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Generation of Glassy Ellipsoidal Particles within an Elastomer by in Situ Polymerization, Elongation at an Elevated Temperature, and Finally Cooling under Strain

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ABSTRACT: When styrene is polymerized within an elastomeric matrix of poly(dimethylsiloxane) (PDMS), spherical particles of polystyrene (PS) are generated and provide considerable reinforcement of the network. If the PDMS–PS elastomer is subsequently drawn at a temperature above the glass transition temperature of the PS, then the particles deform into prolate (rodlike) ellipsoids which retain their shapes when the elastomer is cooled while still in the stretched state. If the deforming force is then removed, the elastomer is observed to retract, but only part of the way back to its original dimensions. The particles themselves were characterized by using scanning and transmission electron microscopy and were found to have axial ratios of approximately 2 and to have their axes oriented in the direction of the high-temperature stretching. The reinforcement they provided was characterized by using stress–strain measurements in elongation at room temperature. In these anisotropic materials, the modulus in the direction parallel to the original stretching direction was found to be significantly higher than that of the untreated (isotropic) PDMS–PS elastomer, whereas in the perpendicular direction it was significantly lower.

Introduction

The reinforcement of elastomers has been successfully achieved by the introduction of a variety of fillers, among them carbon black, silica, and titania.[1–3] Recent studies found that it is also possible to obtain good reinforcement by introducting spherical particles of a glassy polymer,[4–6] a technique in which the monomer was swollen into the network and then polymerized in situ.

Another recent study[7] described a novel method for producing prolate ellipsoidal polymer particles with predetermined axial ratios. The polymer particles were obtained by drawing a polymer film containing spherical glassy polymer particles. In this particular case, the film was poly(vinyl alcohol) and the glassy particles were polystyrene (PS) introduced from a separately prepared PS latex. The film and the PS particles it contained were drawn at a temperature above the glass transition temperature, T_g, of the PS and then cooled in the stretched state.[7] The particles were then isolated by dissolution of the poly(vinyl alcohol) and centrifugation. Electron microscopy showed the particles to have axial ratios close to the values of the draw ratios employed and to be nearly monodisperse in their geometries. These materials are now being used as model substances in the area of colloid science.

The purpose of the present study is to use this new technique[7] in combination with the also new idea of generating glassy PS particles in in situ polymerizations.[4,5] Since the basic point of interest is the presumably anisotropic reinforcement[8] such particles would provide, they would be left in the polymer matrix rather than separated out. Therefore, a polymer much more elastomeric than poly(vinyl alcohol) was chosen, specifically poly(dimethylsiloxane) (PDMS). The PDMS–PS composites thus prepared have been characterized by electron microscopy, and elongation measurements have been carried out both parallel and perpendicular to the drawing direction.

Experimental Details

Preparation of PDMS Networks. Hydroxyl-terminated PDMS (Petrarch Systems Co.) having a number-average molecular weight of 18 000 g mol^{-1} was end linked with tetraethoxysilane (Petrarch Systems Co.) in the undiluted state, in the usual manner.[9,10] The resulting network sheets were extracted with toluene for 3 days at room temperature and then deswelled with methanol. The samples were then dried to constant weight, note being taken of the amount of soluble material thus extracted.

In Situ Polymerization of Styrene. A total of 5 wt % benzoyl peroxide (Lucidol Div., Pennwalt Co.), to serve as a free-radical initiator, was dissolved in styrene (Aldrich Chemical Co.). PDMS sheets were weighed and then immersed in an excess amount of the above solution for 1 h. The swollen samples were placed into jars, which were then filled with nitrogen, sealed, and refrigerated for 4 days, to ensure equilibrium swelling. The polymerization was carried out by then holding these materials at 70 °C for 30 h. The resulting PDMS–PS composites were held under vacuum for 1 day to remove the unreacted styrene monomer.

Preparation of Ellipsoidal Particles. Strips of the composite having the dimensions 20 × 25 mm^2 were cut from the sheets. They were clamped in a stretching frame and drawn at 200 ± 3 °C to the desired value of the draw ratio λ, which is the ratio of the length drawn to that in the original state. Stretching was carried out by operating the frame manually at an average rate of 3–5 cm s^{-1} with the portion of the frame holding the strip immersed in a hot silicone fluid bath.[7] After the desired draw ratios were obtained, the strips, while still stretched, were quenched in a cold water bath, and the silicone fluid was quickly wiped away. The entire process took only a few seconds. After the samples cooled, they were released. The ratio of the retracted length to the original length is designated λ', which is a measure of the permanent deformation after the drawing–retraction process.

Scanning and Transmission Electron Microscopy. Drawn and undrawn PDMS–PS strips were fractured under liquid nitrogen, and the cross-section areas coated with gold. They were examined with a Cambridge 600 scanning electron microscope.

Other pieces of stretched and unstretched PDMS–PS strips were cut by using an ultramicrotome (FC 40 Reichert-Jung Co.) at −130 °C. The slices, which had a thickness on the order of 0.03 μm, were examined in transmission with a Hitachi H-600 electron microscope.

Stress–Strain Measurements. Strips were cut from both the undrawn and drawn sheets, in the latter case both parallel and perpendicular to the drawing direction. Stress–strain isotherms in elongation were obtained for these strips in the usual manner.[9–11] The measurements were made by using a sequence of increasing values of the elongation or relative length of the

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Table I
Preparation and Properties of PDMS Elastomers Filled with Ellipsoidal PS Particles

drawing information			mechanical properties			
λ^a	λ'^b	direction	$\alpha_u{}^c$	f^*_r,^{d} N mm^{-2}	$\alpha_r{}^e$	10^3E_r,^{f} J mm^{-3}
1.0	1.0	isotropic	1.9	0.486	3.61	0.650
1.7	1.3	∥	1.8	0.406	2.64	0.349
1.7	1.3	⊥	2.1	0.533	4.43	0.908
2.2	1.6	∥	1.4	0.312	1.93	0.147
2.2	1.6	⊥	2.2	0.410	3.94	0.588

[a] The draw ratio during the stretching at high temperature. [b] The deformation ratio remaining after retraction. [c] Elongation at which the upturn begins. [d] Nominal force at the rupture point. [e] Elongation at the rupture point. [f] Energy required for rupture.

samples, $\alpha = L/L_0$, where L_0 is the rest length of the drawn strip after retraction. There were frequent inclusions of values out of sequence to check for reversibility. The reduced nominal stress or modulus was calculated from the equation[9,11,12]

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

where $f^* = f/A_0$ is the nominal stress, f the equilibrium force, and A_0 the cross-sectional area of the drawn strip after retraction, in the vicinity of room temperature. All measurements were conducted at 25 °C, and the elongations were generally increased to the rupture point of the sample.

Results and Discussion

The PDMS networks were found to have sol fractions that amounted to approximately 8.9 wt %. This would correspond to a rather large number of dangling chains in the network, but this is probably irrelevant since these will be extensively filled systems. The PS introduced during the in situ polymerizations was 35.0 wt %.

Values of the draw ratio, λ, and the deformation ratio, λ′, after retraction are listed in columns one and two of Table I. It is seen that the values of the ratios after retraction are somewhat smaller than the corresponding draw ratios, but well above the value $\lambda' = 1.0$ corresponding to complete recovery.

This is obviously due to the fact that essentially nondeformable ellipsoidal particles generated during the drawing, and having axes in the direction of the drawing, would prevent the elongated network chains from collapsing back to their undeformed states. Thus, $\lambda' > 1$. Also, since the sample volume must remain essentially constant during the retraction (and drawing), the sample dimensions in the two perpendicular directions do not increase to their original values.

Some scanning electron micrographs obtained for different draw ratios are given in Figure 1. The original in situ polymerized spherical particles have an average diameter of 0.4 μm, which is consistent with previous results.[4] The ellipsoidal particles produced at different draw ratios have different values of the axial ratio (the ratio of length along the long axis to the perpendicular length) that are close to the corresponding draw ratios. Also, the particle axes lie nearly along the draw directions. The transmission electron micrographs represented in Figure 2 show the same characteristics as those of the scanning electron micrographs.

The stress–strain isotherms obtained for the PDMS–PS composites are represented in the usual manner[9,11,12] in Figure 3. The values of the draw ratio, λ, are indicated. The curves for the strips cut parallel and perpendicular to the drawing direction are indicated by ∥ and ⊥, respectively. It is found that the modulus for the strips cut parallel to the stretching direction are higher than those for the perpendicular ones. Also, the unstretched sample has a value of the modulus between those for the stretched samples in these two directions. In an earlier study[8] of prolate ellipsoidal particles oriented in a magnetic field during the curing and in the undrawn elastomer, the oriented particles increased both the parallel and perpendicular moduli, but the former much more than the latter. This difference, relative to the results shown here, is certainly due to the particles in the present study impeding the network from retracting to its initial state, as already described. Also, the parallel samples give earlier and larger upturns in modulus than the unstretched sample, while the perpendicular samples give somewhat later and smaller upturns. Each value α_u of the elongation at the upturn is given in column four of Table I.

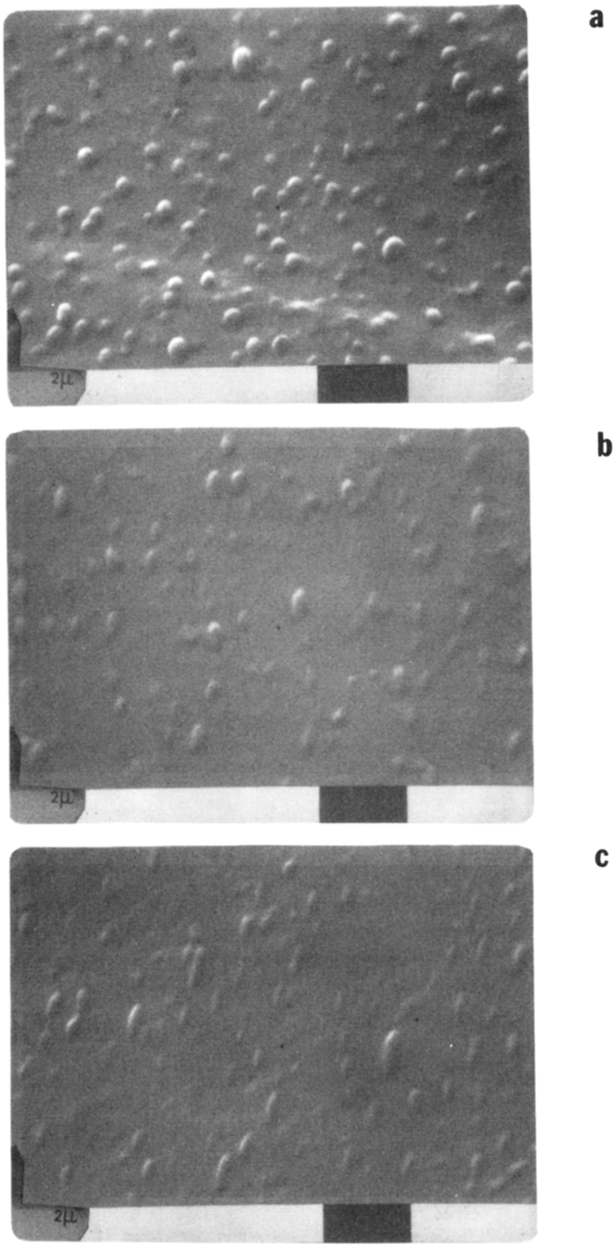

Figure 1. Scanning electron micrographs of a PDMS–PS composite stretched at high temperature and cooled, at different draw ratios: (a) unstretched sample, (b) $\lambda = 1.8$, $\lambda' = 1.4$, and (c) $\lambda = 2.2$, $\lambda' = 1.6$, where λ is the draw ratio during heating and cooling and λ′ ($1 < \lambda' < \lambda$) is what remains of the value of this ratio after the force is removed. The length of the black bar corresponds to 2 μm.

An alternative representation, the nominal stress as a function of elongation, is shown in Figure 4. Values of the ultimate strength, as measured by the nominal stress f^*_r

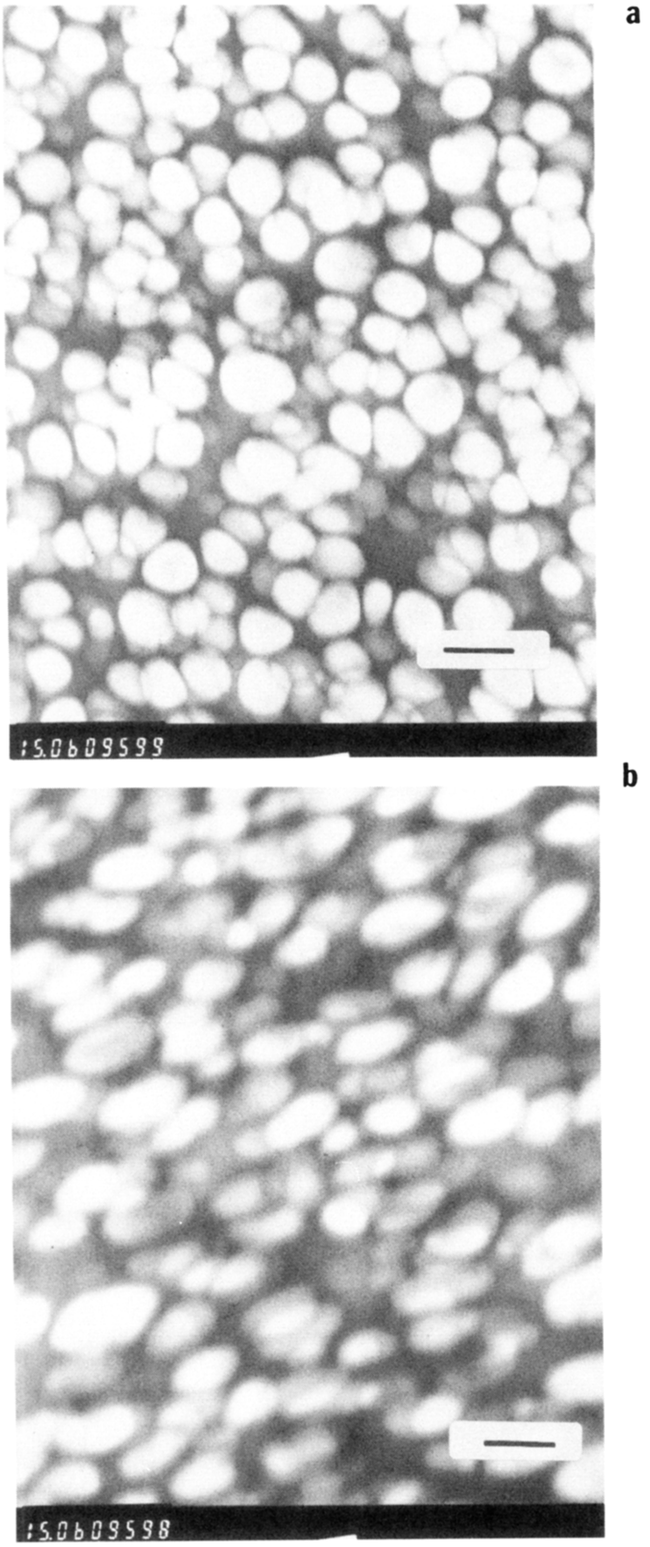

Figure 2. Transmission electron micrographs of a PDMS–PS composite: (a) unstretched sample, (b) stretched sample with $\lambda = 2.2$, $\lambda' = 1.6$. The length of the bar corresponds to 0.5 μm.

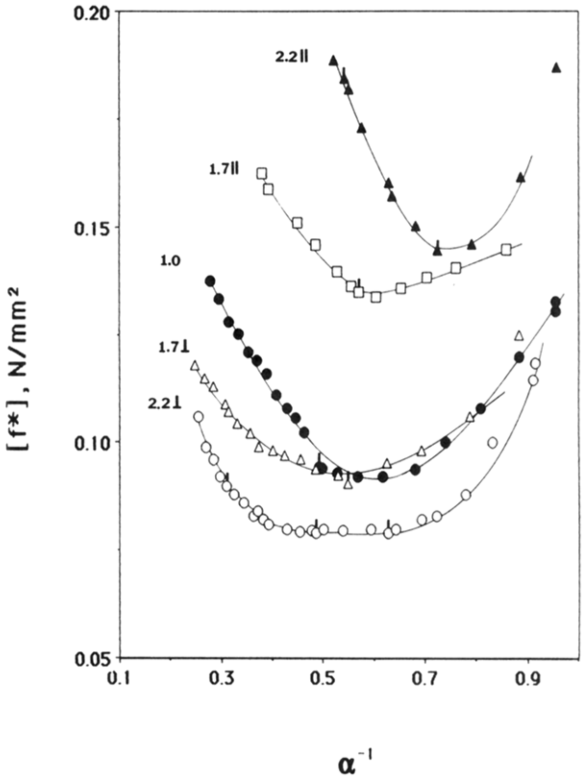

Figure 3. Stress–strain isotherms of the PDMS–PS composites. Values of the draw ratio, λ, and the testing directions are indicated on each curve. The symbols with small tabs represent the data used to test for reversibility.

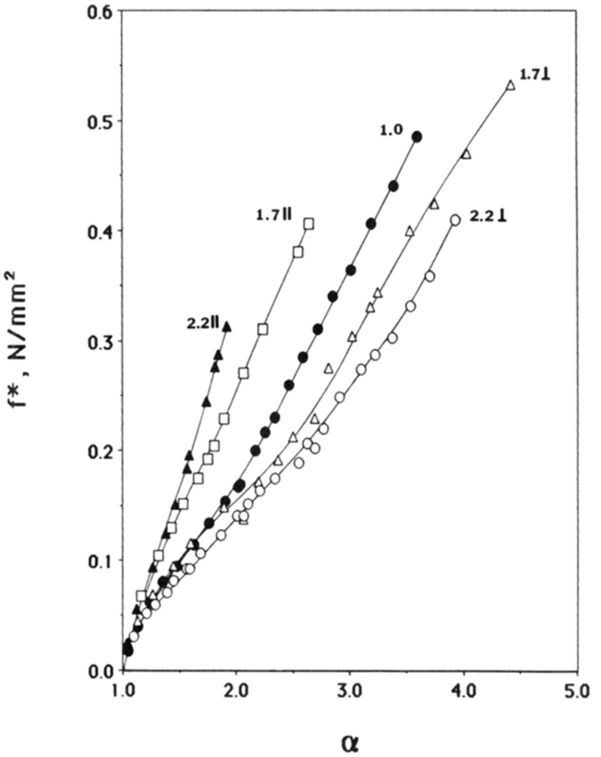

Figure 4. Nominal stress shown as a function of elongation for the same samples described in Figure 3.

at rupture obtained from these curves, are given in column five of Table I. The corresponding values of the maximum extensibility or elongation at rupture α_r are given in the next column. The area under each curve in Figure 4 represents the energy E_r required for rupture, and values of this quantity are given in the final column of Table I. The samples cut parallel have smaller values of f^*_r, α_r, and E_r than those cut perpendicular. In a sense, the network chains in the parallel case are already stretched in the direction in which the elongation is to be imposed and this gives them less extensibility. In the perpendicular case, the chains are still partially compressed and this gives them more extensibility.

The stress relaxation was characterized by $\Delta f^*/\Delta\alpha$, where Δf^* is the difference in nominal stress between its value immediately after the deformation and its value close to

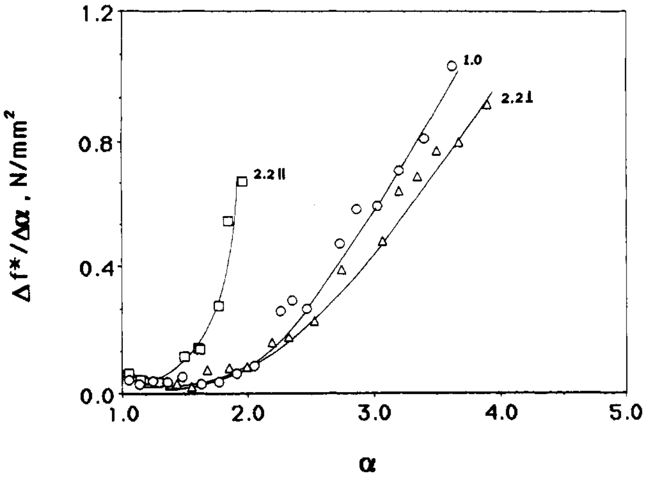

Figure 5. Dependence of stress relaxation on elongation. Values of the draw ratio, λ, and the testing direction are indicated.

elastic equilibrium, while $\Delta\alpha$ is the corresponding increase in the elongation relative to its previous value. Figure 5 shows a plot of $\Delta f^*/\Delta\alpha$ versus elongation for the strips both unstretched and stretched. Each curve is labeled by the draw ratio and the testing direction. It is interesting that the relaxation is small in the initial region but increases rapidly when the elongation exceeds α_u. Similar changes in stress relaxation have been observed in the earlier work cited.[8] In this earlier study, the changes were thought to result from the adsorption of polymer chains onto the filler surface and their partial desorption in response to the applied stresses. In the present case, all the stress-strain isotherms were found to be reversible, so the effect here may simply have been the time-delayed motions of the chains in the viscous elastomeric matrix.

In any case, the techniques described appear to be an intersting way of producing elastomeric materials of controlled anisotropy.

Replacing uniaxial drawing by one that is biaxial (through inflation of sheets[13]) should produce oblate (disk-like) particles. Such experiments are in progress.

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