# Dimensional Stability and Tensile Properties of Drawn Polystyrene Composites

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## Synopsis

Recovery experiments above $T_g$ and tensile tests have been performed on glass bead and short glass fiber–polystyrene composite sheets obtained from extrusion and subsequent hot drawing. A shift procedure has been applied to the recoil data using a WLF equation. The data reported show that both dimensional stability and mechanical properties are enhanced by adding rigid fillers to the drawn thermoplastic matrix. The presence of short fibers reduces strongly the recoverable strain of the oriented material. A simple model able to predict the equilibrium values of the length reversion ratio of glass bead composites is developed and compares well with the experimental data.

## INTRODUCTION

Particulate fillers are often used to improve the dimensional stability of polymeric items obtained through processing techniques such as injection molding, deep drawing, hot stamping, etc. In fact, in these operations the material undergoes large multiaxial deformations which result in molecular orientation and remain as frozen-in stresses during cooling of the material. Once the formed objects are exposed to sufficiently high temperatures, various degrees of spring-back take place and subsequent changes in shape and dimensions occur.[1]

In previous articles[2-4] the effect of draw ratio on fiber orientations, on the extent of damage done to the fibers during processing, and on the recoil kinetics of polystyrene composite sheets is analyzed. The equilibrium value of the length reversion ratio, defined as the ratio of the initial length of a drawn sample to the length of the sample after exposure at a temperature higher than $T_g$, for a time long enough to be sure of having reached the complete recovery of the oriented molecules, has shown to take quantitatively into account the molecular orientation. Using the WLF equation[5] all the experimental data obtained at various temperatures, times and filler content have been correlated by a unique master curve when plotted as fractional distance from equilibrium versus the reduced time.

In the present article, the effect of glass beads and short glass fibers on the dimensional stability and mechanical properties of drawn polystyrene is studied. A simple model able to predict the recoverable strain of bead-filled composites is proposed.

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## EXPERIMENTAL

The drawn composite samples have been obtained with the processing equipment shown schematically in Figure 1. It consists of three parts, namely, the extruder, a section for hot drawing, and cooling of the extruded sheet and the control system.

A Negri and Bossi single screw extruder, 83 cm in length and 3 cm in diameter, was utilized. The barrel possesses four heating zones, one located in the head and three others spaced along the barrel. Each functions independently with a separate on-off control. Thermocouples located along the barrel are connected to a temperature recorder, allowing continuous readout of temperature at various positions in the extruder.

In the study, the screw speed was held constant at 19 rpm and the temperature profile in the extruder was fixed by the four controllers set at 180 (at the head), 170, 160, and 150°C (at the feed section). The extruder die was a slit of 20 mm width and 2 mm height. The hot drawing section was 70 cm long from the exit of the die to the pair of rollers that catches the extruded strip. Between these two points a cooling section was placed, consisting of a slit in which cold water flowed countercurrently to the strip. A molten strip exited from the extruder and passed between the rollers which were driven at a sufficiently high rate to impose an elongational flow. The rollers had rubber surfaces and the distance between them was accurately controlled. They were chain driven by an electric motor whose rotational speed can be varied. The draw ratio (DR), defined as the ratio of the cross section of the strip at die exit $A_0$ to the cross section of the final drawn strip $A$ (i.e., DR = $A_0/A$), was controlled by the speed of the rollers. The draw ratio was measured by cutting a sample strip of length $l$ and weighing the piece. The draw ratio is then given by

$$DR = (A_0/P)\rho l \qquad (1)$$

where $A_0$ is the cross section of the die and $P$, $\rho$, and $l$ are the weight, density, and length of the sample, respectively. The cooling of the strip as it was being drawn was accomplished by the slit put at a fixed position in the cooling section. Both the velocity and temperature of the water were held constant.

The constituent materials used were Montedison's Edistir FA, general purpose polystyrene ($M_w$ = 200,000, $T_g$ = 83°C) and Silenka 8041 E-glass fibers with 95%
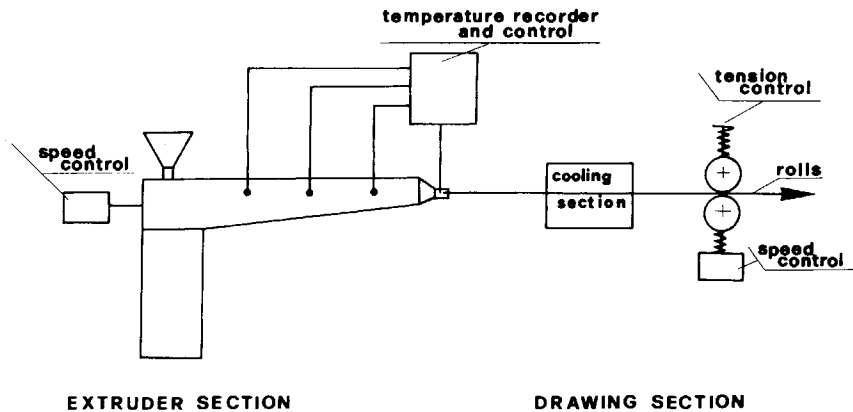


Fig. 1. Sketch of the processing apparatus.

of the fibers having a nominal length of 3 mm and 5% having a nominal length of 6 mm.  The fiber diameter is 10 $\mu$m.  The concentration levels studied ranged from 0.05 to 0.4% by volume of E-glass fiber.  The fiber length after the drawing processes are reduced as shown in ref. 2.  Composites obtained with polystyrene and glass beads also have been studied at concentrations ranging from 0.2 to 3.5% by volume of beads.  The glass beads (Ballotini Europe 3000 CP/01) were washed repeatedly with water to eliminate all mixed dust and extraneous matter, treated with warm diluted hydrochloric acid to dissolve the small amount of iron particles present, and again washed with water to eliminate acidity.  After drying, beads having diameters between 40 and 50 $\mu$m were finally degreased in a Soxhlet extractor, resieved, and then dried to eliminate all the absorbed water.

The polystyrene was first dried at 60°C, in vacuum, for a minimum of 2 hr. The proper weight of glass fibers or glass beads was added and the mixture placed in the feed section of the extruder.  Material was extruded and drawn until the temperature profile in the extruder was constant and the conditions of drawing and cooling were stabilized.  The recoil experiments were performed by immersing the drawn samples into a thermostatic bath filled with glycerol, which is not absorbed into polystyrene.  Specimens were removed after various residence times at temperatures ranging from 108 to 165°C and for residence times as long as 200 min.  The initial length of the samples ($l_0$) cut from the extruded strips was 9 mm.  Longer strips gave a spiral-like shrinkage because of inhomogeneous deformation.[3]  As discussed previously,[2] although the deformation during extrusion, drawing, and recoil is inhomogeneous, the specimens approach homogeneous uniaxial extension in the region around their centerline.  For these reasons the recoil kinetics of drawn composite samples have been studied by measuring the length at the central line using a micrometer with a sensitivity of 0.01 mm.

Tensile tests have been performed on rectangular specimens by means of an Instron 1112 tensile testing machine.  The sample length was 12 cm and the distance between the grips was 6 cm.  An average cross section was determined by weighing each specimen.  The cross-sectional area is defined as $A = P/l\rho$, where $P$ is the sample weight, $\rho$ is the density, and $l$ is the length.  The material density was measured by means of a density gradient column realized with sodium chloride solution having a sensitivity of $2 \times 10^{-4}$ g/cm$^3$ over 1 m of column.

## RESULTS AND DISCUSSION

The recoil kinetics for the polystyrene samples filled with $\phi$ = 0.017% by volume of glass fiber, at a DR = 6.1 and at different temperatures are reported in Figure 2.  The data are plotted as $l_0/l_t$ vs. $t$ and display the same behavior as the unfilled drawn polystyrene previously studied.[2]  At high temperatures an asymptotic equilibrium value $l_f$ is reached.  The data have been superimposed by horizontal shifts to give the master curves shown in Figure 3, relative to a reference temperature of 135°C.

The master curves for materials drawn to different DR are also reported in Figure 3.  The variable $t'$ is related to real time by $t' = t/a_T$, where $a_T$ is the shift factor given by the WLF equation[5] in a modified form

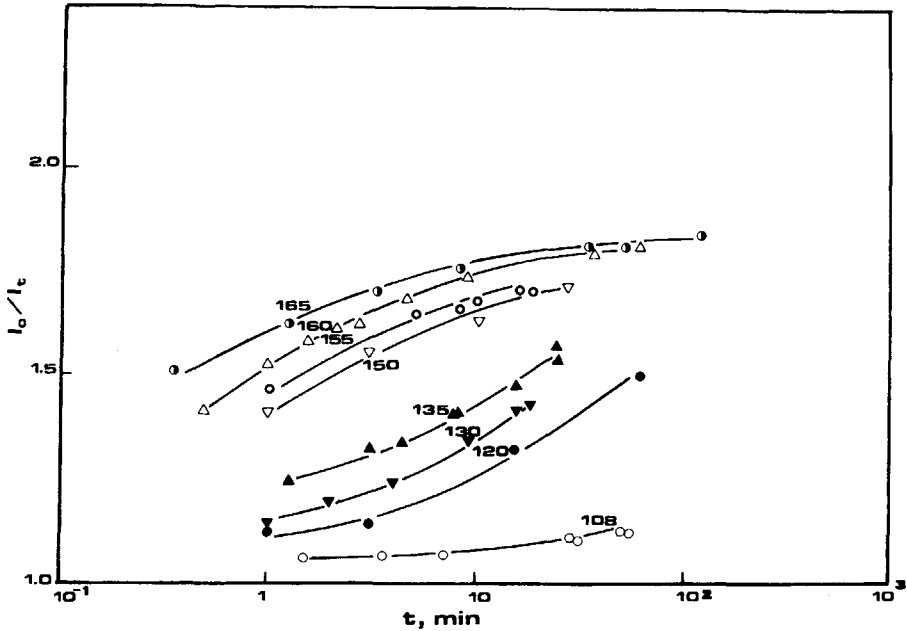$$\log a_T = -C_1(T - T_g)/C_2(T - T_g) - \log a_{T_0}$$

Fig. 2. Recoil of an oriented filled ribbon at different temperatures (°C) above $T_g$, $\phi = 0.017\%$, DR = 6.1.

with $T_g \doteq 83°C$, $C_1 = 13.3$, $C_2 = 47.5°C$, and $a_{T_0} = 1.12 \times 10^{-7}$. The values of $C_1$ and $C_2$ are those reported for polystyrene[5] and used in ref. 3.

In Figure 4 the equilibrium values of the length reversion ratio $l_0/l_f$, relative to glass fiber composites at $\phi = 0.017\%$ are reported as a function of DR indicating a linear relationship between these two variables. The slope of the straight line,
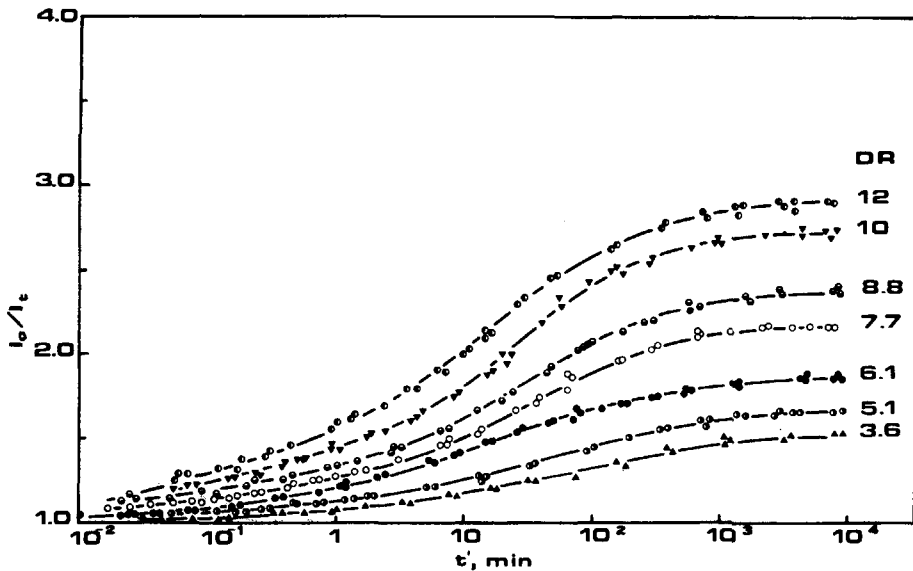


Fig. 3. Recoil master curves referred to 135°C for differently oriented short glass fiber–polystyrene composites. $T_r = 135°C$, $\phi = 0.017\%$.
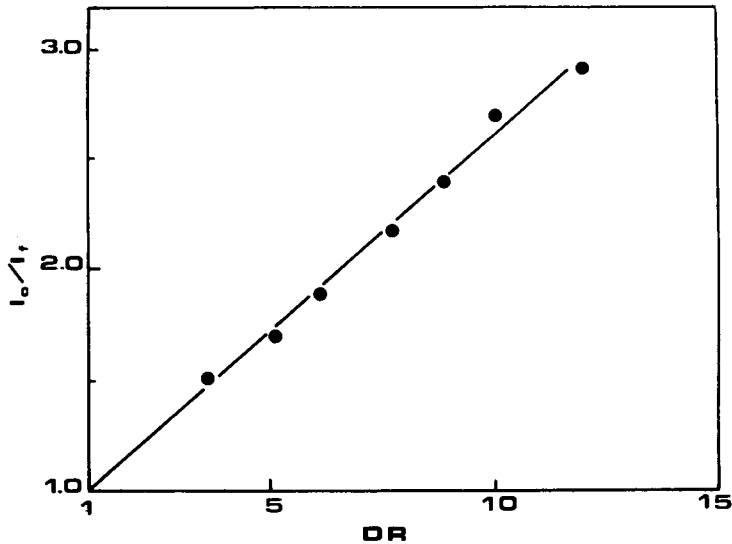
Fig. 4. Equilibrium reversion ratios $l_0/l_f$ vs. nominal drawing ratios DR for 0.017% by volume glass fiber–polystyrene composites.

much lower than unity (i.e., 0.17), shows that only a small part of the imposed deformation is retained as molecular orientation which reveals an elastic recovery when the sample is exposed at $T > T_g$. Similar results have been obtained with unfilled polystyrene and with composites containing glass beads. The values of the slope in the $l_0/l_f$ vs. DR diagram are 0.20 for bead-filled samples and 0.23 for unfilled polystyrene (PS).
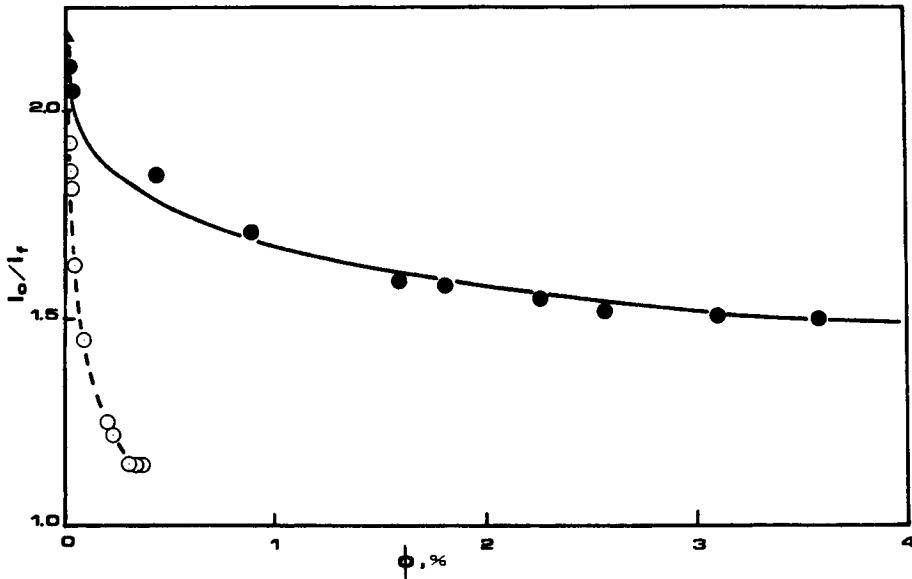


Fig. 5. Equilibrium reversion ratios vs. volume fraction for glass beads and glass fiber–polystyrene composites of nominal drawing ratio 6.1. Beads: (●) experimental, (—) theory; fibers: (○) experimental.
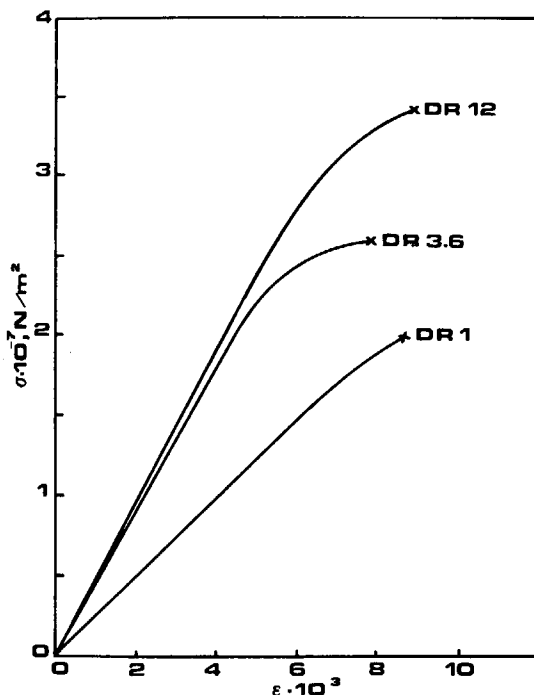
Fig. 6. Stress–strain curves for differently oriented unfilled polystyrene, $T = 25°C$.

One of the possible reasons for this difference in slope could be a different degree of molecular orientation in filled and unfilled samples subjected to the same thermal and mechanical history. The data reported in Figure 5, however, indicate that this is not the case, at least for glass bead composites. In fact, in Figure 5 the experimental values of $l_0/l_f$ relative to bead composites are plotted as a function of volumetric filler content $\phi$, as full dots together with a full line which represents the relation

$$\epsilon_{rf} = \epsilon_{rp}[1 - (\phi/\phi_{max})^{1/3}] \tag{2}$$

In this equation $\epsilon_r$ is defined as

$$\epsilon_r = (l_0 - l_f)/l_0 = 1 - (l_0/l_f)^{-1} \tag{3}$$

and the subscripts $f$ and $p$ refer to the bead-filled composites and the unfilled polymer, respectively; $\phi_{max}$ represents the maximum volume fraction of beads for random packing of large spherical particles and is expected to be equal to 0.63.[6,7] Equation (2) is based on the hypothesis that $\epsilon_{rp}$ represents, under fixed thermal and mechanical history, a property of the drawn polymer both when unfilled or bead filled. Therefore, following the Smith's analysis[8] relative to the strain at break of glass bead composites one obtains eq. (2). Obviously the $\epsilon_{rp}$ and $\epsilon_{rf}$ values are relative to the same mechanical and thermal history (i.e., in our case to the same DR). The good agreement between the experimental data and the predicted values [calculated with $\phi_{max} = 0.63$, $(l_0/l_f)_p = 2.3$ in eq. (2)] indicates that the molecular orientation in the glass-bead-filled system and in the unfilled polymer is the same for a fixed DR. Consequently, the reduction of the length reversion ratio (LRR) in bead composites is only due to the presence
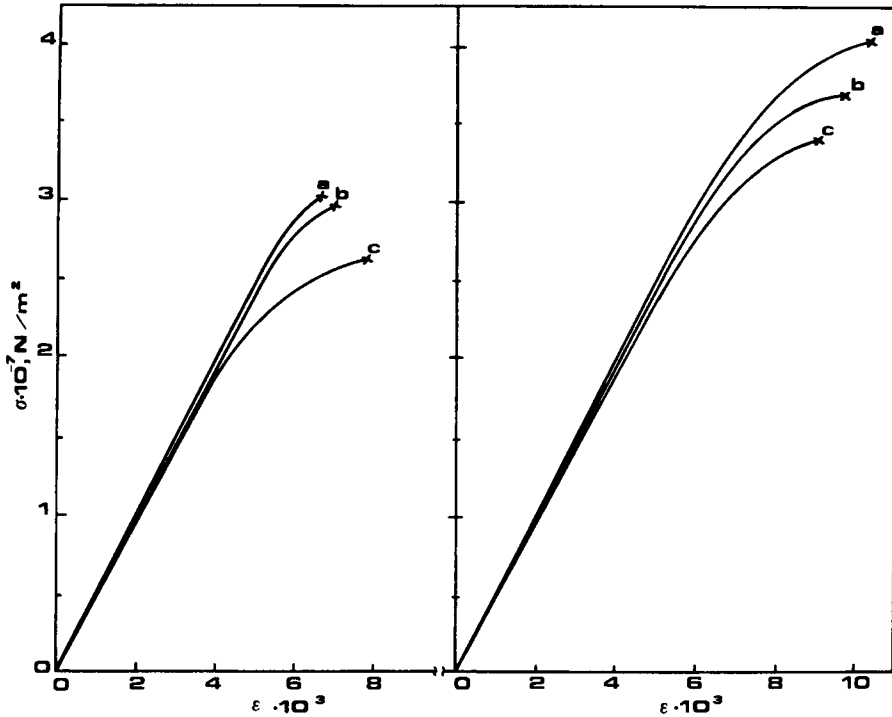
Fig. 7. Stress–strain curves for fiber glass–polystyrene composites, DR = 3.6 (left-hand side); for glass beads–polystyrene composites, DR = 12 (right-hand side) of different filler volume fractions, $T$ = 25°C. $\phi$ (%): Left-hand side (a) 0.44, (b) 0.087, (c) 0; right-hand side (a) 4.6, (b) 0.087, (c) 0.

of beads, which reduces the total amount of relaxing volume. Moreover, the parameter $\epsilon_r$ represents a compressive strain which develops once the material is exposed at $T > T_g$. This value is correlated with the recoverable strain which should be correctly defined as $(l_0 - l_f)/l_f$.

In Figure 5 the equilibrium values of the LRR for fiber-filled composites are also reported. In this system the filler effect on the dimensional stability is much stronger than for bead composites. In fact, at very small fiber concentrations ($\phi$ = 0.35%), $l_0/l_f$ is reduced from a value of 2.3 (i.e., 130% of the deformation of unfilled PS) to a value of 1.15 (i.e., 15% of deformation). Also in this case, the decrease of the equilibrium values of LRR as a consequence of filler content can be attributed to the effect of fibers on the recovery process more than on the amount of molecular orientation of the polymeric matrix at a fixed DR. This is also supported by the mechanical data that will be discussed later.

The stronger influence on the equilibrium value of the LRR of the glass fibers with respect to the glass beads is probably due to a different recovery mechanism. In fact if one puts an unfilled drawn specimen with fixed ends at $T > T_g$, after some time the internal stresses relax without modifying the shape of the sample, while, if the ends are free to move, the specimen creeps until an equilibrium value of LRR is reached. It is possible to assume that the fibers act as constraints for a certain amount of polymer surrounding them and consequently the fiber-filled specimens partly creep and partly stress relax. The stress relaxation contribution on the overall process increases at increasing fiber content.
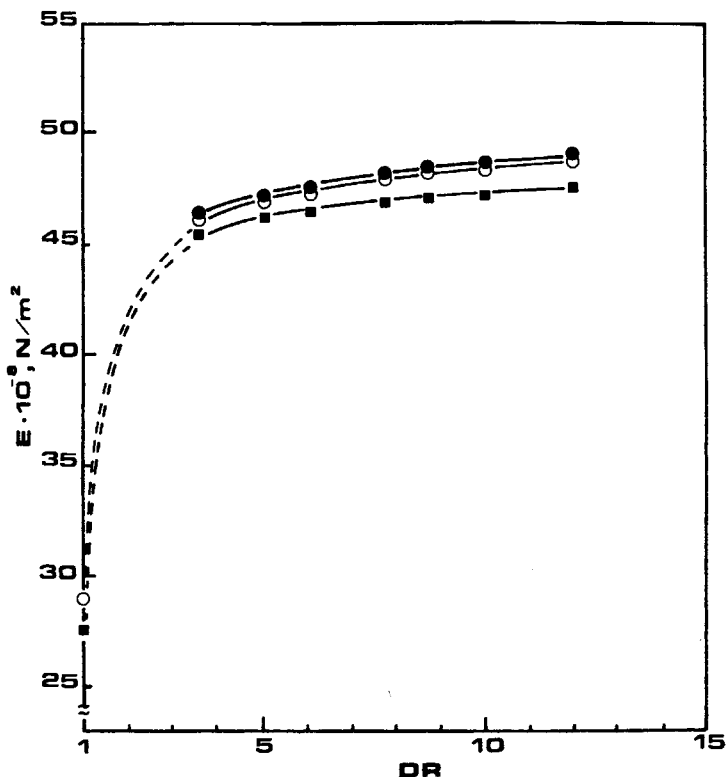
Fig. 8. Elastic moduli for unfilled (■), glass bead (O), and glass fiber (●) polystyrene composites at different drawing ratios, $T = 25°C$; $\phi = .087\%$.

The stress–strain curves obtained at room temperature on unfilled PS at different DR in the direction parallel to the drawing axis are reported in Figure 6. The tensile behavior changes from a typically brittle response to a more ductile type behavior for draw ratios going from 1 to 12. The brittle–ductile transition can be attributed to the effects of both molecular orientation and thermal stresses. Under fixed conditions of cooling, the oriented surface layers are quenched more rapidly than in the interior, resulting in a state of tension internally and a state of compression near the surface.

Upon subsequent tensile deformation, crazes and microvoids initiate in the interior of the specimens, where there is a state of pretension, and then propagate normal to the drawing axis toward the surface. The surface being both oriented and in a state of compression has a higher resistance to microcrack propagation and thus tends to inhibit catastrophic failure. Thus, it is possible to develop a greater degree of microvoiding (i.e., irreversible deformation) prior to catastrophic failure. Moreover, the increase in axial tensile strength arising from the uniaxial orientation of glassy polymers has been theoretically predicted by Sternstein and Rosenthal.[9]

Tensile stress–strain data have also been obtained for polystyrene composites and are reported in Figure 7. The presence of beads enhances the ductile behavior of the unfilled resin as already shown for similar systems.[10,11] The stress–strain behavior relative to the fiber composites indicates, however, that the presence of fibers reduces the polymer ductility. This premature failure
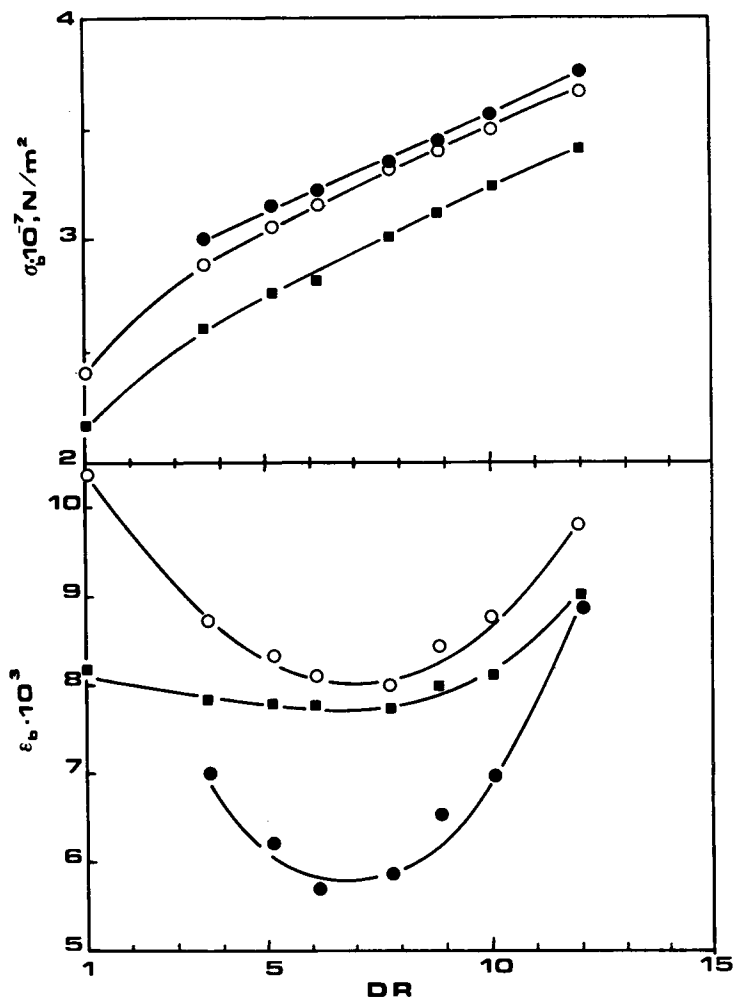
Fig. 9. Ultimate properties for unfilled (■), glass bead (O) and glass fiber (●), polystyrene composites at different drawing ratios, $T = 25°C$. Stress at break (upper part) and strain at break (lower part); $\phi = 0.087\%$.

could be attributed to the stress concentrations around the fiber which are well oriented in the direction of applied stresses.[2]

In Figure 8, the elastic moduli of unfilled PS and composites containing 0.87% of glass fibers and glass beads, respectively, are reported as a function of DR. The value relative to DR = 1 has been obtained from compression-molded specimens prepared from drawn material. All the mechanical properties obtained from such materials are similar to those reported in ref. 12 relative to polystyrene molded from as-received pellets. The modulus increases rapidly at increasing DR, up to DR = 3.5 and then increases slowly. This effect of DR on the elastic modulus is similar to that on birefringence[13] or on the tensile strength[9] reported in literature for similar systems. The effect of filler on the modulus, however, is very small as expected for this very low filler content. But the data clearly show that the molecular orientation of the matrix in both fiber and bead composites is the same of that of the unfilled polymeric matrix at the
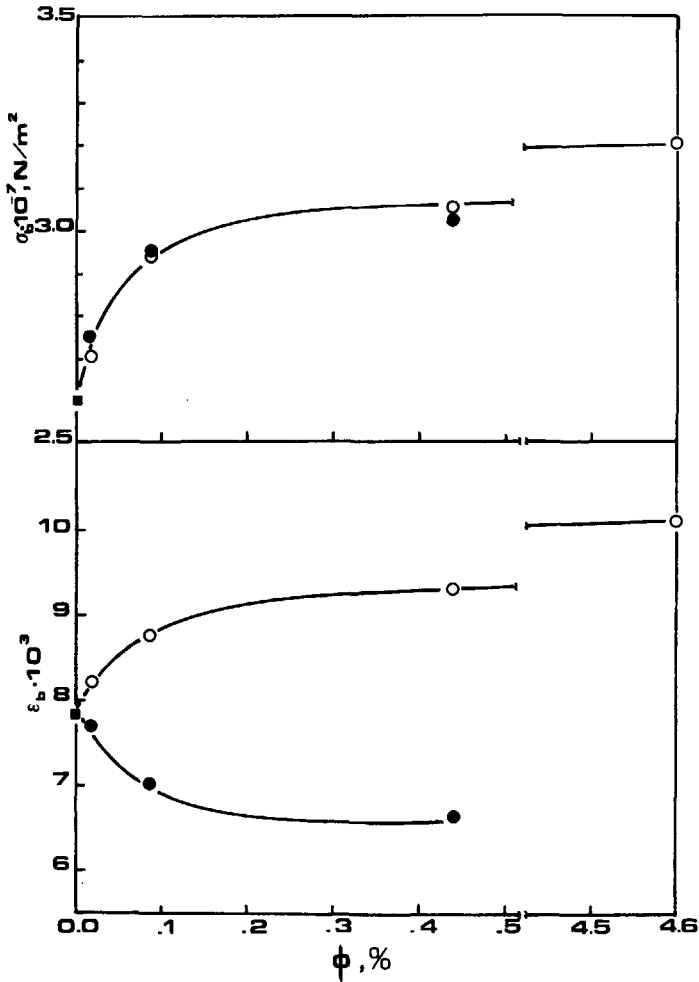
Fig. 10. Ultimate properties for glass bead (O) and glass fiber (●) polystyrene composites at different filler volume fractions of drawing ratios 3.6 at $T = 25°C$. Stress at break (upper part) and strain at break (lower part).

same DR. This, once more, indicates that the strong reduction of the equilibrium values of LRR should be attributed to the relaxation process and not a low molecular orientation induced during the drawing process.

In Figures 9 and 10 the ultimate tensile properties of PS, PS/glass bead, and PS/glass fibers are reported as function of DR and volumetric filler content $\phi$. The strain at break $\epsilon_b$ of the composite is decreased at increasing DR and then increases. This behavior could be atrributed to microvoid formation during the drawing process. But once the molecular orientation is high enough, the oriented molecules assist in the crack stopping mechanism. As also expected, theoretically,[9] the strength of drawn materials increases with DR.

In conclusion, recovery experiments have shown that small amounts of short glass fibers can enhance the dimensional stability of oriented polystyrene sheets. This effect has been demonstrated not to be due to a reduction in molecular orientation of the polymeric matrix. A model to predict the equilibrium values

of the length reversion ratio of glass bead composites is developed and compares well with experimental data.

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