers of polystyrene and poly(4-vinylphenol) were studied as compatibilizers for organic−inorganic composite (OIC) materials. The concept is to use these polymers to reduce the interfacial tension in incompatible OIC materials. This should reduce the particle size of the dispersed inorganic phase and improve adhesion between the components, resulting in better optical and mechanical properties. Dynamic mechanical and ultimate physical properties, as well as transmission electron micrographs, are provided as evidence for the compatibilization of polystyrene and titania produced in situ. These results clearly show that the domain size of the dispersed phase can be reduced and the mechanical properties improved with compatibilizers. Perhaps surprisingly, poly(4-vinylphenol) homopolymer was also found to be an effective compatibilizer in polystyrene−titania composites. An alternate compatibilization mechanism is proposed for the homopolymer.

Introduction

Morphology and phase separation control are critical in the generation of organic−inorganic composite (OIC) materials via in situ polymerization of metal alkoxides in organic polymers. These materials generally exhibit higher stiffness and hardness, although toughness is reduced. It has been shown[1−18] that highly transparent, homogeneous OIC materials can be produced using differing means to control morphology. High degrees of homogeneity have been achieved using organic polymers functionalized with trialkoxysilane groups that can coreact with added inorganic monomers, such as tetraethoxysilane (TEOS), thereby retarding phase separation.[4−8] Homogeneity has also been obtained without the use of trialkoxysilane functionalization by selecting polymers with appropriate backbone structures that can interact with the growing inorganic oxide network.[9−18] Polymers such as poly(methyl methacrylate) (PMMA),[10−12] poly(vinyl acetate) (PVAc),[9] poly(vinylpyrrolidone),[11,13] poly(*N*,*N*-dimethylacrylamide),[11] and poly(ethyloxazoline)[18] were shown to hydrogen bond with silanols on silicate networks. This apparently retards phase separation during vitrification. Organic substituents such as ethylene oxide side chains are also effective in controlling phase separation, as illustrated by the generation of transparent materials with poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) and a variety of inorganic monomers.[14,15]

Although effective, there are limitations to the methods described above in controlling phase separation in OIC materials. The use of trialkoxysilane functionality requires synthetic methodology and appropriate coupling agents to modify the polymers. The resulting polymers are hydrolytically unstable, which creates storage problems. Additionally, the use of trialkoxysilane functionality does not ensure homogeneity in the composite. This was demonstrated for both epoxy[19] and polyester[20] systems in which gross phase separation was observed even with polymers functionalized with triethoxysilane pendant groups. Not all unfunctionalized polymers interact sufficiently with the inorganic oxide networks to retard phase separation. In particular, hydrophobic polymers generally will not yield homogeneous composites. Many high-temperature polymers are quite hydrophobic and have limited interaction with the inorganic oxides. Thus, it is desirable to develop alternate means to homogenize organic polymers and inorganic oxide networks in order to optimize composite properties.

Organic polymer blends generally are inherently incompatible. Often a third constituent, or compatibilizer, can be added to improve the blend properties.[21−23] Effective compatibilizers are random, graft, or block copolymers.[23] In a simplistic sense, compatibilizers are selected for a blend of polymers A and B such that part of the compatibilizer is miscible with polymer A and the other is miscible with polymer B. The compatibilizer diffuses to the interface between the two immiscible polymers and reduces the interfacial tension, thereby reducing the dispersed-phase particle size. Additionally, the compatibilizer can increase the adhesion between the two phases.

It is of interest to determine whether block, graft, and random copolymers of styrene (S) and 4-vinylphenol (VPh) can be used as compatibilizers to improve the properties in OIC materials. Poly(4-vinylphenol) (PVPh) interacts strongly with silica,[24] suggesting that copolymers with this monomer might be effective compatibilizers. To test this approach, it was necessary to choose an organic polymer that was inherently incompatible with the growing inorganic oxide network but would either be miscible or show some degree of preferential interaction with the polystyrene portion of the compatibilizer. Three polymers were deemed suitable for the

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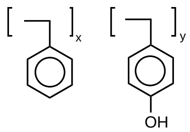
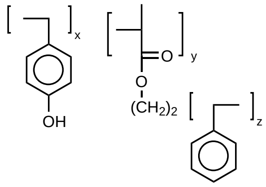
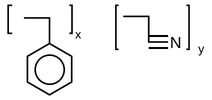
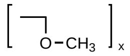
Table 1. Polymer Structures

chemical name	structure
poly(styrene-*block*-4-vinylphenol)	
poly(4-vinylphenol-*graft*-styrene)	
poly(styrene-*co*-acrylonitrile)	
poly(vinyl methyl ether)	

study, polystyrene, poly(vinyl methyl ether) (PVME), and poly(styrene-*co*-acrylonitrile) (SAN). Although SAN is not miscible with PS, there exists strong internal repulsion between the S and AN portions of the SAN copolymer. In addition, a positive Flory–Huggins interaction parameter between S and VPh has been found to be positive as measured by our group[25] by differential scanning calorimetry (DSC). A series of low molecular weight polystyrenes and poly(vinylphenols) were blended and their miscibilities determined by DSC. All blends were found to be immiscible, showing two distinct glass transition temperatures with minimal shifts, even at molecular weights as low as 800 for PS and 2820 for PVPh. One can calculate[26] a value for the Flory–Huggins interaction parameter from these data to be ca. 0.25 between S and VPh. Thus, in the framework of the binary interaction model, there is a driving force for the S portion of S-*co*-VPh to find the S portion of SAN. This report describes the use of PVPh-containing polymers as compatibilizers in improving homogeneity in composites generated from the in situ polymerization of metal alkoxides in PS, PVME, and SAN. Ultimate and dynamic mechanical properties, as well as transmission electron micrographs, are provided.

Experimental Section

Tetrahydrofuran (THF) (Kodak, reagent grade) and 4-ethylphenol (Kodak) were used as received. Titanium isopropoxide ($Ti(^iPrO)_4$) was obtained from Fluka, and zirconium butoxide ($Zr(BuO)_4{\cdot}BuOH$) was obtained from Alfa Products. Both metal alkoxides were used as received. Table 1 depicts the chemical structures for the polymers that were used. Polystyrene was purchased from Scientific Polymer Products and purified by precipitation in methanol, resulting in $\bar{M}_w$ = 275 000 with $\bar{M}_w/\bar{M}_n$ = 2.4, determined by size exclusion chromatography (SEC). Poly(styrene-*co*-acrylonitrile) (SAN) was Tyrill 880 (Dow Chemical) and contained *ca*. 23 wt % acrylonitrile (AN). Poly(vinyl methyl ether) (PVME) was obtained as a toluene solution from Scientific Polymer Products. Most of the toluene was removed by rotary evaporation prior to redissolution of the polymer in THF.

Compatibilizers. A variety of block, graft, and random copolymers of P(S-*co*-VPh) were studied. Table 2 lists the copolymers as well as the molecular weights and compositions. Poly(4-vinylphenol) was synthesized as described in ref 27 and had $\bar{M}_w$ = 67 500 (PS equivalents) and $\bar{M}_w/\bar{M}_n$ = 1.7. The PS-*co*-PVPh random copolymer was also synthesized as previously described.[27]

Table 2. P(VPh-*co*-S) Copolymers for Compatibilization

sample	structure	av no. of PS arms	MW peak	wt % PVPh
b	diblock	1	141 000	50–60
g1	graft	6.7 of 13K each	113 000	<20
g2	graft	2.8 of 13K each	120 000	70
r	random		$\bar{M}_w$=108 000,[a] $\bar{M}_w/\bar{M}_n$ = 3.91	55

[a] Absolute molecular weight.

Block copolymers [P(S-*b*-VPh)] were prepared, as described by Nakahama,[28] by living, anionic polymerization and sequential addition techniques. Styrene monomer was initiated in THF (10% wt/vol) at −78 °C with *sec*-butyllithium (1.3 M in cyclohexane), and polymerization was allowed to proceed for 20 min to ensure complete conversion. The *p*-(*tert*-butyldimethylsiloxy)styrene monomer was added via syringe to the orange poly(styryllithium) anion, and the color immediately changed to yellow. Polymerization of the second block was allowed to proceed for 1 h, and degassed methanol was finally added to terminate the polymerization. The polymers were isolated by precipitation into methanol, vacuum filtration, and drying in vacuo overnight at 80 °C. In all cases, the yields were quantitative, and compositions as determined by ^1H NMR were in excellent agreement with calculated compositions based on monomer charges. Molecular weight distributions were typically less than 1.25, and molecular weights were predictable based on the ratio of total monomer to initiator. The poly(vinylphenol) block was readily generated by removing the protecting group in THF at 60 °C for 4–6 h with hydrochloric acid catalyst. The polymer was purified by precipitation into water to remove the residual acid.

Graft copolymers [P(VPh-*g*-S)] were prepared by conventional free-radical copolymerization of a methacrylate-terminated polystyrene oligomer (Sartomer, 13 000 g/mol) and *p*-((*tert*-butyloxy)carbonyl)oxy)styrene (TBOC styrene) (Kodak). Typically, 25% solids in THF were used with VAZO 64 (Du Pont) as the radical initiator at 64 °C. The polymerization was allowed to proceed for 48 h, and yields were typically 80–85%. The polymer was isolated by precipitation into methanol, vacuum filtration, and drying in vacuo for 18 h at 80 °C. The protected graft copolymer was readily dissolved in deoxygenated dioxane, and trifluoroacetic acid was added as the catalyst to remove the (*tert*-butyloxy)carbonyl protecting group. The reaction was allowed to proceed at reflux for 24–48 h. ^1H NMR confirmed the quantitative removal of the protecting groups to generate the poly(vinylphenol) backbone. The polymer was isolated by precipitation into water to remove all traces of acid catalyst, and a second precipitation into cyclohexane/hexane removed any incorporated polystyrene macromonomer. SEC confirmed almost complete removal of residual macromonomer (less than 5% remained).

Prehydrolysis of Titanium and Zirconium Alkoxides. The titanium or zirconium alkoxides were prehydrolyzed in a manner similar to a procedure reported by Wilkes and coworkers.[29,30]

Method I. Titanium isopropoxide (5 g) was dissolved in THF (5 g), and a premixed solution of isopropyl alcohol (20 g), water (0.6 g), and 10 N HCl (0.1 g) was added dropwise with continuous mixing. Alternatively, THF (9 g) was mixed with zirconium butoxide (5 g), and a premixed solution of isopropyl alcohol (15 g), water (0.2 g), and 10 N HCl (0.05 g) was added.

Method II. THF (5 g) was mixed with 10 N HCl (0.1 g) and added with continuous mixing to titanium isopropoxide (5 g). Some water may be present in the THF, as no precautions were used to dry it.

Generally, prehydrolysis of zirconium butoxide resulted in precipitation of zirconium oxide; however, samples could be successfully prepared using method I if done carefully. Alternatively, hydrolysis and condensation of the alkoxides could be effected in situ by allowing atmospheric moisture to diffuse into the composites. No other source of water was added in these cases. In this report, if prehydrolyzed metal alkoxides were used, it will be noted. Otherwise, the reaction was effected using atmospheric moisture.

Preparation of Composites. Composite samples were prepared by dissolving the polymer in THF at a concentration of 5 wt % for PS and SAN or 25 wt % for PVME. The PS–PVPh copolymer (or PVPh homopolymer) was dissolved separately in THF at 2.5 wt %. The inorganic component was introduced by adding an appropriate amount of stock solution from prehydrolysis (ph) method I or II or by adding the inorganic alkoxide directly, as described above. Variations on the order of addition and the drying temperature, as well as prehydrolysis of the titanium, were tested. The best results for PS were obtained by first mixing the polymer and compatibilizer followed by addition of the inorganic monomer. The resulting solutions were generally yellow–orange and were immediately cast into Teflon dishes and covered with an inverted crystallization dish to allow slow solvent evaporation. This permitted moisture from the air to contact the sample, effecting polymerization of the metal alkoxide. Both the SAN/Ti and PVME/Ti composites for TEM characterization were prepared with prehydrolyzed Ti (method II). In the case of the PVME composites, the alkoxide was mixed initially with the copolymer and then added to PVME. Samples for mechanical testing were cut to the desired shape and cured at 100 °C *in vacuo* for 3 h.

Two variations on the order of mixing were evaluated. Generally the polymer and copolymer (compatibilizer) were mixed followed by metal alkoxide addition. Unless otherwise noted, this order of addition was used. Alternatively the alkoxide was first mixed with the compatibilizer solution, and then the polymer solution was added. Although the latter method exhibited more gelation problems due to the strong interaction of PVPh with the metal alkoxide, the resulting film appearances and the composite morphologies were not substantially different with either method of addition.

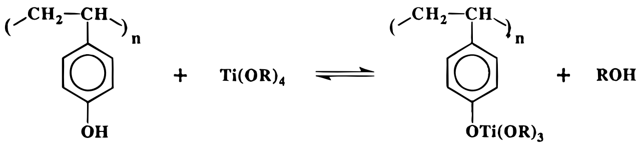
Nomenclature. A shorthand notation is used to identify the composites. The relative weight ratios of the components in the starting solutions will be noted. The copolymer used as a compatibilizer is identified in Table 2. Thus, a composite made from 2 g of PS, 1 g of titanium isopropoxide, and 0.05 g of block copolymer would be designated PS/Ti/b, 2/1/0.05. It is important to note that these are the initial feed ratios and that the Ti content represents the weight percentage of titanium alkoxide, not TiO_2.

Physical Property Measurements. Dynamic mechanical thermal analysis (DMA) was performed using a Rheometrics solids analyzer RSA II at 10 Hz over a temperature range from −100 to 300 °C, with a heating rate of 2–3 °C/min. Mechanical properties were measured on a Sintech 20 testing machine. Miniature dogbone samples, ASTM D638M-III format, were tested at a constant crosshead speed of 2.5 mm/min (strain rate = 0.1 min^{-1}). Dogbone samples were machined from polymer sheets by rough cutting samples on a water-cooled MK Model MG-125 DS diamond saw and machining to final test format on a TensilKut Model 10–88 router. The samples were then cured as described above. The engineering stress was calculated using the average cross-sectional area. Strain was calculated using the crosshead displacement and an effective gauge length. The tensile modulus was analyzed using a linear regression fit of the initial slope of the stress–strain curve.

PS and SAN samples for transmission electron microscopy (TEM) were prepared by first sectioning the material at ambient temperature on a Reichert Ultracut E and producing sections of about 95 nm in thickness. These sections were examined using a JEOL 100CXII microscope at 100 kV. The PVME samples were sectioned under liquid nitrogen conditions. The samples were then dry-transferred to the TEM grids where they were dry-pressed and examined under cryo conditions. The intrinsic contrast between the TiO_2 and the organic polymers was sufficient, and no additional staining was required.

Results and Discussion

Preparation of Composites. The concept for this work relies upon the strong interactions between inorganic oxides and polymers containing acid or hydroxyl functionality; one such polymer is PVPh. The addition of titanium alkoxides to solutions of PVPh results in immediate gelation. However, prehydrolyzing (ph) titanium isopropoxide (method I) prior to addition to PVPh results in a stable solution, and a transparent orange film is obtained upon casting and drying. Using method II to prehydrolyze the titanium alkoxide results in gel formation upon mixing with PVPh. Gelation of the PVPh/Ti solutions is presumably due to alcohol exchange on the titanium, resulting in cross-linking from the formation of covalent Ti–phenol bonds, as shown below. The addition of tetraethoxysilane (TEOS) (and 4 equiv of 0.15 N HCl) to PVPh produces a transparent film, whereas the addition of prehydrolyzed (method I) zirconium butoxide to PVPh results in a clear gel. These results are indicative of strong interactions between the inorganics and PVPh.



Differences in results between methods I and II likely arise from the fact that substantially more water (2 equiv) is added in method I, producing more extensive hydrolysis. The resulting Ti species (method I) are partly polymerized and have less residual OR groups to exchange with the phenolic polymer. Thus, the species resulting from methods I and II would be expected to interact differently with PVPh. Method I results in Ti species that presumably interact predominantly by hydrogen bonding between the phenol and TiOH groups, whereas method II results in species predominantly interacting by alcohol exchange.

Block, graft, and random copolymers of styrene and VPh (P(S-*co*-VPh)) were synthesized. As discussed above, the PVPh portion of the copolymer strongly interacts with the inorganic phase. In order to utilize these copolymers as effective compatibilizers, organic polymers must be chosen that are miscible (or interact favorably) with the PS portion of the copolymers. Several candidates are obvious,[31] such as PS, PVME, SAN, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), and tetramethyl bisphenol A polycarbonate (TM-BPAPC). PS, PVME, and SAN all formed opaque, white composites when titanium was added, in the absence of compatibilizer. This is a desirable result because compatibilization can only be tested in inherently incompatible composites. Unexpectedly, TM-BPAPC and PPO were found to form transparent films when combined with titanium isopropoxide (with no added compatibilizer). It is not clear whether these polymers are inherently compatible with the titania or whether Ti species act in a catalytic way to degrade or react with the polymer. For the present study, we have focused upon PS/Ti, PVME/Ti, and SAN/Ti for morphological characterization and PS/Ti for mechanical property determination.

Table 3 lists the samples (ph denotes prehydrolyzed metal alkoxide) and their physical appearance, the average particle sizes of the dispersed inorganic phase, and the weight percentages of compatibilizer and metal oxide. The percentage of metal oxide is calculated from the known amount of Ti in the feed, assuming full conversion to MO_2. The retention of Ti in the fully cured samples was verified by neutron activation analysis. As noted in the Experimental Section, the order of mixing

Table 3. Samples

components	feed ratio	wt % TiO_2	wt % copol	appearance[a]	particle size (av)[b]
PS/Ti	2/0.5	6.6		opaque	
PS/Ti	2/1	12.3		opaque	0.5−1 μm
PS/Ti/b	2/0.5/0.025	6.5	1.2	opaque	
PS/Ti/b	2/0.5/0.050	6.4	2.3	clear	10−20 nm
PS/Ti/b	2/0.5/0.075	6.3	3.4	clear	<10 nm
PS/Ti/b	2/0.5/0.10	6.3	4.5	clear	<10 nm
PS/Ti/b	2/0.5/0.15	6.1	6.5	clear	<10 nm
PS/Ti/b	2/0.5/0.20	6.0	8.5	clear	
PS/Ti/b	2/0.7/0.07	8.7	3.1	clear	<10 nm
PS/Ti/b	2/0.7/0.14	8.4	6.0	clear	<10 nm
PS/Ti(ph)/b	2/0.5/0.05	6.4	2.3	clear	
PS/Ti/b	1/1/0.02	21.6	1.5	opaque	
PS/Ti/b	1/1/0.10	20.3	7.2	translucent	
PS/Ti/b	2/1/0.05	12.1	2.1	opaque	0.25 μm
PS/Ti/b	2/1/0.10[d]	11.8	4.2	clear	<10 nm
PS/Ti/b	2/1/0.20	11.3	8.1	clear	<10 nm
PS/Ti/r	2/0.5/0.025	6.5	1.2	translucent	0.1−0.2 μm
PS/Ti/r	2/0.5/0.05	6.4	2.3	clear	0.1−0.2 μm
PS/Ti/r	2/0.5/0.10	6.3	4.5	clear	0.1−0.2 μm
PS/Ti/r	2/0.5/0.20	6.0	8.5	clear	50−100 nm
PS/Ti/r	2/1/0.10	11.8	4.3	clear	
PS/Ti/PVPh	2/0.5/0.0125	6.6	0.6	opaque	0.2−0.5 μm
PS/Ti/PVPh	2/0.5/0.025	6.5	1.2	opaque	0.1−0.2 μm
PS/Ti/PVPh	2/0.5/0.05	6.5	2.3	clear	0.1−0.2 μm
PS/Ti/PVPh	2/0.5/0.10	6.3	4.5	clear	50−100 nm
PS/Ti/PVPh	2/0.5/0.20	6.0	8.5	clear	25−100 nm
PS/Ti/EPH	2/1/0.05	12.1	2.1	opaque	0.5−1 μm
PS/Ti/EPH	2/1/0.10	11.8	4.2	opaque	0.5−1 μm
PS/Ti/EPH	2/1/0.20	11.3	8.1	opaque	0.5−1 μm
PS/(Ti/g1)	2/(1/0.10)[c]	11.8	4.2	opaque	
PS/(Ti/g1)	2/(1/0.20)[c]	11.3	8.1	translucent	
PS/Ti/g2	1/1/0.1	20.3	7.2	gelled	
SAN/Ti(ph)	2/1[d]	12.3		opaque	0.5−1.0 μm
SAN/Ti(ph)/b	2/1/0.20	11.3	8.1	translucent	<10 nm
PVME/Ti(ph)	2/1	12.3		opaque	1 μm
PVME/(Ti(ph)/b)	2/(1/0.10)[c]	11.8	4.2	translucent	20−50 nm
PVME/Ti(ph)/b	2/1/0.20[d]	11.3	8.1	translucent	<10 nm
PS/Zr	2/1			opaque	1−5 μm
PS/(Zr/g1)	2/(1/0.1 and 0.2)[c]			translucent	

[a] All samples without the copolymer were white, all samples with added copolymer were yellow. [b] The size of the dispersed (TiO_2) phase, as determined by TEM or SEM. [c] For these samples, the alkoxide was first added to the copolymer solution, then the resulting solution was added to the polymer solution. [d] Also mixed as in (*c*).

was studied. It was thought that differences might result by first reacting the copolymer with the metal. Qualitatively, no significant differences were observed in the DMA results or sample morphology with PS using either order of addition.

Two general trends were noted. Firstly, as the weight percentage of Ti or compatibilizer increased, shrinkage and crack formation upon drying increased. Composites prepared with PS, which is inherently brittle, were therefore limited to less than 10 wt % TiO_2 in order to produce crackfree specimens for mechanical property determination. Secondly, although some of the solutions were more turbid with increasing copolymer concentration, the resulting films actually became more translucent or clear.

Gelation due to interactions between the compatibilizer and metal alkoxide can be a problem, impairing the dispersion of the components prior to casting. Zirconium alkoxide addition led to more gelation than did titanium under similar conditions, but prehydrolysis was effective in minimizing gelation. The morphologies of the resulting films do not seem to be dramatically affected by the use of prehydrolysis or direct addition of inorganic monomers. Several different graft, block, and random copolymer compositions were investigated. Not surprisingly, gelation was a more pronounced problem as the PVPh content of the copolymer increased. However, a minimum concentration of PVPh is required for efficient compatibilization. A composition of about 50% PVPh was found to be optimal. It has been suggested[32] that the optimum block copolymer for efficient polymer−polymer compatibilization is one that is very symmetric, that is, one where the block lengths are about the same.

Morphology. Scanning electron micrographs (not shown) of the fracture surface of PS/Ti, 2/1, show a large degree of phase separation. The fracture surface of this same PS/Ti composition but with 8.1 wt % block copolymer revealed that the addition of the compatibilizer dramatically improved the sample homogeneity and seems to have affected the fracture mechanism, as evidenced by differences in the fracture surfaces. Figure 1 shows TEMs of these same composites with increasing amounts of compatibilizer. It is evident that the inorganic phase size has been significantly reduced, from 0.5−1 mm in PS/Ti to <10 nm upon addition of the block copolymer.

Figure 2a shows a TEM of SAN/Ti, 2/1. In contrast to the PS sample, the Ti was prehydrolyzed. As was the case with PS, large inorganic domains of about 0.5−1.0 mm were obtained. Figure 2b shows a TEM of this same SAN-to-Ti ratio with 8.1 wt % block copolymer added. Again note the size reduction of the inorganic phase to <10 nm. Slightly different morphologies were observed with PVME, as indicated in Figure 3. Figure 3a shows a TEM of PVME/Ti (ph), 2/1. Unlike the PS and SAN examples, the inorganic domains appear as dense spheres approximately 1 mm in diameter. Some

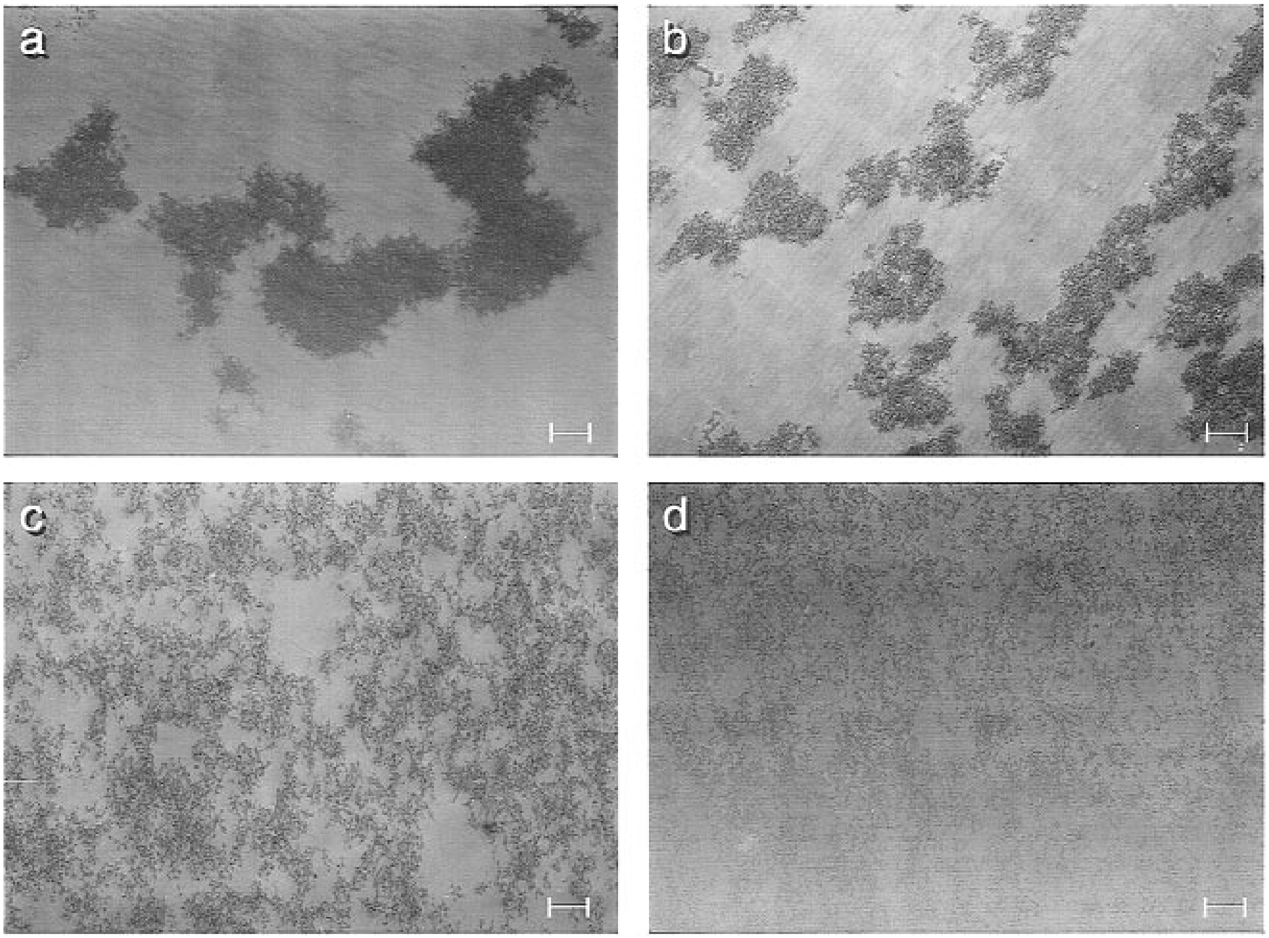


Figure 1. Transmission electron micrographs of PS/Ti, 2/1, composite with (a) 0 wt %, (b) 2.1 wt %, (c) 4.2 wt %, and (d) 8.1 wt % block copolymer. Fiducial bar = 250 nm.

of the spheres were fractured upon sectioning. Figure 3b shows the same PVME/Ti composition with 4.2 wt % block copolymer. The inorganic domains were substantially smaller (20–50 nm) and more homogeneously dispersed.

The SEM and TEM results indicate that P(S-*b*-VPh) block copolymers are effective in reducing the inorganic phase size and dispersing TiO_2 in each of the three polymer systems. Improved dispersion of the inorganic phase should result in improved mechanical properties. Unfortunately, the 2/1 PS/Ti loadings studied by TEM are 12.3 wt % TiO_2 and were too brittle for mechanical testing.

The morphology of the PS/Ti, 2/0.5, series (shown in Figure 4), with only half the Ti as in the previous samples, is similar. When the diblock was added at 2.3 wt %, the size of the titania particles decreased to about 10 nm. These small titania particles aggregate into clusters ranging from 50 to 250 nm in size. The clusters are more loosely formed than in the composites with more titania (compare Figure 1b with Figure 4a), and the individual titania particles are more visible in the micrograph.

The morphology for the PS/Ti, 2/0.5, series with added random copolymer was different from that with the diblock. Although small differences were observed, the size of the titania particles remained approximately 0.05–0.2 μm in diameter, regardless of the amount of added copolymer (within the range 1.2–8.5%). However, as the copolymer concentration was increased, the inorganic phase became more dispersed, forming what appeared to be more of a network structure. Also, the titania phase seems to become less dense as the concentration of copolymer increases, which is inferred from the decreasing resolution and contrast in the TEMs. Figure 5 shows TEMs of PS/Ti, 2/0.5, with 2.4 and 8.5 wt % random copolymer. This micrograph should be compared with Figure 4 showing TEMs of similar compositions with block copolymer. Addition of the block copolymer results in much smaller and well-dispersed TiO_2 phases.

One question is whether the phenolic copolymers are actually serving as compatibilizers as described earlier in this report or whether the phenolic moieties simply modify the polymerization mechanism of the inorganic monomers. To test this, the small molecule 4-ethylphenol (EPH) was substituted for the copolymer. EPH has been shown to be a good model for PVPh in heats of mixing studies of polymer blends.[27] Figure 6 shows TEMs for 2/1 PS/Ti with 2.1 and 8.1 wt % EPH. These composites have roughly the same amount of phenol as composites with 4.2 and 16 wt % block copolymer (with 50% VPh). Thus, Figure 6 should be compared with Figure 1. Clearly the block copolymer is much more efficient at compatibilization. In fact, the inorganic domain size was virtually independent of the amount of added EPH, suggesting that the phenolic moieties are not simply affecting the titanium alkoxide reaction kinetics.

One additional comparison was made, using PVPh homopolymer in place of the copolymers. PVPh is highly immiscible with PS, so it would be anticipated to be ineffective as a compatibilizer. Figure 7 shows TEMs of PS/Ti, 2/0.5, with 1.2, 4.5, and 8.6 wt % PVPh,

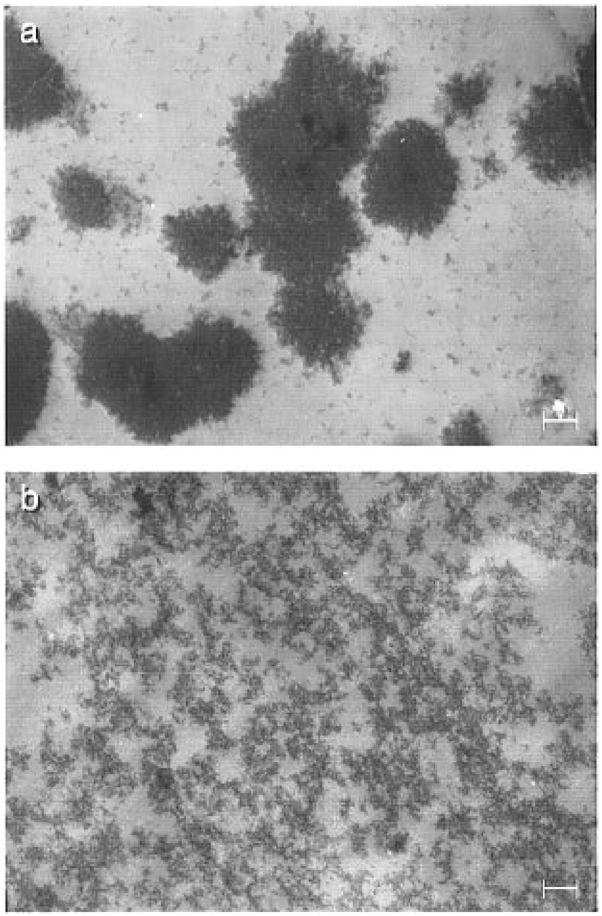
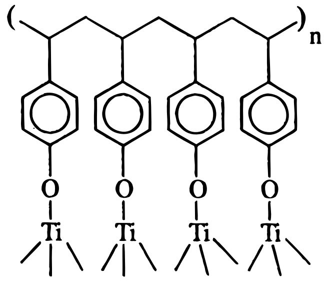


Figure 2. Transmission electron micrographs of (a) SAN/Ti, 2/1, and (b) SAN/Ti, 2/1, with 8.1 wt % block copolymer. Fiducial bar = 250 nm.

respectively. The addition of increasing amounts of PVPh substantially improved the composite homogeneity, similar to the results with the random copolymer. This effect was seen in the mechanical properties, which will be discussed below. It is probable that PVPh interacts strongly either with the titanium alkoxide monomer (via alcohol exchange) or with the growing titania particles (via extensive hydrogen bonding). Such extensive interaction could effectively shield both the surface of the titania and the phenolic OH groups. If the interactions were extensive enough, the exterior of the particles could appear very similar to PS, as shown below.



This type of shielding may account for the enhanced homogeneity observed with added PVPh. Such shielding could also produce an emulsification effect in which the polymer prevents titania aggregation and gross phase separation. The results with PVPh homopolymer were surprising and the explanation speculative at this time.

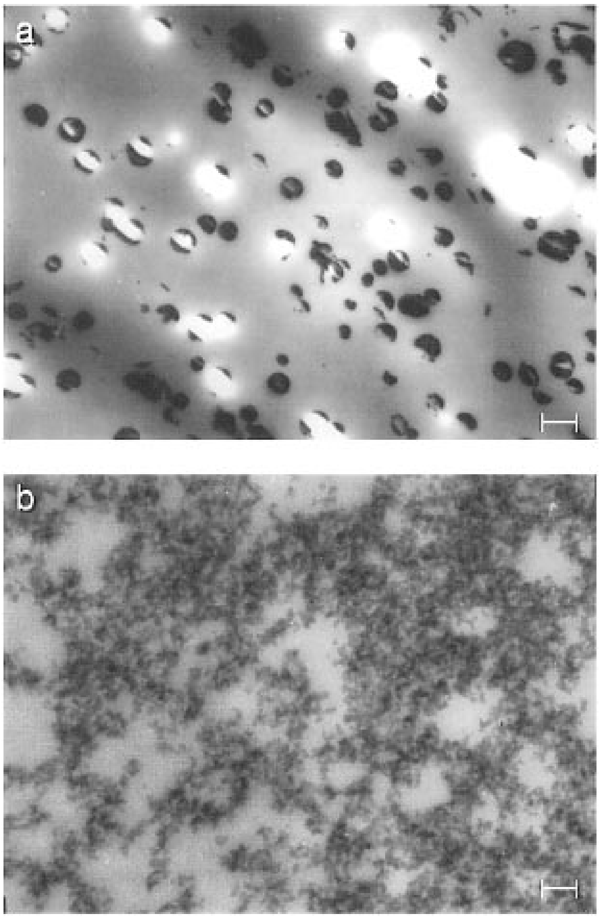


Figure 3. Transmission electron micrograph of (a) PVME/Ti, 2/1, and (b) PVME/Ti, 2/1, with 4.2 wt % block copolymer. Fiducial bar = (a) 3.6 μm, (b) 250 nm.

Mechanical Properties. The storage (E') and loss (E'') moduli, obtained from DMA, are shown in Figure 8 for a series of PS/Ti, 2/0.5, composites with increasing amounts of block copolymer. At the lowest copolymer loading, 1.2 wt %, no rubbery plateau in the elastic modulus above the T_g of PS is observed, as is also the case for PS/Ti. However, addition of a minimum of 2.4 wt % copolymer resulted in a clearly defined plateau in E' (above T_g) extending to 300 °C. The value of the plateau modulus was found to increase with increasing amounts of copolymer (at least up to 6.5 wt %) with little corresponding increase in T_g (given by the maximum in E''). It is important to note that a plateau in E' above T_g is obtained in these composites with TiO_2 loadings of only about 6 wt %. These results should be compared with the results for MEEP, PMMA, and PVAc composites with TEOS in which a threshold value of about 12–15% SiO_2 was required to observe a plateau in the modulus.[9-15] However, the magnitude of E' in the plateau region is much lower for the compatibilized PS/Ti composites (ca. 10^6 Pa) than was for the PVAc/TEOS composites (ca. $>10^7$ Pa), for example. This is consistent with cross-linking, as opposed to the presence of a load-bearing, continuous, inorganic network that was proposed for the PVAc system.[9]

Figure 9 shows E' plots for PS/Ti, 2/1, with 4.5 wt % block and random copolymer or PVPh homopolymer. Well-defined plateau moduli of about 1.9×10^6 Pa are observed in all cases. The E' plots are virtually indistinguishable for each of the added compatibilizers, even though there are substantial morphological differences between the samples. Apparently the morphological

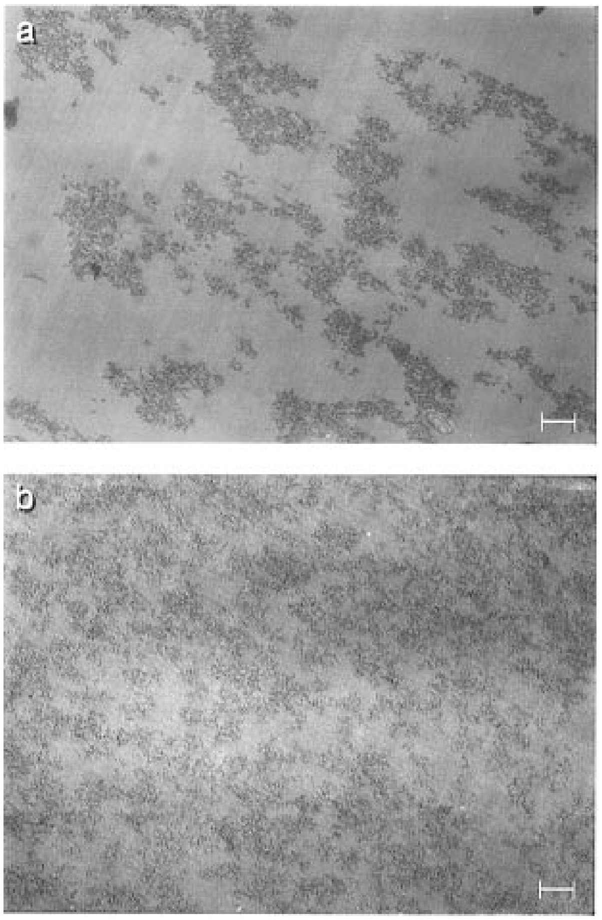


Figure 4. Transmission electron micrograph of PS/Ti, 2/0.5, with (a) 2.3 wt % and (b) 6.5 wt % block copolymer. Fiducial bar = 250 nm.

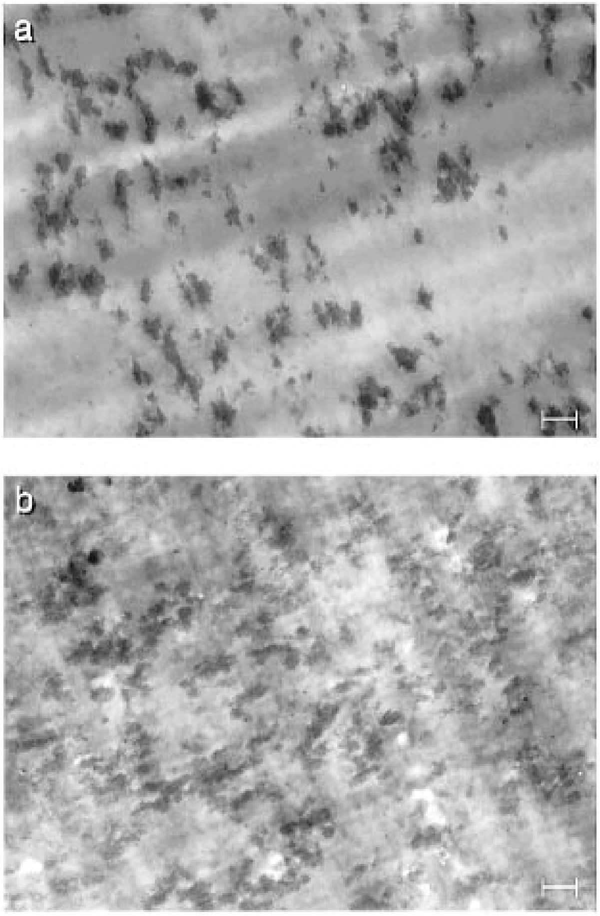


Figure 5. Transmission electron micrograph of PS/Ti, 2/0.5, with (a) 2.3 wt % and (b) 8.1 wt % random copolymer. Fiducial bar = 250 nm.

differences observed by TEM do not dominate the mechanical properties. It is obvious, however, by comparison of these samples to PS/Ti that the addition of PVPh-based compatibilizers substantially improves mechanical properties.

Figures 10–12 show plots of the results obtained from the measurement of ultimate mechanical properties of the compatibilized polystyrene with 6.5–8.5 wt % titania (PS/Ti, 2/0.5). A fiducial bar representing the typical average standard deviation obtained for these measurements is shown in each figure. The results are plotted as a function of wt % VPh in the compatibilizer to compare equivalent amounts of phenol functionality. A maximum is observed in the mechanical properties as a function of wt % compatibilizer, which is typical of the use of compatibilizers in organic polymer blends. At high compatibilizer loadings, the samples become brittle and develop cracks upon drying. The exception to this is the PVPh homopolymer composites, which exhibit steadily increasing moduli with increasing PVPh. In general, the optimum amount of compatibilizer appears to be between 2 and 3 wt %.

Figure 10 illustrates that in the absence of compatibilizer, the addition of titanium alkoxides is found to substantially reduce the modulus of PS. (PS has a tensile modulus of about 2177 ± 228 MPa, a break stress of 33 ± 4 MPa, and a break strain of 1.6 ± 0.2%.) These samples are grossly phase separated as indicated by their opacity. Poor adhesion between the PS and inorganic phase and the presence of voids as a result of the macroscopic phase separation would lead to inferior mechanical properties. Addition of 2–3% of the block copolymer substantially improved the modulus to above that of polystyrene. The random copolymer was also effective in improving the modulus values, although less so than the block copolymer. It appears that the maximum in modulus is shifted to a lower loading with the random copolymer. Although slight differences in the results between compatibilizers may be artifacts owing to data scatter and sample defects, the modulus was improved over that of PS and substantially improved over that of PS/Ti by the addition of block or graft copolymer or PVPh homopolymer. The improvement in properties is likely a result of the reduced size and better dispersion of the titania particles and possibly better adhesion between these and the PS matrix.

Similar results were obtained for both elongation at break and break stress. Although none of these values are as large as for pure PS, there is substantial improvement over the values with no compatibilizer. An interesting trend was noted for the random copolymer in that no maximum as a function of composition was observed for both the elongation at break and break stress. This result merits more attention; however, data scatter may be the dominant effect. Of primary importance is the fact that improved modulus values can be obtained, relative to pure PS, with only minimum loss of elongation at break and break stress.

Conclusions

The results demonstrate the viability of using compatibilizers for improved properties in OIC materials. The PS, SAN, and PVME systems were test cases, and the physical properties shown here are only illustrative

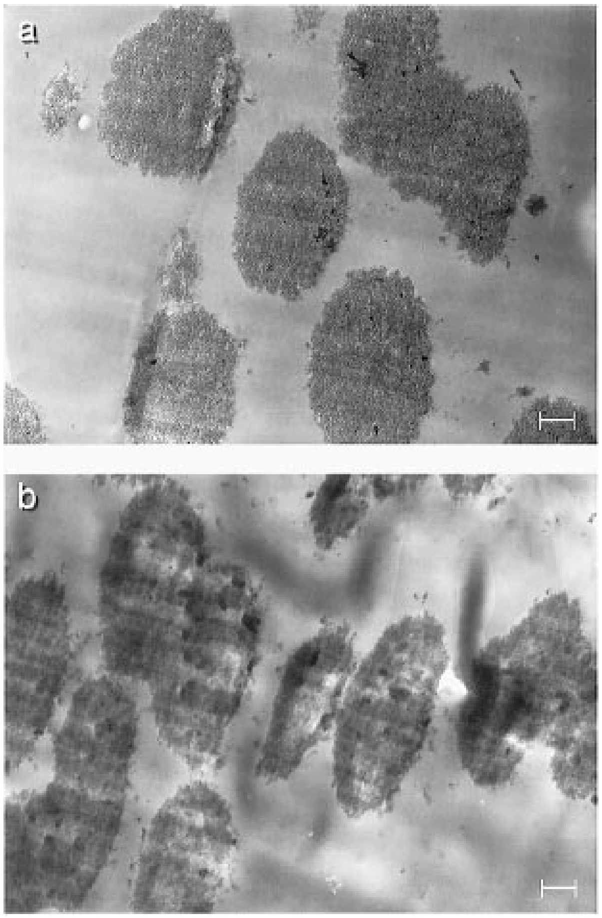


Figure 6. Transmission electron micrograph of PS/Ti, 2/1, with (a) 2.1 wt % and (b) 8.1 wt % ethylphenol. Fiducial bar = 250 nm.

of what compatibilizers may provide in these types of systems. The compatibilizer allowed homogeneous introduction of titania to organic polymers with which it is inherently incompatible. Microscopy results indicated that the size of the dispersed inorganic phase could be substantially reduced in these composites by addition of the compatibilizer. DMA results showed that a plateau in the tensile modulus above the T_g of PS could be obtained with added compatibilizer and that this plateau was obtained at very low titania loadings. The samples were found to stretch substantially above their T_g but did not fail. Ultimate mechanical properties showed that the effect of the compatibilizer on the mechanical properties was generally optimized at about 2−3 wt % copolymer. Modulus values could be improved by over 200 MPa with virtually no change in break stress and only a slight depression in elongation at break relative to PS. When compared to the incompatible PS/Ti composite, much larger increases in modulus and break stress were obtained.

Block copolymers of PS and PVPh (50/50) were found to be most effective at reducing the size of the dispersed titania phase. However, there were virtually no discernible differences in mechanical properties of the composites containing either block or random copolymers or PVPh homopolymer. The effectiveness of the homopolymer in compatibilizing the PS and titania was surprising and is apparently not due simply to modification of the polymerization mechanism of titanium isopropoxide, as the small molecule 4-ethylphenol also proved to be ineffective.

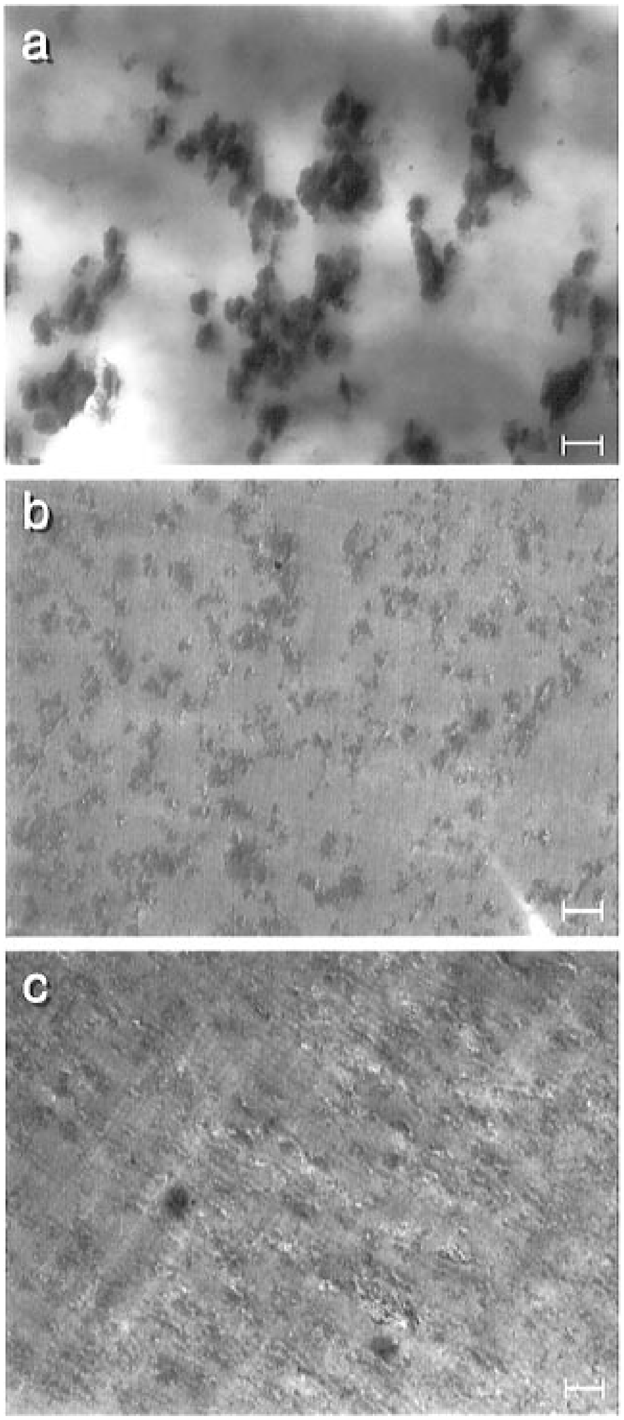


Figure 7. Transmission electron micrograph of PS/Ti, 2/0.5, with (a) 1.2 wt %, (b) 4.5 wt %, and (c) 8.5 wt % PVPh. Fiducial bar = 250 nm.

A possible explanation for the observed results may be that two differing types of compatibilization mechanisms are operative. The mechanism of block copolymer compatibilization may be similar to that described for organic polymer blends in that the VPh block binds to the surface of the titania particles, with the PS block extending into the PS matrix. On the other hand, the random copolymer or PVPh homopolymer may be coating the inorganic particles, with few polymer chains extending into the PS matrix. The compatibilizer shields the titania particles, resulting in a PS-like surface due to the fact that the phenolic OH groups are directed toward titania, allowing dispersion of the particulates in the PS phase. Note that this would also effectively shield the OH groups from the PS matrix,

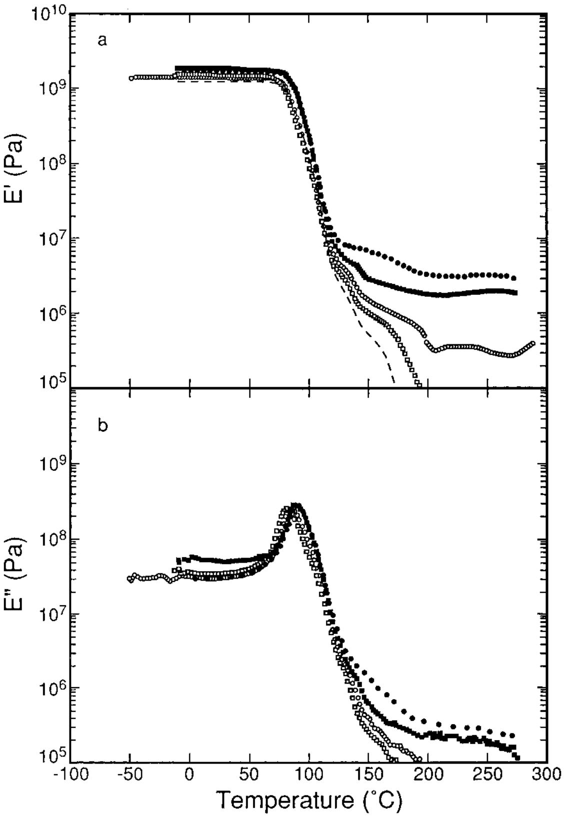


Figure 8. DMA spectra (a) E' and (b) E'' of PS/Ti, 2/0.5, with (□) 1.2, (○) 2.3, (■) 4.5, and (●) 6.5 wt % block copolymer: dashed curve is PS/Ti, 2/0.5, with no added block.

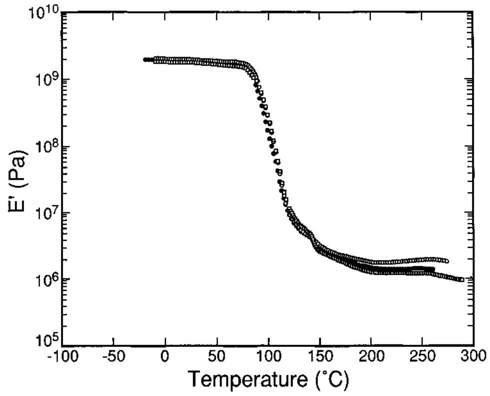
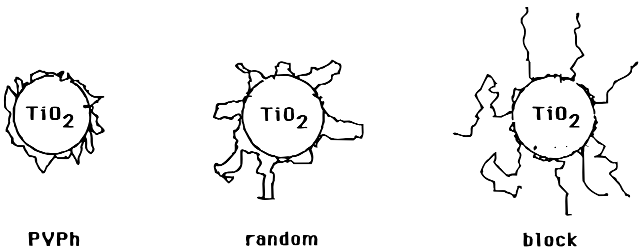


Figure 9. DMA spectrum (E') of PS/Ti, 2/0.5, with 4.5 wt % (○) block, (□) random, and (●) PVPh.

which otherwise would drive phase separation. These models are, however, only speculative at this time.



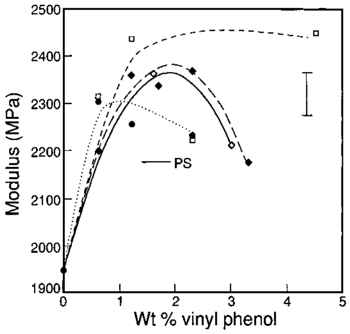


Figure 10. Tensile modulus vs percent compatibilizer for (◆) PS/Ti/b 2/0.5; (◇) PS/Ti/b, 2/0.7; (●) PS/Ti/r, 2/0.5; and (□) PS/Ti/PVPh, 2/0.5. The fiducial bar represents the typical average standard deviation.

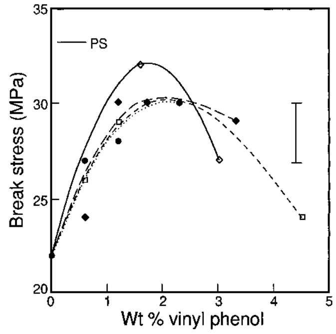


Figure 11. Break stress vs percent compatibilizer for (◆) PS/Ti/b, 2/0.5; (◇) PS/Ti/b, 2/0.7; (●) PS/Ti/r, 2/0.5; and (□) PS/Ti/PVPh, 2/0.5. The fiducial bar represents the typical average standard deviation.

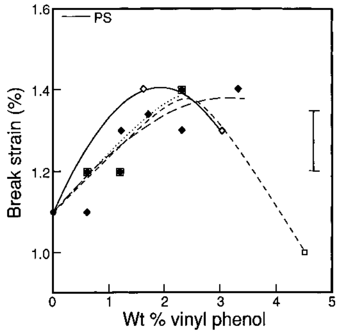


Figure 12. Elongation at break vs percent compatibilizer for (◆) PS/Ti/b, 2/0.5; (◇) PS/Ti/b, 2/0.7; (●) PS/Ti/r, 2/0.5; and (□) PS/Ti/PVPh, 2/0.5. The fiducial bar represents the typical average standard deviation.

It is interesting that moderate values of E' in the elastic region above T_g are obtained at titania loadings at least as small as 6.5 wt %, in contrast to results obtained previously on other systems such as PVAc or PMMA. It may be that the PVPh-containing polymers become part of the reinforcing "network" via cross-linking, as opposed to a purely inorganic oxide network being formed.

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