Method for Generating Oriented Oblate Particles in an Elastomer and Characterization of the Reinforcement They Provide

Shuhong Wang, Ping Xu, and J. E. Mark*

Department of Chemistry and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221-0172

Received March 29, 1991; Revised Manuscript Received June 18, 1991

ABSTRACT: It was found to be possible to generate glassy ellipsoidal particles having an oblate shape by the following sequence of steps: (i) in situ polymerization of styrene in a poly(dimethylsiloxane) network, (ii) biaxial deformation of the resulting particles at an elevated temperature by means of either compression or inflation of a sheet of the filled elastomer, and (iii) finally cooling the sample under this strain. The existence of oblate (disklike) particles oriented nearly coplanar with the plane of the resulting sheet was confirmed by scanning electron microscopy. Stress–strain measurements in elongation to the rupture points were performed on strips of the resulting composites. Making the systems anisotropic in this way was found to increase the modulus and ultimate strength but to decrease the elongation at rupture relative to the isotropically filled materials.

Introduction

Reinforcement of polymer composites is obviously affected by the size, shape, and spatial distribution of the filler particles. Since anisotropy in mechanical properties can be very useful in some applications, it is of particular interest to determine the effect of particle shape on reinforcement. In the case of asymmetric (nonspherical) particles, their degree of orientation within the polymeric matrix also assumes considerable importance.

There have been several theories for predicting the modulus and strength of particulate-filled polymeric composites,[1] particularly those filled with nonspherical particles. In one such analysis,[2] Chow found that both the shape and degree of orientation can greatly affect the deformation behavior of such materials and predicted the five elastic moduli for composites containing aligned ellipsoidal fillers that are either prolate (rodlike) or oblate (disklike). In the case of aligned particles that are prolate, the greatest reinforcement is expected when the stretching direction is parallel to the particle axis. In the case of aligned particles that are oblate, it should be greatest perpendicular to the particle axis (i.e., for forces that are in the "plane" of the disk). There are very few experimental studies relevant to these predictions, because of difficulties in aligning such anisotropic fillers. One novel way to obtain elastomeric systems of this type is to employ filler particles that are sufficiently magnetic to align in response to an external magnetic field applied during the curing process (which converts a polymer into a cross-linked network and thus locks the particles into place).[3]

In a recent alternative approach, ellipsoidal particles having prolate shapes were generated by in situ polymerization in an elastomeric network.[4] The elastomer was poly(dimethylsiloxane) (PDMS), and the monomer chosen to be polymerized was styrene, so as to yield hard, glassy particles of polystyrene (PS). Swelling the network with portions of styrene containing a peroxide and then heating it generated the desired particles in roughly spherical shapes. The resulting, isotropically filled elastomer was drawn uniaxially at a temperature above the glass transition temperature T_g of PS and then cooled in the stretched state. Prolate PS particles were thus introduced and their reinforcing effects characterized.

The present investigation extends this in situ technique to the preparation of ellipsoidal particles that are oblate rather than prolate by using biaxial extension rather than uniaxial. To facilitate comparisons, the same elastomer and filler were used. The particles thus generated in these PDMS–PS composites were characterized by scanning electron microscopy, and elongation measurements were used to characterize the reinforcement they provide.

Experimental Details

Preparation of PDMS Networks. A sample of hydroxyl-terminated PDMS (Petrarch Systems Co.) having a number-average molecular weight of 18 000 was end-linked with tetraethoxysilane (Petrarch Systems Co.) in the undiluted state in the usual manner.[5,6] The resulting network sheets were extracted with toluene for 3 days at room temperature and then deswollen with methanol. They were then dried to constant weight, note being taken of the amount of soluble material thus extracted.

In Situ Polymerization of Styrene. Benzoyl peroxide (Lucidol Division, Pennwalt Co.) was dissolved in styrene (Aldrich Chemical Co.) to a concentration of 5 wt % to serve as a free-radical initiator. The extracted PDMS sheets were weighed and then immersed in an excess amount of this solution for 1 h. After swelling, the sheets were removed from the solution and placed into jars, which were then filled with nitrogen and sealed. They were then refrigerated for 4 days to ensure equilibrium distribution of the styrene–peroxide solution. The polymerization of the styrene thus introduced was carried out at 70 °C for 30 h.[7,8] The resulting PDMS–PS composites were dried under vacuum for 1 day to remove any unreacted styrene monomer.

Preparation of Oblate Particles. There are two ways of deforming the spherical particles thus prepared into oblate shapes. In the compression method, pieces of PDMS–PS composites with approximate dimensions of 20 × 20 × 1 mm^3 and measured thickness were placed between two aluminum plates. Four clamps located on the four sides of the plates were used to exert the required compressive forces. The entire assembly was immersed in a hot silicone oil bath at 200 ± 3 °C for ca. 15 s and then quenched in a cold-water bath.[4,9] After cooling, the samples were removed from the plates.

The inflation method employed a circular sample sheet having a central test area approximately 20 mm in diameter. It was mounted over the top of an open cylindrical pressure chamber, as shown in Figure 1. The device is essentially a simplification of the apparatus previously used to determine stress–strain isotherms in biaxial extension.[10,11] The sample sheet was inflated by forcing silicone oil into the chamber, which was then sealed. The chamber and the attached inflated sheet were then immersed in a hot oil bath at 140 ± 3 °C for a few seconds and then put into a cold-water bath. The sample sheet was removed from the mount after it had completely cooled.

In both techniques, the ratio of the final value of the sample thickness to its original value was designated the permanent deformation λ'', as was done previously.[4]

0024-9297/91/2224-6037$02.50/0 © 1991 American Chemical Society

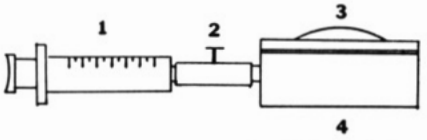

Figure 1. Apparatus for making the PS particles oblate and aligning them by means of inflation of a network sheet: (1) syringe; (2) valve; (3) inflated sample sheet; (4) pressure chamber.[10]

Table I
Mechanical Properties of Poly(dimethylsiloxane) Elastomers Filled with Polystyrene Particles

method	λ'' [a]	$[f^*]_r$,[b] N mm^{-2}	α_r[c]	f^*_r,[d] N mm^{-2}	10^3E_r,[e] J mm^{-3}
untreated	1.0	0.148	4.38	0.641	1.06
compression[f]	0.76	0.151	2.75	0.395	0.368
	0.66	0.158	2.43	0.356	0.275
	0.58	0.169	2.39	0.374	0.279
inflation[f]	0.71	0.154	2.90	0.427	0.405
	0.64	0.165	2.85	0.449	0.404

[a] Permanent deformation ratio. [b] Modulus at rupture. [c] Elongation at rupture. [d] Nominal force at rupture. [e] Energy required for rupture. [f] Method used for making the particles oblate and aligning them.

Scanning Electron Microscopy. Sectioning of the samples was carried out with a sharp razor blade, with one cross-section taken parallel to the sample plane, and another perpendicular. Each cross-sectional area was coated with gold and then examined with a scanning electron microscope (Stereoscan 90, Cambridge Instruments).

Stress–Strain Measurements. Strips for the stress–strain measurements in elongation were cut from the central region of each of the sheets, and their isotherms were determined at 25 °C in the usual manner.[5,6,12,13] Data were taken using a sequence of increasing values of the elongation or relative length of the samples, $\alpha = L/L_0$, where L_0 is the rest length of the heat-treated strip after retraction. The reduced nominal stress or modulus was calculated from the equation[5,12,13]

$$[f^*] \equiv f^*/(\alpha - \alpha^{-2}) \quad (1)$$

where $f^* = f/A_0$ is the nominal stress, f the equilibrium force, and A_0 the initial cross-sectional area of the treated strip after retraction. Measurements were carried out to the rupture point of each of the samples.

Since these samples are expected to be anisotropic, it would be desirable to measure their moduli perpendicular to the sheet as well. This would be almost impossible to do using the design of the present experiment, however. The technique requires that a relatively thin sheet of the composite be used, and it would be very difficult to carry out stress–strain measurements of the required precision perpendicular to the plane of the film.

Results and Discussion

The value of the soluble fraction of the PDMS networks was ca. 9 wt %, which is probably unimportant since they were then extensively filled, specifically to 45.0 wt % PS.

After the deformation at the elevated temperature and cooling under strain, the samples had values of permanent deformation ratio λ'' significantly less than 1. Their values are given in column two of Table I. This is obviously due to the deformed PS particles which, because of their asymmetry and rigidity, prevent the elastomeric matrix from retracting to its original dimensions.

The existence of oblate particles was confirmed by the scanning electron micrographs shown in Figure 2. The pictures were taken from the sample with a permanent deformation ratio $\lambda'' = 0.66$, and the oblate particles were generated by the compression method. Part a shows the cross-section surface parallel to the sample plane, and the observed circles represent top views of the disklike particles. Part b shows the cross-section surface perpendicular to the sample plane, and the observed ellipses thus represent side views of the particles. Both prespectives indicate good alignment of the particles relative to the plane of the sample sheet.

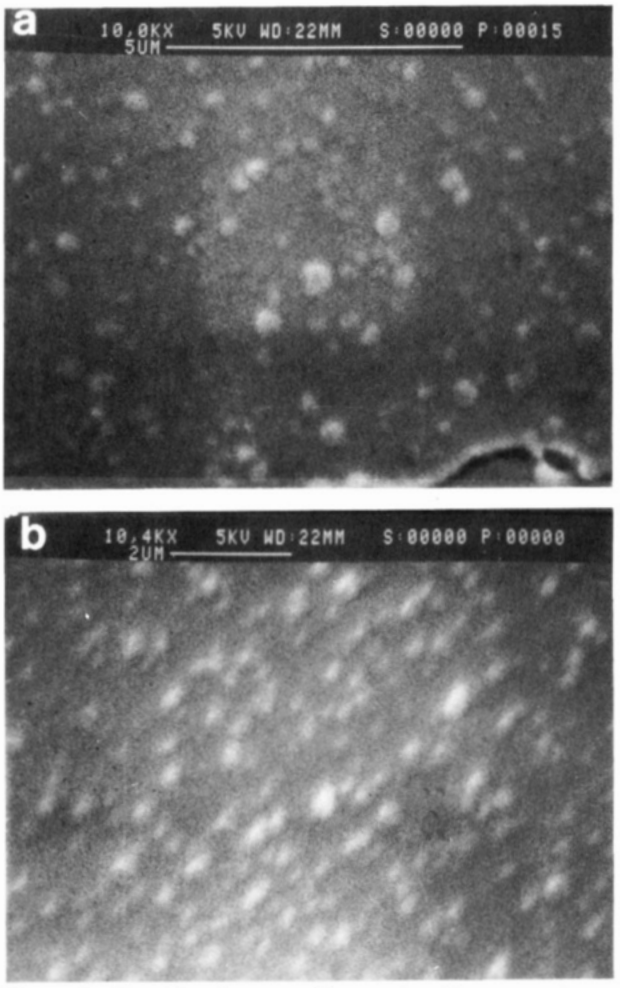

Figure 2. Scanning electron micrographs of cross-sections of a PDMS network filled with oblate PS particles generated by the compression method: part a, cross-section surface parallel to the sample plane; part b, cross-section surface perpendicular to the sample plane.

The stress–strain isotherms for the samples produced by the compression method are presented in Figure 3, and those from the inflation method are shown in Figure 4. The permanent deformation ratio is indicated for each curve. The results in the two figures show the same trend, indicating that both techniques gave the desired particle shapes and orientations. Figure 5 shows the results in Figure 3 in an alternative representation, with the nominal stress plotted against elongation. The area under each curve in Figure 5 represents the energy E_r required for rupture. From these figures, it is seen that the treated samples have moduli and ultimate strengths, as measured by $[f^*]_r$, that are higher than those of the untreated sample. Presumably these quantities in the direction perpendicular to that investigated would show changes in the opposite direction, but a different type of stress–strain apparatus would have to be employed for such measurements. The values of the elongation α_r at rupture are smaller, as might be expected, since the network chains in the treated case are already stretched by the particles in the direction in which the elongation is to be imposed and this gives them less extensibility.[4] This would also explain the decreased values of E_r and f^*_r. It is also interesting to note that the treated samples give upturns in modulus that were larger

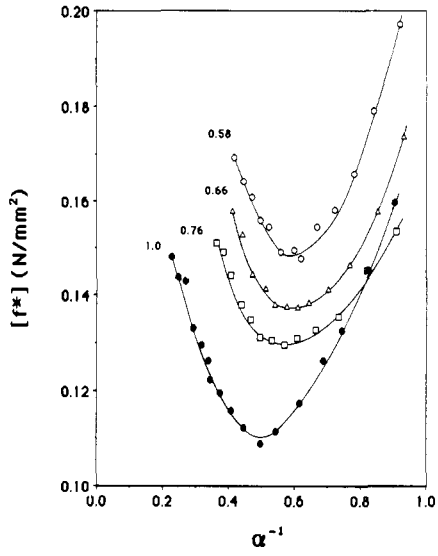

Figure 3. Stress–strain isotherms for the PDMS networks filled with oblate PS particles generated by the compression method. Values of the permanent deformation ratio λ″ are indicated for each curve.

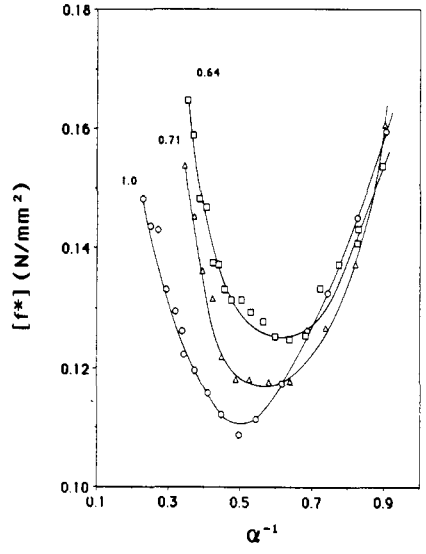

Figure 4. Stress–strain isotherms for the PDMS networks filled with oblate PS particles generated by the inflation method. Values of the permanent deformation ratio λ″ are indicated for each curve.

and occurred at lower elongations. The specific values of these ultimate properties are all given in the last four columns of Table I.

Comparing these results with those obtained earlier on composites filled with prolate particles,[4] one can see that the reinforcement provided by the aligned oblate particles in the direction perpendicular to their principal axis is similar to that of the aligned prolate particles in the direction to their axis. These results seem to be in agreement with the theoretical predictions reported by Chow.[2] Quantitative comparisons between this theory and the present experimental results are difficult, however, because the in situ generation of particles causes considerable deformation of the elastomeric matrix. This could

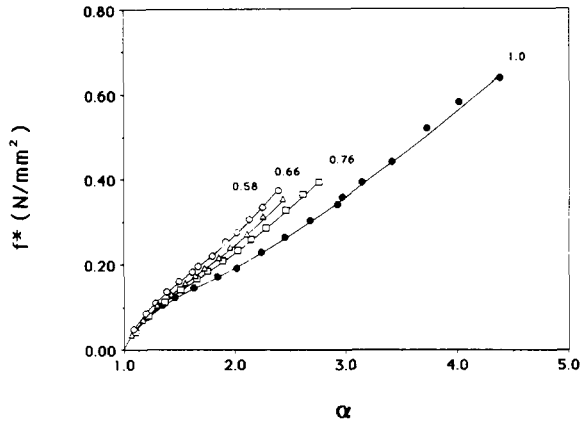

Figure 5. Alternative representation of the results shown in Figure 3.

be avoided, of course, by using un-cross-linked PDMS and then dissolving the polymer away from the particles so that they could be recovered.[9] They could then be blended into another sample of PDMS before curing, thus avoiding this deformation. The particles would presumably be randomly arranged, however, unless somehow aligned in a separate step prior to cross-linking. Studying elastomers containing oblate particles that are randomly oriented would, of course, be interesting in its own right.

Such oblate particles separated from the polymer matrix in which they were generated should also be extremely useful as model substances in the area of colloid chemistry. This was, in fact, precisely the reason ellipsoidal particles of *prolate* shapes were generated and separated out by Nagy and Keller.[9] Anticipated uses include testing of the theories of light, X-ray, and neutron scattering from such asymmetric particles, the viscosities of their solutions, their diffusion coefficients, and the nature of their asymmetry-induced aggregation into anisotropic phases.

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR 89-18002 (Polymers Program, Division of Materials Research), and we wish to thank Mr. E. G. Clark of the University of Cincinnati Department of Materials Science and Engineering for help with the electron microscopy.

References and Notes

(1) Ahmed, S.; Jones, F. R. *J. Mater. Sci.* **1990**, *25*, 4933.
(2) Chow, T. S. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 959.
(3) Sohoni, G. B.; Mark, J. E. *J. Appl. Polym. Sci.* **1987**, *34*, 2853.
(4) Wang, S.; Mark, J. E. *Macromolecules* **1990**, *23*, 4288.
(5) Mark, J. E.; Sullivan, J. L. *J. Chem. Phys.* **1977**, *66*, 1006.
(6) Mark, J. E. *Adv. Polym. Sci.* **1982**, *44*, 1.
(7) Fu, F.-S.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2229.
(8) Fu, F.-S.; Mark, J. E. *J. Appl. Polym. Sci.* **1989**, *37*, 2757.
(9) Nagy, M.; Keller, A. *Polym. Commun.* **1989**, *30*, 130.
(10) Xu, P.; Mark, J. E. *Rubber Chem. Technol.* **1990**, *63*, 276.
(11) Xu, P.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 355.
(12) Mark, J. E.; Flory, P. J. *J. Appl. Phys.* **1966**, *37*, 4635.
(13) Mark, J. E.; Erman, B. *Rubberlike Elasticity. A Molecular Primer*; Wiley-Interscience: New York, 1988.

Registry No. PS, 9003-53-6.