TREATMENT OF FIBROUS MATERIALS IN GLOW DISCHARGE.

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ABSTRACT

Continuous treatment of loose fibers in glow discharge was investigated with various reactor designs. When the fiber web was confined between two net-structured belts, considerable surface modification was obtained, as proven by x-ray photoelectron spectroscopic surface analysis. The treatments of wool resulted in increased yarn and fabric strength,and abrasion and shrinkage resistance.

INTRODUCTION

Effects of electric discharges on surface chemical modification have been studied on various textile-like materials (1). In the case of artificial polymeric materials these changes commonly resulted in the improvement of adhesion properties (2). Because natural fibers, such as cotton and wool, have more complex surfaces and are more reactive, surface modifications have much more pronounced effects. Kassenbeck (3) has reported the treatment of wool, while Stone and Barrett (4) found important changes in the properties of cotton. Such treatments did not alter the strength of the single fibers or their bulk properties, but the surface changes resulted in higher cohesion between individual fibers and therefore in higher yarn strength and fabric tear strength. In addition, the increased crosslinking at the surface has been reported to improve abrasion resistance (5). The major effect on wool is a dramatic decrease in felting shrinkage (6). A study of the chemical structure of the surface of glow discharge modified wool indicated that the basic reactions of wool in glow discharge are oxidation and elimination of the sidechains of the protein molecules (7,8). Scanning electron microscope studies indicated noticeable physical changes in surface structure only after more extensive treatment (9). Corona treatment of wool in fibrous form, to obtain practical control of shrinkage, has appeared technically feasible (10). Wool treated as yarn or fabric in radiofrequency discharge also showed important benefits; in most cases no disadvantage appeared. Unfortunately, when complete prevention of shrinkage was attempted by more vigorous treatment of wool in the form of yarn or fabric, many protruding surface fibers were singed. Although hardly visible, these fine burnt fibers resulted

in a harsh feel, or at least their entanglement with each other caused undesirable noises when the yarn was unrolled. To get a more thorough, uniform treatment and avoid overtreating surface fibers, the direct treatment of loose wool fibers by rf glow discharge was studied. The main objective is a continuous process that allows convenient treatment of enough material for adequate testing. In this paper we report not only the physical and chemical modifications of loose fibers treated in rf glow discharges but, also, various reactor designs tested for this purpose.

EXPERIMENTAL

The wool used in these experiments was scoured fine wool with a diameter of 15μ to 20μ. The wool was extracted before use with a mixture of benzene and methylalcohol mixture (3:2 by volume) . The surface changes caused by rf glow discharge were determined with both batch and continuous reactors.

The simplest batch reactor (# I) has been described previously (11). Wool fibers were fastened to a microscope slide at their ends by narrow strips of adhesive tape. This slide was then placed in the center of the cylindrical reactor and treated under various reaction conditions. This provided 20-40 mg of treated material.

Larger quantities, up to 1 gram could be treated in another reactor (# II) previously used for fabric treatments (12). In this case the fibers in the form of a thin web were draped around a glass tube placed concentrically in the large cylindrical reactor. Since the reactor was rotated back and forth between the electrodes, while at the same time the ground electrode was also moved back and forth along the axis of the reactor, an improved treatment could be obtained without noticeable burning. Contact with the glass surface, however, prevented a consistently uniform treatment.

In another reactor design (# III), a fiber web was carefully rolled up on a small spindle. The spindle was placed on a winding mechanism inside a vacuum jar with an opening in its bottom. The opening led to a vertical reactor with appropriate electrodes. The reactor,in turn, was connected at its bottom to another vacuum jar to collect the fibers. While the wool was slowly unwound in the upper container, it was gravity-fed through the reactor and treated with rf plasma.

A large, but still batch-type operation could be carried out in a reactor (# IV) designed by the Surface Activation Corporation (SAC) (13). This reactor used low frequency discharge (2000 Hz). Rolled up fabric inside the reactor is pulled (full width, single layer) by an internal drive mechanism between a set of electrodes. In order to allow fiber treatment the fibers were drafted to form a web 75-cm wide (15g/m). This was rolled up between two 80 m open mesh belts. These conveyor belts were made of nylon and polyester with two different openings : 4-mm^2 squares and 15-mm^2 hexagons. This sandwich arrangement was unrolled and pulled between the electrodes in the same way as fabric. After treatment,the fibers were removed, spun into yarn, and tested.

A small scale reactor (# V) for the continuous treatment of loose fibers is shown in schematic in Fig. 1. Its basic principle is the same as used for the reactor to treat yarns (14). The material is introduced through a long "capillary slit" with a cross-section of 50 mm x 0.75 mm instead of a 1 mm capillary tube . The reactor is

divided into segments by three vacuum locks on each side. The rollers not only advance the material through the reactor, but also help to seal one segment from neighboring ones. The reactor is made of aluminum, but the two large sides of the reactor chambers, each of which measures 200 mm x 80 mm x 20 mm, are Pyrex glass windows to allow capacitative excitation. The reactor was designed with two consecutive chambers which allowed not only double exposures but, alternatively, grafting treatment in the second chamber. This grafting is the subject of a separate report.

The wool fibers were drafted into a 50 mm wide thin continuous web (1.2 g/m) and introduced to this reactor between two endless belts to avoid stress on the web. Several kinds of belting were tested including, besides the net-like materials described above, types made from paper,polyethylene and cotton without perforations. These were tested as a means to minimize air leakage to the reactor chamber along the belts. When solid belts were used the upper belt was lifted from the web surface as it entered the plasma chamber to allow greater exposure of the fibers to the glow discharge. Cotton belts provided the best seal but, even with 30 l/min pumps connected at A,B and C, the pressure in the reactor chamber could not be lowered below 50 torr.

To get a better vacuum, instead of adding more vacuum locks at the reactor entrance and exit, the whole reactor was enclosed in a tubular container shown in Fig. 2. The container was constructed of a PVC tube with appropriate connections for vacuum and electricity. At both ends, a specially designed double slit system allowed the entrance and exit of the belt-web system with little loss of vacuum. A 300 l/min pump evacuated the outer container to 30 to 40 torr. When the reactor was then evacuated, the pressure in the reaction chambers decreased to 1 to 2 torr depending on the rate at which the wool was introduced. The speed of the belts was generally 60 to 120 cm/min. At higher speeds the pressure in the chamber increased. At 1 to 2 torr, a glow discharge could be created by a 100 W rf generator using copper plates slightly smaller than the Pyrex glass windows. Two identical generators were required to excite both chambers simultaneously when longer treatment was needed. The characteristics of the various reactors are summarized in Table I.

Surface analysis of the fibers was by x-ray photoelectron spectroscopy (XPS) as described (15).

RESULTS AND DISCUSSION

Treating small amounts of fibers in batches (reactor # I) quickly produced considerable surface modification. As determined by XPS, an air plasma at 2 torr and 70 W caused almost a 200% increase in the oxygen/carbon and nitrogen/carbon ratios after 30 seconds. Fig 3. depicts the effect of exposure time on the atomic ratios. An immediate increase in atomic ratios is followed by some decrease with continued exposure. Undoubtedly, the protein breaks into smaller water-soluble fragments since the surface atomic ratios of the treated wool decrease after gentle rinsing. The decrease in the sulfur/carbon ratio is especially noticeable. In untreated wool this ratio was 0.057 S/C; with 0.013 and 0.044 for hexa- and bivalent sulfur, respectively. After the wool has been treated in the large batch reactor (# II), this relationship is reversed in favor of the hexavalent sulfur : 0.048 & 0.021, respectively, with the total slightly higher than in the untreated

fibers. After the treated fibers were rinsed with water, however, the total S/C ratio, 0.048, was less than for untreated wool, with 0.018 & 0.030 ratios for the hexa- and bivalent sulfur, respectively. As shown in Fig. 3, O/C and N/C ratios were also decreased by rinsing; though these values remained higher than before treatment. It appears that plasma treatment breaks up some of the protein molecules, as well as oxidizing side-chains.

Before treating the wool fibers confined between open-mesh belts in the large reactor (# IV), small scale tests were made in reactor # I, to determine the possible shielding effect of the sandwiching netted belts. When small amounts of wool fiber were enclosed between either type of net material and treated with glow discharge as described above, the surface chemical studies showed less change in the atomic ratios but the effect of confinement between the open-mesh belts was small.

Large-scale tests were then carried out in the SAC reactor (# IV) with exposure times of 2 to 4 minutes. The atomic ratios were found to be, on the average, 20% to 30% less than with rf excitation, but this is not necessarily attributed to the lower frequency. In addition, some variation was observed depending on the position from which the sample was taken. This might have been caused by the inhomogeneity of the plasma. However, no harshening of the surface was observed and the textile properties were improved. For instance, the strength of the yarn spun from plasma treated fibers was 25% to 46% higher than that of the control, while the wool treated in the form of yarn showed only a 17% to 30% increase. This confirmed our expectation of a more thorough treatment for the fibers.

The shrinkage of a knitted sample was between 5.5% to 9.6% in comparison to 49% for the untreated sample. Although samples knitted from directly treated yarn had even less shrinkage, between 0% to 7%, these values resulted from a long study. Similar tests to find optimum conditions for the large reactor (# IV) have not been feasible. Interestingly, abrasion resistance also showed less improvement in this large-scale treatment. In particular, when the net with larger openings was used, wide variation was observed and in some cases a decrease of 10% to 15% was found. In the case of the smaller meshed belting, the improvement in abrasion resistance was between 40% to 70%. This improvement is in the same range as with directly treated yarns.

Evidently, the glow discharge can penetrate the net to cause the desired surface modification of the wool, but the net still takes up some of the energy. When the small scale continuous reactor (# V) was tested with the open-mesh belts, the improvement in strength and shrink resistance was only about 50% of that realized with the large reactor (# IV), even though the smaller reactor had the higher power density. The results were improved when the reactor was modified to allow separation of the belts before entering the reaction chamber. After the separation of the belts the wool was not so closely confined to them and improvements were obtained even when the belts were not perforated. Nevertheless, even under the best conditions only 80% of the possible improvement could be achieved in reactor V. This degree of shrinkage control is inadequate. It appears that the belting should be completely outside of the glow discharge zone, since maximum improvement was realized in treating loose wool directly in the vertical small scale-batch reactor (# III).

CONCLUSION

The glow discharge treatment of loose fiber webs provides improvements similar to those obtained by treating yarn or fabric, but a more uniform treatment is obtained, and overtreating surface fibers is avoided. The main problem is to provide for large scale continuous treatment of a very open, fragile web. An appropriate scale up of the continuous reactor described here appears, with some modification, to provide a suitable model for that purpose.

REFERENCES

(1) A.E.Pavlath, Plasma Treatment of Natural Materials, in Techniques and Application of Plasma Chemistry, edited by J.R. Hollahan and A.T. Bell (Wiley, New York, 1974)
(2) R.H. Hansen and H.J. Schonhorn, J. Polymer Sci. B4. 203 (1964)
(3) P. Kassenbeck, U.S. Patent 2,977,745 (1961)
(4) R.B. Stone and J.R. Barrett, Text. Bull 88. 65 (1962)
(5) A. Barretta, Ann. Sci. Textiles, Belges, 20.(2) 44 (1972)
(6) A.E. Pavlath and R.F. Slater, Appl. Poly. Symposia, 18. 1317 (1971)
(7) A.E.Pavlath and K.S. Lee, Proc. 5th Intern. Wool Textile Res. Conf. 1975, edited by K. Zeigler (Deutsches Wollforschunginstitute, Aachen 1976),III. 263
(8) K.S. Lee and A.E. Pavlath, ibid, III. 275
(9) W.H. Ward, ibid, II. 458
(10) W.J. Thorsen and R.Y. Kodani, Textile Res. J. 36. 651 (1966)
(11) M.M. Millard, J.J. Windle and A.E. Pavlath, J. Appl. Polym. Sci. 17. 2502 (1973)
(12) A.E. Pavlath and K.S. Lee, J. Macromol. Sci.-Chem.,A10(3), 619 (1976)
(13) A. Bradley and J.D. Fales, Chemtech, 1971. 232
(14) M.M. Millard and A.E. Pavlath, Textile Res. J. 42. 460 (1972)
(15) A.E. Pavlath, K.S. Lee and G.H. Robertson, Vacuum, 25. 157 (1975)

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Reference to a company and/or product named by the Department is only for the purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

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TABLE I
Characteristics of various reactors used in the experiments.

Design #	Volume of glow ml	Max. power W	Remarks
I	300-400	75-80	Best pressure 0.2 torr
II	1200-1400	250-300	Best pressure 0.6-0.8 torr
III	1600	250-300	Best pressure 1-1.2 torr
IV	appr. 10^5	2000	Actual reactor volume was 3000 l; pressure 1.5-2 torr
V	300	75-80	Best pressure 1.4-1.6 torr

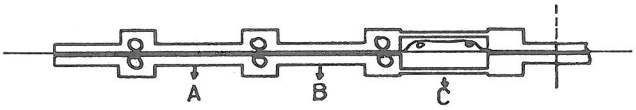

Fig. 1
Continuous small-scale reactor
for glow discharge treatment of loose fibers

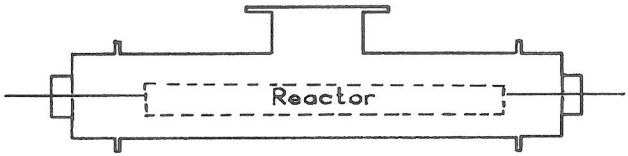

Fig. 2
PVC tube-container for reactor in Fig. 1.
(Length= 450 cm, diameter= 30 cm)

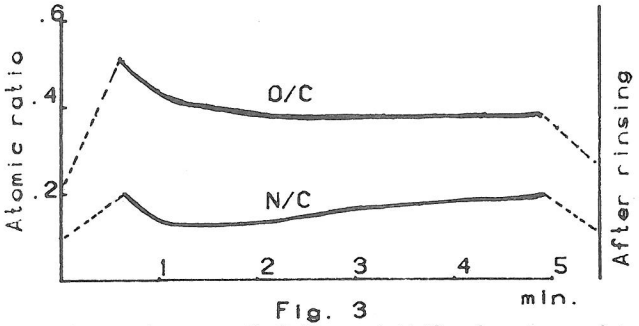

Fig. 3
Time dependence of O/C and N/C atomic ratios
on glow discharge treated wool fiber surface.