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Effects of Dispersion and Aggregation of Silica in the Reinforcement of Poly(methyl acrylate) Elastomers

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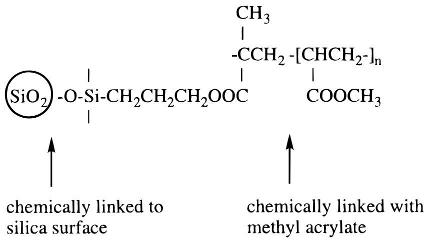
Composites were prepared from methyl acrylate monomer and silica particles to which 3-(trimethoxysilyl)propyl methacrylate groups had been grafted. The silica particles were bonded onto poly(methyl acrylate) through participation of their methacrylate groups in the polymerization of the methyl acrylate to form an elastomeric matrix. If the polymerization was done promptly after the ingredients were mixed, the silica particles were randomly dispersed. On the other hand, if sufficient time was permitted, the particles spontaneously formed regular arrays within the monomer which, on polymerization, yields the elastomer. Finally, if the particle dispersion was first dried and then blended into the monomer prior to polymerization, an aggregated arrangement was obtained. Although the elastomers having regularly ordered silica dispersions exhibited novel optical properties, they showed little difference in mechanical properties relative to those with randomly dispered silica. The elastomers having aggregated silica, however, had significantly improved mechanical properties, relative to the other two types. This is consistent with frequent observations in the rubber industry that halting compounding short of complete filler dispersion can give the best balance of mechanical properties.

Introduction

Organic−inorganic composites frequently consist of inorganic particles or fibers dispersed in a polymer matrix. They are of considerable interest and importance since they frequently provide properties that are optimal combinations of those of the separate organic and inorganic materials.[1−6] In addition, some composites can exhibit properties that are totally absent in the separate one-phase materials. In these composites, the dispersed phase is normally of micron size and is agglomerated and irregularly dispersed. There are two possible departures from these general characteristics which might be exploited for obtaining new properties from such composites. The first is to minimize particle size, and this has already opened a new and currently active research area known as “nanotechnology”.[7] The second is to control the dispersion of the particles. For example, an ordered embedding of particles in the polymer matrix can give rise to some very unusual properties, such as the optical effects described below.

Scheme 1. Sketch of the Structure of the PMA/TPM−Si Composites



Specifically, several of us recently reported the preparation of poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) composites filled with 3-(trimethoxysilyl)propyl methacrylate coated silica (TPM−silica).[8−10] The substituted methacrylate acts as a bonding agent, in that its trimethoxysilyl groups are hydrolyzed in a sol−gel reaction that bonds them to the silica surfaces. The resulting composite materials exhibited iridescence and other interesting optical properties. This apparently arises from Bragg diffraction of visible light by the colloidal crystalline arrays of the monodisperse amorphous silica particles, which typically have diameters on the order of 150 nm. The regular particle arrangements obtained are stable, since the methacrylate groups of the TPM are chemically bonded to the polymeric matrix, as shown in Scheme 1.

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The colloidal crystalline structure can be controlled by variation of the number of particles, by stretching elastomeric composites in which they reside, or by swelling the composite with more monomer followed by a second polymerization.[10]

Not surprisingly, it has been the optical properties of such composites that have been the most extensively studied.[10] Their other properties remain largely unknown, although there has been some work on related systems.[11−14] For example, an additional extremely important application of such composites occurs when the polymer matrix is elastomeric (as in the case of the PMA). This would be to provide an answer to the longstanding question in the rubber industry on the advantages or disadvantages of carrying out compounding so as to disperse reinforcing filler as completely as possible.[15−19] The complication in the usual compounding situation is the fact that the shearing stresses sufficient to break up particle aggregation are also sufficient to cleave some of the elastomeric chains. The present investigation was therefore carried out to provide clarification of this issue, preparing the PMA colloidal silica systems in such a way as to obtain particle dispersions that were random, regular, or aggregated. Of particular interest, of course, were the mechanical properties of these three types of filled elastomers. Also of interest, however, were their dynamic mechanical behavior and their thermal properties, including their glass transition temperatures.

Experimental Details

Synthesis of the PMA/TPM−Silica. Details of the preparation of TPM-coated silica particles and their use in ordered composite PMA films are reported elsewhere.[8−10] In this investigation, the desired particle concentrations were 35, 40, and 45 wt % and were obtained by diluting a master batch of 48 wt % dispersion with more methyl acrylate (MA) monomer. Each of the MA−silica dispersions[10] was mixed with 0.25 wt % of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone and was then poured into a sandwiched glass cell. Two of these cells had dimensions of 1 in. × 3 in. × 264.5 μm, and two others 2 in. × 3 in. × 396 μm. Two of the mixtures were immediately photopolymerized, but two of the other cells were placed horizontally in an oven maintained at 25 °C for 6−8 h. The two mixtures which were immediately polymerized gave composites with randomly distributed particles, while the two placed in the oven had sufficient time to form colloidal crystals, and thus the desired regular arrangements of the silica particles.[10] In both cases, the photopolymerization of the monomer and the methacrylate groups on the TPM−silica gave permanence to the arrangements obtained.

To form the aggregated TPM−silica, concentrated methanolic dispersions of 153 nm TPM−silica particles were dried at room temperature, followed by overnight vacuum-drying at 25 °C. The resulting aggregated particles were then redispersed in MA to form a concentrated dispersion of 53 wt % particles. As before, the desired particle concentrations of 35, 40, and 45 wt % were obtained by diluting the 53 wt % dispersion with more MA. These mixtures were immediately photopolymerized, as described above.

Scanning Electron Microscopy. Composite films were microtomed at room temperature parallel to the film plane using a Sorvall RMC-MT 6000 instrument, and the surfaces were coated with Au−Pd under vacuum in a Hummer II sputter coater. Images were recorded with a JEOL JSM-35U scanning electron microscope (SEM) at 25 kV and 30 000 magnification. Images near the top and bottom of each film were found to be similar.

Measurements of Mechanical Properties. For these measurements the sample films were cut into strips with dimensions 20 × 4 × 0.34 mm^3. Relatively static tensile tests were carried out on these strips using an Instron tester.[20] The rate of elongation was 0.5 in./min, and measurements were carried out to the rupture points.

Equiaxial extension is equivalent to uniaxial compression, and permits additional characterization of the static mechanical properties of these materials. This type of deformation is important since results obtained by it and by uniaxial elongation constitute a full spectrum of stress−strain behavior of a material. For these measurements, the samples were cut into circular films with dimensions of 50 × 50 × 0.34 mm^3. The biaxial extension was imposed by inflation of these sheets in a laboratory-built apparatus constructed essentially as described elsewhere.[21,22] Data thus obtained were converted into values of the compression ratio α and compression stress f^*.[23] The compression ratios were obtained from the dimensions of the samples before and after inflation. Values of f^* were calculated from[22]

$$f^* = pr/(2d_0\alpha^2) \tag{1}$$

where p is the measured inflation pressure, r is the radius of curvature of the inflated sheet at the applied pressure, and d_0 is the initial thickness of the sample film. These measurements were also carried out to the rupture points.

Dynamic mechanical tests were performed to characterize the response of a material to periodic stresses. When carried out over a wide range in frequency and temperature, these tests are especially sensitive to the chemical and the physical structure of a material.[24,25] The tests were conducted on strips of dimensions 20 × 4 × 0.34 mm^3, using a Rheometrics Solid Analyzer RSA II (Rheometrics, Inc., New Jersey). First a static strain scan was made for every sample strip to determine suitable values of the pretension; thereafter, both frequency sweeps and temperature sweeps were carried out.

Thermal analysis is also important, since it can, for example, provide information on such properties as thermal stability and transition temperatures between physical states. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were therefore carried out, using a Polymer Laboratories (PL) Thermal Science DSC system with nitrogen as purging gas. The baseline calibration was performed with sapphire, while second-stage calibrations were performed with indium, silicon, and zinc references, to achieve temperature readings within ±0.5 °C. The heating rate employed was 10 °C/min. Of particular interest in these

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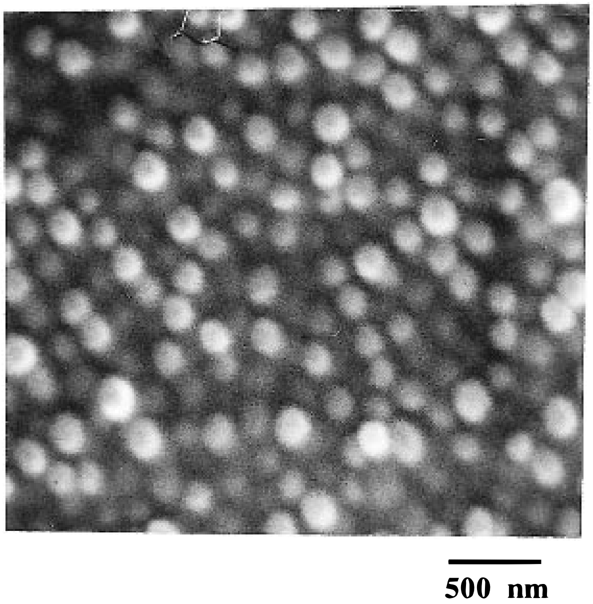

Figure 1. Electron microscopy results for a sample containing randomly dispersed silica particles. In these first three figures, the composites had 40 wt % silica and had been microtomed parallel to the film plane.

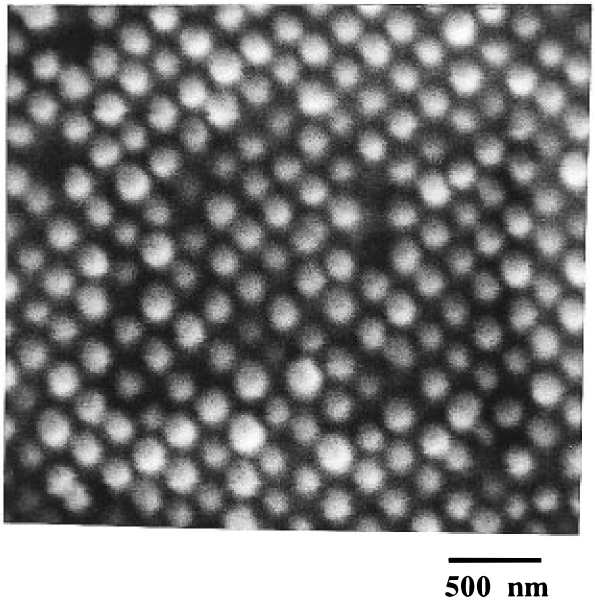

Figure 2. Electron microscopy results for a sample containing regularly dispersed silica particles.

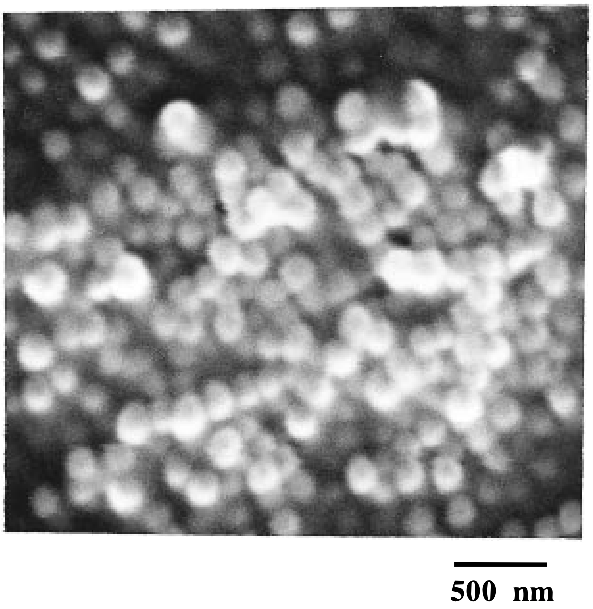

Figure 3. Electron microscopy results for a sample containing aggregated silica particles.

experiments were changes in the temperature profiles that would permit identification of the glass transition temperatures.

Results and Discussion

Scanning Electron Microscopy. The relevant SEM images reported here pertain to films microtomed parallel to the film plane for (i) disordered particles in a composite that was polymerized immediately after filling the cell, (ii) regularly arranged particles in a composite that was polymerized after formation of colloidal crystals, and (iii) aggregated particles obtained by redispersing a dried sample of TPM−silica into monomer shortly before polymerization. These results are shown in Figures 1−3, respectively. The first demonstrates the random arrangements of the particles, the second the hexagonal order of the particles in a plane that contributes to Bragg diffraction,[13,14] and the last the degrees of aggregation of the redispersed particles.

Static Mechanical Properties. Representative stress−strain plots for these PMA/TPM−silica composites in elongation are shown in Figure 4; additional isotherms are presented elsewhere.[20] Selected important mechanical properties are summarized in Table 1. It can be seen that the strength of PMA is dramatically increased by the presence of the TPM−silica. For example, the Young's moduli of the filled elastomers (35−45 wt % silica) were 10 to more than 100 times higher than that of unfilled elastomer. At the same time, the strain at rupture decreased markedly from 1400% for an unfilled sample to 40% in the case of 45% filler. This is consistent with general observations[11,23] that introduction of filler into an elastomeric matrix increases its strength but decreases its extensibility. Of greater importance is toughness, which is the energy needed to break the sample and is thus the area under a stress−elongation curve. Although it decreases at the higher TPM−silica contents, it is worth noting that only the composites with aggregated silica have greater toughness than unfilled PMA. This is because the composites with randomly dispersed silica and regularly dispersed silica have relatively small extensibilities, as documented in Table 1.

The effect of the silica dispersion and aggregation on the stress−strain properties is illustrated further in Figures 5 and 6. It is clear from these results and others shown elsewhere[20] that the composites with randomly dispersed and regularly dispersed silica have almost identical stress−strain isotherms. Thus, making the dispersion highly regular can lead to novel optical properties,[10] but this does not have much effect on static mechanical properties. This is reminiscent of the effect of network chain-length distribution on elastomeric properties; there is essentially no effect unless the distribution is made peculiarly bimodal by the end-linking of mixtures of very short and very long function-

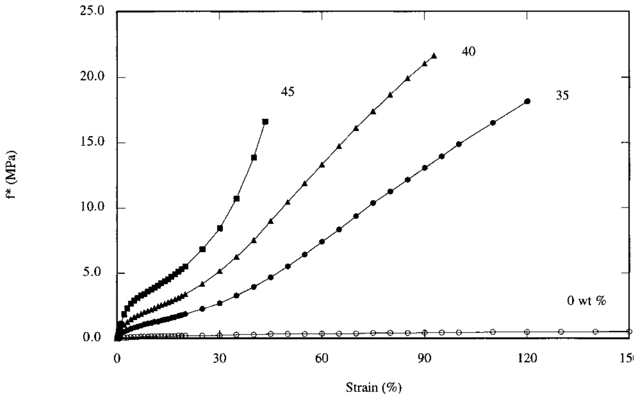

Figure 4. Representative stress−strain isotherms for some PMA/TPM−silica composites having regularly dispersed silica. The rate of elongation was 0.5 in./min, and the silica contents are specified for each curve.

Table 1. Some Mechanical Properties of the PMA/TPM−Silica Composites in Elongation

TPM−silica (wt %)	type	Young's modulus (MPa)	strain at rupture (%)	toughness (J/m^3 ×10^7)
0		2.07	1419	1.54
35	rand[a]	20.3	120	1.01
	reg[b]	19.4	121	0.97
	agg[c]	29.9	254	2.24
40	rand[a]	30.1	98.2	1.13
	reg[b]	29.2	92.8	0.98
	agg[c]	68.6	184.	1.80
45	rand[a]	126	46.2	0.36
	reg[b]	80.8	43.6	0.33
	agg[c]	262	127	1.02

[a] Randomly dispersed silica. [b] Regularly dispersed silica. [c] Aggregated silica.

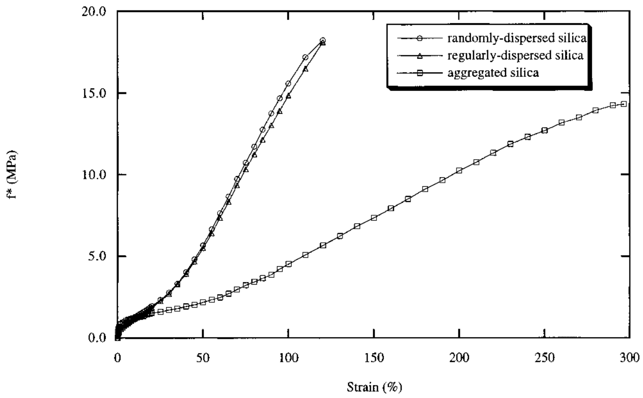

Figure 5. Effect of dispersion and aggregation of the silica on the mechanical properties of the composites having a silica content of 35 wt %.

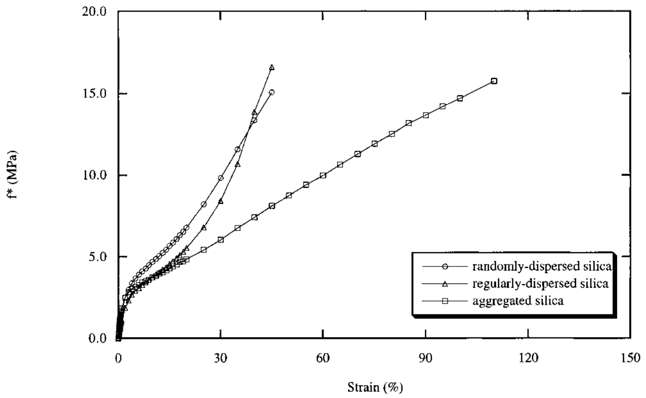

Figure 6. Effect of dispersion and aggregation of the silica on mechanical properties, but for composites having a silica content of 45 wt %.

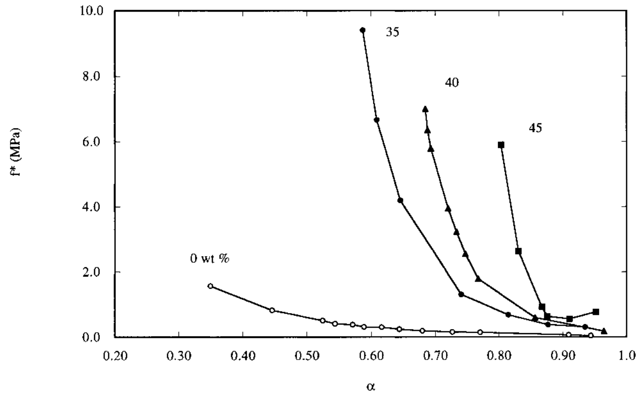

Figure 7. Compression stress−compression ratio relationships for the composites with regularly dispersed silica.

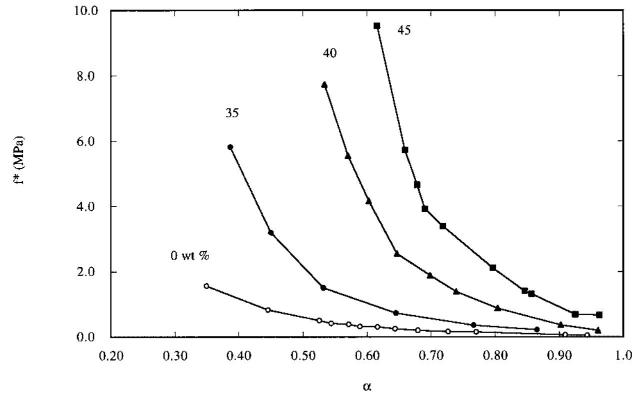

Figure 8. Compression stress−compression ratio relationships for the composites with aggregated silica.

ally terminated chains.[26−29]

The composites with aggregated silica are seen to exhibit isotherms with much improved properties, particularly their extensibilities. Their improved mechanical properties relative to the other two types is consistent with frequent observations in the rubber industry that halting compounding short of complete filler dispersion can give the best balance of mechanical properties. At least part of the explanation may reside in the nature of the "bound rubber"[15−19] in the vicinity of the aggregates, but this is largely conjecture. Some analytical theory would be very useful in this regard, and computer simulations already show some promise in giving molecular insight into the elastomer reinforcement process in general.[30]

Figures 7 and 8 show stress−strain isotherms in compression for PMA/TPM−silica composites having regularly dispersed silica and aggregated silica, respectively.[22] The corresponding ultimate properties are summarized in Table 2. It is seen that the deformations

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Table 2. Ultimate Mechanical Properties in Compression (Equibiaxial Extension) for the Composites Having Regularly Dispersed Silica or Aggregated Silica

type of silica	content (wt %)	compression ratio	compressive stress (MPa)	compression energy[a] ($J/m^3 \times 10^5$)
	0	0.350	1.57	2.53
reg[b]	35	0.587	9.41	7.62
	40	0.684	7.00	4.67
	45	0.803	5.91	2.38
agg[c]	35	0.387	5.83	7.00
	40	0.533	7.74	8.85
	45	0.616	9.53	9.91

[a] Calculated from $E = \int \alpha f^* \mathrm{d}\alpha$. [b] Regularly dispersed silica. [c] Aggregated silica.

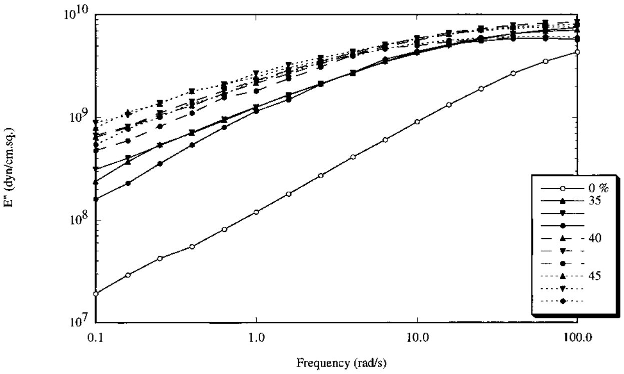

Figure 9. Frequency dependence of the loss modulus for the composites at room temperature. Solid triangles, randomly dispersed silica; inverted solid triangles, regularly dispersed silica; filled circles, aggregated silica.

at rupture in compression decrease with increase in silica content and that the composites with aggregated silica have higher compressibilities. This parallels the results in uniaxial elongation. It is also seen that the composites with aggregated silica have higher compression energies at rupture than do the composites with regularly dispersed silica. This is mainly because of their higher compressibilities.

Dynamic Mechanical Properties. Figure 9 shows the effect of frequency on the loss modulus E'' for the composites. The results for the storage modulus E' were similar, and are shown elsewhere.[20] The moduli were found to increase continuously as the frequency increased, but with a leveling off, and the effect of frequency became progressively less pronounced as the silica content increased. Apparently, at higher frequencies some of the motions cannot keep up with the frequency changes. This was more evident in the case of the loss modulus.

The effects of temperature on E'' and loss tangent tan δ for some of the composites are shown in Figures10 and 11. Additional results are shown elsewhere.[20] A sharp drop of E' near 25 °C[20] indicates that the glass transition occurs near this temperature. Well above the glass transition temperature T_g, a rubberlike plateau in E' is observed which extends to at least 100 °C.[20] Since cross-linked polymers generally exhibit a plateau in E' above T_g (the magnitude of which is a function of the molecular weight between cross-links),[31] this is consistent with the fact that the composites are cross-linked by the silica.

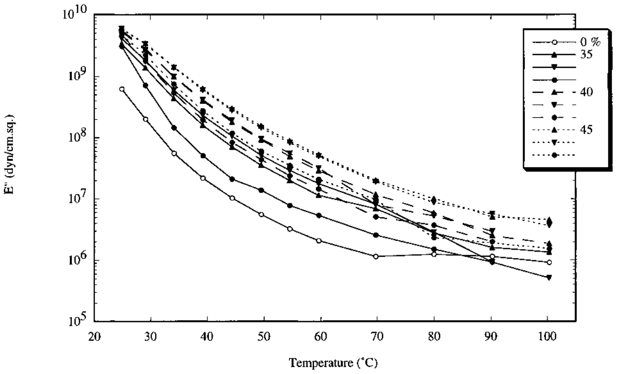

Figure 10. Temperature dependence of the loss modulus at a frequency of 10 rad/s; see legend to Figure 9.

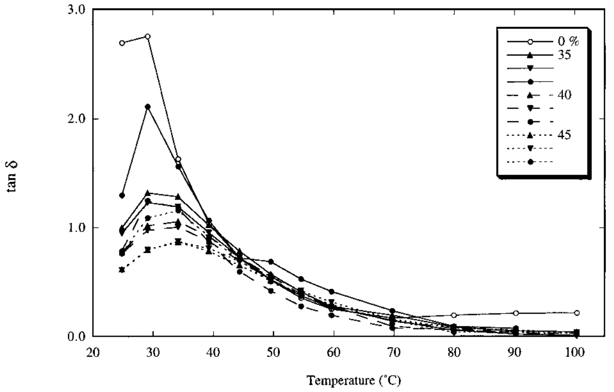

Figure 11. Temperature dependence of loss tangent at a frequency of 10 rad/s; see legend to Figure 9.

Values of E'' are seen to decrease as the temperature increases, but the loss tangent reaches a maximum at around 30−35 °C. This is due to the asynchronous change of storage and loss modulus with temperature. At higher temperatures, the moduli differ for different silica loadings, but there is not much difference in the values of loss tangent. This suggests that with increase of temperature, the interaction between the PMA networks and silica particles weakens, the energy lost in this interaction is minimized, and the energy lost in the PMA network chains dominates.

As in the case of the more static mechanical properties, the composites with randomly dispersed silica and regularly dispersed silica behaved very similarly. This was much more evident with regard to the effects of frequency.

Thermal Properties. These composites all showed very similar thermogravimetric curves,[20] as is illustrated in Figure 12. In all cases, the composite films undergo initial weight loss between 90 and 100 °C and further loss between 375 and 410 °C. The amounts of residue left after the analyses are compared with the theoretical amounts of silica based on elemental compositions in Table 3. The amount of silica left and the amounts calculated are in close agreement, as expected from the polymer matrix and the TPM groups decomposing, and leaving only silica particles as residue. Similar results have been observed for polyimide−silica hybrids where the amount of silica residue was proportional to the initial amount of tetraethoxysilane used to generate the silica in situ.[31]

Figure 13 shows the glass transition region in the DSC curves for selected composites, with additional results reported elsewhere.[20] Generally speaking, the

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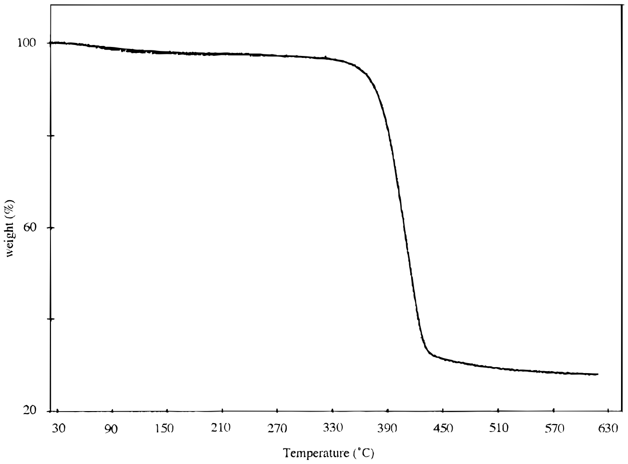

Figure 12. Representative thermogravimetric curve, for the composite having 35 wt % randomly dispersed silica. The heating rate was 10 °C/min.

Table 3. Comparisons of TGA Results and Elemental Analyses for Silica Residues

TPM−silica content (wt %)	TGA residue (wt %)	calcd residue (wt %)[a]
35	31.2	31.1
40	32.2	35.4
45	37.0	40.1

[a] Calculated as SiO_2 remaining after loss of all C, H, and excess O.

influence of silica content on the T_g was found to be small. This is consistent with previous reports that an increase in filler content can cause T_g of a composite to increase, decrease, or stay unchanged, depending on the specific polymer−filler system.[32−34] Changes in T_g were found to be much more pronounced in the case of PMMA/silica composites,[13] and Table 4 compares the effect of silica on T_g for these two materials. In the case of the PMMA, the composites have higher values of T_g than the unfilled polymer, and an increase in silica content increased T_g at least slightly. The reasons for this difference in behavior for these composites, and for others,[32−34] are not clear at the present time.

Conclusions

This investigation extends methods previously used for preparing composites having novel optical properties by placing silica particles in regular arrays within a polymeric matrix. In the present case, the matrix was an elastomer and the particle arrangements produced ranged from regular to random, to aggregated. The levels of reinforcement provided by the particles were essentially the same for the regular and random arrangements, but significantly improved in the case of the aggregated particles. This result is consistent with attempts in the rubber industry to control compounding of elastomers so as to obtain good dispersions of reinforcing filler particles without completely eliminating their aggregation into larger structures.

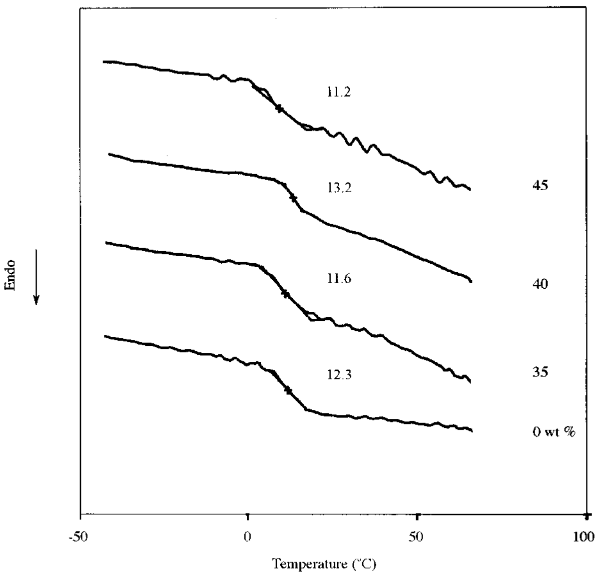

Figure 13. Differential scanning calorimetry curves for some composites having randomly dispersed silica. The heating rate was 10 °C/min. The amount of silica and the value of the glass transition temperature are indicated for each curve, and the ×'s locate the approximate positions of the transitions.

Table 4. Comparison of Effect of Silica on the Glass Transition Temperature of PMA/TPM−Silica and PMMA/TPM−Silica Composites

	T_g (°C)	
TPM−silica content	PMA	PMMA
0	12.2	102
35 wt % randomly dispersed	11.6	116
35 wt % regularly dispersed	10.1	124
35 wt % aggregated	9.7	N/A

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