Chemical and Mechanical Properties of Methyl Methacrylate-Grafted Wool Fiber

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SYNOPSIS

Since it has been reported in the literature that polymer-grafted wool fibers have better acid and alkali resistances and dye uptake, the present study was carried out using $KBrO_3$ and substrates such as Fe (II), Co (II), cysteine, cystine, tyrosine, and urea for graft copolymerization of methyl methacrylate (MMA) onto wool. Acid and alkali resistances, dye uptake, and dry tensile strength of the resulting graft copolymers were studied.

INTRODUCTION

The grafting process may lead to three major effects on wool: (i) opening of the surface structure of the wool, thereby causing damage to the defense pattern of the wool molecule: (ii) causing partial degradation of the polypeptide chain, which can make the wool backbone vulnerable to further chemical attack; (iii) grafting the backbone by welding of methyl methacrylate (MMA) polymer chains to it and protecting it from the attack of chemicals. It has been reported in the literature that polymer-grafted wool fibers have better acid and alkali resistances and dye uptake.[1] But, the dry tensile strength of wool was generally not improved by graft copolymerization.[2-5] However, poly(methyl methacrylate) (PMMA)-grafted wool by the initiator system $KBrO_3 - VO_2^+$ improved the dry tensile strength of the fiber enormously (10-time increase).[1] Hence, the present study was carried out using $KBrO_3$ and substrates such as Fe(II), Co(II), cysteine, cystine, tyrosine, and urea for graft copolymerization of MMA onto wool. The resulting graft copolymers were subjected to acid and alkali treatments. Dye uptake and dry tensile strength were also determined.

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EXPERIMENTAL

Preparation of graft copolymer samples were reported in an earlier paper.[1]

Acid Solubility

Wool (grafted as well as control samples) (0.1 g) was treated with 6*N* HCl at 65°C for 60 min. The fibers were filtered and washed several times with distilled water, dried at 110°C, and weighed. The percentage loss in weight of the wool gave the acid solubility.

Alkali Solubility

Alkali solubility was determined by the method of Harris.[6] Wool (grafted as well as control samples) (0.1 g) was treated with 10 mL 0.1*N* NaOH at 65°C for 60 min, the fibers filtered and washed with distilled water, then washed twice with aqueous acetic acid, and finally washed several times with distilled water. This was then dried at 110°C and weighed. The percentage loss in weight of the wool gave the alkali solubility.

Dye Uptake

Dyeing of wool fibers was carried out both with the grafted and control samples using the dye alizarin blue. Dyeing was conducted for 1 h at 60°C using

1% of the dye, 15% Glauber's salt, and 10% acetic acid, and the liquor-to-wool ratio was maintained at 100 : 1.[7] After this, the wool sample was filtered through an IG3 sintered crucible and the optical absorbance of the filtrate was measured using a (UV–Vis) spectrophotometer (Spectronic 20) at 591.7 nm. From these results the dye uptake by the wool fibers was computed.

Tensile Property

The tensile strength of the fiber (grafted and control) was determined using an Instron tensile tester at a crosshead speed of 0.5 cm/min. The diameter of the wool sample was calculated using a piler micrometer. The cross-sectional area was found using the relationship:

$$\text{Cross-sectional area} = \pi d^2/4,$$

where d = diameter of the fiber.

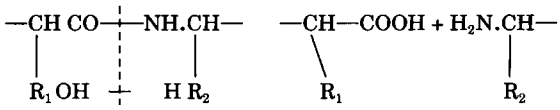
The breaking load of the fiber was also determined. The tensile strength was found out from the data using the expression:

$$\text{Tensile strength (kgf/cm}^2\text{)} = \frac{\text{Breaking load in kg}}{\text{Cross-sectional area in cm}^2}.$$

RESULTS AND DISCUSSION

Acid Solubility

The principal action of aqueous solutions of acids and alkalis on proteins is to hydrolyze them, i.e., to split the complex molecule into simpler derivatives by a process of hydrolytic fission at the polypeptide bonds.



The nature of hydrolysis depends on the nature of the hydrolyzing agent. Thus, acids and alkalis show characteristic differences. It is assumed that all forms of hydrolysis are due to the action of water that is catalyzed by hydrogen or hydroxyl ion—as the case may be.

Wool keratin is an ampholyte, i.e., it contains both acidic and basic groups and hence is capable of combining with both basic and acidic substances. With fairly strong acids such as hydrochloric acid, complete binding of acid occurs. At a pH of approximately 1, such acids cause swelling and, under certain conditions, cause dissolution of the protein, whereas the cystine content of wool is unaffected by acids.

At lower percentages of grafting, resistance to acid action was not observed (Table I). In fact, the acid solubility increased from 0 graft-on to approximately 15% graft-on wool sample. This showed degradation of polymer chain to a small extent during the grafting reaction. During the graft copolymerization process, amino acid residues were prone to attack by initiators and the new linkages formed by the polymer chains were less when compared to high graft-on. Thus, the polypeptide chains in lower graft-on were protected only to a smaller extent when compared to high graft-on wool. This may be the cause for the higher solubility of lower graft-on wool in hydrochloric acid. In all systems studied, when the percentage grafting increased resistance to acid solubility also increased (Table I). Both the backbone (polypeptide chain) as well as the free amino acid side chains were protected to withstand acid hydrolysis under this condition.

Table I Acid Solubility of Natural and Grafted Wool Fibers

	Acid Solubility						
% Grafting	$KBrO_3$	$KBrO_3$–Fe (II)	$KBrO_3$–Co (II)	$KBrO_3$–cysteine	$KBrO_3$–cystine	$KBrO_3$–tyrosine	$KBrO_3$–urea
0	22.9	22.9	22.9	22.9	22.9	22.9	22.9
5	35.5	23.0	26.0	24.5	27.5	27.0	24.0
10	24.5	23.0	26.5	28.5	28.5	29.0	25.5
20	21.5	17.5	21.5	16.0	25.0	21.5	20.5
30	17.5	14.5	18.0	12.0	20.0	19.0	15.0
35	—	14.0	16.0	10.0	20.0	16.0	13.0

Table II Alkali Solubility of Natural and Grafted Wool Fibers

% Grafting	Alkali Solubility						
	$KBrO_3$	$KBrO_3$–Fe (II)	$KBrO_3$–Co (II)	$KBrO_3$–cysteine	$KBrO_3$–cystine	$KBrO_3$–tyrosine	$KBrO_3$–urea
0	13.7	13.7	13.7	13.7	13.7	13.7	13.7
5	13.6	13.5	13.5	13.3	13.0	13.5	13.6
10	12.8	13.4	13.4	12.8	12.5	13.4	13.3
15	12.1	13.3	12.9	12.3	12.2	13.3	13.1
20	11.8	13.2	12.5	12.1	11.9	13.2	13.0
25	11.6	12.0	12.2	11.8	11.8	13.0	12.7
30	11.4	11.1	11.4	11.6	10.0	12.4	12.6
35	11.3	10.7	10.7	11.3	—	11.3	12.3
40	10.3	10.3	10.0	10.9	—	—	—
45	—	9.9	—	10.5	—	—	—

The acid resistance shown by the wool fibers is found to follow the order given below when different reducing agents are involved in the grafting process:

cysteine > Fe(II) > urea > $KBrO_3$ alone

> Co(II) > tyrosine > cystine.

Alkali Solubility

One of the main effects of alkalis on wool is the destruction of the cystine disulphide group. The alkali solubility increases when the wool is degraded either by peptide-bond breakdown or rupture of the disulphide bonds. Moreover, disorientation of the macromolecular structure resulting from the breaking of hydrogen bonds alone also greatly increases the alkali solubility (although no covalent bonds have been broken). Alkali solubility decreases greatly when the disulphide bond is replaced by a more stable link. Alkali solubility decreases also when entirely new crosslinks are introduced by a chemical process.[8]

The experimental results showed that alkali solubility values of grafted wool have decreased in all seven systems studied (Table II). But, they differ in extent of decrease in solubility although the same monomer and oxidant were used for the grafting reaction. In the presence of different reducing agents, the order of decrease in solubility shown by the grafted wool fibers was as follows:

cystine > Fe(II) > cysteine > Co(II)

$\simeq$ $KBrO_3$ alone > tyrosine > urea.

A possible explanation is that the attack of different redox initiators on the wool fiber may be expected to differ. For example, wool from the $KBrO_3$–urea system gave least resistance to solubility because urea would have more pronounced attack on the —s—s— bond of the wool fiber. Further, the

Table III Dye Uptake of Natural and Grafted Wool Fibers

% Grafting	% Dye Uptake						
	$KBrO_3$	$KBrO_3$–Fe (II)	$KBrO_3$–Co (II)	$KBrO_3$–cysteine	$KBrO_3$–cystine	$KBrO_3$–tyrosine	$KBrO_3$–urea
0	66.1	66.1	66.1	66.1	66.1	66.1	66.1
5	92.0	77.0	76.0	86.0	87.0	83.0	85.0
10	91.5	87.0	85.0	91.0	89.5	93.0	95.0
15	87.0	87.0	90.5	82.0	91.5	90.0	94.0
20	82.5	87.0	84.5	74.5	92.0	89.5	89.0
30	82.5	83.0	85.0	73.0	89.5	87.0	80.0

orientation of grafted chains and or the new crosslinks formed on the backbone may have weakened the fiber.

Dye Uptake

Wool is partly crystalline and partly amorphous. Due to polymer grafting, the amorphous region is increased in wool, resulting in an increase in the dye uptake. It has already been reported that polymer-grafted wool had better dyeability than ungrafted wool.[1] In the present work also, in all systems studied the grafted wool gave better dye uptake than ungrafted wool (Table III). In ungrafted wool, during penetration complex dyes experience resistance at the surface (and near surface) of wool. When the surface structure is opened due to grafting, dye penetration becomes much easier, resulting in an increase in the dye uptake. This may be one of the reasons for the increase in the dye uptake of grafted wool. But, at higher graft-on percentages the uptake of dye decreased to lower values, even lower than that of the control sample. The dye penetration is made more difficult at higher graft-on percentages. Here, the opened structure of the surface would have been closed by the formation of a greater number of grafted chains on the backbone. Second, the reduction in the amount of wool present in higher graft-on fibers results in a decrease in the active sites; hence, even though the amorphous region has increased at higher conversion the dye uptake has decreased at higher percentage of grafting (Table III).

Tensile Strength

The dry strength of wool fiber is greatly influenced by the number of peptide bonds present in it. Hence, the breakdown of a relatively small number of peptide bonds can lead to extensive weakening of fibers, e.g., for a 30% hydrolysis of peptide bonds an 80% decrease in dry tensile strength was noticed.[9] The strength of dry fiber is further strengthened by interchain hydrogen bonding and not by covalent crosslinks. Water and other chemical agents can swell the wool fiber and break these hydrogen bonds. However, dilute salt solutions increased the strength of wool by dehydrating the same. As wool contains large amounts of reactive groups, it can adsorb and retain various chemicals that come into contact with it. These chemicals can also modify the elastic properties of wool.[9] The copolymerization can result in glueing of the fibers in fixed positions in the matrix, thus inhibiting their movement. The groups responsible for conferring affinity for water may be either masked or occupied by the polymer; the polymer may also fill the dead space (the space not occupied by the fiber molecules), making the fiber's moisture-retaining power lower and increasing its stiffness. The penetration of other reagents into the fiber may also be affected.

Without exception, all systems studied in this present investigation produced wool grafts with su-

Table IV Tensile Strength of Wool Before and After Grafting

System	% Grafting	Tensile Strength, GPa
Ungrafted wool	0	0.056
$KBrO_3$–MMA–wool	41.10	0.094
	35.52	0.091
	25.86	0.088
	14.98	0.089
	4.90	0.089
$KBrO_3$–Fe (II)–MMA–wool	90.58	0.104
	49.30	0.097
	28.26	0.070
	20.00	0.066
	13.58	0.070
$KBrO_3$–Co (II)–MMA–wool	44.30	0.086
	39.52	0.071
	30.22	0.078
	20.22	0.074
	11.66	0.069
$KBrO_3$–cysteine–MMA–wool	44.74	0.152
	32.14	0.138
	30.08	0.136
	18.30	0.069
	8.14	0.091
$KBrO_3$–cystine–MMA–wool	43.70	0.070
	34.18	0.065
	26.84	0.060
	19.20	0.061
	6.20	0.057
$KBrO_3$–tyrosine–MMA–wool	38.10	0.093
	33.18	0.086
	28.66	0.065
	17.06	0.064
	11.48	0.064
$KBrO_3$–urea–MMA–wool	35.76	0.097
	26.44	0.072
	19.34	0.089
	9.34	0.085
	4.58	0.070

perior tensile strength values to that of the control. Though the same oxidant was used throughout, in all systems studied, depending on the reducing agent used, the tensile strength value had changed. Excellent tensile strength was imparted to the grafted wool by the $KBrO_3$–cysteine system. A three-time increase was noticed for a 45% graft-on. The next best results were from the $KBrO_3$–urea and $KBrO_3$–Fe(II) systems (Table IV).

Support for the tensile property values also comes from the acid resistance shown by grafted wool. Of the various systems studied, $KBrO_3$–cysteine gave the highest resistance toward the action of acid. This showed that the polypeptide main chain was fortified by some secondary linkages. The least acid resistance was shown by the cystine–$KBrO_3$. In the tensile property also, the latter system gave the least improvement.

The dye uptake measurement also indicated a similar trend regarding the strength of the grafted fibers. $KBrO_3$–cysteine gave minimum dye uptake either due to stronger bond formation or the reactive groups being masked as the result of grafting reaction. It was also interesting to note that the $KBrO_3$–cystine system took up the largest amount of dye.

CONCLUSION

In all systems studied, the resistance to acid solubility was shown at higher pH values and alkali solubility decreased when the percentage grafting increased. The grafted wool gave better dye uptake than ungrafted wool fiber, but at higher graft-on percentages the uptake of dye decreased to lower values, even lower than that of the control sample. As $KBrO_3$ may be affecting graft copolymerization in a milder way, leaving the wool backbone intact, without exception all systems studied produced wool grafts with superior tensile strength values to that of the control.

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