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Mechanical properties of a poly(methyl acrylate) nanocomposite containing regularly-arranged silica particles

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SUMMARY

In an earlier investigation, poly(methyl acrylate) nanocomposites containing silica particles were found to have novel optical properties when the particles were regularly spaced rather than randomly located.The availability of these materials was used to determine whether there was any difference in the particles' reinforcing ability between ordered and random arrangements. The two types of composites were compared using near-equilibrium mechanical property measurements in uniaxial or equi-biaxial deformation, and dynamic mechanical properties measurements. It was found that having the filler particles regularly arranged had little effect on these properties, and that there was no anisotropy in their mechanical behavior. Related experiments could possibly be used to clarify the long-standing question of the importance of particle aggregation in elastomer reinforcement.

Key words: Nanocomposites, poly(methyl acrylate) elastomers, silica, mechanical properties, reinforcement, organic-inorganic hybrid materials

INTRODUCTION

Organic - inorganic composites are playing increasingly-important roles in research and in numerous applications. They can frequently provide properties which are combinations of those of the original organic and inorganic materials.[1-6] In addition, some composites can exhibit properties that are totally absent in the separate one-phase materials. In one novel approach, Sunkara et al.[7,8] reported poly(methyl acrylate) (PMA) composites filled with 3-(trimethoxysilyl)propyl methacrylate coated silica (TPM-Si). In these composites, TPM was chemically attached to silica particle surfaces and was chemically crosslinked with the PMA matrix as shown in Fig 1. The monodisperse silica particles crystallize into a face-centered cubic lattice in the liquid monomer, and crystalline order is retained as the monomer polymerizes to form the elastomer. This type of ordered nanocomposite is iridescent because the regular arrangements of the silica particles diffract visible light. Such optical properties of theTPM-Si/PMA composites have been studied but most of their other properties still remains unknown, although there has been some work on related systems.[9] This report describes some of their mechanical properties. It was decided to exploit the availability of these materials to determine whether there was any difference in the particles' reinforcing ability between these two arrangements. It was of particular interest to compare the two types of com-

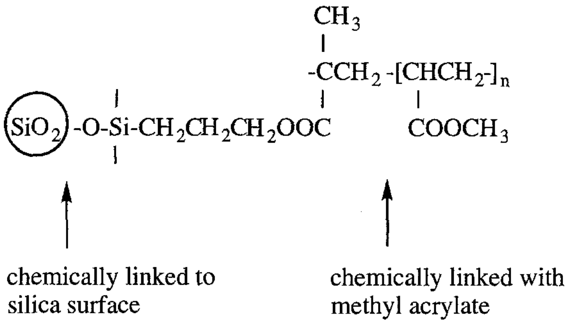

Fig. 1. Sketch of the structure of the elastomeric composites.

posites using near-equilibrium mechanical property measurements in uniaxial or equi-biaxial deformation, and dynamic mechanical property measurements.

PREPARATION OF COMPOSITES

The TPM-Si/PMA composites were synthesized by photoinitiated free-radical polymerizations.[7] A concentrated dispersion of 153 nm diameter TPM-Si in methyl acrylate (MA) was made by dialyzing TPM-Si particles in a methanolic dispersion with MA. This original dispersion was diluted with MA to make dispersions which contain 45, 40, and 35 wt % of TPM-Si. The dispersions having theseTPM-Si concentrations were loaded into glass cells, along with 0.2 wt % of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA). Polymerization was initiated with a medium-pressure Hg lamp either immediately upon preparation of these precursor samples (i. e., before crystallization), or after a period of time (8 - 12 hr) required to obtain particle crystallization (as judged by good diffraction effects). This was done to have the silica particles randomly dispersed in the first set of samples, but regularly dispersed in the second.

MECHANICAL PROPERTY MEASUREMENTS

Tensile tests were carried out on an Istron tester for three pairs of TPM-Si filled PMA sample films: 35, 40, and 45 wt % of TPM-Si in MA with the polymerizations started either before and after the crystallization. Two sample strips were cut perpendicularly from each film to investigate the possible presence of orientation within the samples; the two directions were referred as X and Y. Sample dimensions were 20 x 4 x 0.34 mm^3.

Equi-biaxial deformation tests were also carried out, for further clarification of the stress-strain properties of these composites. The apparatus employed is described elsewhere,[10] with only minor modifications. Dynamic mechanical properties can also provide much information on the morphology of organic/inorganic composite systems. Therefore the dynamic mechanical properties of these composites were measured on a Rheometics Solid Analyzer, using both frequency sweeps and temperature sweeps.

RESULTS AND DISCUSSION

Some typical stress-strain plots of these samples are shown in Fig. 2. It can be seen that the strength of PMA is dramatically increased by the presence of the TPM-coated silica, with Young's moduli of the filled PMA being 10 to 60 times higher than that of unfilled PMA for 35 to 45 wt % TPM-Si. At the same time, the strain at rupture of PMA decreased markedly from 1400 % for an unfilled sample to 50 % when filled with 45 % of TPM-Si. This is consistent with the general observation[9,10] that introduction of filler into an elastomeric matrix increases its strength but decreases its extensibility.

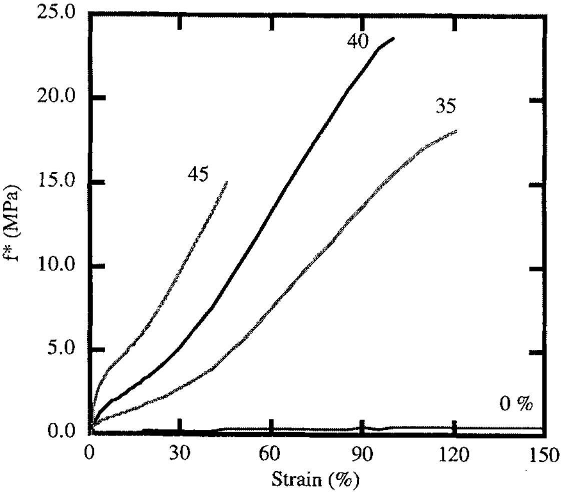

Fig. 2. Typical stress-strain plots of silica-PMA nanocomposites with different silica contents, using a relatively low deformation rate of 0.5 in/min. These composites were polymerized before crystallization, and therefore have randomly-arranged filler particles.

Fig. 3 illustrates the effect of the TPM-Si crystallization process on the stress-strain behavior. It can be seen that the stress-strain properties of these TPM-Si/PMA composites are almost identical at the same filler loading, irrespective of whether they were polymerized before or after particle crystallization. Fig. 4 compares the effect of sample directions, and demonstrates an absence of anisotropy in the stress-strain behavior. Thus Figs. 3 and 4 suggest that although the crystallization process is critical to the TPM-Si/PMA composites' optical properties, it doesn't have much effect on their stress-strain properties.

The results for the equi-biaxial deformation tests are shown in Fig. 5, in which the reduced stress $[f^*] = f^*/(\alpha - \alpha^{-2})$ is plotted against reciprocal elongation

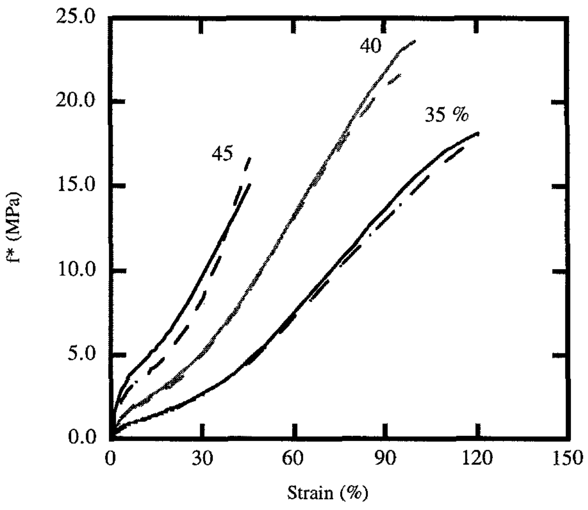

Fig. 3. The effects of particle crystallization on some properties of the silica-PMA composites. The solid lines denote samples polymerized before the particles could crystallize, and the dashed lines samples polymerized after particle crystallization.

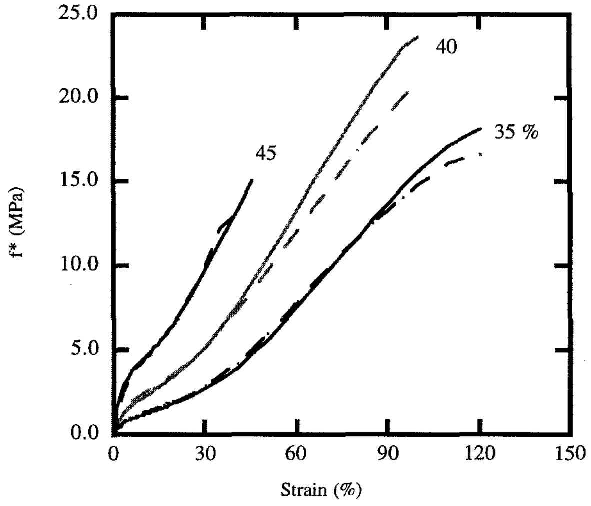

Fig. 4. Effects of sample direction on the stress-strain properties of the silica-PMA composites polymerized before crystallization. The solid lines denote samples cut in the X direction, while the dashed lines denote samples cut in the Y direction.

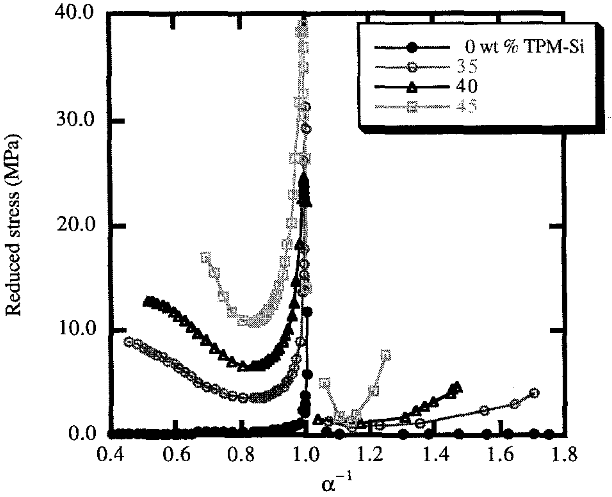

Fig. 5. Reduced stress - reciprocal elongation plots of TPM-Si/PMA composites with different TPM-Si contents. These composites were polymerized after crystallization, and the experimental data were obtained using uniaxial and equi-biaxial deformations.

(α^{-1}), with f* being nominal stress (defined as the applied force divided by the cross sectional area of the sample), and the elongation α being the ratio of deformed sample length to initial length. The results of some tensile tests are included for purpose of comparison. One interesting observation is that the reinforced composites show upturns in reduced stress in both elongation (tensile tests, $\alpha^{-1} < 1$) and compression (biaxial deformations, $\alpha^{-1} > 1$). As expected, the unfilled PMA does not exhibit any upturns at all.[9,10]

Some typical dynamic mechanical curves showing the frequency dependence of complex modulus E* are shown in Fig. 6. It was found that composites with the same TPM-Si content have the same frequency dependence, which means that the crystallization of the TPM-Si particles does not affect this property. As indicated by the empirical equation of Eilers and van Dijk,[11] the shear modulus increases with volume fraction of filler according to

$$G_e / G_{eo} = [1 + 1.25\, \phi / (1 - \phi / \phi_m)]^2 \qquad (1)$$

where G_e is the equilibrium modulus of filled polymer, G_{eo} is the equilibrium modulus of the unfilled polymer, ϕ is volume fraction of filler, and ϕ_m is a maximum volume fraction corresponding to close packing, which may be bet-

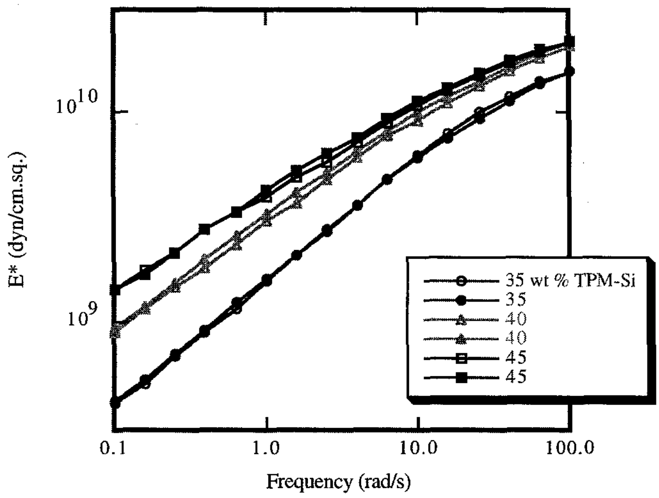

Fig. 6. Frequency dependence of complex modulus E* for some composites having various TPM-Si contents. The unfilled symbols denote samples polymerized before crystallization, and the filled symbols denote samples polymerized after crystallization.

ween 0.74 and 0.80. This equation predicts that the moduli are dependent only on filler loading, in agreement with the results presented here.

It is concluded that there is no anisotropy of mechanical properties for these TPM-Si/PMA composites. Also, the crystallization process which is critically important for attaining novel optical properties in these composites does not have much effect on their mechanical properties. This is reminiscent of the fact that network chain length distributions in unfilled elastomers have little effect on mechanical properties, unless very unusual *bimodal* distributrions are obtained by endlinking mixtures of very short and very long chains.[12] Related experiments on the present filled elastomers, however, could possibly be used to clarify the long-standing question of the importance of filler aggregation on elastomer reinforcement.[13]

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