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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>

THERMAL AND MECHANICAL PROPERTIES OF SOME POLY(METHYL ACRYLATE)/SILICA COMPOSITES WITH INTENTIONALLY SUPPRESSED INTERFACIAL BONDING

Guru S. Rajan^a; James E. Mark^a; Edward E. Seabolt^b; Warren T. Ford^b

^a Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH, U.S.A. ^b Department of Chemistry, Oklahoma State University, Stillwater, OK, U.S.A.

Online publication date: 24 June 2002

To cite this Article Rajan, Guru S. , Mark, James E. , Seabolt, Edward E. and Ford, Warren T.(2002) 'THERMAL AND MECHANICAL PROPERTIES OF SOME POLY(METHYL ACRYLATE)/SILICA COMPOSITES WITH INTENTIONALLY SUPPRESSED INTERFACIAL BONDING', *Journal of Macromolecular Science, Part A*, 39: 1, 39 – 51

To link to this Article: DOI: 10.1081/MA-120006517

URL: <http://dx.doi.org/10.1081/MA-120006517>

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THERMAL AND MECHANICAL PROPERTIES OF SOME POLY(METHYL ACRYLATE)/SILICA COMPOSITES WITH INTENTIONALLY SUPPRESSED INTERFACIAL BONDING

Guru S. Rajan,¹ James E. Mark,^{1,*}
Edward E. Seabolt,² and Warren T. Ford²

¹Department of Chemistry and the Polymer Research Center,
The University of Cincinnati, Cincinnati, OH 45221-0172

²Department of Chemistry, Oklahoma State University,
Stillwater, OK 74078

ABSTRACT

Poly(methyl acrylate)/silica composites were prepared using a silane coupling agent designed to suppress the bonding between the silica and the acrylate elastomeric matrix. These composites were characterized using a scanning electron microscope, a differential scanning calorimeter, thermogravimetric analyzer, and an Instron mechanical tester. The mechanical properties of these materials were much poorer than those of the corresponding composite having a silane giving strong interfacial bonding, thus documenting the effects of these interactions on the reinforcement of a typical elastomeric material.

Key Words: Poly(methyl acrylate); Elastomer; Composites; Thermal properties; Mechanical properties; 3-Chloropropyltrimethoxysilane; 3-(Trimethoxysilyl)propyl methacrylate; Silica; Filler Dispersion

*Corresponding author. E-mail: markje@email.uc.edu

INTRODUCTION

Organic-inorganic composites are of considerable interest and importance because they provide properties that are synergistic of both the inorganic particles and polymer matrix in which they are dispersed [1–19]. For example, optimization of particle size in the nanoscale size range has opened a novel and exciting research field in the areas of nanotechnology and nanocomposites [12]. In addition to improvements in mechanical properties, regularly dispersed particles in a polymer matrix even exhibit unusual optical properties [9, 11, 14].

But the most important still unsolved problem is the nature of the bonding between the filler particles and the polymer chains [18]. The mechanical performance of a composite depends on the adhesion between the dispersed and the continuous phases. If the surface of the filler is incompatible with the polymer, the phases separate and there is agglomeration of the filler. The filler surface, however, can be modified with alkyl-trialkoxysilanes to improve adhesion between the filler and the polymer [20]. The network chains can then be adsorbed onto the filler surfaces thereby increasing the effective degree of crosslinking. Moreover, this effect can be strong if some reactive surface groups are present on the particles leading to more crosslinking or endlinking of the polymer chains.

Covalent chemical bonding between the filler particles and the polymer matrix (“chemisorption”) can be dominant and restrict the movement of polymer chains relative to the filler surface when high stresses are applied [18]. Even if these interactions are absent, long-range van der Waals forces between the filler surface and elastomer matrix can lead to “physisorption”. Both these types of adsorption contribute to reinforcement. A filler particle may be considered a high functionality crosslink, but can also participate in molecular rearrangements under strain. The distribution of end-to-end vectors of the chains, and network chain mobility are affected by the volume taken up by the filler. The presence of fillers not only segregates the molecules in its vicinity and reduces entanglements, but also reduces the segmental mobility of the adsorbed polymer chains.

It has long been recognized that the size, structure, and surface nature of filler particles play important roles in the reinforcement of elastomers [21–26]. The particle size determines the interfacial area between polymer and filler, aggregate-aggregate distance, and dispersion and distribution of the filler in the matrix. Smaller size is a prerequisite for enhancement of reinforcement in filled-polymer systems. Filler structure is a geometrical parameter, which determines the restriction of the movement of polymer chains during deformation. The nature of the surface dominates the polymer-filler interactions, filler aggregate-aggregate interactions, etc.

There are a number of theoretical approaches that account for the interactions between filler particles and a host elastomer [27–37]. In this paper,



however, only those literature results that clearly illustrate the influence of covalent bonding, or the absence thereof, between the polymer and the filler on the mechanical properties of filled elastomers will be given emphasis. The specific goal is obviously to understand the behavior of the present PMA/silica composites, which will use 3-chloropropylsilane to intentionally suppress covalent bonding between the two phases [38–49].

Kraus [38] showed the influence of filler attachments on modulus and effective crosslink density for styrene-butadiene rubber (SBR) filled with either easy processing channel carbon black (EPC) or graphitized channel black at the same structural level. Significant improvements in crosslink density and 300% modulus for EPC carbon black compared with unfilled and graphitized channel black filled SBR showed that EPC carbon black interacted strongly with the polymer while the graphitized black interacted very little.

Gent et al. [39–41] considered the apparent softening effect in tensile stress-strain measurements to occur because the effective load-bearing in the material is reduced due to the presence of vacuoles. The beads he investigated, and therefore, the corresponding vacuoles, were regarded as uniform spheres, which were distributed in a regular, not random, manner.

Medalia [42, 43] demonstrated that the volume of any occluded rubber should be added to the filler volume, which results in a larger “effective” volume of reinforcing agent. He also showed that extrudate swell of rubber compounds could be predicted well for fillers of different structure levels if such an effective filler volume correction is used.

Polmanteer and Lentz [44] studied the effect of structure and polymer-filler linkages on modulus and crosslink density for elastomers of polysiloxane (“silicone”), SBR, and poly(ethylene co propylene) (EPM) filled with trimethylsiloxy -treated silica fillers. Vulcanizates of these filled elastomers were measured in two environments: (1) toluene, and (2) toluene in an ammonia atmosphere designed to cleave any polymer-filler linkages present. The mechanical behavior was found to be influenced by the concentration of effective network chains (sum of chemical crosslinks and the effective physical crosslinks that result from trapped entanglements). The number of network chains (or crosslink density) increased with increasing filler structure in toluene, but the number of network chains decreased considerably (by 21–47%) in the presence of the ammonia-modified atmosphere. Data showed that over 40% of the total effective network chains are dependent on polymer-filler interactions. The results demonstrated that polymer-filler bonds are required, in combination with occluded volume, in order to achieve a significant increase in both modulus and crosslink density.

Blackley and Sheikh [45–47] studied the effects of surface treatment of bead-filled poly(ethyl acrylate) (PEA) elastomers on mechanical properties. The chemical interaction between the surface of filler particles and the elastomer matrix was varied by varying the nature of the glass surface [45].



The results for the tensile stress-strain properties of these PEA elastomers containing various concentrations of beads indicated that the stiffening effects of the beads increased as the adhesion between the beads and matrix was improved [46]. If the beads were treated so as to minimize the adhesion to the matrix, then they were actually found to cause an apparent softening of the material! This effect was explained by assuming that beads merely served to increase the void content of the material and thereby effectively reduced the cross section of the material available for load bearing.

Vondracek and Pouchelon [48] demonstrated the effects of ammonia atmosphere on the tensile set and swelling in silica-filled silicone rubber. The silicas used (fumed and precipitated) differed from each other by their specific surface area and/or surface nature. This study showed that the ammonia-induced chemical cleavage of hydrogen bonds results from the simultaneous action of mechanical or physical stress and the chemical effect of the ammonia. Tensile deformation of silica-filled silicone vulcanizates in an ammonia environment resulted in a permanent deformation or set which critically depended on silica contents, while the unfilled vulcanizates yielded no permanent deformation.

Maaref et al. [49] showed that blends of Zeolite 13X fillers and polystyrene exhibited no reinforcement effects, but the pseudo interpenetrating polymer networks (PIPNS) showed significant increases in tensile strength with increasing filler content. There was no reinforcement for either the blends or PIPNs of Vycor glass filler because of their large particle size. The PIPN samples, however, gave larger values of the tensile strength relative to the corresponding blended samples. This could be possibly be due to increased interactions in the PIPNs. This conjecture was supported by thermal analysis, electron microscopy, and small-angle X-ray scattering studies.

These studies document earlier results on the various effects of elastomer-particle interactions on mechanical properties, the primary subject of the present investigation.

Earlier investigations reported a novel approach to the preparation of poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) composites filled with 3-(trimethoxysilyl)propyl methacrylate-coated silica (TPM-Silica) [9, 11, 13–17, 19]. TPM was grafted to the colloidal silica, which was prepared from tetraethoxysilane (TEOS). The elastomeric matrix was formed by the polymerization of methyl acrylate (MA) in the presence of TPM-silica particles to form PMA/TPM-silica composites [19]. The particles were attached to the PMA by covalent bonding between the coupling agent and the matrix.

Either randomly dispersed, or regular arrays (ordered dispersions), or aggregated PMA/TPM-silica composites were obtained, depending on when the polymerization was performed after the ingredients were mixed. If the polymerization was done immediately after the ingredients were mixed, the filler particles were randomly dispersed. When the polymerization was done



after sufficient time was allowed, the silica particles formed regular arrays. As final alternative, aggregated particles were obtained when the particle dispersion was first dried and then mechanically blended into the monomer prior to polymerization [19].

Elastomers containing aggregated silica showed a dramatic improvement in mechanical properties compared to the other two types of filler arrangements, in spite of the fact that the regular arrays were of particular interest since they exhibited novel optical properties. The results can be attributed to the good dispersions of reinforcing filler particles without completely eliminating their aggregation into larger structures, and to the methacrylate groups of the TPM being chemically bonded to the polymer matrix.

The present investigation was carried out to elucidate the extent to which the mechanical properties of PMA/TPM-silica composites depend on the chemical interaction between the coupling agent and the matrix. In this study, 3-chloropropyltrimethoxysilane (CP) was used as the silane coupling agent. CP groups are effective for dispersal of the colloidal silica into MA, but do not have the unsaturated groups to copolymerize with the MA. The resulting interactions are therefore mostly physical in nature, with little if any chemical bonding. Specifically, we report the (1) synthesis; (2) formation of colloidal crystals in the monomer dispersions; (3) attempts at retaining the colloidal crystals during polymerization; (4) scanning electron microscopy (SEM) images of dispersed and aggregated CP-silica in the composites; and (5) thermal and mechanical properties of PMA/CP-silica composites. Aggregated and randomly dispersed PMA/CP-silica composites were emphasized, because regular arrays and randomly dispersed PMA/TPM-silica composites were known to exhibit similar mechanical properties.

EXPERIMENTAL

Materials

Most of the materials were purchased from the Aldrich Chemical Company. TEOS and CP were distilled under vacuum, and absolute alcohol (Fisher) was distilled shortly before use. Ammonium hydroxide (Fisher), MA, and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were used as obtained. Dialysis of CP-silica in MA was done using a Spectra-Por (cellulose ester dialysis membrane) with a molecular weight cut-off of 50,000 and a diameter of 22 nm [14].

CP-Silica Particles

Colloidal dispersions of silica particles were prepared by the hydrolysis and condensation of TEOS in aqueous ammoniacal ethanol using the



Stober method [14]. CP was coated onto these particles to form chloropropylsilica by the procedure of Philipse and Vrij [14, 50]. These coated particles thus lack the methacrylate groups used in the TPM to bond the particles to the PMA [14, 19]. The particles had an average diameter of 155 nm (according to transmission electron microscopic measurements). The dispersion of CP-silica in ethanol was transferred to methanol by dialysis. The methanolic dispersion was then concentrated to yield a 56 wt% particle dispersion, and the particles were then transferred to MA by dialysis. The methods employed were those reported for the preparation of TPM-silica from trimethoxypropylsilyl methacrylate [14]. Chemical analysis of the filler obtained gave: Anal. Found: C, 9.91; H, 2.70; N, <0.05; Si, 39.13; Cl, 12.09 [50].

Randomly Dispersed CP-Silica Particles

For the randomly dispersed PMA/CP-silica composites, a 54.3 wt% solids dispersion of CP-silica in methyl acrylate was diluted to 1.5 mL to give dispersions having 34, 39, or 46% solids content. In addition, 2.7–3.0 mg of the photoinitiator, DMPA, was mixed into each sample. The dispersions were transferred to 2.5 cm × 7.5 cm × 396- μ m thick glass sandwiched cells which were then sealed, and the monomer polymerized immediately at room temperature by irradiation with a 450-W medium pressure Hg lamp [14]. No colloidal crystals were observed, neither in the monomer dispersion nor in the polymerized film [50].

Aggregated CP-Silica Particles

For the PMA composite containing aggregated CP-silica, a 100 mL sample of a methanolic CP-silica dispersion was evaporated in air at room temperature until solvent was no longer discernible. It was then dried at 80°C for 24 hours to produce a white, caked powder. The powder was dried further under vacuum at room temperature for 24 hours. A 3.18 g sample of the powder was mixed with 5.8 g of the MA monomer in a polyethylene bottle, shaken mechanically, and sonicated until the particles appeared to be completely dispersed. Evaporation of the MA from a weighed amount of dispersion under nitrogen left 47.8% of solid. This 47.8%-solids dispersion was diluted with more MA to give 1.9 mL each of dispersions having 35, 41, or 43 wt% solids, and then 3.4–3.7 mg of DMPA was mixed into each of them. Using the same method as for the randomly dispersed samples [14], the dispersions were transferred to glass sandwiched cells, sealed, and the monomer polymerized at room temperature. The density of the CP-silica particles was taken to be 1.80 g cm⁻³ [50].



Scanning Electron Microscopy

The surfaces of the composite films were coated with Au-Pd under vacuum. Images were recorded with a Hitachi S-4000 Scanning Electron Microscope at 20 kV and 25,000 magnification.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements were carried out on a TA Instruments DSC 2010 Differential Scanning Calorimeter with nitrogen as purging gas. The experiments were performed from -20 to 50°C at a heating rate of $10^{\circ}\text{C}/\text{min}$.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was done on a TA Instruments TGA 2050 Thermogravimetric Analyzer with nitrogen as purging gas. Tests were conducted from 30 to 630°C at a rate of $10^{\circ}\text{C}/\text{min}$.

Mechanical Testing

Mechanical property measurements were carried out on sample strips with dimensions $20 \times 4 \times 0.34 \text{ mm}^3$ using an Instron tester at a rate of $12.7 \text{ mm}/\text{min}$, to the rupture point.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

The SEM images of the composites are shown in Figs. 1 and 2. The disordered particles in the composite that were polymerized immediately after mixing the ingredients resulted in random arrangements of the particles, as shown in Fig. 1. The aggregated particles obtained by redispersing a dried sample of CP-silica into monomer shortly before polymerizing yielded aggregation, as demonstrated in Fig. 2.

Differential Scanning Calorimetry

The DSC results for the PMA/CP-silica composites are shown in Table 1. The glass transition temperature T_g increased with increasing silica content even though the influence of the filler on the T_g is not large.



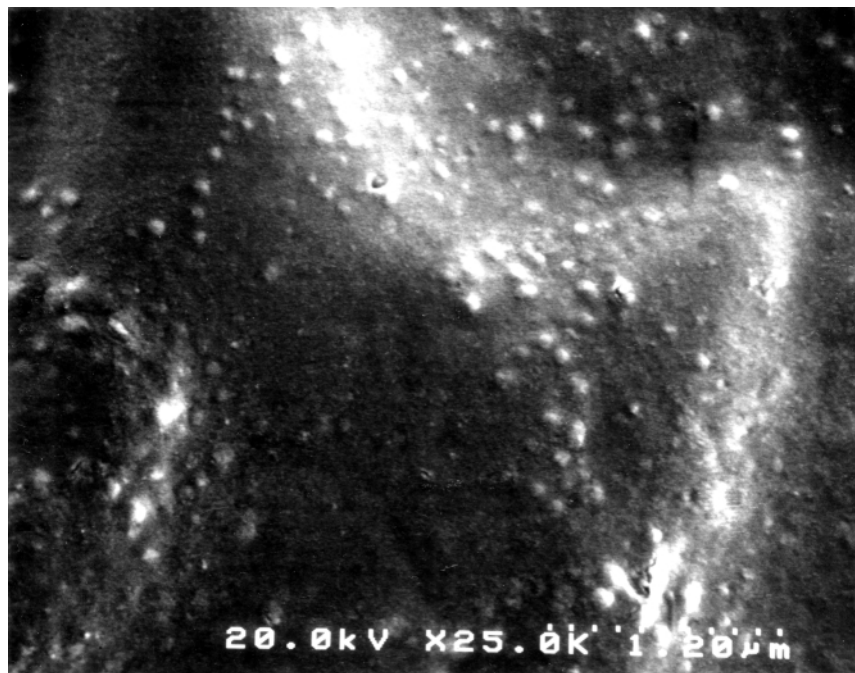


Figure 1. Electron micrograph of the randomly dispersed PMA/CP-silica composite.

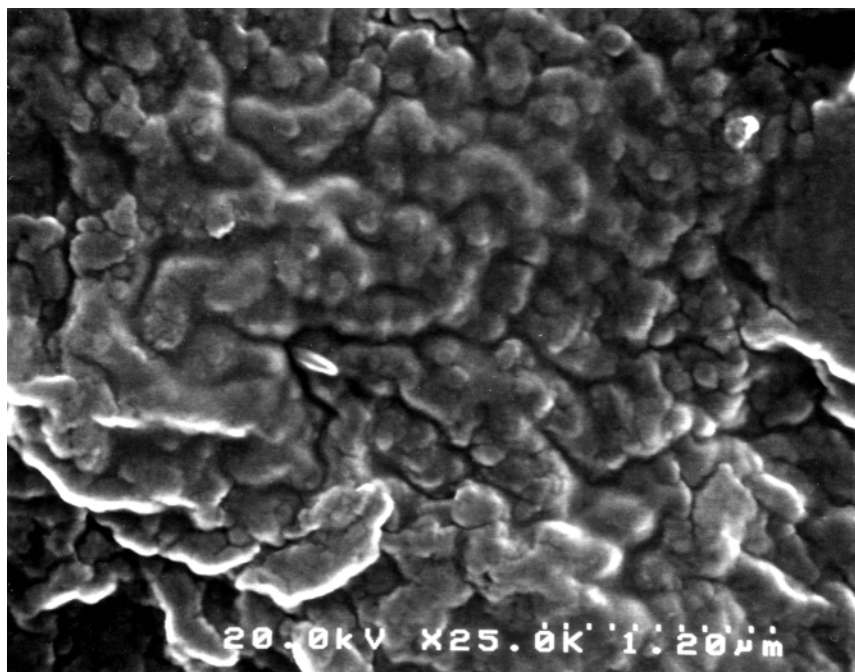


Figure 2. Electron micrograph of the aggregated PMA/CP-silica composite.

Table 1. Glass Transition Temperatures of the PMA/CP-Silica Composites (°C)

Filler Wt%	Filler Aggregation	
	Randomly Dispersed	Aggregated
0	13.1	13.1
35	13.5	13.2
40	14.2	14.1
45	14.7	14.2

Randomly dispersed silica composites had higher values of T_g than those with the aggregated silica. These results are in agreement with some of the trends reported in literature. Specifically, the introduction of filler particles may increase or decrease the T_g of a composite as the filler content increases, or may not be affected at all, depending on the specific polymer-filler system [5153]. Kraus and Gruver found that the T_g of a styrene-butadiene copolymer increased only 0.2°C for every ten parts per hundred by reinforcing carbon black added [54]. Pu et al. have shown that values of the T_g of the aggregated-particle composites were lower than those of the composites with randomly dispersed particles [19].

Thermogravimetric Analysis

TGA results are shown in Table 2. The composites remained stable up to 340°C and decomposition of the organic components was complete at about 425°C. The weight percent of residue for 35, 40, and 45 wt% of randomly dispersed particles and aggregated particles were 31.6, 34.4, and 37.9% and 33.0, 35.1, and 38.4%, respectively. The thermogravimetric curves showed behavior similar to that reported by Pu et al. [19].

Table 2. Thermogravimetric Values of the Residue Wt% for the PMA/CP-Silica Composites

Filler Wt%	Filler Disposition	
	Randomly Dispersed	Aggregated
0	5.57	5.57
35	31.6	33.0
40	34.4	35.1
45	37.9	38.4



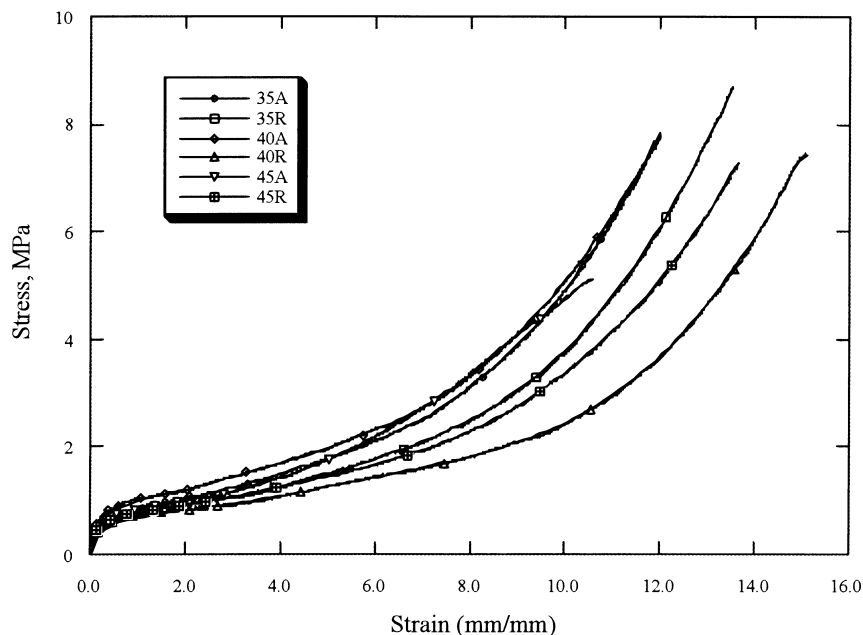


Figure 3. Stress-strain isotherms for the randomly-dispersed (R) and aggregated (A) PMA/CP-silica composites.

Mechanical Properties

In the present investigation, the mechanical property results are shown in Fig. 3 and Table 3. They indicate that CP does essentially nothing to improve the tensile modulus and strength of the PMA composites. This is, of course, consistent with the view that these deactivated filler particles have no reinforcing capacity and merely contribute to the void content of the material. The measured elongations at break are those of the elastomer

Table 3. Mechanical Property Results for the PMA/CP-Silica Composites

CP-Silica (wt%)	Disposition	Young's Modulus, MPa	Strain at Rupture, % $\times 10^{-3}$	Toughness, MPa
0	—	2.07	1.42	15.4
35	Random	2.70	1.35	37.6
	Aggregated	3.17	1.20	32.6
40	Random	3.27	1.51	35.5
	Aggregated	3.95	1.19	34.3
45	Random	4.03	1.36	34.2
	Aggregated	4.25	1.06	24.0



matrices. The increase in extensibilities for these PMA/CP-silica composites compared to that of PMA/TPM-silica composites is, of course, consistent with decreased chemical bonding in these CP materials. The birefringence of such PMA/CP-silica composites were of the same order of magnitude as that of the unfilled elastomer. This suggested that there was no large change in the orientational behavior of the composites in the absence of polymer-filler bonding [55].

The Young's modulus of the aggregated silica-filled elastomers was higher than the other type and increased with increasing percent filler in both cases. The data are about the same as those for the unfilled PMA sample reported by Pu et al. [19]. CP groups are effective for dispersal of the colloidal silica into MA but do not copolymerize with the MA. Since chloropropylsiloxanes are good solvents for PMA, after polymerization, the CP groups on the silica solvate the PMA but only occasionally covalently link to the PMA via chain transfer during radical polymerization. The PMA/CP-silica composites have mainly van der Waals attractions between the silica and the PMA elastomer. Even though CP groups solvate the PMA, the van der Waals attraction between the CP groups and the PMA matrix would be much weaker than the covalent bonds that strengthen the PMA/TPM-silica composites.

Reinforcements with hard domains can increase stiffness and resistance to fracture [18, 56–59]. Such stiffness increases involve a hydrodynamic effect, shape factor, and occlusion of rubber into the void space of filler aggregates. However, regardless of the particle size, interfacial area, and degree of dispersion, fillers will have no reinforcing effect unless there is good polymer-filler interaction. The properties are not improved if there is only poor or occasional bonding of the elastomer to the filler. In the absence of such bonding, aggregation does not improve the properties. In addition, even strain amplification of the polymer matrix would be reduced if the polymer molecules are unable to effectively anchor onto the filler surface.

CONCLUSION

SEM clearly demonstrated the dispersion, random or aggregated, of the CP-silica particles in the elastomeric composites. The T_g of the PMA/CP-silica composites increased with increasing wt% of filler. Randomly dispersed particles gave higher values compared to that from the aggregates. TGA results showed that the residue wt% of the composites increased with increasing wt% of the silica particles. The Young's modulus increased, but not significantly, and the extensibilities are essentially those of the unfilled elastomer. As expected, the physical interactions between the CP groups and the PMA matrix were much weaker than the covalent bonds that strengthen the PMA/TPM-silica composites.



ACKNOWLEDGMENTS

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grants DMR-00-75198 (to JEM) and DMR-98-12523 (to WTF) (Polymer Program, Division of Materials Research).

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Received August 1, 2001



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