Properties of Some Wool Keratin Copolymers

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SUMMARY

The properties of keratin following the formation of polymers in situ have been studied. It is important to determine any effects of the initiatory system on keratin in order to assess the role of the added polymer. The water content of the copolymer usually differs from that of the keratin and polymer measured as separate entities and influences the observed physical properties. Deposition of polymer has little direct effect on properties unless reaction with the keratin structure occurs. Observed physical properties suggest that polymer is predominately formed in the matrix component.

The cells of the fiber cuticle, forming the outer 10% of the fiber, overlap to form scales with the free end always directed towards the fiber tip. Thus polymer applied to the surface of a keratin fiber may mask the natural scales and greatly alter the properties of fiber assemblies. In such cases it is usually desired to restrict polymer formation to the actual surface either by the application of reactive preformed polymers which are capable of grafting to active groups at the keratin surface, or by causing two extremely reactive bifunctional compounds to react at the fiber surface to form a polycondensation polymer, e.g., polyamides are formed by the reaction of a diamine and a diacid chloride. The accumulated chemical and electron

microscope evidence suggests that the polymer is covalently bonded to sites in the wool fiber.

Surface modifications which change the properties of fiber assemblies cause little change in the properties of single fibers. Of greater interest therefore is the internal deposition of polymer inside keratin. Many studies have been made of the formation of polymers within keratin fibers, most frequently using vinyl monomers. Initiation of polymerization is usually achieved by irradiation or by allowing the fibers to absorb a chemical initiator either before or during polymerization. If irradiation is carried out prior to placing the keratin in the monomer, the subsequent formation of polymer is termed pre-irradiation grafting.

The location of polymer within wool fibers may be substantially modified by adjusting the polymerization conditions. For instance, deposition of polymer may be restricted to near-surface locations by allowing only short contact times between the fibers and monomer or by conducting a diffusion-controlled polymerization. However, the histological distribution of polymer following polymerization throughout the keratin fiber is of great interest in the interpretation of copolymer properties in relation to fiber structure. In terms of the structure of wool keratin there is no evidence of preferential deposition in any of the various histological components, i.e., cuticle, cell membranes or cortical cells, or of any region consisting entirely of homopolymer for polymer distributions of less than 100% on the original weight of wool [1].

It is the purpose of this paper to present some of the properties exhibited by such copolymers and interpret these in terms of the structural features of keratin, the location of the added polymer, and the possible interactions between keratin and polymer. Measurements have been made of sorption properties, densities, load-extension relations, torsional rigidity, and thermal stability of various copolymers where significant property modifications are observed. For the most part the amount of added polymer in the samples was less than 100% on the original weight of wool.

EXPERIMENTAL

The deposition of polymer within wool fibers was achieved by polymerization in situ from aqueous monomer solutions using several initiator systems; ferrous ion-hydrogen peroxide [2], potassium persulfate [3], and pre-irradiation in vacuo with γ-rays from a ^{60}Co source [4] at a dose rate of 10^6 R/hr for 24 hr. The conditions of polymerization were as given in

the appropriate references. Polymerization from the monomer vapor phase was obtained by preabsorption of α, α'-azobisisobutyronitrile (AZBN) into wool fibers before exposing them to an oxygen-free atmosphere of acrylonitrile vapor at 60°C.

Water sorption isotherms were determined gravimetrically. The samples were suspended from a calibrated quartz spiral spring balance mounted in an evacuable glass sorption chamber and the temperature controlled to ±0.01°C. Increments of water vapor pressure were read from a wide bore differential mercury manometer and the corresponding change in sample weight calculated from the spring extension. The equilibrium water content (EWC) was expressed as the weight per cent of the original wool content. Formic acid uptakes were measured in a similar manner. Densities of modified wools were determined in a density gradient column charged with carbon tetrachloride and toluene.

Load-extension data before and after treatment were obtained for individual fibers immersed in water using a Cambridge Extensometer. Extension before treatment was terminated at 15% extension, the fiber released and relaxed in water at 50°C for 1 hr prior to the polymerization treatment. The complete load-extension curve of an unmodified fiber may be deduced from the shape of the curve up to 15% extension [5]. After treatment the fiber was loaded in the Extensometer until break. Torsional rigidity measurements of fibers before and after deposition of polymer were made by techniques which have been described elsewhere [6]. The fibers were twisted in water and in Analar glycerol at 20°C at a constant rate of 13.82 rad/min for a period of 5 min.

The relative thermal stability of wool fibers containing polymer was estimated from the longitudinal stability of the fibers immersed in water in a sealed tube at 130°C [7].

RESULTS AND DISCUSSION

Sorption Properties

Typical changes in the water vapor sorption isotherms for keratin-polyacrylonitrile copolymers are shown in Fig. 1. The changes are not uniform over the whole range of the isotherm. The increased water content at high humidities illustrated by Curve B - a pre-irradiation initiated polymerization - occurs because of chain scission during the irradiation. The amount of degradation is variable and could be minimized by using a
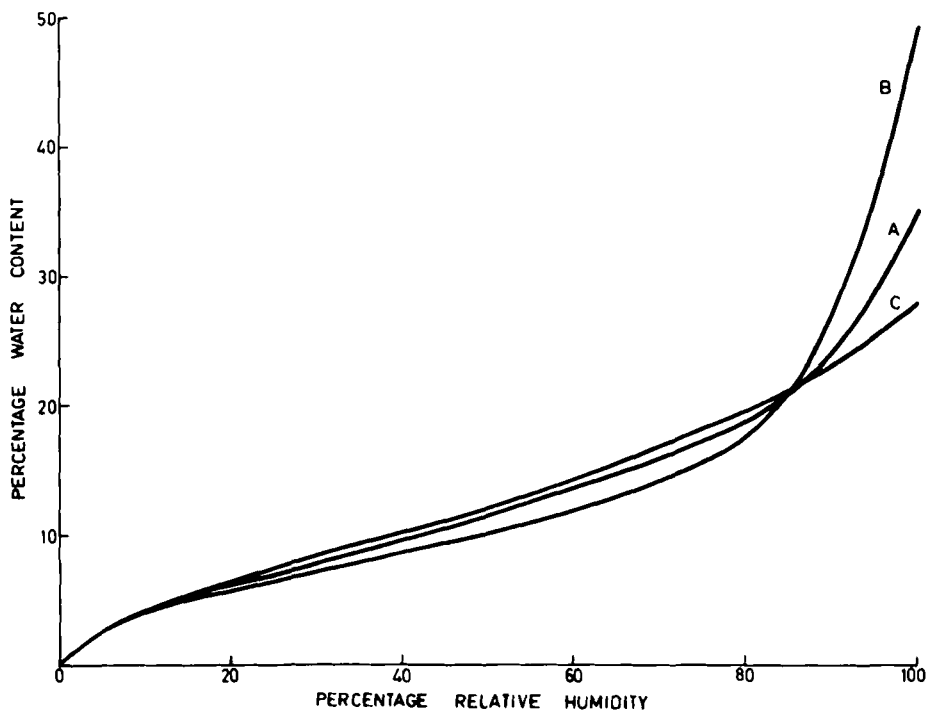
Fig. 1. Water vapor isotherms at 35°C of wool and wool-PAN copolymers. The water content is expressed as a wt% of the original weight of wool. A, Unmodified wool. B, Wool + 22% PAN (preirradiation initiation). C, Wool, + 54% PAN (Fe^{2+}/H_2O_2 initiation).

lower radiation dosage. The copolymer formed using chemical initiation has a reduced water content at high humidities (see Curve C). A similar reduction below the combined water contents of keratin and polymer measured independently has been observed with other keratin copolymers even when the polymer is water soluble [8]. Chain entanglements in the copolymer may be responsible for some reduction of water content following deposition of water-soluble polymers. However, the reduction of water content for the keratin-polyacrylonitrile system to less than that of wool alone indicates that the presence of polymer has brought about exclusion of water.

At low humidities sorption by the keratin-polyacrylonitrile copolymers is additive, i.e., the wool has no effect on water sorption by the polymer and the polymer has no effect on water sorption by wool. The increased water

content of the copolymer at intermediate humidities for the chemically initiated polymerization and a decrease of water content for the irradiation initiated sample in the same range point to marked differences in the two copolymers. The isotherm of the keratin-water system can be described by an equation of three terms representing the association of water molecules to the strongly binding hydrophilic groups $-NH_3$ and $-COO^-$, the association of water molecules with weakly binding sites such as peptide bonds and hydroxylic side-chains and the formation of a multilayer [9]. From an analysis of the isotherms represented by Curves B and C of Fig. 1, it is apparent that the chemically initiated copolymer has a greater amount of water associated with weakly binding sorption sites. This represents a lowering of the average energy of association with these sites while radiation grafting causes an increase in the average energy of association. Such an effect could arise because of differences in packing density of the two samples. It should be emphasized here that chemically initiated polymerization to lower polymer contents also leads to reduced water contents in this intermediate humidity range.

Density

The change in density with polymer content for chemically initiated keratin-polyacrylonitrile copolymers is shown in Fig. 2. There is an initial increase in density as polymer is deposited in the keratin indicating an efficient packing of the chains. The subsequent decrease in density is greater than expected for the polymer composition of the system. Therefore with increasing polymer contents the packing of the polypeptide and polymer chains is less efficient. For radiation initiated keratin-polyacrylonitrile copolymers a higher density is obtained for the same polymer content. This confirms the variability in packing efficiency of keratin copolymers which could affect the water content in the intermediate humidity region of the copolymer-water isotherm.

Swelling in Formic Acid

A measure of the effective constraints to swelling of keratin can be obtained from the saturation uptake of a swelling agent such as formic acid. Where degradation of the keratin has occurred, greater quantities of formic acid are absorbed. In general, the deposition of polymer by chemical initiation has little effect on the uptake of formic acid even in those instances when the water sorption is less. Thus we find that the deposition of polyacrylonitrile does not reduce the formic acid uptake expressed as a function
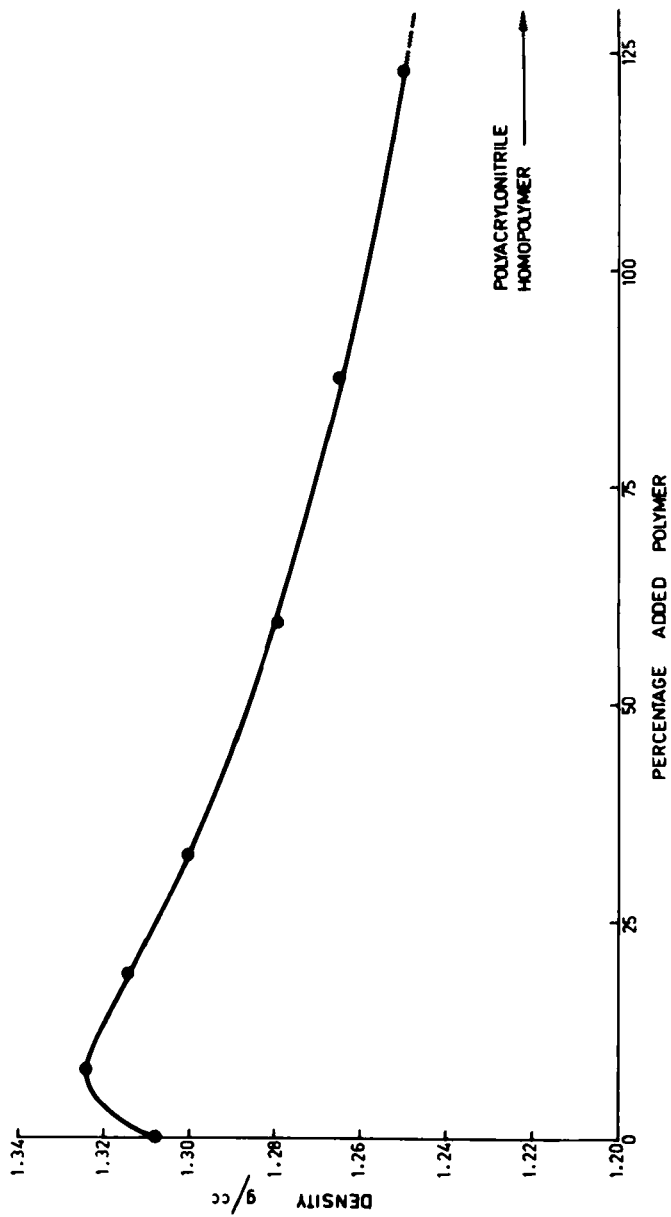
Fig. 2. Density as a function of added polymer content of wool-PAN copolymers (Fe^{2+}/H_2O_2 initiation).

of the original weight of wool. This would indicate that no additional constraints to swelling have been introduced. However, the deposition of polymers such as poly(divinylbenzene) substantially reduce the subsequent formic acid uptake by the keratin copolymer and this reduction indicates the introduction of additional constraints to swelling, probably via a cross-linked network. Resorcinol-formaldehyde resins and methacrylic acid-chromium chloride complexes also introduce additional constraints to swelling.

Load-Extension Relations

The general shape of the load-extension curves of copolymers remain similar to that of keratin. A typical set of load-extension curves in water are shown in Fig. 3 for unmodified wool and wool containing polyacrylonitrile at two levels. Two extremes of behavior are evident. For the low amount of added polymer the fiber appears stiffer over the whole range. This must be interpreted in the light of the sorption data which showed a lower saturation water content for such fibers. Thus the load-extension curve is similar to that of the same fiber with a lower water content. On the other hand the load-extension curves of fibers with high levels of polymer deposition show a considerable change in behavior.

When a keratin fiber is extended, the initial stiff region, known as the Hookean region, represents the stretching of secondary bonds which hold the structure together. The decrease in the Young's modulus, which corresponds to the longitudinal extension of a fiber within this Hookean region, indicates that the deposition of polymer has disrupted some of these secondary bonds. With extension into the yield region, the fiber extends very rapidly with increase of load because of the change from an α-helical to an extended chain configuration and the effect of polymer is to increase the yield modulus. This indicates that the polymer interferes with the extension of the α-helices. At the end of the yield region ($\sim 30\%$ extension in water) the fiber stiffens due to the opposition to extension by covalent bonds. The presence of polymer, however, causes the fibers to break under a smaller load than for unmodified fibers so that the copolymer does not in fact show a post-yield region.

This behavior is general for copolymers of keratin although differences in water sorption properties modify the load-extension relation to some extent. Initiation procedures which cause rupture of disulfide bonds weaken the keratin structure and the copolymer may appear to be less stiff than the unmodified fibers. Such an effect is observed following chemical initiation by potassium persulfate. It should be noted that the
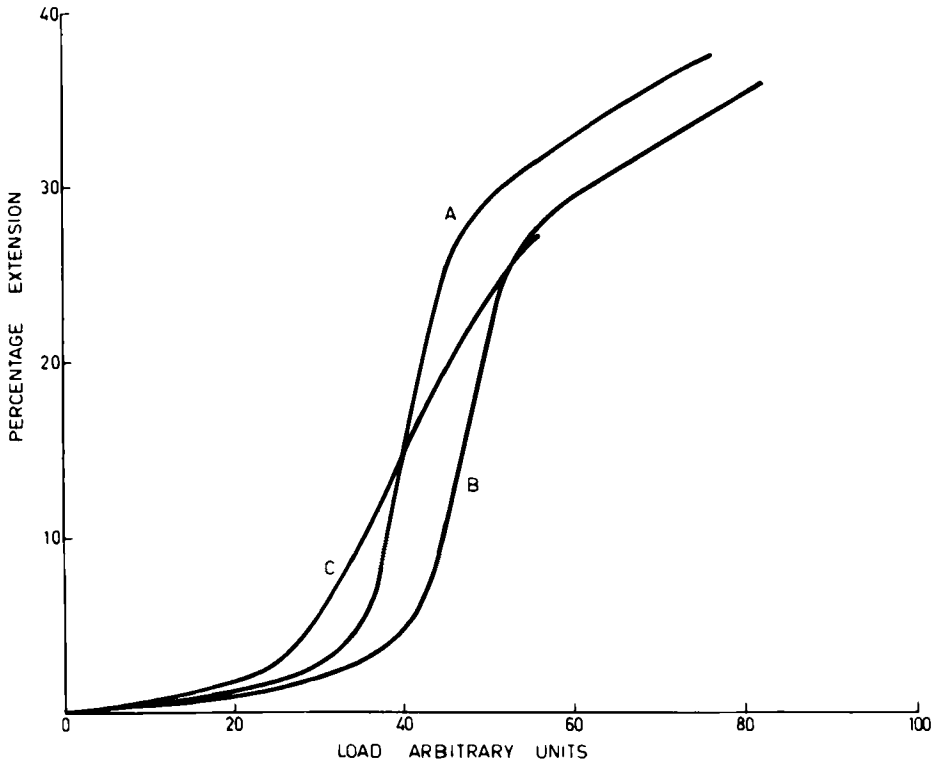
Fig. 3. Load-extension curves of wool and wool-PAN copolymers in water. A, Unmodified wool. B, Wool + 12.5% PAN. C, Wool + 87.5% PAN.

deposition of poly(divinylbenzene) is similar in effect to the deposition of polyacrylonitrile despite the additional constraints to swelling introduced with the former treatment.

Torsional Modulus

Torsional measurements on keratin fibers reflect the mechanical properties of the matrix. Internal deposition of polymer may be considered in three categories: 1) the introduction of a reagent which causes changes in the dimensions and water content of the fibers, 2) the rupture of covalent bonds within the structure, and 3) the introduction of additional cross-links.

Measurements were made of torsional modulus and torsional relaxation of fibers twisted in water and in Analar glycerol. The torsional moduli of the

dry fibers were relatively unaffected by the deposition of polymer. In general, where a large amount of polymer was added to the keratin there was an increase in the wet torsional moduli as would be expected for a reduced water content. Where the treatment resulted in covalent bond breakdown as with pre-irradiation or potassium persulfate initiation, the wet torsional modulus of the copolymer was reduced. On the other hand poly(divinylbenzene) caused an increase in wet torsional modulus above that expected from a change in the saturation water content of the co-polymer. This indicates an increase in effective cross-linking. In all cases there was an increase in rate of relaxation of torque suggesting that there is a steric effect causing an increase in the internal viscosity of the structure and an initial high torque which decays at constant twist.

Thermal Stability

Keratin fibers heated in water may undergo an α-β transformation, i.e., the α-helical conformation assumes an extended chain conformation. Contraction in fiber length follows such a transformation and the contraction behavior can be related to the so-called melting point of the α-helical component of the fibers [7]. The extent of contraction is determined by the temperature of heating and the properties of the nonhelical components of the fiber.

The contraction behavior of keratin copolymers in water is relatively un-affected by the deposition of polymer in most instances despite changes in the saturation water content. However, the following effects on the subsequent contraction were obtained. 1) Slower contraction corresponding to an increase in melting temperature of $10°C$ for wool fibers copolymerized with sodium acrylate. 2) A reduction in the extent of contraction of wool fibers copolymerized with divinylbenzene. 3) A decreased thermal stability if the initiation step involved rupture of disulfide bridges, e.g., potassium persulfate initiator.

Further evidence of the role of disulfide bonds was obtained from the thermal stability of wool fibers in which half of the cystine residues were modified by reduction with tributyl phosphine. Subsequent carboxymethylation of thiol groups with iodoacetic acid was carried out in some cases. The reduced fibers showed a marked decrease of thermal stability irrespective of further reaction of the thiol groups. The deposition of polyacrylonitrile in reduced fibers proceeded at twice the rate when thiol groups were present, but the addition of polyacrylonitrile did not alter the thermal stability of the reduced fibers in either case. Thus the rupture of disulfide bonds may have a marked effect on polymerization rates but the subsequent thermal

stability is independent of polymer formation and is determined by the extent of cystine breakdown.

CONCLUDING REMARKS

The increased torsional modules taken in conjunction with the reduced swelling in formic acid of poly(divinylbenzene) copolymers of keratin suggests the formation of additional cross-links in the matrix portion of the fiber. The additional fact that changes in the load-extension curves are similar to the changes observed after the deposition of polymers such as polyacrylonitrile suggests that these cross-links are not affecting the micro-fibrillar regions. A similar conclusion may be drawn from the contraction behavior of the poly(divinylbenzene) copolymer showing no effect on the thermal stability but a marked decrease in the extent of fiber contraction. Thus the α-helical conformation appears unaffected but there is an increased resistance to deformation of the whole fiber. It appears, therefore, that the deposited polymer appears to be preferentially located in the matrix component of keratin fibers. The stabilization of the α-helical conformation by polymerization of sodium acrylate in keratin does not require the polymer to be located within the microfibrils but does suggest interaction of the polymer with reactive groups in the microfibrils.

The properties of keratin dominate the properties exhibited by the copolymers. However, by a suitable choice of added polymer and conditions of polymerization it is possible to give additional, and hopefully desirable, properties to the copolymer. An understanding of the changes in sorption properties of the copolymer is important because of the marked influence of water content on the observed physical properties. The mode of initiation is important because of possible reaction with the keratin structure and subsequent effects on properties. Polymerization from the vapor phase using AZBN initiator gave copolymers whose properties were essentially the same as copolymers of similar polymer content obtained by chemical initiation with the Fe^{2+}/H_2O_2 system.

Variations in the mode of initiation may determine whether or not the added polymer is covalently bonded to the keratin structure. The formation of thiol groups by the reduction of cystine residues or the creation of free radicals leads to grafting at these sites. However, the contribution of the added polymer to the properties of the copolymer appears to be independent of initial grafting.

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