Stress relaxation measurements on wool + polyacrylonitrile graft copolymers

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With 2 figures and 2 tables

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1. Introduction

The incorporation of synthetic polymers, particularly those prepared from vinyl monomers, into the wool fibre has been of considerable interest for many years (1). It has been shown that extremely large amounts of polymer can be incorporated whilst retaining the essential morphology of the keratin structure. Such polymer composites do show quite different mechanical properties and the incorporation, for example, of polyethylacrylate can yield an elastomeric wool fibre (2).

Vinyl monomers can be incorporated into wool by a variety of initiatory systems. Arai, Negishi, Komine, and Takeda (3) have shown that methyl methacrylate can be copolymerized with wool without the formation of homopolymer. Digestion of the wool has isolated the vinyl polymer and analysis has shown (4) that the polymer is terminated at each end by an amino acid residue one of which is probably cystine and the site of initiation. Clearly the product is a graft copolymer with the grafts acting as extended intermolecular crosslinks. Two features may be expected from the presence of the graft; an alteration in the mechanical properties through the introduction of new crosslinks, and since the fibre swells in order to accommodate the polymer (5), there will be a loosening of part of the internal structure of the wool fibre.

The polymerization of acrylonitrile inside wool fibres using the ferrous ion-hydrogen peroxide initiatory system has been examined in detail by D'Arcy, Hall, and Watt (6). Microscopic examination has shown the fibre to be free of surface grafted polymer. Swelling in formic acid followed by extraction with dimethylformamide + formic acid mixtures produced only a small weight loss. Extraction of fibre cross sections on the electronmicroscope grids did however indicate that a small amount of homopolymer was produced (7). On this evidence it is reasonable to conclude that most of the polyacrylonitrile forms a graft copolymer although the location of the grafts with respect to the keratin molecule still remains to be established. Electron microscopic examination does not indicate any preferential deposition of polymer in any of the histological components of the fibre (8). Within the cortical cells it may be expected (9) that polymer forms mainly in the matrix although there is an indication that the microfibrils may be affected since the low angle X-ray reflections become more diffuse with the incorporation of polyacrylonitrile (10).

An examination of some of the physical properties of wool + polyacrylonitrile copolymers has already been made. Watt (5) and Watt and D'Arcy (11) have shown that the water vapour isotherms are modified by the presence of the polymer except at about 85% R.H. when the isotherms cross and the moisture regain shows no dependence on the polyacrylonitrile composition. Stress-strain diagrams show the effect of grafting but since the water content is also modified it is not possible, from the work already reported, to draw firm conclusions concerning the dependence of the mechanical properties on copolymer composition. An examination of the relative changes in the torsional and extensional moduli at 50% R.H. has been made by Simpson (12) and significant changes observed in the compositional range up to 25% w/w polyacrylonitrile.
This is the region of greatest interest in the technological application of this copolymer system.

Work on wool fibres carried out over a number of years has generally shown that the stress-strain diagram is a relatively insensitive indicatrix of the effect of chemical modification. The time dependent properties, in particular the relaxation of stress after the application of a small strain, are found to be much more sensitive and this technique has been used for the examination of wool graft copolymers containing up to about 90% w/w polyacrylonitrile. The additional effect of variation in the rate of stress relaxation through variation in the water content of the various copolymers has been minimised by making measurements at 85 R.H. and 35 °C as suggested by the isotherms given by Watt (5).

2. Experimental

Fibres of Corriedale wool (batch ref. SW 1) which had been modified by the internal deposition of polyacrylonitrile using the ferrous ion-hydrogen peroxide method were available from the work of D’Acy, Hall and Watt (6). Weight uptakes were determined on the basis of the dry weight of the wool.

In the mechanical measurements prior selection was made to avoid fibres having exceptional variation in diameter. Fibres chosen for use were de-aged by immersion for 10 min in a buffer mixture of pH 7 and then conditioned in the apparatus under zero strain for 24 h prior to the experiment. The apparatus was similar to that described by Feughelman (13) the stress on the fibre being determined with a Statham transducer type G 1. The apparatus was maintained at 35 °C and the humidity kept at 83% R.H. through the use of saturated KBr solutions.

At the commencement of an experiment the fibre of length approximately 5 cm was given a strain of 5% the rate of strain being kept constant at 1%/sec. A strain of this magnitude takes the fibre beyond the yield point to a region where the mechanical properties show their most significant change with copolymer composition (5, 12). Stress relaxation measurements were continued for 24 h. A significant amount of variability was observed and it was necessary to examine a large batch of fibres from each preparation. Needles and Sarsfield (14) have also reported increased variability in the tensile properties of wool graft copolymerized by dye-sensitized photopolymerization in the case of a number of acrylic monomers.

For the evaluation of the stress in the fibre it has been assumed to be of circular cross-section. Measurements of fibre diameter were made at a large number of points along its length using a calibrated image splitting eyepiece. The stress in the fibre after 0.1 min from the start of loading has been taken as the reference point (f~) for the purpose of normalizing the stress data.

3. Results

The force required to maintain a constant strain in the fibre will be proportional to the number N of molecular chain segments effectively opposing the force. If in order to allow the force to decrease it is assumed that these segments become either broken or displaced according to a first order rate equation,

$$-\frac{dN}{dt} = kN$$  \[1\]

where k is the appropriate rate constant it is then straightforward to show that the stress will be given by,

$$\ln\left(\frac{f}{f_0}\right) = -kt$$  \[2\]

where $f_0$ is the stress at zero time. However in stress relaxation experiments it is not easy to determine $f_0$ since the strain in the fibre is not produced instantaneously. Instead the stress developed after a fixed time interval, in this case 0.1 min, has been taken as the effective zero point.

The experimental data when plotted according to eq. [2] did not give a single value for the rate constant.

A satisfactory agreement was obtained by considering the observed stress relaxation to be accounted for by two decay processes characterized by the rate constants $k_a$ and $k_b$. That is eq. [2] was replaced by,

$$\beta = (1 - B) \exp(-k_a t) + B \exp(-k_b t)$$  \[3\]

where B is an adjustable parameter taking values up to unity, and $\beta = f/f_0$.

In the analysis of the data this equation was fitted to the data at three points so that,

$$\beta_1 = (1 - B) \exp(-k_a t_1) + B \exp(-k_b t_1)$$

$$\beta_2 = B \exp(-k_b t_2)$$

$$\beta_3 = B \exp(-k_b t_3)$$  \[4\]

from which,

$$\ln B = (t_3 \ln \beta_2 - t_2 \ln \beta_3)/(t_3 - t_2)$$

$$k_a = -\ln[(\beta_1 - B \exp(-k_b t_1))/(1 - B)]/t_1$$

$$k_b = \ln(\beta_2/\beta_3)/(t_3 - t_2).$$  \[5\]

The values of $\beta_1$, $\beta_2$ and $\beta_3$ were chosen after the best curve had been drawn through large scale plots of the data for each copolymer sample. Evaluation of the parameters $k_a$, $k_b$ and B was easily arranged through the use of a short computer program and the results are given in table 1.

1) The equilibrium water content is here expressed as the weight of water per gram of dry wool in the copolymer. Polyacrylonitrile is an almost completely hydrophobic material.