Modification of Cotton, Rayon, and Silk with Urethane Acrylate under Ultraviolet Radiation

A. S. BASHAR, MUBARAK A. KHAN, K. M. IDRISS ALI

Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, P.O. Box 3787, Dhaka, Bangladesh

Received 30 November 1995; accepted 15 April 1996

ABSTRACT: Ten different formulations were developed with Ebcryl 264, a urethane acrylate in combination with other monofunctional monomers in the presence of some additives and coadditives. Thin films prepared from these formulations under ultraviolet (UV) radiation were characterized. Natural fibers such as cotton, rayon, and silk were treated with the formulations and cured under UV radiation. Their physical and mechanical properties were studied. It was found that the tensile strength (TS) of cotton, rayon, and silk was significantly increased as a result of this treatment under UV radiation (TS_{cotton} = 150%, TS_{rayon} = 30%, and TS_{silk} = 40%). Elongation of cotton and silk increased to 380 and 50%, respectively. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1703–1711, 1997

Key words: natural fibers; urethane acrylate; UV radiation; tensile strength

INTRODUCTION

Natural polymers play an important role in the advancement of modern technology. Every individual type of polymer has its own applications. Natural polymers are obtained from natural fibers such as jute, flax, cotton, rayon, silk, etc. Some are used for making carpets, carrier bags, and decorative articles, while others are used in making beautiful apparel. Among the above natural fibers, the present report deals with only cotton, rayon, and silk. Cotton is composed of natural cellulose; rayon is derived as a by-product from paper pulps that are made with bamboo, green jute, etc. Rayon is obtained as thread from the viscous material left after the pulp preparation. Silk is composed of protein material derived from insects. In the previous report[1] cotton, rayon, and silk were modified through graft copolymerization with methylmethacrylate (MMA) under ^{60}Co γ radiation. Silk obtained the maximum grafting (35%) among them with MMA under the γ source, but the tensile strength did not increase at all for any of them. Recently it was reported[2–5] that jute materials (fiber, yarn, and hessian cloth) could be conveniently grafted with urethane acrylate oligomer in the presence of some additives and coadditives under ultraviolet (UV) radiation, with enhancement of tensile properties (strength and elongation). But the jute materials, grafted under ^{60}Co γ radiation did not increase the tensile strength of the grafted product. These findings led us to undertake the modification of cotton, rayon, and silk under UV radiation (in place of γ radiation). In fact, some other workers grafted cotton with MMA[6,7] in the presence of ceric ion, dyes,[8] and hydrogen peroxide[9,10] containing swelling solvents. Davis and Garnett[11] grafted cotton with styrene using alcohols as swelling solvents. However, Shukla and Athalye[12] grafted cotton with hydroxyethylmethacrylate (HEMA) under UV radiation, but they did not find out what happened to the strength of the grafted cotton. There is very

Correspondence to: Dr. K. M. Idriss Ali.

little work on the modification of rayon. However, recently some workers modified silk yarns by grafting them with HEMA under UV[13] and plasma[14] radiations. Tsukada et al.[15] studied properties of the silk that was grafted with MMA or other monomers under thermal techniques.

The present study reports on the modification of cotton, rayon, and silk under UV radiation with urethane acrylate combined with other additives and coadditives. These additives and coadditives were used for the enhancement of rhelogical properties of jute, a natural fiber.[2–5]

EXPERIMENTAL

Materials

White cotton yarn was collected from the local market; rayon thread was procured from the Karnafuli Paper Mills situated at Chittagong, Bangladesh. Silk yarn was obtained from the Rajshahi Silk Mills. Each of the samples (200-cm long) was dried at 105°C until constant weight was achieved.

Ebcryl 264 (EB), a urethane triacrylate oligomer with an aliphatic backbone, was procured from IAEA and was used without further purification. The oligomer, being a highly viscous material, was diluted with some reactive diluent monofunctional monomers such as *N*-vinylpyrrolidone (NVP), 2 ethylhexyl acrylate (EHA), MMA, and methyl acrylate (MA). They were procured from Merck. Methyl ethyl ketone (MEK), a product of BDH Co., was used as the antibubbling agent. Diallyl phthalate (DP) was used as a plasticizer and was obtained from Aldrich Chemical Co. Photoinitiator Irgacur 184 was used to initiate the radical formation reaction under the UV radiation.

Method

Polymer Films

Ten different formulations were developed with the oligomer (Ebcryl 264) in combination with other additives in the proportions shown in Table I. Thin polymer films were prepared with these formulations under UV radiation on a glass plate (8×3 cm). The plate was coated with the formulated solution using a 0.018-in. bar coater (Abbey Chemicals Co., Australia). The UV radiation was obtained from a Minicure (MC-200-UV) device of IST-Technique (Germany). The UV lamp (254–313 nm) gave 2-kW energy with an efficiency margin of ±1%. A pendulum hardness tester (Labotron, Byke) was used to determine the film hardness of the UV-cured film. The gel content was determined by extracting the UV-cured film with hot acetone for 48 h in a Soxhlet extractor. A known weight of the cured film was wrapped in stainless steel that was put in the Soxhlet for extraction with hot acetone. The weight difference before and after the extraction yielded the gel content. Because the film was very soft and sticky on the plate, it could not be peeled off the plate; so, tensile properties such as strength and elongation were not measured.

Substrates

The substrate (cotton, rayon, or silk) sample was pulled through the developed formulation contained in a beaker at a speed of 4 m/min so that it would simultaneously pass under the UV radiation of the Minicure. In some cases, treated substrate was passed several times under the UV lamp in order to ascertain the full curing of the substrate. The cured substrate was extracted in hot acetone for 48 h to remove unreacted chemicals and to determine the extent of polymer that was crosslinked with the substrate. Therefore, the extent of polymer uptake was calculated as percent polymer uptake = $100(W_e - W_0)/W_0$, where W_e is the weight of the cured sample after the extraction and W_0 is the weight of the virgin sample.

Tensile properties of the cured substrates were determined directly with Instron (model 1011), equipment for the measurement of tensile properties. The crosshead speed was 0.03 m/min; its load capacity was 500 lb and efficiency was within ±1%. The results obtained were within ±2%.

Water uptake of treated and untreated samples was determined by immersing the substrates in water contained in a static water bath at 25°C. The samples were kept immersed with suitable weights tied to the samples. The uptake of water was periodically monitored to find the profile of water uptake.

RESULTS AND DISCUSSION

This report deals with preparation of polymer films under UV radiation with 10 different formu-

Table I Composition of Different Formulations

Chemicals (w/w %)	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
EB	30	25	25	20	15	15	15	15	15	15
NVP	30	25	20	20	20	15	10	20	20	20
EHA	30	40	35	35	35	35	35	30	30	25
MMA			10	10	10	15	20	15	10	15
MA			5	10	10	10	15	20	20	
MEK	5	5	5	5	5	5	5			
I	2	2	2	2	2	2	2	2	2	2
DP	3	3	3	3	3	3	3	3	3	3
V	21	13	15	8	8	5	11	8	4	9

EB, Ebcryl 264; NVP, *N*-vinylpyrrolidone; EHA, 2-ethylhexyl acrylate; MMA, methyl methacrylate; MA, methyl acrylate; MEK, methyl ethyl ketone; I, photoinitiator (Irgacure 184); V, viscosity (mps at 25°C); DP, diallyl phthalate.

lations developed with Ebcryl 264 and the characterization of these films. The second phase of the report deals with the treatment of natural fibers, particularly cotton, rayon, and silk, with the formulated solutions and then cured under the UV radiation and the study of the change of their physical and mechanical properties.

Polymer Films

Pendulum Hardness

Thin polymer films were prepared with the formulated solutions of oligomer (Ebcryl 264) under UV radiation. Film hardness was determined with the pendulum method while the cured film was still on the glass plate. Pendulum hardness (PH) is plotted (Fig. 1) against the number of passes under the UV lamp. The hardness increased with the number of passes, attained a maxima for most of the cases, and then decreased at higher UV radiation. The decrease of film hardness could have been caused by the degradation of the cured polymer at higher doses. The excessive radiation could have damaged the surface of the cured film. There may be some other factors that could cause reduction of film hardness. Some of the films attained the maximum PH at the 8th pass while others attained it at the 10th pass. However, PHs of formulations 1, 2, and 8 (F1, F2, and F8) increased even after the 12th pass. The highest PH value was obtained by F7 that contained the maximum content of MMA in the formulation. F7 was followed by F6. The lowest PH was found in F10. In fact, the films (F8, F9, and F10) that did not contain MEK, the antibubbling agent, showed substantially lower film hardness.

Gel Content

Gel content of the UV-cured films is plotted in Figure 2. Observe that the gel content mainly increases with UV dose. But most of the films attain the maximum gel at the sixth pass. However,

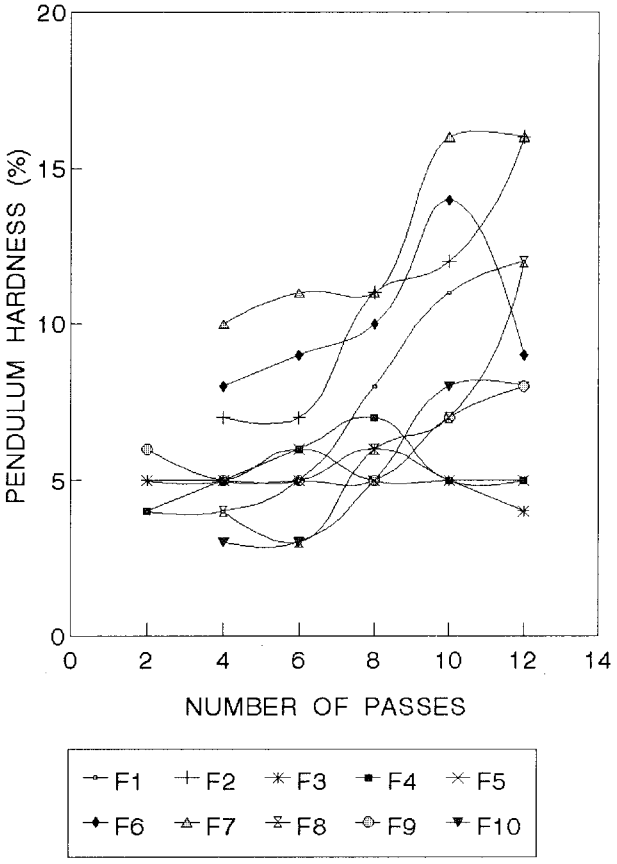

Figure 1 Pendulum hardness of UV-cured polymer films against number of passes.

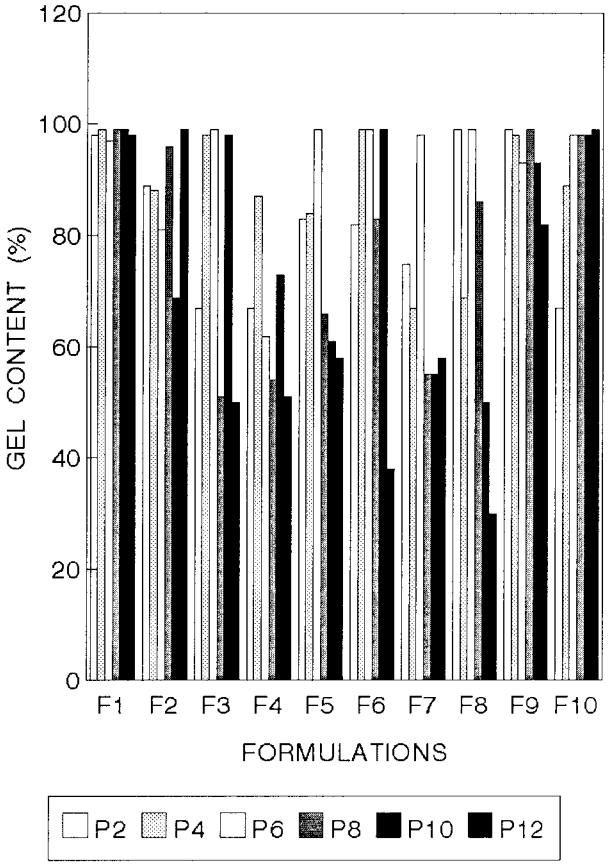

Figure 2 Gel content of UV-cured polymer films against formulations as a function of passes.

there are some films that show the maximum gel content at the fourth pass. The decrease of gel at higher doses may be explained as above that the high dose damaged and degraded the polymer. The overall highest gel content was obtained by formulation F1. The lowest gel content was given by F4. The highest PH (Fig. 1) was achieved by F7 whereas the highest gel content was obtained by F1 (Fig. 2). Gel content and film hardness are both represented by the crosslinking density. Film hardness represents the crosslinking density at the surface of the film while gel content represents the crosslinking density present in the entire film. F1 contained the highest amount of NVP, which is a unique compound[16–18] and is known to make better augmentation through its carboamide (—N=CO—) group between the oligomer chain. The UV-cured films were very soft and sticky on the glass plate because of the high proportion of EHA, a low glass transition temperature (T_g) monomer, and DP present in all the formulations. Thus, the films could not be peeled off the plates and the tensile properties could not be determined.

Cotton, Rayon, and Silk Substrates

Cotton, rayon, and silk samples were treated with these formulations and then cured under UV radiation. Polymer uptake is the amount of polymer that adheres to the irradiated substrate after the solvent extraction. Cotton achieved the highest polymer uptake (400%) among the three substrates and that was with formulation F4 at the second pass under the UV lamp (Fig. 3). Formulations F1–F5 and F10 produced higher uptake values with cotton at the second pass after which the polymer uptake decreased (data not shown). On the other hand, formulations F6–F9 produced low uptake values at the second pass. Such polymer uptake behavior with rayon (Fig. 4) and silk (Fig.

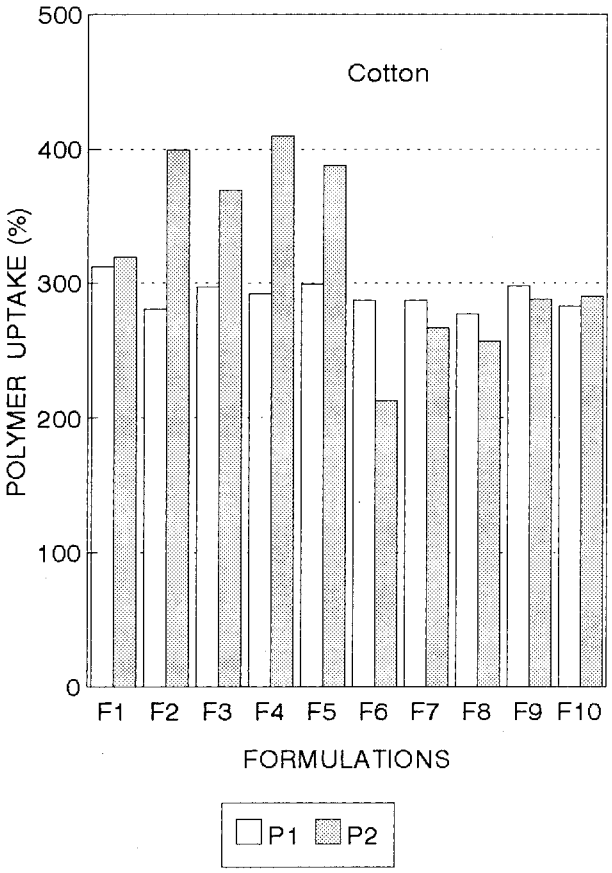

Figure 3 Polymer uptake of different formulations with cotton as a function of passes under a UV lamp.

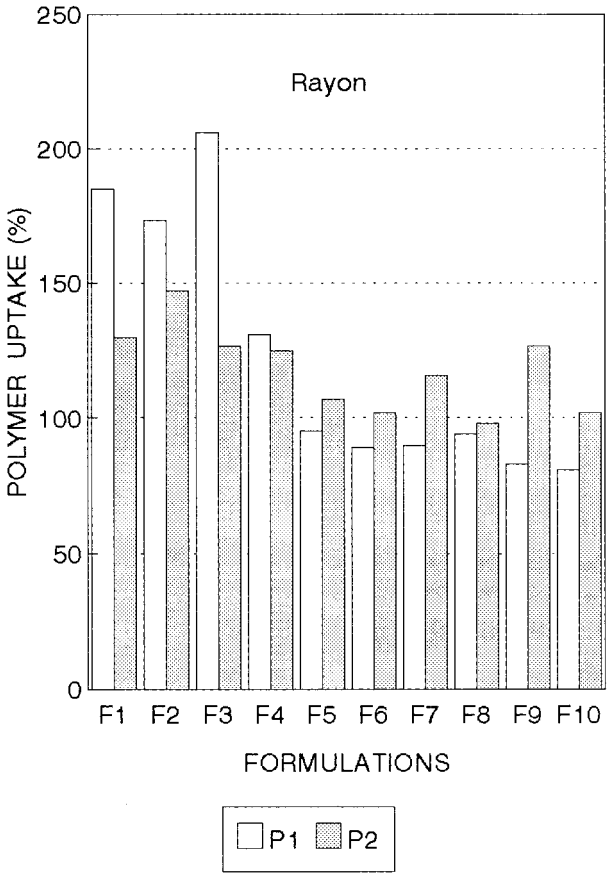

Figure 4 Polymer uptake of different formulations with rayon as a function of passes under a UV lamp.

5) was little different than that with cotton. In the case of rayon, the highest uptake value was obtained with F3 (200%) and the lowest with F8. Formulations F1–F4 induced low uptake values at the second pass, unlike formulations F5–F10, which produced the increased uptake values at the second pass, after which there was no increment of the uptake values with rayon. But silk required more radiation to produce higher uptake values. In most of the cases, three passes were required to obtain the maximum uptake values. The higher uptake value (150%) was obtained with F1 at the third pass under the UV lamp (Fig. 5).

Cotton achieved the highest amount of polymer uptake (400%) compared to rayon (200%) and silk (150%). These values were obtained with different formulations (cotton with F4, rayon with F3, and silk with F1) at different UV doses. The amount of grafting achieved under UV radiation with urethane acrylate was really significant for diversified applications of these materials.

Tensile Properties

Tensile properties (strength, TS, and elongation at break, Eb) of treated and untreated samples of cotton, rayon, and silk were determined. Change of these properties was noted and expressed as factors. Thus, TS factor, T_f, is the ratio of TS of the treated substrate to that of untreated one; that is, $T_f = \mathrm{TS}_{\mathrm{treated}}/\mathrm{TS}_{\mathrm{untreated}}$. Similarly, elongation factor $E_f = \mathrm{Eb}_{\mathrm{treated}}/\mathrm{Eb}_{\mathrm{untreated}}$.

Cotton

There was a significant enhancement of TS of the treated cotton thread as a result of this treatment. All the formulations increased the TS values of cotton under the UV radiation. This enhancement was between 80 and 150% as shown in Figure 6 where T_f is plotted against formulations as a function of passes under the UV lamp. The highest increment in TS value was obtained with formulation F10 under one pass of UV radiation; a

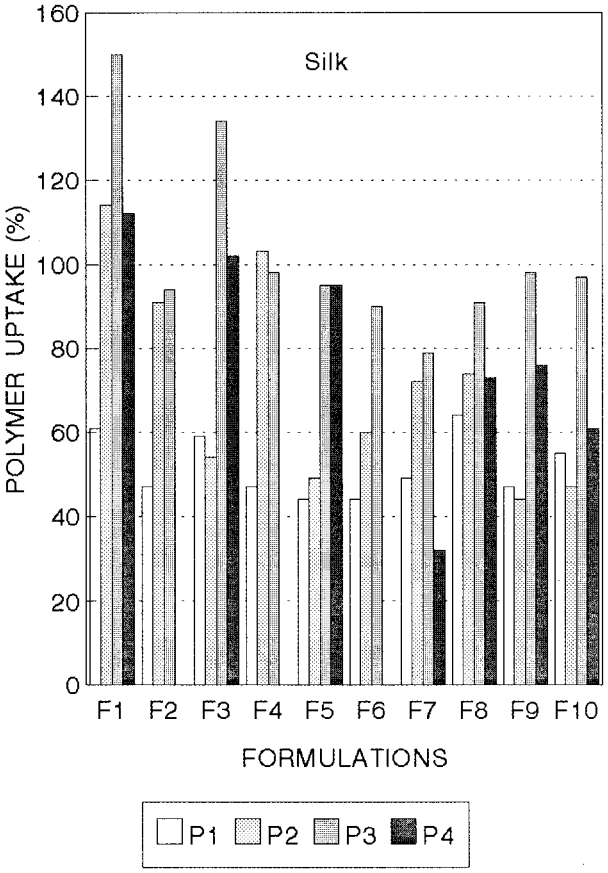

Figure 5 Polymer uptake of different formulations with silk as a function of passes under a UV lamp.

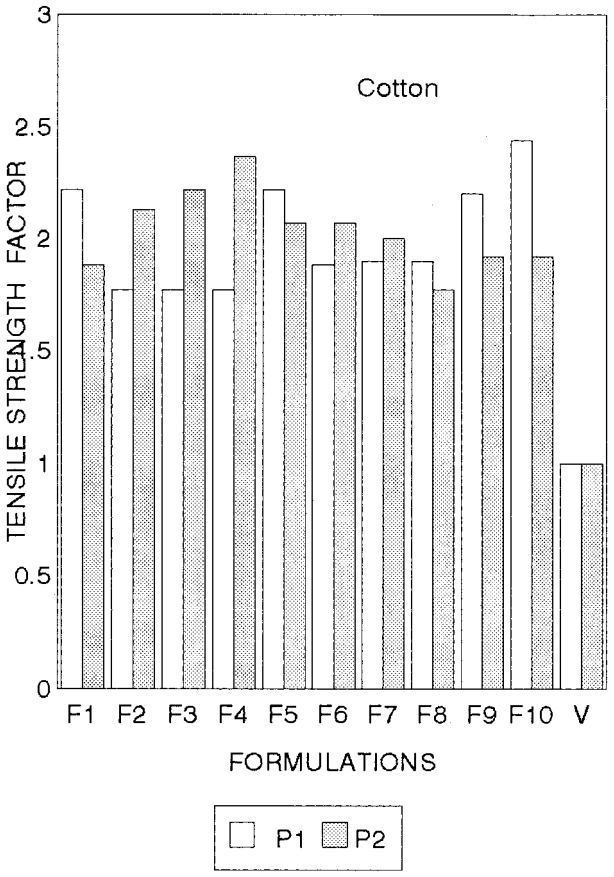

Figure 6 Tensile strength factor of cotton against different formulations as a function of passes under a UV lamp.

further increase in UV dose decreased the tensile property of the cotton in most of the cases; thus, TS values were decreased in the second pass with formulations F10, F9, F8, F5, and F1. However, in formulations F2, F3, F4, F6, and F7, there was an increase of TS by the second pass under UV radiation. This is a significant achievement in obtaining substantial enhancement of TS of the cotton materials treated with all the formulations developed. These formulations not only increased the tensile strength of the treated cotton thread, but also increased the stretchability (elongation) of the cotton thread. The results of enhancement of Eb are given in Figure 7, where elongation factor is plotted against formulation as a function of UV radiation represented by number of passes. The treated cotton thread could be stretched up to 380% more than the untreated cotton. However, there was variation of the stretching ability of the treated cotton that was dependent on the type of formulations used. All the formulations induced stretching ability of the treated cotton under the UV radiation. Formulations F1, F2, F3, F4, F6, and F10 registered higher elongation by the second pass under UV radiation. This is a very important achievement and finding in the study on modification of cotton to be used in diversified applications.

Rayon

The tensile strength factor, T_f, of the rayon system is shown in Figure 8 against different formulations. Most of the formulations decreased the TS of the treated rayon in the second pass under UV radiation, except formulation F7 where the TS values were the same at both passes and in F1 where there was more of a decrease in the first pass than in the second pass. There was enhancement of TS of the treated rayon samples with formulations F2, F5, F6, F8, F9, and F10 that oc-

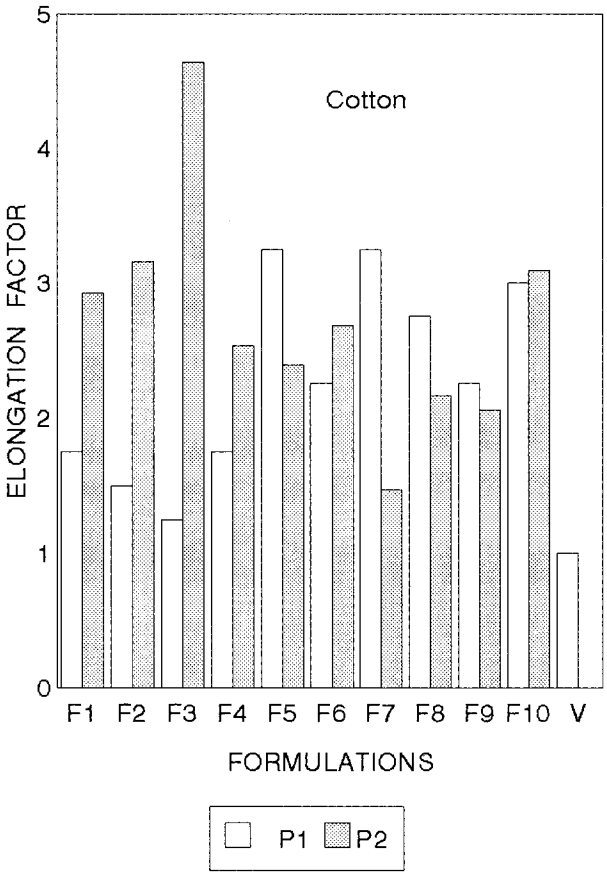

Figure 7 Elongation factor of cotton against different formulations as a function of passes under a UV lamp.

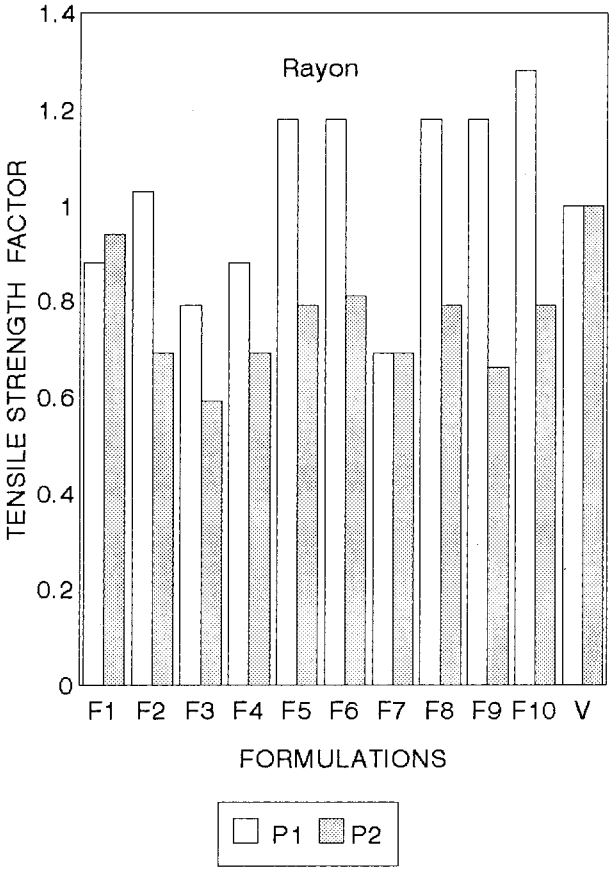

Figure 8 Tensile strength factor of rayon against different formulations as a function of passes under a UV lamp.

curred by the first pass of the UV radiation. The highest increase (about 30%) was obtained with formulation F10. However, there were other formulations that decreased the TS of the treated rayon substrate.

There was a substantial decrease of the elongation factor of the treated rayon materials. This decrease was between 20 and 80% as shown in Figure 9 and was further aggravated by increasing the UV dose from one pass to two passes. The above behavior is unlike that of cotton under similar conditions and treatment. Although rayon obtained increased grafting up to 200%, its tensile properties (TS and Eb) were also reduced.

Silk

Silk is a polymer composed of protein moieties. The physical characteristics of silk fibers are really difficult to change or modify. The present study revealed a significant increment of TS of the silk yarns that were soaked in specially formulated solutions and cured under UV radiation. TS factor of the treated silk material is shown in Figure 10 against the formulation as a function of UV dose. The TS decreased in the first pass and then increased with the number of passes under UV radiation, represented by P1, P2, P3, etc., respectively, for the first pass, second pass, and so on. It was also observed that almost all the formulations induced increased strength to the silk substrate in the second pass under UV radiation. This trend of increments in TS values continued up to four or five passes. The highest TS values (40%) were attained by formulation F5 in the fourth pass and that was maintained in the fifth pass. Formulations from F7 to F10 yielded almost the same extent of TS increment (about 38%) in the third pass under UV radiation. In the previous report[1] it was possible to increase the TS value of silk by 4% only under ^{60}Co γ irradiation (the silk was treated with MMA + NVP + urea). The

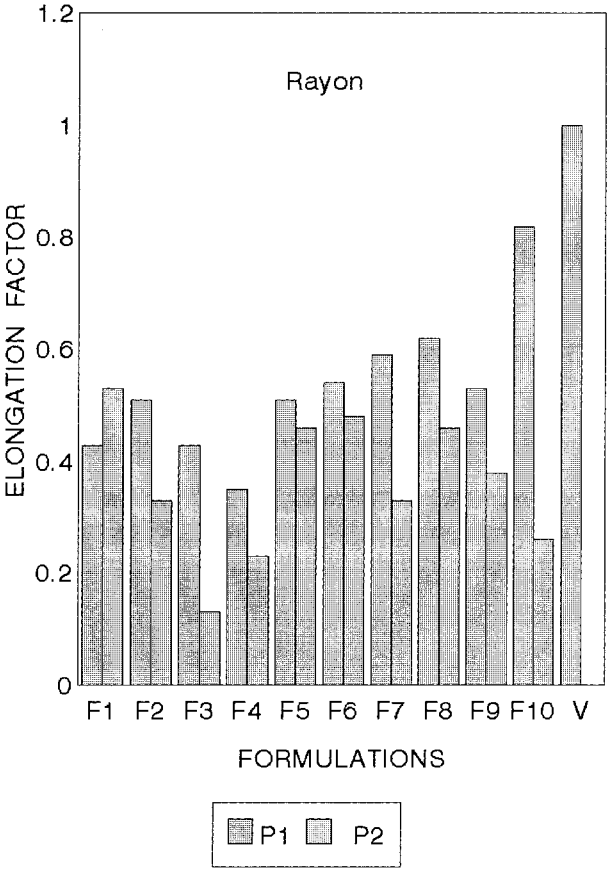

Figure 9 Elongation factor of rayon against different formulations as a function of passes under a UV lamp.

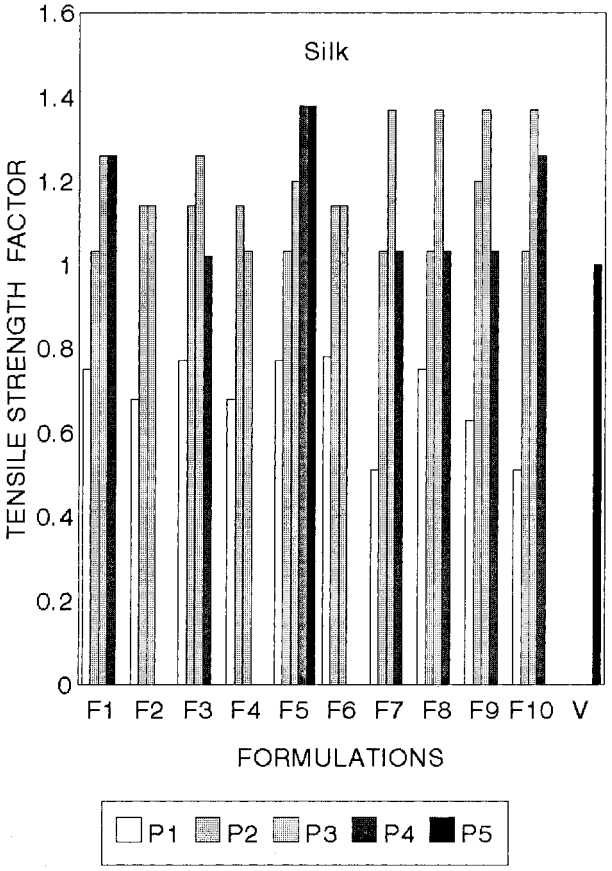

Figure 10 Tensile strength factor of silk against different formulations as a function of passes under a UV lamp.

40% TS increment of the silk thread with formulation F5 is a significant achievement.

As a result of this treatment of silk with these formulations, there was decreased elongation for almost all the formulations except F1–F3 (Fig. 11); there was a slight increase of Eb in the first pass for these formulations and then the Eb decreased. However, there were some formulations like F5 and F8 that induced increased elongation to the treated silk in the third pass under UV radiation. The highest elongation was obtained by F5, and that was about 50% more than that of the virgin (untreated) silk yarns. This is also a significant achievement in the study of silk.

Water Uptake

Water uptake by the treated and untreated samples was monitored at 25°C. The results are shown in Figure 12, where water uptake is plotted against soaking time. Almost all the samples attained the maximum water uptake within the initial 10–15 min; there was a plateau after 25 min of soaking time in the treated samples while the untreated samples still continued to soak very slowly in the water. The untreated cotton gained water uptake up to about 60% whereas the treated cotton could soak up water by less than 10%. The untreated rayon achieved the highest uptake of water by 95% within 150 min, but the treated rayon had only 20% water uptake. The untreated silk sample soaked up the least amount of water (45%) and the treated silk obtained 20% water uptake.

CONCLUSION

In the study of modification of cotton, rayon, and silk with urethane acrylate combined with other additives under UV radiation, all three species (cotton, rayon, and silk) gained substantial

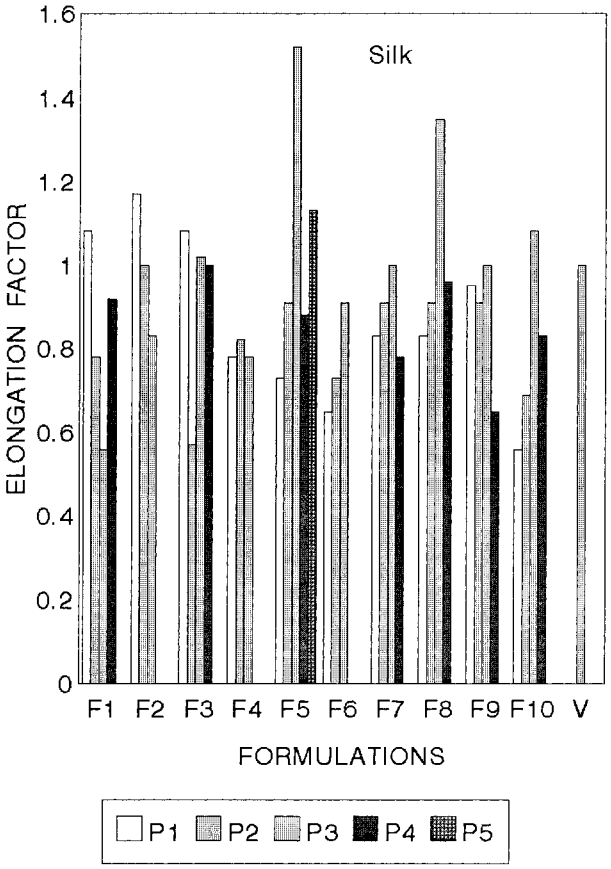

Figure 11 Elongation factor of silk against different formulations as a function of passes under a UV lamp.

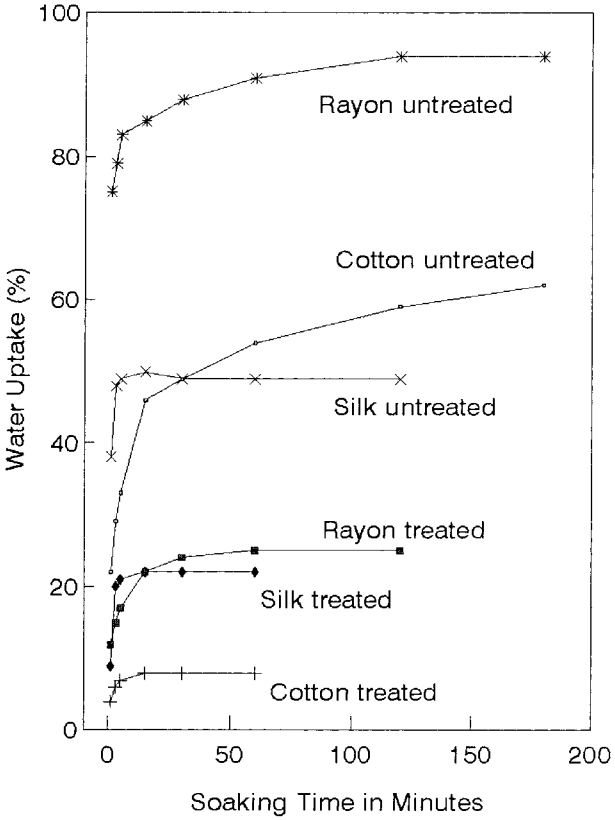

Figure 12 Water uptake by treated and untreated cotton, rayon, and silk against soaking time.

strength as a result of this treatment under the UV radiation (cotton by 150%, rayon by 28%, and silk by 40%). Similarly, it was possible to stretch/elongate the treated species to a significant extent: cotton by 380% and silk by 50%. However, the treated rayon lost its stretching ability. In the history of modification of cotton, rayon, and silk, the present investigation reveals promising results that are to be considered during diversified applications of these materials.

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