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Radiation-Initiated Polymerization in Aged Wool Keratin

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ABSTRACT

A mutual irradiation technique for polymerization from the vapor phase has been used to internally deposit a number of polymers in wool. Prior to the polymerization step wool samples were aged by conditioning at 80° C in the presence of monomer and water vapors. This treatment modified the tensile properties of the wool; producing stronger fibers with a reduced stress relaxation. These changes can be reversed by saturation with water. The irradiation levels used were not sufficient to modify the changes produced by aging. Polymerization from the vapor phase enabled copolymers to be formed without disturbing the aged state of the wool substrate. The sorption and tensile properties of the copolymers have been examined and it appears that the effects of aging are retained by a wool-poly(methyl methacrylate) copolymer even after relaxation in water.

The phenomenon of aging is observed when an appreciable time is required for molecular structures to reach equilibrium following a change of environment or a mechanical distortion and is encountered in many macromolecular materials. During aging, pronounced changes in physical properties may occur. Recent work has illustrated that some aging effects of wool keratin may lead to desirable textile applications [1, 2]. However, one of the major difficulties in any attempts to utilize, in practical situations, the desirable effects of aging is that following a change of environment the macromolecular structure moves towards a new equilibrium condition, with a consequent change of properties. Thus it would sometimes be advantageous to stabilize the structure in the desired aged condition. It has been shown that some of the desirable attributes of aged wool cloth can be retained by subsequent deposition of a suitable resin within the wool fibers [3].

The exact mechanism of the aging process is not known. The secondary and higher structures of the polypeptide chains in keratins are strongly hydrogen bonded. Whenever a keratinous structure is subjected to a change in environmental conditions, molecular stresses may be set up. In the case of humidity changes the water content alters with consequent dimensional variations. The water content may rapidly attain an equilibrium value but the keratin-water complex may not reach its equilibrium state for an extremely long time. Although wool fibers swell both radially and axially, the swelling is anisotropic [4]. The mechanical stresses due to swelling cause rupture of the hydrogen bonded network, allowing a decay of swelling stresses. Reformation of a network may then occur and probably involves the formation of new hydrogen bonds in equilibrium with the stress-free state. Structural rearrangement following absorption of water is evidenced by long-term changes in conductivity of wool fibers [5] and by the observation of two-stage water absorption under certain conditions [6]. Each hydrogen bond that reforms may require additional hydrogen bond rearrangements to produce an equilibrated configuration with minimum energy under constant environmental conditions. In practice the difficulty of maintaining a truly constant environment means that the material is being required to approach a new equilibrium configuration every time its environmental conditions change.

Wool fibers conditioned at intermediate relative humidities undergo aging, and some physical properties, such as the stress-strain relationship, are altered. The magnitude of the change depends both on the time and temperature of the conditioning process, and on the state of the fiber in the unaged condition. An equilibrium condition in water is attained very quickly and immersion of wool fibers in water to give a reproducible zero for mechanical tests is a well-established practice. Standard, and mechanically reproducible, unaged fibers are obtained in this way since saturation with liquid water or exposing to high humidities of water vapor disturbs the equilibrium state established at lower humidities. Thus the fibers become unaged with respect to the lower humidities.

In order to stabilize the fiber in its aged state it would seem necessary to maintain the hydrogen bonded network of the substrate in its minimum energy configuration and to prevent rearrangements to higher energy levels from occurring under changing humidity conditions. Leeder and Wemyss [3] have formed resin within the fibers of an aged wool fabric without disturbing the aged state and have shown that such treatment can preserve some of the advantages of the aged fabric even after saturation in water. Deposition of polymer in wool fibers substantially alters their water sorption properties. The introduction of monomer from the vapor phase together with water vapor prior to inducing polymerization would seem to be another effective way of stabilizing wool fibers in the aged condition. Radiation provides a convenient means by which polymerization of a monomer in the vapor phase in contact with a solid substrate may be initiated.

General discussions of the effect of radiation on polymers have been published [7, 8]. Most natural fibers appear to degrade on irradiation and the effect increases with increasing dose. There is little evidence of dose rate effects. Irradiation of fibers in the presence of monomer vapor (mutual irradiation) usually gives higher polymer yields for a given dose than the post-irradiation method in which the fibers are irradiated, then placed in contact with monomer. It is difficult to deposit polymer in dry keratin, but with mutual irradiation techniques high polymer yields can be obtained by the addition of water which swells the keratin structure and facilitates penetration of monomer to the sites of the initiating radicals [9]. This paper investigates the feasibility of using radiation to deposit polymer within aged wool fibers without altering the desirable properties produced by the aging process.

EXPERIMENTAL

Polymerization Procedure

An accurately weighed wool sample was placed in the polymerization tube (see Fig. 1). Three radial indentations, I, supported the wool sample away from the bottom of the tube. A small side arm, T, drawn out to a capillary, enabled a hypodermic needle to be inserted into the tube below the wool sample. Requisite amounts of distilled water and monomer liquid were introduced from a hypodermic

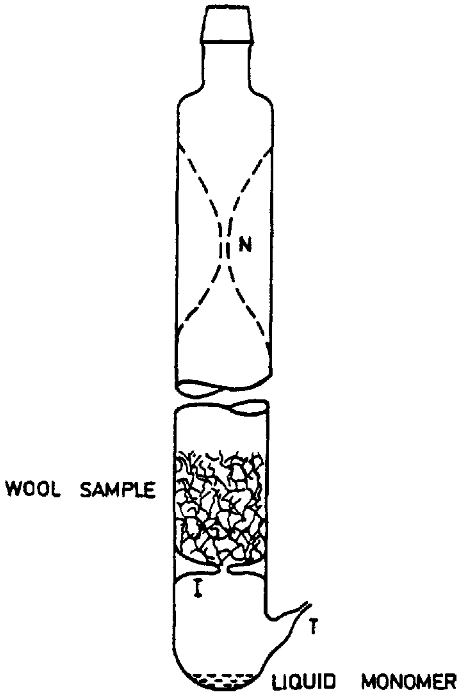

FIG. 1. Diagrammatic representation of a polymerization tube showing position of wool sample above the liquid monomer.

syringe. With the base of the tube immersed in liquid nitrogen the capillary was sealed off and the tube was evacuated. It was then isolated from the pump, the liquid nitrogen removed, and the frozen water and monomer allowed to thaw so as to liberate any dissolved gases. This procedure was repeated twice to ensure complete removal of dissolved gases from the system before the tube was sealed off at the capillary neck, N.

Accelerated aging was carried out by placing the sealed tube in an oven at 80° C for 48 hr after which time the tube and its contents were allowed to cool slowly to room temperature. The amount of water introduced was sufficient to give a water content of approximately 16% in the wool sample. Because the wool was in a sealed tube this water content would not vary greatly with the temperature.

After aging, the sealed tubes were irradiated in a ^{60}Co gamma radiation facility at the Australian Atomic Energy Commission. The dose rate was 3.9×10^5 rads/hr. The irradiated tubes were opened and the wool samples washed in a suitable solvent to remove any homopolymer and reweighed. The copolymer yield was calculated as the percentage increase in the weight of the wool sample.

Mechanical Tests

Force-extension data were obtained by forming a single wool fiber into a loop in a holder mounted in an Instron stress measuring apparatus. Mounted fibers were equilibrated and measured under standard atmospheric conditions of 20° C and 65% r.h. The fibers were stressed at a constant rate of strain of 1.7%/sec. Stress relaxation was determined by holding the fibers at a fixed length and determining the decay of stress as a function of time. To determine the behavior in extension of unaged fibers, the mounted fiber was relaxed in distilled water at 50° C for 1 hr, conditioned, and stretched again.

Sorption isotherms were determined gravimetrically by suspending wool samples from a calibrated quartz helical spring mounted in an evacuable glass chamber which had provision for admitting thoroughly deaerated vapor. The pressure of the admitted vapor was read from a wide-bore differential mercury manometer. An efficient air thermostat encased the apparatus and enabled the temperature to be controlled to within ±0.01°C. Changes in the sample weights were followed by measuring the spring extension with a cathetometer. The equilibrium weight of the vapor being sorbed was expressed as a percentage of the original weight of wool.

RESULTS

Properties of Aged Fibers

The effects of the time of aging on the stress-strain relationship for Merino wool fibers are summarized in Table 1. The first column refers to the time that the fibers which had been relaxed by immersion in distilled water at 50°C had been held under the test conditions of 65% r.h. and 20°C. It can be readily seen that the rate of increase of percentage stress at 4% strain is initially high and subsequently diminishes so that the measured stress tends toward an equilibrium value. In practice attainment of an equilibrium value takes an exceedingly long time; experience in this laboratory [10] has indicated that aging proceeds at a measurable

TABLE 1. Stress-Strain Data for Aging of Wool Fibers

Time of aging (days)	Percentage stress at 4% strain	Percentage residual stress after 30 min at 1.5% strain
0	100.0	21.7
1	103.0	22.2
2	104.4	22.7
4	105.8	23.3
7	107.4	24.2
14	109.1	25.6
21	110.0	26.7
28	110.2	27.3

rate up to 5 years under these conditions. However, equilibrium is established more quickly at higher temperatures and humidities. The stress relaxation behavior of wool fibers is also affected by aging. The residual stress, after having been stressed to 1.5% strain and held at that strain for 30 min, is given, as a percentage of the original stress, in Column 3.

Figure 2 shows the effect of accelerated aging on the stress-strain curve of a Merino wool fiber. The solid curve, A, is for wool which was aged by being held at 80° C with 16% water content for 96 hr, and the dashed curve, B, was obtained after the fiber was relaxed in distilled water at 50° C to restore it to the unaged state. For both curves a small stress is required to decrimp the wool fiber and the zero strain is taken as the intercept on the abscissa, obtained by extrapolation of the linear portion of the Hookean region of the curve for the fiber in the unaged state. The gauge length of the extensometer remained fixed, and the linear portion of the Hookean region of the curve for the aged fiber, when extrapolated, cuts the abscissa at a positive strain. This indicates that the fiber has lengthened during the aging process. The Hookean region of the curves shows that the aged fiber exhibits a higher Young's modulus. Because the fiber is being strained at a constant rate, an overshoot of stress can be observed. This maximum in the stress-strain curve emphasizes that the state of the fiber is being changed by mechanical deformation. Increased stiffness in the Hookean region probably results from extra strength being imparted to the fiber through a hydrogen bonded

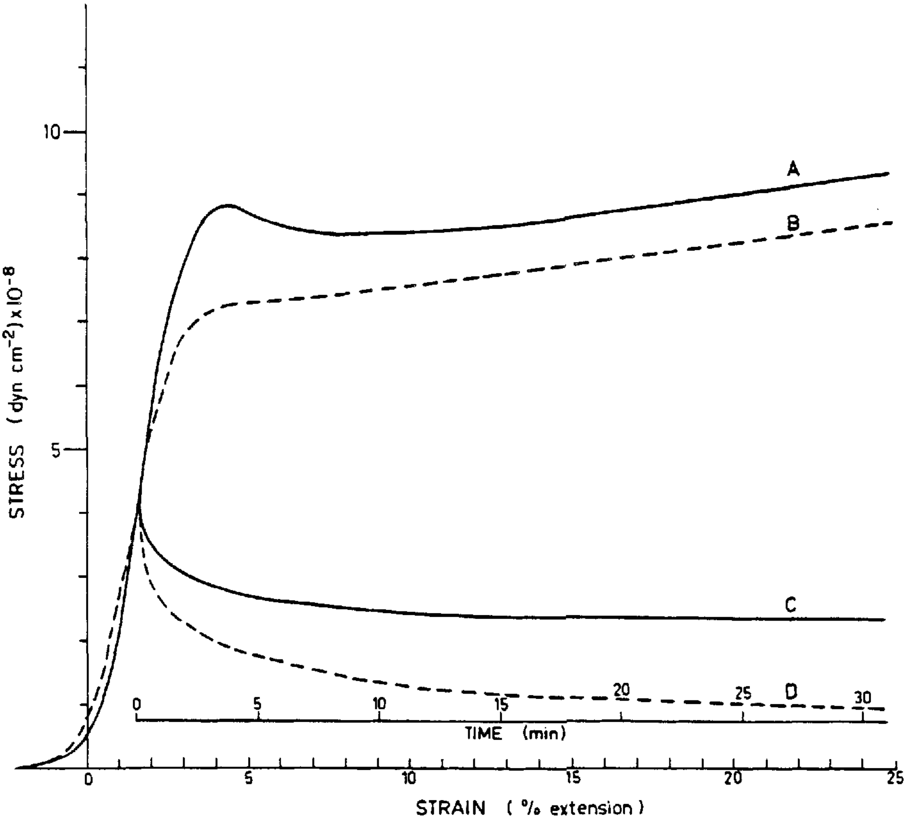

FIG. 2. Stress-strain curves of a Merino wool fiber at 20°C and 65% relative humidity. (A) Fiber has been aged at 80°C and 16% water content for 96 hr. (B) Same fiber unaged by relaxation in water at 50°C for 1 hr. (C) and (D): Stress relaxation curves as a function of time from 1.5% strain for the aged and unaged fibers, respectively.

network being formed in a condition of minimum energy. The overshoot results from the cooperative rupture of a number of bonds as the fiber begins to yield. The development of this pronounced overshoot is not evident for fibers aged at room temperature for long periods (as long as 14 years). Well into the yield region the two curves are parallel so that the same additional force is required for further extension of the aged or unaged fibers in this region.

The relaxation of stress with time, when held at a constant strain of 1.5% after straining in the Hookean region, is also shown as Curves C and D for the aged and unaged fibers, respectively. The subsidiary abscissal axis is a time scale for the stress relaxation and has its origin coinciding with the time of attaining the constant strain level of 1.5%. The amount of relaxation in the aged fiber is markedly reduced.

Aging in the Presence of Monomer

Wool samples with 16% water content were heated to 80°C for 48 hr in the presence of monomer vapors in equilibrium with their liquid phases. There were no significant changes in the extent of the modification after conditioning at 65% r.h. and 20°C from those observed after aging under similar conditions in the absence of monomer vapor.

Effect of Radiation on Properties of Wool Fibers

Earlier workers [7, 8] have shown that the tensile properties of wool fibers are not significantly effected by radiation doses of up to 5 Mrads. Higher doses produce progressive reductions in fiber strength. Figure 3 shows the effects of irradiation of dry wool, in vacuo, on the stress to produce 4% extension (Curve A), equilibrium water content at saturation (Curve B), and equilibrium formic acid content at saturation (Curve C). The sensitivity of each of these properties to the effects of gamma irradiation is quite different, with the equilibrium uptake of formic acid vapor at saturation providing the most sensitive measure of changes in the wool structure. Torsional modulus also provides a sensitive measure of radiation effects and in all cases the effect of the modification increases with radiation dosage. However, the extent of modification due to irradiation is not only dependent on dosage, but also on the conditions under which the irradiation is carried out. The changes in the above properties are increased by the presence of either water vapor or air, with the greatest change being produced when both are present during irradiation. However, in no case did we find a significant change of the measured properties for a dosage of less than 5 Mrads.

The question of whether irradiation would modify the structure of aged wool sufficiently to change the stress-strain behavior has been examined and data is tabulated in Table 2 for dosages of 5 Mrads.

Control wool fibers were taken from an unaged wool sample and

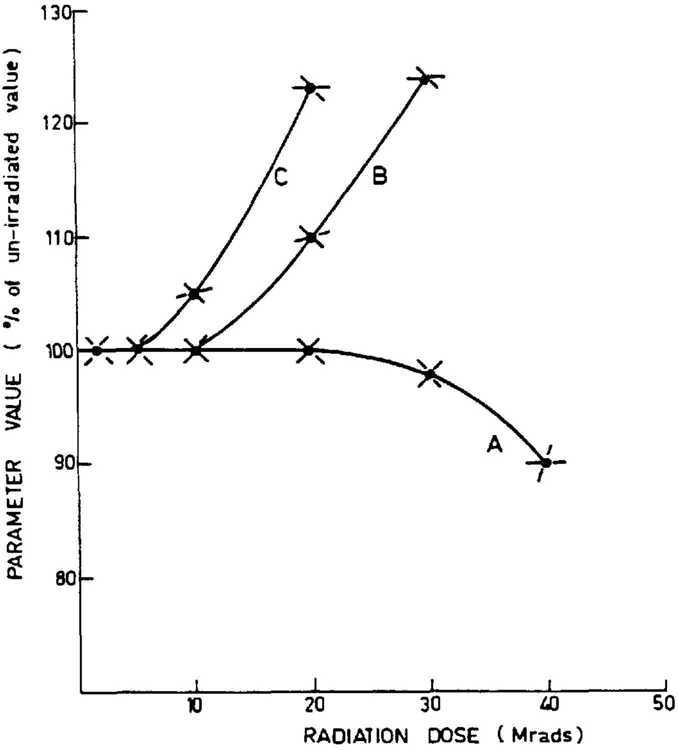

FIG. 3. Percentage change in the value of a physical parameter of wool fibers as a function of irradiation dose. (A) Stress at 4% strain. (B) Saturated water content. (C) Saturated formic acid content.

were not irradiated. A second sample was irradiated in the unaged state. Other fibers were aged for 48 hr at 80°C and 16% water content, with and without monomer vapor present, before irradiation. The aged fibers exhibited changes in their stress-strain behavior characteristic of the aging process, even after irradiation. The effect of varying the dose rate was not investigated.

Formation of Polymers in Situ

The deposition of polymers was initiated by the irradiation of wool samples while exposed to monomer vapor. The presence of inhibitor

TABLE 2. Mechanical Properties of Aged and Irradiated Wool (Dose: 5 Mrad)

	Yield point		Young's modulus (dynes cm^{-2}) × 10^{-8}	
	Strain (% extension)	Stress (dynes cm^{-2}) × 10^{-8}	Hookean region	Yield region
Control	2.45	7.10	2.81	0.70
Unaged wool	2.5	7.05	2.80	0.70
Wool aged in presence of H_2O	3.75	8.95	3.25	0.68
Wool aged in presence of H_2O and monomer	3.7	9.0	3.30	0.69

in the monomer liquid at the bottom of the tube effectively prevented the formation of large amounts of homopolymer in the liquid but did not suppress polymerization in the wool fibers. The monomers used, the conditions of polymerization, and the amount of polymer formed are tabulated in Table 3.

TABLE 3. Formation of Wool Copolymers

Monomer	Monomer concentration, % (by weight) of wool	Radiation dose (Mrad)	Polymer yield % weight increase (on weight of wool)
-	-	5.0	0.0
Vinyl acetate	100.0	5.0	30.2
Vinyl acetate	40.0	0.75	7.4
Methyl acrylate	100.0	5.0	85.4
Ethyl acrylate	100.0	5.0	78.0
Ethyl acrylate	40.0	0.75	28.2
Methyl methacrylate	100.0	5.0	80.2
Styrene	100.0	5.0	27.0
Acrylonitrile	100.0	0.75	60.0
Acrylonitrile	100.0	5.0	80.0
Isoprene	100.0	5.0	8.0
Isobutylene	100.0	5.0	1.0
Vinyltriethoxysilane	100.0	5.0	33.8
Ethyltriethoxysilane	100.0	5.0	33.4

The stress-strain relationships of wool fibers containing polymer were determined before, and after, the fibers were relaxed in distilled water at 50°C and the ratios (expressed as a percentage of the relaxed value) of the stress at 4% strain are tabulated in Table 4. The percentages of residual stress remaining in the fibers after the fiber was held at a constant

TABLE 4. Physical Properties of Wool Copolymers

Polymer	Polymer add-on weight (%)	Stress ratio at 4% strain $\left(\frac{\text{unrelaxed}}{\text{relaxed}} \times 100\right)$	Stress relaxation from 1% strain (% residual stress)		Water content at 65% r.h. and 20°C (%w/w on weight of wool)
			Unrelaxed	Relaxed	
Control	-	110.5	80.0	60.5	15.0
Ethylacrylate	28.2	118.2	67.0	61.5	16.8
Methyl methacrylate	80.2	100.0	84.0	67.9	15.5
Styrene	27.0	112.0	71.4	55.1	13.6
Acrylonitrile	60.2	122.1	79.5	47.0	15.1
Isoprene	8.0	113.5	83.0	67.3	15.9
Vinyltriethoxysilane	33.8	113.2	83.6	64.0	18.7
Ethyltriethoxysilane	33.4	116.1	80.8	61.5	15.2

1.5% strain for 30 min are tabulated, and the ratio of the residual stress in the unrelaxed fiber to that in the relaxed fiber is given. The water contents of the copolymers at 65% r.h. are given in Column 6 of Table 4.

DISCUSSION

The changes with aging in the stress-strain relationships of wool fibers are indicative of the modification of physical properties of macromolecular systems in which rearrangements at the secondary or higher structural levels follow mechanical deformations. The values of the measured stress, to produce a 4% strain at a constant rate of strain, and the residual stress at 1.5% strain both approach equilibrium values, although the rate of change in the stress relaxation is clearly slower than the rate of increase in stiffness of the fibers. The equilibrium being approached is defined by the environment of the fibers and represents a rearrangement of the fiber structure to attain stress equilibrium. A new aging process will be initiated and a new equilibrium will be approached if the environmental conditions are distrubed. The difference in the time taken to establish a new equilibrium value of fiber stiffness compared to the rate of stress relaxation highlights the difficulty in determining when the aging process has been completed, since the time necessary to reach a constant value for any physical property will depend upon the property being measured.

The time taken to reach an equilibrium or near equilibrium structure and hence a constant value for all measured physical properties is reduced, in the case of wool, by elevated humidities and increased temperatures. Complete equilibrium seems to be achieved within a few minutes at 50° C when wool is immersed in distilled water. Such treatment can repeatedly produce a wool fiber which is in a convenient standard state for aging studies. The increase in the residual stress in aged fibers is to be expected if a more strongly hydrogen bonded network free of any internal stresses is built up during the aging process.

The effects of radiation on the mechanical properties of wool fibers which are illustrated in Fig. 3 show that there is little change in the stress at 4% strain until about 25 Mrads have been absorbed by the wool. At radiation doses above this level there is a greater weakening of the fiber. Increases in equilibrium saturation vapor absorption became evident at doses as low as 5 Mrads in the case of formic acid vapor and 10 Mrads in the case of water. By contrast, Zahn [11] has reported that a dose of 10 Mrads in the presence of air decreased the uptake of water vapor by wool. An increase in the amount of vapor absorbed from a saturated atmosphere has been used as a measure of the rupture of covalent bonds in the keratin network [12]. Formic acid vapor is a more sensitive sorbate than water in this respect because the hydrogen bonded network is so severely ruptured by this penetrant that swelling is limited only by the constraints imposed by covalent bonds or chain entanglements. The results suggest that the irradiated wool has suffered rupture of covalent bonds and the substrate is then able to swell more easily to accommodate greater amounts of absorbed material. The increased swelling in water will also follow from the rupture of covalent bonds but the hydrogen bonded network also imposes restraints on swelling. The relative increases in formic acid and water vapor uptake are similar to the ratios obtained following chemical attack on covalent cross-links [13], and this would suggest that the hydrogen bonded network is not greatly affected by irradiation.

The differences in sensitivity of various physical techniques for detecting radiation effects on wool illustrate the necessity of choosing criteria with relevance to the properties which determine the suitability of wool for its practical end use.

The facts that wool can be aged in the presence of monomer vapors and that irradiation does not change the properties of the aged fibers makes possible radiation-initiated polymerization to form a copolymer with aged wool fibers. That a copolymer can in fact be formed under these annealing conditions is readily apparent from Table 3. The presence of water vapor, while promoting aging of the fibers, probably is advantageous to the polymerization process. The substrate is swollen so that the relatively large monomer molecules, which would normally enter the wool fiber only slowly, are able to be absorbed by wool from the vapor phase. It has already been demonstrated [14, 15] that the presence of water vapor during irradiation of wool-monomer systems leads to higher polymer deposition yields. Under these conditions the polymer will be distributed throughout the wool fibers and not restricted to the near-surface regions as is observed for diffusion-controlled polymerizations.

When the aging process takes place after the fibers have been equilibrated with monomer and water vapors, the subsequent free radical polymerization, initiated by the irradiation process, yields a copolymer free from additional internal stresses which normally result from the concentration gradient set up by monomer diffusing into the substrate. The presence of inhibitor effectively prevented the formation of homopolymer in the liquid monomer phase during irradiation so that all the polymer was formed within the wool fibers. This enabled high copolymer yields to be obtained with a limited amount of monomer and, in fact, provides an effective means of controlling the copolymer composition.

The acrylic monomers gave high conversions under these conditions, the ethoxysilanes and styrene gave intermediate polymer yields, and low yields were given by isoprene and isobutylene. Vinyl acetate showed marked evidence of serious chemical degradation of the wool by the monomer during the aging stage so that the polymer yield for this monomer may be understated due to weight loss from the wool.

The stress-strain relationships of the copolymers, although showing modifications, remain similar to those exhibited by wool; this indicates that the tensile properties of the copolymers are predominately determined by the substrate and not the added polymer. Direct comparison of the stress relaxation data for the various copolymers is complicated since the fibers have differing water contents under the test conditions. Table 4 shows that, with the exception of poly(methyl methacrylate), added polymer causes a greater reduction in stress at 4% strain when the copolymers are deaged by relaxation in water, i.e., there appears to be a greater effect owing to rearrangement of the hydrogen bonded network in the copolymer. In the case of poly(methyl methacrylate) copolymer, no deaging effect is apparent. This would suggest that the copolymer formed with this monomer has had its internal hydrogen bonded structure stabilized so that there is no tendency for a lower energy state to be produced by the rearrangement of hydrogen bonds. That stress relaxation takes place in the wool-poly(methyl methacrylate) copolymer suggests that the unchanged stress at 4% strain after relaxation in water follows from a stabilization of the stress-free configuration of the aged wool substrate.

The formation of wool copolymers by the technique of aging the wool in the presence of monomer vapor followed by radiation-induced polymerization has been demonstrated. The properties of the copolymer fibers are predominately those of the wool substrate but may show modifications of tensile and sorption properties, the extent of which depends on the monomer chosen.

REFERENCES

[1] H. J. Katz, Text. Res. J., 36, 874 (1966).
[2] J. Delmenico and A. M. Wemyss, J. Text. Inst., 60, 78 (1969).
[3] J. D. Leeder and A. M. Wemyss, J. Appl. Polym. Sci., 15, 507 (1971).
[4] I. C. Watt, Text. Res. J., 35, 1072 (1965).
[5] J. E. Algie and I. C. Watt, Text. Res. J., 35, 922 (1965).
[6] I. C. Watt, Text. Res. J., 30, 644 (1960).
[7] R. D. Gilbert and V. Stannett, Isotopes Radiat. Technol., 4, 403 (1967).
[8] H. A. Rutherford, Radiation Effects in Organic Materials (R. O. Bolt and J. G. Carroll, eds.), Academic, New York, 1963, Chap. 11.

[9] J. A. Gervasi and V. Stannett, J. Appl. Polym. Sci., 10, 1217 (1966).
[10] B. J. Rigby and T. W. Mitchell, J. Text. Inst., In Press (1972).
[11] H. Zahn et al., Proceedings of the 2nd United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 29, UNESCO, 1958, p. 233.
[12] I. C. Watt, Nature, 201, 923, (1964).
[13] I. C. Watt and J. D. Leeder, Trans. Faraday Soc., 60, 1335 (1964).
[14] A. A. Armstrong and H. A. Rutherford, Text. Res. J., 33, 264 (1963).
[15] W. S. Simpson, Cirtel, Paris, 3, 359 (1965).

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