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
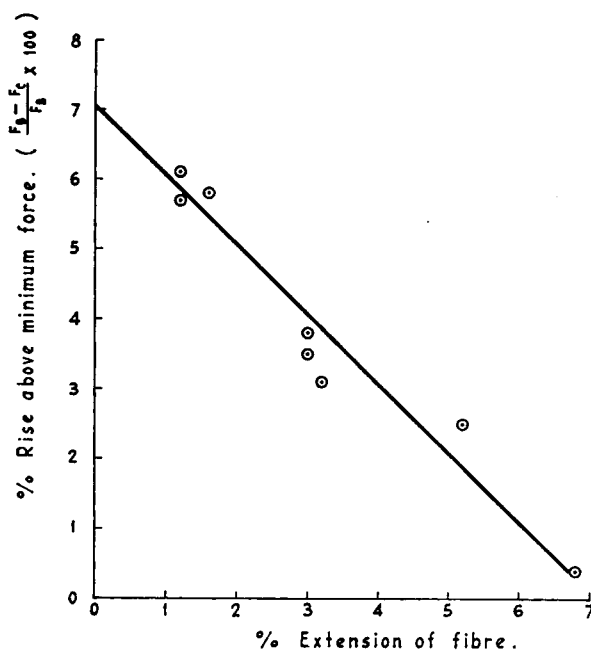
with time, the effect on torsional rigidity is more marked, being almost wholly dependent on the mechanical properties of the portion of the fiber weakened by the water penetration.

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-

munication we wish to report two new methods of grafting methyl methacrylate to natural rubber in latex form.

One procedure consists in irradiating commercial natural rubber latex in the presence of a vinyl monomer with ultraviolet light using water-soluble photosensitizers, such as ferric ion pairs $Fe^{3+}Cl^-$ and $Fe^{3+}OH^-$, in a nitrogen atmosphere. The mechanism of such photopolymerizations has been the subject of a detailed investigation,[2,3] and it has been shown that the primary photochemical process involves an electron transfer followed by the dissociation of the primary product to generate a free radical which initiates vinyl polymerization:

$$Fe^{3+}X^- \xrightarrow{h\nu} Fe^{2+}X$$
$$Fe^{2+}X \longrightarrow Fe^{2+} + X^*$$
$$X^* + M \longrightarrow M^*$$
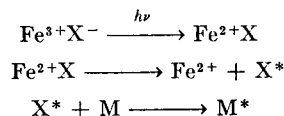
where X represents a radical, e.g., Cl or OH, and M is the vinyl monomer.

In a typical experiment, when 200 cc. of rubber latex containing approximately 5 g. of total solids/100 cc. were irradiated with 2.8 g. of methyl methacrylate monomer using the $Fe^{3+}Cl^-$ photosensitizer, nearly 75% of methyl methacrylate was grafted to natural rubber. It is of interest to report that in similar experiments with acrylonitrile, no grafting was achieved although there was considerable homo-polymer, formation.

Another procedure consists in the use of hydrazine as the initiator of polymerization in emulsion. The mechanism of initiation of polymerization by hydrazine has been investigated in this laboratory,[4] and evidence has been obtained in favor of an initiation reaction involving the hydrazyl radical formed by one-electron oxidation of hydrazine by metallic ion under the appropriate reaction conditions.[5]

$$N_2H_4 + M^{x+} \longrightarrow N_2H_3^* + M^{(x-1)+} + H^+$$
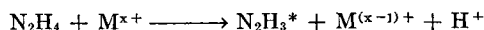
where M^{x+} represents a one electron oxidant.

In the presence of oxygen, the primary process must presumably be the same since a direct reaction between hydrazine and oxygen is considered improbable.[6] When methyl methacrylate is polymerized in the presence of commercial natural rubber latex using hydrazine under conditions of autoxidation of the latter catalyzed by cupric ions, a considerable amount of grafting was achieved. In a typical experiment where 28 g. of methyl methacrylate was polymerized in commercial latex containing about 40 g. of total solids under conditions of autoxidation of hydrazine with $10^{-4}M$ cupric ions as the catalyst at room temperature, the reaction was complete in six hours with nearly 50% of the methyl methacrylate grafted to the rubber. The graft copolymer, pure rubber, and polymethyl methacrylate were separated by using the appropriate solvent extraction procedures which have been employed by previous investigators.[7]

The details of this investigation, together with the properties of the graft copolymers prepared from rubber and various vinyl monomers, will be the basis of a subsequent publication.

References

1. L. C. Bateman, *Ind. Eng. Chem.*, **49**, 704 (1957).
2. M. G. Evans, M. Santappa, and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).
3. C. C. Menon and M. Santappa, *Can. J. Chem.*, **35**, 1267 (1957).
4. C. C. Menon and S. L. Kapur, *Current Sci. (India)*, **27**, 245 (1958).
5. C. C. Menon and S. L. Kapur, unpublished results.
6. W. C. E. Higginson, *Chem. Soc. (London)*, **Spec. Publ. No. 10**, 105 (1957).
7. B. C. Sekhar, *Rubber Chem. & Tech.*, **31**, 430 (1958).

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Thermodynamic Parameters of Poly(ethylene Oxide) in Aqueous Solution

Recently, the results of an extensive study of the solution properties of high molecular weight poly(ethylene oxide) were discussed by the authors.[1] One of the major points of interest in this study was the inverse solubility-temperature relationship of this polymer in water solution. This phenomenon was interpreted in terms of a hydrophilic-hydrophobic balance in the polymer structure and in terms of the
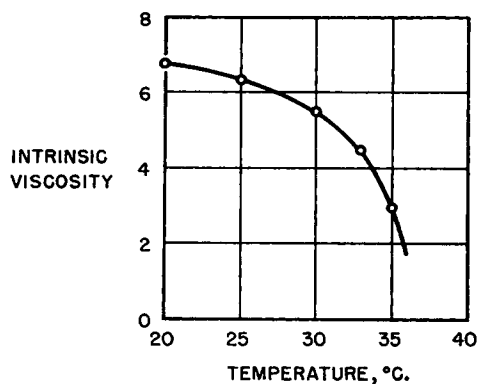

Fig. 1. Intrinsic viscosity of a high molecular weight poly(ethylene oxide) at temperatures near the upper limit of solubility in 0.45 M potassium sulfate solution.

increase in the activity of the neutral polymer molecule as the temperature was increased. A further insight into the factors determining the solution properties of this polymer can be gained following the theory of Fox and Flory[2] with respect to the temperature dependence of the intrinsic viscosity.

In Fig. 1, the intrinsic viscosity of a sample of poly(ethylene oxide), of about four million molecular weight, is shown as a function of temperature in 0.45 M potassium sulfate solution. If 35°C. is taken as the precipitation temperature of an infinite molecular weight polymer, then using the expression for the molecular expansion factor, α, of Fox and Flory[2]