LETTERS TO THE EDITORS

Temperature Stability and Homogeneity of Polystyrene–Polyethylene Grafts*

In a previous publication[1] it was demonstrated that ionizing radiation can be used to graft polystyrene onto polyethylene in three different ways. The polyethylene can be immersed in styrene and the system then irradiated (Type I graft). The polyethylene can be irradiated first in air and then immersed in styrene (Type II graft). Finally, the polyethylene can be irradiated in a vacuum and then immersed in styrene (Type III graft). It was also shown in the same publication, by means of photomicrographs, that Type I and Type II grafts are inhomogeneous, containing inclusions of what is apparently polystyrene homopolymer. Type III grafts appeared homogeneous. Two questions now arose. First, is there any graft copolymer formed at all in Type I and Type II grafts? Second, are Type III grafts truly homogeneous or are the inhomogeneities smaller than the resolution of the microscope (about 0.5 μ)? It was thought that a study of the thermal stability of the grafts would shed some light on the problem.

Experimental

Samples of graft copolymer were prepared from low density polyethylene film as explained in reference 1. The Type I graft contained 37.7% styrene, the Type II graft contained 23.9% styrene, and the Type III graft contained 52% styrene. Several specimens of each type of graft were placed on a hot stage of a polarizing microscope and heated at the rate of 0.5°/min. while their behavior was being observed at very low magnification. X-ray diffraction diagrams were also made of the unheated grafts and were visually observed.

Results and Discussion

The behavior of the Type III graft was the simplest. Except for changes in birefringence, apparently nothing happened until a temperature of about 197°C. was reached. At this point it became opaque as if it had separated into two phases. This is above the melting point of either polyethylene and polystyrene. It is reasonable to suppose that if the polystyrene were grafted to the polyethylene, separation would occur only at higher temperatures. The specimen was heated in air and the separation noted at 197°C. was probably due to oxidation of the graft.

The Type I and Type II grafts show quite different behavior. At 140°C. the Type I specimen begins to show opacity, probably due to phase separation. At 200°C. there seems to be an additional phase separation. The Type II specimen shows very similar results except that the second phase separation occurred at a somewhat lower temperature. In view of the heterogeneous nature of the Type I and Type II grafts as demonstrated in reference 1, these results are

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consistent with the following hypothesis. The bleeding that occurs at 140°C. is due to polystyrene homopolymer. That occurring at higher temperatures is due to oxidative scission of the graft. This means that Type III consists wholly of grafted copolymer whereas Types I and II consist of both homopolymer and graft copolymer.

Visual inspection of the x-ray diffraction diagrams and comparison with unirradiated and ungrafted polyethylene shows no gross changes in the sharpness of the rings, indicating that the bulk of the grafting probably occurred in the amorphous regions of the polymer.

The behavior of the birefringence seems anomalous. The original polyethylene film showed some birefringence due to orientation during processing. The Type I and Type III grafts (37.7 and 52% styrene, respectively) showed very little if any birefringence. The birefringence, however, increased sharply in the range of 95 to 107° for Type I and 85 to 115° for Type III. This birefringence persists until above 195° and it remains when the grafts are cooled to room temperature. Type II (23.9% styrene) is birefringent at room temperature. This birefringence drops at first, then starts to increase again above 115°C. We are at present unable to explain this anomaly, but it may be related to short chains of polystyrene acting as crosslinks for polyethylene. Since the grafting was done at room temperature, it may be expected the crosslinking occurred in an oriented fashion.

Reference

1. D. Ballantine, A. Glines, G. Adler, and D. J. Metz, J. Polymer Sci., **34,** 419 (1959).

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A Note on the Diffusion of Water into a Dry Keratin Fiber

Fujita and Kishimoto[1] have followed the diffusion of penetrants into polymeric solids by measuring the rate of decay of stress in the solid kept at constant extension. Similar experiments are being carried out by the authors on the penetration of water into single stretched wool fibers (Corriedale wool, wet fiber diameter about 50 μ). The force in the fibers was measured by having the fibers attached to an electrical resistance strain gage in the form of a Wheatstone Bridge from which the out-of-balance current was recorded. The stress in a wool fiber, held at a fixed extension in water at 20°C., decayed rapidly and after one hour reached a steady value. At this stage the water around the fiber was replaced by dry Analar glycerol, giving an atmosphere for the fiber
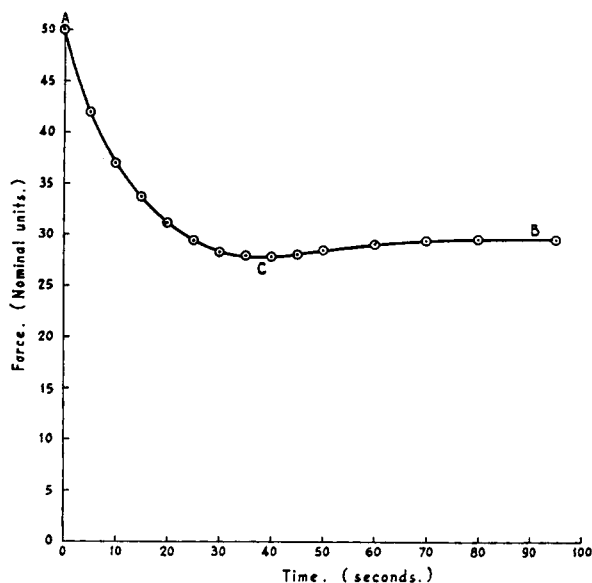
Fig. 1. Change in force in a single Corriedale wool fibre (47 μ diameter in water), stretched to 1.2% extension, when the fiber is taken from 0% R.H. into water. Force at A corresponds to the equilibrium force at 0% R.H. and force at B to the equilibrium force in water.

Fig. 2. $(F_B - F_C)/F_B$ plotted against extension at which the wool fibers were held, where F_B = equilibrium force in water and F_C = minimum force during the experiment when the fiber is taken from 0% R.H. into water. The extension was applied and measured on the fiber originally in water.

equivalent to 0% R.H. The force in the fiber rose rapidly in a few minutes to a fixed value which remained unchanged indefinitely (no resolvable change was recorded over a period of hours). When the fiber's atmosphere was then replaced by water, the force in the fiber dropped and came to equilibrium at the original value recorded just before glycerol immersion. The rate at which this force drops was carefully observed, and for extensions less than about 7% for wool fibers an unusual effect was recorded. As the water entered the fiber the force in the fiber dropped to a minimum value in about half a minute. Then the force rose to a value which was 6% above this minimum when the fiber extension was in the "Hookean" region (i.e., less than 2%) (see Figs. 1 and 2). This result corresponds closely to the effect observed by Mackay and Downes[2] of the torsional rigidity falling to a minimum in less than one minute followed by a slower increase of torsional rigidity to an equilibrium value. In their case, where the fiber atmosphere changed from 0% to 94% R.H., the torsional rigidity reached an unrecorded minimum, which could have been close to zero.

The above correspondence between the variation of torsional rigidity and longitudinal force in a fiber with time can be explained in terms of the two-phase model for wool fibers, described elsewhere.[3] It is proposed that the fiber consists of two phases, a water inpenetrable phase and a matrix which is accessible to water. The matrix has been associated with the matrix of the microfibril-matrix structure of keratin described by Fraser and MacRae.[4] Further, the water penetrable phase is mechanically weakened by a large factor in the presence of water. Also, consideration of this model shows that the torsional rigidity is dependent almost entirely on the mechanical properties of the matrix phase, whereas the longitudinal force is the sum of the forces in each phase. This explains why, although torsional rigidity and longitudinal force in a fiber during moisture uptake vary together
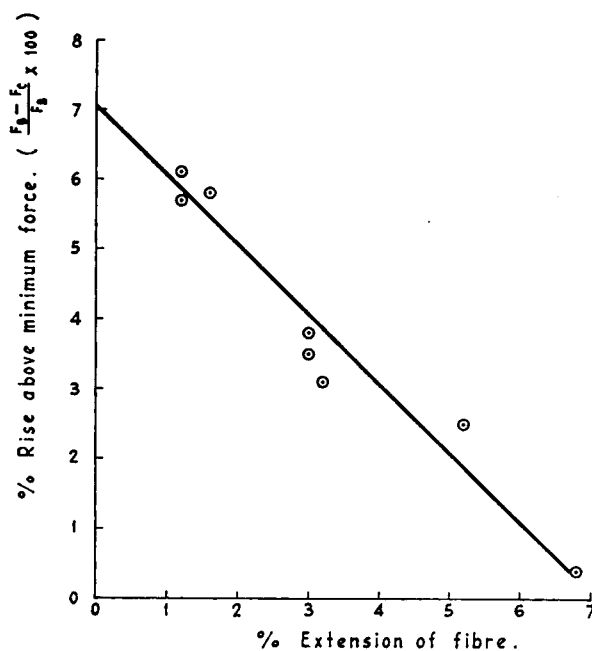
with time, the effect on torsional rigidity is more marked, being almost wholly dependent on the mechanical properties of the portion of the fiber weakened by the water penetration.

References

1. H. Fujita and A. Kishimoto, *J. Polymer Sci.*, **28,** 547 (1958).

2. B. H. Mackay, and J. G. Downes, *J. Appl. Polymer Sci.*, in press.

3. M. Feughelman, *Textile Research J.*, in press.

4. R. D. B. Fraser, and T. P. MacRae, *J. Chem. Phys.*, **28,** 1120 (1958).

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Graft Polymerization of Methyl Methacrylate with Natural Rubber in Emulsion

Recently considerable interest has been attached to the graft polymerization of vinyl monomers with natural rubber and several procedures have been described.[1] In this com-