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Attila Pavlath[a]; Kay Sue Lee[a]
[a] U.S. Department of Agriculture, Western Regional Research Laboratory Agricultural Research Service, Berkeley, California

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Glow Discharge Induced Graft Polymerization of Nonvolatile Monomers on Wool

ATTILA PAVLATH and KAY SUE LEE

Western Regional Research Laboratory
Agricultural Research Service
U.S. Department of Agriculture
Berkeley, California 94710

ABSTRACT

Nonvolatile monomers were grafted to wool by exposure to rf glow discharge under vacuum. The amount of grafting was limited to an average of 2 to 5% weight uptake. With increasing impregnation the amount of graft decreased, and mostly extractable homopolymers formed. Increasing the intensity of the glow discharge above a certain level is also detrimental because at this point the rate of degradation exceeds the rate of polymerization.

INTRODUCTION

Grafting onto wool is a widely studied field since the deposition of polymers on or in the fibers can actually confer new properties on the fibers or improve on existing properties. Considerable success has been achieved by those working in the areas of shrink-, soil-, and flameproofing [1-4]. Polymers merely deposited are not necessarily grafted. Deposition may occur without the formation of any chemical bond between the wool protein and the polymer molecule. The polymer chain may be so entangled or trapped that it is only slowly removed during washing and drycleaning. However, the strength of this essentially physical combination is not uniform throughout the fiber. Occasional weak spots form which might become evident only after repeated cleaning.

Hence various chemical and radiation methods have been studied to create active sites capable of initiating polymerization on the wool surface [5]. If the wool fiber is swollen, free radicals can form very easily inside the fiber, and extensive grafting occurs—in some cases as high as 50 to 100% by weight [6]. Since most of the problems with wool are associated with its surface characteristics only, surface grafting is sufficient. Actually, grafting throughout the fiber may cause undesirable side-effects such as reduced tear strength and swelling.

To date, there has been relatively little utilization of glow discharge for the graft polymerization of compounds to the surface of wool [2, 7] as compared with other textile fibers such as cotton and polyester. Recently, fluoropolymers were successfully grafted to wool by exposing it to a glow discharge created in a mixture of argon and fluorocarbon monomers [8]. This is not practical in every case since many desirable monomers have no vapor pressure. In addition, the creation and maintenance of glow discharge in the presence of organic vapors becomes more and more difficult with an increasing number of atoms in the monomer requiring extremely low operating pressure. Even when a glow can be created, monomer decomposition occurs to a certain degree before polymerization. Therefore, it may be advantageous to use nonvolatile monomers. Earlier, we reported [7] the successful grafting of nonvolatile monomer. We now wish to report the results of a further study involving the graft polymerization of a number of nonvolatile monomers to wool by exposing impregnated yarn and fabric to rf glow discharge.

EXPERIMENTAL

Chemicals

With a few exceptions, most of the monomers were commercial products (CP) used without further purification. Some of them were prepared through direct bromination: tribromo-m-aminobenzenesulfonic acid from m-aminobenzenesulfonic acid in aqueous HCl solution [9], and dibromopropyldiallylphosphate and borate from the corresponding triallyl derivatives in $CHCl_3$ solution at room temperature. The tribromo-m-aminobenzenesulfonic acid was recrystallized from methanol, and the others were used after the elimination of chloroform in vacuum.

Impregnation

Water-soluble monomers were applied at room temperature from aqueous solution; in other cases chloroform or dimethylformamide was used as a solvent. When chloroform was the solvent and the wool was presoaked in methanol, larger amounts of impregnation were obtained. Before impregnation, the wool was exposed for a short time to a mild glow discharge. Such pretreatment probably accelerated the impregnation through ionic scouring of the surface. This pretreatment was in the range of less than 10% exposure in relation to the power used and time of application during subsequent grafting. Pretreatment was found to be especially beneficial when impregnating from aqueous solutions, since glow discharge treatment develops a highly hydrophilic surface [10]. The reaction conditions are very flexible, and no real dependence on time and power could be noticed throughout a wide range.

The monomers were applied from 15 to 20% solutions in sufficient quantities to cause up to 30 to 40% uptake if totally adsorbed. In order to insure uniform distribution, the fabric swatches (150 × 150 mm) were treated in flat dishes, whereas yarn was treated on a continuously rotating horizontal spindle. After a 1-hr treatment, the wool was first drip dried and then dried in vacuum at room temperature to prevent thermal polymerization. In general, the monomer uptake was around 50% of the theoretically calculated amount.

Equipment

The glow discharge was created by an rf generator (13.56 Mc) using capacity coupling. The yarn was treated in a capillary tube-type reactor to permit continuous operation under vacuum [11]. This capillary apparatus is not adaptable to fabric. Hence special equipment was designed for the treatment of swatches (Fig. 1). The fabric was placed on a glass tube located concentrically inside a cylindrical reactor to assure uniform exposure under the glow discharge. Even though the diameter of the inner tube was selected to permit smooth accommodation of the swatch surface without bulging or overlapping, the intensity of the plasma was not uniform throughout the reactor axis or cross-section. Burned spots resulted, especially at higher power settings.

In order to eliminate uneven treatment, two simultaneous independent motions were introduced. One was the rotation of

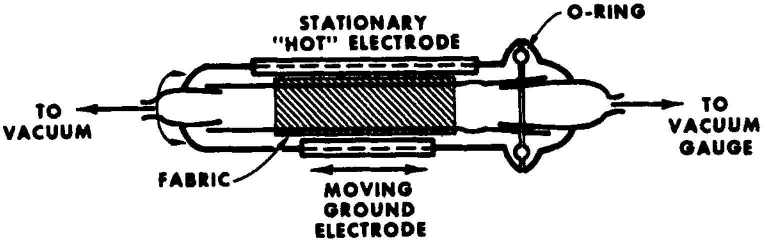

FIG. 1. Rotating reactor for the treatment of wool swatches in glow discharge.

the reactor on its axis between the electrodes in a full clockwise and counterclockwise 360° motion. The other was a 15-cm back and forth movement of the ground electrode in the direction of the axis of the reactor. The cycles of these two movements were different: 35 and 25 sec, respectively. Since the treatment time was generally at least 5 min, the effects of possible hot spots were averaged out throughout the surface of the swatch. There was no burning and only occasional, but uniform, yellowing at the upper limit of the applied power range.

Determination of Graft

Treated samples were rinsed five times at room temperature with the excess of the corresponding solvents, and then air-dried in a constant humidity room. The quantitative uptake was determined by weight increase. The qualitative identification of the graft and the monitoring of relative changes was accomplished by the x-ray photoelectron spectroscopy technique described earlier [12].

RESULTS AND DISCUSSION

We have reported earlier [7] the grafting of nonvolatile, highly fluorinated monomer to wool using glow discharge. Although polymerization was induced, a larger part of the forming polymer was not grafted. After repeated extraction, up to 2% polymer which could not be eliminated remained on the wool. In later work this grafting was used to determine the individual effect of glow discharge components on wool [13].

In this study the grafting of three different types of compounds was attempted. The first group included sodium salts of readily polymerizable monomeric acids, such as acrylate and vinyl sulfonate. These ionic polymers are potential shrinkproofing agents in the case of their chemical grafting [1]. However, for protection against felting shrinkage, approximately 25% grafting by weight is needed. While such grafting could be achieved, it was accompanied by a considerable decrease in the tear strength of wool. Since grafting by glow discharge is limited mostly to the surface, the overall uptake would be in small enough quantities to avoid altering the strength of the wool yet, hopefully, sufficient for complete shrinkproofing.

The results obtained under various conditions are summarized in Table 1. It appears that the amount of polymer retained on wool after exposure to glow discharge and consecutive aqueous extraction is in the same range: 3 to 5%, regardless of the amount added on before glow discharge treatment. Actually, increasing the amount of impregnation may reduce the amount of grafted polymer.

The effects of glow discharge, in contrast to gamma radiation, are confined essentially to a thin outer layer of the fiber which is generally not more than 100 Å. If impregnation is increased, the surface of the wool will be covered to a greater depth by the monomer. Thus the glow initially will activate the monomer and start the growth of the polymer chain. This can grow toward the surface of the wool, but attachment to wool will depend on chain termination resulting from interaction of the growing polymer with a functional group on the wool protein molecule. The number of sites available for such interaction is limited; therefore the statistical probability for grafting decreases if the glow cannot have direct contact with the wool surface. Glow discharge can create active sites almost anywhere on the protein polymer. Treatment of wool with gamma radiation demonstrated that various radicals are rapidly formed throughout the protein chains in considerable quantities [14] without breaking of the chain, unless high doses are used [15].

The experimental results were in good agreement with this theory though, in the case of these compounds, the grafting showed small variation. The shrinkproofing tests, however, readily demonstrated the detrimental effects of high impregnation: shrinkproofing decreased rapidly as impregnation increased. Unfortunately, even in the best case no better than 80% protection was observed against felting shrinkage. The grafting could not be improved by longer exposures and higher power settings. Concurrent with the polymerization, surface etching or ionic scouring also occurs. This, actually, is the dominating reaction once the polymerization is completed. The decomposition of grafted polymer can be demonstrated, even in the case of highly stable fluoropolymers, in the presence of glow discharge [16].

TABLE 1

Monomer	Power (W)	Time	Form of wool	Uptake before discharge (wt%)	Uptake after discharge and extraction (wt%)
Na-acrylate	25	1 sec	Yarn	10.5	4
	75	0.7 sec	Yarn	10.5	4
	75	0.7 sec	Yarn	15.0	3
	50	10 min	Fabric	10.0	5
	100	5 min	Fabric	10.0	4
	100	10 min	Fabric	10.0	3
	100	10 min	Fabric	15.0	2
	200	5 min	Fabric	10.0	3
	200	10 min	Fabric	20.0	3
Acrylic acid then neutralization with Na_2CO_3	25	1 sec	Yarn	15.0	4
	75	0.7 sec	Yarn	15.0	3
	50	5 min	Fabric	10.0	4
	100	10 min	Fabric	15.0	4
Na-vinyl sulfonate	75	1 sec	Yarn	5.5	2
	100	10 min	Fabric	10.0	3
	200	10 min	Fabric	10.0	3

The second group of nonvolatile compounds to be grafted to wool were halogenated esters of possible value for flameproofing applications. Included among these were methacrylates, phosphates, and borates. The solid monomers could be deposited on wool in large quantities from $CHCl_3$ solution. Such impregnated wool, however, was very stiff after the glow discharge treatment. Most of the uptake was removed during extraction since the thick-layered deposit was almost exclusively on the outside. The application of methanol or dimethylformamide caused the wool fibers to swell, and the hand of the fabric was much softer after glow discharge treatment, even at high impregnation levels. The results are summarized in Table 2.

The detrimental effects of higher amounts of impregnation, power, and exposure time are more pronounced in this case. Degradation is especially noticeable with the brominated compounds, since the formation of elementary bromine through oxidative degradation causes considerable discoloration under severe reaction conditions. Also, at lower power settings, the higher amount of apparent grafting might be augmented by another factor. The successfully surface grafted material is likely to trap these larger molecules easily inside of the fiber, thus preventing their extraction. This entrapment is not just simply due to thermal polymerization, because with use of lauryl methacrylate and hexamethylenediacrylamide the amount of grafting was much higher after glow discharge treatment than after several hours of treatment at 80°C. The gas temperature of the glow discharge averages about 50°C.

The third group of compounds, brominated aromatics, really cannot be considered as monomers under normal grafting conditions, but the effect of the glow discharge is more powerful and some grafting can be expected. As observed with some of the compounds of group two, glow discharge opens the bond homolitically and generated aryl radicals can react with active sites also created by glow discharge on the protein chain. Aromatic compounds were selected because of their high stability. However, even these compounds underwent strong degradation, especially tribromophenol and tribomoaniline, as shown in Table 3.

The two compounds which showed some grafting were tetrabromophthalic anhydride and tribromo-m-aminobenzenesulfonic acid. Even with higher power settings, the decomposition was small in contrast to tribromophenol and tribromoaniline which discolored at lower levels of exposure. Nevertheless, the degree of grafting was considerable, although x-ray photoelectron spectroscopic analysis revealed that on the outermost layer, bromine was rapidly eliminated (as summarized in Table 4), and oxidation was the dominant reaction. The resulting graft was quite strong even though a great deal was removed in an accelerated washing test

TABLE 2

Monomer	Power (W)	Time (min)	Uptake before discharge (wt%)	Uptake after discharge and extraction (wt%)
Pentabromophenyl methacrylate	50	5	15	6
	50	10	15	8
	50	20	15	10
	50	10	10	6
	100	5	10	2
	100	10	15	6
	200	10	10	2
Pentachlorophenyl methacrylate	50	5-5	12	4
	100	10	12	2
Dibromopropyldiallylphosphate	100	5	30	8
	200	10	25	4
Triallyphosphate	100	5	25	-
Dibromopropyldiallylborate	100	5	25	2
	200	10	25	-
Lauryl methacrylate	100	10	15	6
	-	2 hr (80°C)	15	1
Hexamethylenediacrylamide	100	10	15	8
	-	2 hr (80°C)	15	2

TABLE 3

Compound	Form of wool	Power (W)	Time	Uptake before discharge (wt%)	Uptake after discharge and extraction (wt%)
Tribromoaniline	Yarn	75	0.7 sec	15	-
	Fabric	50	5 min	15	1
Tribromophenol	Yarn	75	0.7 sec	15	-
	Fabric	50	5 min	15	1
Tetrabromophthalic anhydride	Yarn	75	1 sec	10	5
	Yarn	75	1 sec	18	5
	Fabric	100	10 min	15	6
	Fabric	200	10 min	15	3
Tribromomethanilic acid	Yarn	75	1 sec	12	5
	Yarn	75	1 sec	18	3
	Fabric	100	10 min	20	7
		200	10 min	20	4

TABLE 4. Surface Analysis of Glow Discharge Treated Impregnated Wool by XPS. Relative Ratio of Oxygen, Nitrogen, Sulfur, and Bromine to Carbon

Compound	Impregnation (%)	Stage	Oxygen	Nitrogen	Sulfur	Bromine
Tetrabromophthalic anhydride	12	Before d.c.	0.97	0.27	Trace	0.07
		After 1st d.c.	1.25	0.38	0.06	0.02
		After 2nd d.c.	1.18	0.33	0.10	Trace
		After washing	0.78	0.35	Trace	Trace
	20	Before d.c.	0.95	0.29	-	0.08
		After 1st d.c.	1.35	0.52	0.07	0.03
		After 2nd d.c.	1.25	0.4	0.10	Trace
		After wash	1.19	0.35	Trace	Trace
Tribromomethanilic acid	13	Before d.c.	1.05	0.32	0.02	0.05
		After 1st d.c.	1.25	0.41	0.09	0.01
		After 2nd d.c.	1.64	0.49	0.13	Trace
		After wash	0.91	0.32	Trace	Trace
	20	Before d.c.	0.95	0.22	0.05	0.14
		After 1st d.c.	1.50	0.51	0.13	0.05
		After 2nd d.c.	1.58	0.42	0.15	Trace
		After wash	1.1	0.38	Trace	Trace

using detergent. Simple extraction was not sufficient for the removal of brominated aromatics after glow discharge treatment.

Compounds of the second and third groups were tested for flameproofing. Only tetrabromophthalic anhydride and tribromo-m-aminobenzenesulfonic acid showed any flame-resistance after extraction. Even though considerable grafted chemical remained after detergent washing, there was not enough left to achieve a flameproof fabric. Chemical grafting experiments indicated that a minimum of 8 to 10% uptake is required for this purpose [9].

CONCLUSIONS

Low-temperature glow discharge can cause the polymerization of nonvolatile monomers adsorbed on wool. Grafting will occur if the impregnation is low enough to allow the active particles from the glow discharge to create free radicals on the protein chain. At higher levels of impregnation, mostly homopolymers are created; these are easily removed through extraction. This cannot be counteracted by higher power settings and longer residence times because of the competing ionic scouring of the newly formed polymer that occurs under more vigorous reaction conditions. The generated free radical is not only capable of initiating polymerization, but also can couple with other nonpolymerizable free radicals. The present method is limited to low level grafting where the maximum level achievable is strongly dependent on the applied substrate.

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