

Chemical Factors Affecting Soiling and Soil Release from Cotton-Containing Durable Press Fabric. VIII. Grafting of Polyester/Cotton Blend Fabrics with Carboxyl-Containing Polymer*

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Synopsis

Fabric samples of polyester/cotton blend were graft copolymerized to different levels (add-ons) with poly(acrylic acid) and poly(methacrylic acid) using the mutual γ -irradiation technique and the Fe^{2+} - H_2O_2 redox system, respectively. The copolymers so obtained were given durable press treatments with and without conventional nonionic softener using DMDEU as the crosslinking agent. The susceptibility of the copolymers before and after crosslinking to aqueous and nonaqueous oily soiling and their ability to release the soils were examined. It was found that hydrophilization of the surface of polyester/cotton blend through grafting with the said carboxyl-containing polymers brings about a significant improvement in the resistance of the blend to aqueous and nonaqueous oily soil particularly after crosslinking in presence of nonionic softener. A certain improvement in the ease of oily soil removal could be achieved by grafting. The opposite holds true for aqueous soil release. Soiling and soil release depends on the magnitude and method of grafting, medium of soiling, as well as the formulation of crosslinking treatments. The effect of grafting on some properties of the blend fabric before and after crosslinking was also examined.

INTRODUCTION

Soiling and soil release are complex phenomena involving the interrelationships of the nature of the fiber surface, a fiber-fabric structure, soil, chemical finish, and detergent. Out of several variables which collectively contribute to the problems of soiling and soil release, only some have been taken into account in studies of soiling and soil release carried out so far.¹ Recent reports from this division²⁻⁸ have dealt with the effects of chemical modification of cotton through introduction of carboxyl-containing groups or polymer in its structure, or through inclusion of CMC, conventional soil release finishes, or poly(acrylic acid) on the soiling and soil release characteristics of crosslinked cottons.

The present work is undertaken with a view to clarify the effects of grafting of polyester/cotton blend fabric with carboxyl-containing polymer on the soiling and soil release properties of the fabric before and after durable press treatments.

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EXPERIMENTAL

Polyester/Cotton Blend Fabric

Mill scoured and bleached plain weave (23 picks \times 23 ends/cm) polyester/cotton blend fabric was used throughout this investigation. Chemical analysis of the blend shows that it contains polyester and cotton at a ratio of 49.7:50.3. Unless otherwise stated, this blend fabric will be regarded as the untreated control.

Reagents

Hydrogen peroxide, ferrous ammonium sulphate, and magnesium chloride hexahydrate were of reagent grade chemicals. Acrylic acid and methacrylic acid were freshly distilled before used. Dimethyloldihydroxyethylene urea (DMDEU) was used as the crosslinking agent. This was supplied by BASF, West Germany, under the commercial name Fixapret CPA[®]. As a nonionic softener, 50% Velustrol PA[®], supplied by Hoechst, West Germany, was used.

Grafting of Poly(methacrylic Acid) onto Polyester/Cotton Blend

Samples of polyester/cotton blend fabric (15 \times 40 cm) were immersed in 0.1% aqueous ferrous ammonium sulphate solution for 15 min at room temperature. The samples were then squeezed to ca. 75% wet pickup and dried at ambient conditions. The samples were then rolled to have a form of a cylinder and introduced in glass cups (5 ϕ \times 40 cm height) containing the aqueous polymerization solution. The latter consisted of methacrylic acid, hydrogen peroxide, and distilled water. A material-to-liquor ratio of 1:20 was used. The polymerization reaction was carried out at 90°C under continuous stirring. Different graft levels (add-ons) were achieved by varying the methacrylic acid concentration (2.5–10%) and/or reaction time (60–180 min). After the desired reaction time, the samples were repeatedly extracted with boiling distilled water till constant weight.

Grafting of Poly(acrylic Acid) onto Polyester/Cotton Blend

Strips of the blend fabric (30 \times 6 cm) were impregnated in aqueous solution of acrylic acid for 1 h at room temperature using a material to liquor ratio of 1:10. This was then placed in the Co-60 cell to effect mutual irradiation grafting at a dose of 1.5 Mrad. Irradiation were provided by the 8000 ci Co-60 gamma source of the Middle Eastern Regional Radioisotope Centre, Cairo. Different add-ons were obtained by varying the acrylic acid concentration from 5% to 12%. Homopolymer formation was removed through several extraction with boiling water till constant weight, as indicated above in case of poly(methacrylic acid).

Carboxyl Content

Determination of the carboxyl content in blends bearing carboxyl-containing graft polymer was carried out according to a reported method,⁹ which is based on similar method described elsewhere.¹⁰

Crosslinking Treatment

Unless otherwise stated, the crosslinking treatment was carried out as follows. Fabric samples were padded through two dips and two nips in a solution containing DMDEU (120 g/L) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (20 g/L) to a wet pickup of ca. 75%. At this point, the fabric was stretched back to its original dimensions on pin frames for drying, then for curing. Drying was carried out for 5 min at 100°C and curing for 5 min at 160°C. The samples were then conditioned at 65% relative humidity and 25°C for 48 h before testing for soiling and soil-release properties.

Aqueous Soil

Aqueous soil was prepared as follows: to 10 g of carbon black were added 90 mL distilled water and 1 g dispersing agent (Irgasol DA gran., Ciba-Geigy, Switzerland). This was placed into a stoppered bottle half-filled with glass balls and shook mechanically using a shaking machine for 30 min. The result of this was a smooth, uniform soil mixture. This stock solution was diluted with water so as to have aqueous soil-mixture consisting of aqueous stock soil mixture:water 1:99.¹¹

Nonaqueous Oily Soil

Nonaqueous oily soil was prepared as follows: 10 g of carbon black and 90 g of motor oil were ground in a mortar with a hand pestle until the material were uniformly mixed. Dilute soil dispersions were prepared by diluting the stock mixture with carbon tetrachloride so as to give nonaqueous oily soil consisting of oily stock soil mixture:carbon tetrachloride 1:99.¹¹

Soiling

Fabric samples were padded one dip, one nip through the soil dispersions under a tight squeeze roll pressure. The samples were then dried at ambient conditions.¹¹

Laundering

The soiled samples were laundered at 65°C in a small washing machine (Calor 2000, France) using a solution containing 7.5 g/L detergent (Ariel®, made in France by Procter and Gamble) at a material-to-liquor ratio of 1:100. (Ariel is a synthetic detergent based on perborate builder.) Three washing cycles, 5 min. each, were given followed by three water rinses in the same washing machine.¹¹

Soiling and Soil Removal Measurements¹²

A Beckman Spectrophotometer Model 26 with an integrating sphere adjusted manually to 1 mm opening slit at 700 nm wavelength using an MgSO_4 plate as a reference was employed to monitor the magnitude of soiling and soil removal. Four measurements were made on each side of the sample (10 × 10 cm) to give

a total of eight readings. The latter were averaged to give a single value. All samples were measured against a white background consisting of four layers of filter paper. Since all treated samples and the corresponding controls have essentially equal initial reflectance before soiling, it was decided to use reflectance values as the means of estimating the soil content after soiling and the extent of soil after laundering; thus^{13,14}

$$K/S = (1 - R)^2/2R$$

where R is the reflectance (measured at wavelength 700 nm) and K and S are the absorption and scattering coefficients, respectively.

$$\text{degree of soiling (DS)} = (K/S)_{su} - (K/S)_{uu}$$

$$\text{percentage of soil removal (DSR)} = \frac{(K/S)_{su} - (K/S)_{sw}}{(K/S)_{su} - (K/S)_{uu}} \times 100$$

where $(K/S)_{uu}$ refers to the K/S value for unsoiled unwashed sample, $(K/S)_{su}$ refers to the K/S value for soiled unwashed sample, and $(K/S)_{sw}$ refers to the K/S value for soiled washed sample.

Crease Recovery

A Wrinkle Recovery Tester, T. J. Edwards, Inc., Boston, was used for crease recovery measurement throughout the present work.¹⁵

Tensile Strength

The tensile strength and elongation at break (warp and weft) were measured on the tensile strength testing machine type FMGW 500 (Thuringer Industriewerk, Rauenstein) at 25°C and 65% relative humidity. The results quoted are the means of 10 breaks for each warp and filling with a test length of 20 cm at a constant breaking time of 20 s.

Rating

Samples were evaluated for rating by comparison with the standard samples of "Wash 'n' Wear Standards" of AATCC distributed by T. J. Edwards, Inc., Boston.¹⁶

Moisture Regain

The moisture regain was determined by the vacuum desiccator method with sodium nitrite to give 65% RH at $21 \pm 1^\circ\text{C}$.

Water Imbibition

The water imbibition was determined by impregnating the conditioned samples (65% RH at $21 \pm 1^\circ\text{C}$) in water for 15 min, then centrifuged (4000 rpm) for 10 min. The weight of conditioned sample before impregnation and after

centrifugation were recorded. Water imbibition (WI) was calculated as follows:

$$\text{WI (\%)} = [(A - B)/B] \times 100$$

where A and B are the weights of centrifuged and conditioned samples, respectively.

Drop Disappearance

The drop disappearance was measured by allowing a drop of water to fall on the sample and the time needed for this drop to disappear was then measured.¹⁷

Water Transport

Evaluation of water transport, as a measure of wettability properties of samples under investigation, was carried out as per a reported method.¹⁸

RESULTS AND DISCUSSION

Aqueous Soiling

Samples of polyester/cotton blend were grafted copolymerized to different levels (add-ons) with poly(acrylic acid) and poly(methacrylic acid) using the mutual γ -irradiation technique and the Fe^{2+} - H_2O_2 redox system, respectively. The different copolymers so obtained together with the control (untreated sample) were subjected to soiling with aqueous dispersion of carbon black. Results of the degree of soiling are given in Tables I and II.

It is obvious (Table I) that grafting of the polyester/cotton blend with poly(acrylic acid) reduced the degree of soiling to a considerable degree irrespective of the magnitude of grafting within the range studied. Nevertheless,

TABLE I
Aqueous Soiling and Aqueous Soil Release Properties of Polyester/Cotton Blend Fabric Grafted with Poly(acrylic Acid) before and after Crosslinking with DMDEU (120 g/L) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (20 g/L)^a

Add-on (meq COOH/ 100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	0.531	88.5	0.660	85.4	0.712	80.5
41.66	0.261	76.8	0.594	85.2	0.419	88.5
88.38	0.234	57.9	0.541	93.0	0.342	89.4
139.56	0.356	49.8	0.479	93.1	0.170	86.3
150.00	0.391	46.3	0.399	92.4	0.148	80.8
222.19	0.469	45.4	0.325	88.8	0.142	75.2

^a The mutual irradiation method was used to initiate grafting of poly(acrylic acid) onto the blend.

TABLE II
Aqueous Soiling and Aqueous Soil Release Properties of Polyester/Cotton Blend Fabric Grafted with Poly(methacrylic Acid) before and after Crosslinking with DMDEU (120 g/L) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (20 g/L)^a

Add-on (meq COOH/ 100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	0.531	88.5	0.660	85.4	0.712	80.5
29.83	0.115	57.5	0.706	95.5	0.370	87.7
35.19	0.126	53.5	0.667	92.8	0.375	88.9
52.90	0.152	49.3	0.659	93.6	0.380	88.9
99.95	0.140	39.2	0.635	88.5	0.399	87.7
111.00	0.152	39.8	0.635	85.8	0.414	88.0

^a The Fe^{2+} - H_2O_2 redox system method was used to initiate grafting of poly(methacrylic acid) onto the blend.

the resistance to soiling decreased appreciably by increasing the magnitude of grafting; in full contrast to 100% cotton.³

Table II shows the results of the degree of soiling obtained with blend samples grafted with poly(methacrylic acid) using Fe^{2+} - H_2O_2 redox system. As can be seen, introduction of such a carboxyl-containing polymer in the blend imparts a significant soil resistance property to the blend regardless of the magnitude of grafting, similar to grafting with poly(acrylic acid) using the irradiation technique. However, a comparison between the degree of soiling obtained with the poly(acrylic acid)-blend graft copolymers and poly(methacrylic acid)-blend graft copolymers (Tables I and II) would indicate that: (a) while the degree of soiling increases appreciably by increasing the magnitude of grafting of poly(acrylic acid), it marginally increases by increasing the magnitude of grafting of poly(methacrylic acid) and (b) at roughly equal add-ons the latter copolymers acquired much greater soil resistance than the former. This implies that either the method of grafting or the vinyl moiety of the acid or both play a role in aqueous soiling of the polyester/cotton blend; opposite to 100% cotton.³

The resistance of the blend graft copolymers to aqueous soiling as compared with the control (untreated polyester/cotton blend) could be associated with a decrease in the capillary rise between fibers in the yarn or within interyarn spaces in the fabric. Since the fabric in question is made of two entirely different fibers, i.e., polyester and cotton, the decrease in capillary rise brought about by grafting could be expected to depend upon (a) nature, amount, molecular weight, molecule weight distribution, and frequency of the graft and (b) share of the polyester and cotton components of the blend as a backbone for the graft. Current data (Tables I and II) suggest that with the radiation method, grafting occurs throughout the blend components, i.e., on polyester as well as on cotton, which in turn lead to modification of both components. While modification of the cotton component causes perhaps a decrease in capillary rise,³ modification of the polyester component may bring about an increase by opening up the compact structure of the polyester. Indeed, the decrease in soil resistance by increasing the magnitude of irradiation grafting substantiates this. With the Fe^{2+} - H_2O_2 redox system, grafting would be essentially confined to the cotton component, since

polyester fibers was found to be not amenable to grafting with poly(methacrylic acid) under similar conditions. As a consequence, there is a significant decrease in capillary rise between cotton fibers, which is further assisted by the relatively lower capillary rise of polyester fibers in the blend yarn. This and the higher rate of dissociation of poly(methacrylic acid) as compared with poly(acrylic acid)³ would account for the higher soil resistance properties obtained with poly(methacrylic acid)-blend graft copolymers than poly(acrylic acid)-blend graft copolymers.

When poly(acrylic acid)-blend graft copolymers of relatively low add-ons were crosslinked with DMDEU in the presence and absence of softener, the degree of soiling is enhanced substantially. The opposite holds true for copolymers having relatively high add-ons (Table I). Furthermore, the presence of softener is advantageous in improving the soil resistance properties of the crosslinked copolymers, opposite to the crosslinked control with which presence of softener enhanced the degree of soiling.

Table II shows the effect of DMDEU treatments in the presence and absence of softener on the ability of poly(methacrylic acid)-blend graft copolymers induced by Fe^{2+} - H_2O_2 redox system to pick up aqueous soil. It is clear that crosslinking treatments enhances significantly the degree of soiling of both the untreated blend (control) and the blend copolymers. However, the enhancement in the degree of soiling of the grafted blend by crosslinking is significantly higher than that of the control. Furthermore, the degree of soiling of the grafted blend samples after crosslinking in the absence of softener is significantly higher than in its presence. There is also a tendency that the degree of soiling of the grafted blend samples increases by increasing the magnitude of grafting. At any event, however, the degree of soiling of the grafted blend samples after crosslinking in the presence of softener is significantly lower as compared with the corresponding crosslinked control. In the absence of softener, on the other hand, the degrees of soiling of the crosslinked grafted blend samples are comparable with that of the crosslinked control. An indication of this is that the presence of softener during crosslinking of the said grafted blend samples is advantageous in imparting a good degree of soil resistance to poly(methacrylic acid)-blend graft copolymers, similar to poly(acrylic acid)-blend graft copolymers induced by γ -irradiation.

With the above in mind, it may be concluded that hydrophilization of the surface of the polyester/cotton blend through grafting with carboxyl-containing polymers brings about a significant improvement in soil resistance of the blend, particularly after crosslinking of the grafted blend with DMDEU in presence of nonionic softener, similar to 100% cotton.³

Aqueous Soil Release

Table I shows the soil release properties of blend samples copolymerized with poly(acrylic acid) to different add-ons. The latter are expressed as meq COOH/100 g blend copolymer. It is seen (a) that grafting of the blend with poly(acrylic acid) reduces significantly the ease of soil removal and (b) that the ease of soil removal decreases as the graft add-on increases. The same phenomenon was observed when 100% cotton was grafted with carboxyl-containing polymers.³ Similar results are also obtained when the blend was copolymerized

with poly(methacrylic acid), as shown in Table II. However, the reduction in ease of soil removal exerted by poly(methacrylic acid) is much more than that caused by poly(acrylic acid) even at approximately equal add-ons.

Since the grafted poly(methacrylic acid) is confined to the cotton component in the blend, as already indicated, current data suggest that more hydrophilization of cotton component in the blend through grafting is not suitable at all for imparting soil release characteristics to the blend fabric. Indeed, the reverse occurs and ease of soil removal is seriously impaired. Hydrophilization of both blend components, i.e., cotton and polyester, proved inadequate for improving the soil release characteristics since ease of soil removal is impaired though to a lesser degree as compared with hydrophilization of the cotton component only.

Failure of grafting of carboxyl-containing polymer to polyester/cotton blend suggests that the grafted blend, though it may acquire high affinity to the water than the soil, the blend offers an ideal resting place for the soil. Grafting seems to open up the blend structure, thereby facilitating penetration of soil particles and assessing association and formation of larger soil particles which are difficult to be removed during laundering by virtue of their entrapment between the swollen grafted fibers. This and the possibility that the grafted chains fails in bringing about a balance between hydrophilicity and hydrophobicity in the blend would account for the lower soil release characteristics observed with the grafted samples.

When the control (untreated polyester/cotton blend) was treated with the crosslinking formulation containing DMDEU and $MgCl_2 \cdot 6H_2O$, the soil release characteristics of the blend decreases. A further decrease in the soil release characteristics of the blend occurs upon incorporation of nonionic softener in the crosslinking formulation. On the other hand, when the grafted blend samples were given similar treatments, soil release characteristics are enhanced significantly. Even in the presence of softener, substantial soil removal is observed with the grafted samples (Tables I and II). Crosslinking seems to create a sort of balance between hydrophilicity and hydrophobicity in the blend, thereby improving the soil release characteristics. Since the control does not show any improvement, and indeed crosslinking impairs its soil release properties, and since the improvements in soil release characteristics are very significant in case of grafted samples, it is possible to state that crosslinking increases the energy of the grafted blend-soil interface than the energy of the control-soil interface.

A close examination of the data given in Tables I and II indicate that polyester/cotton blend fabric grafted with poly(acrylic acid) using the irradiation method exhibited better soil release properties than blend fabric grafted with poly(methacrylic acid) using $Fe^{2+}-H_2O_2$ redox system at roughly the same add-on. This is observed before crosslinking. After crosslinking the soil release properties of both graft copolymers are comparable. Furthermore, crosslinking masks the differences in soil release properties caused by variation in the magnitude of the add-on to a great extent, and the presence of the graft in the blend diminishes the adverse effect of the softener.

Nonaqueous Oily Soiling

Table III shows the effect of grafting of polyester/cotton blend with acrylic

TABLE III

Nonaqueous Oily Soiling and Nonaqueous Oily Soil Release Properties of Polyester/Cotton Blend Fabric Grafted with Poly(acrylic Acid) before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L)^a

Add-on (meq COOH/ 100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	1.306	87.2	1.306	88.9	1.473	60.8
41.66	0.753	97.7	0.719	97.9	1.135	86.3
88.38	0.715	92.8	0.632	97.5	1.058	95.5
139.56	0.715	85.6	0.674	93.3	0.985	90.8
150.00	0.662	86.1	0.615	92.6	0.902	87.3
222.19	0.653	87.4	0.456	87.9	0.746	84.8

^a The mutual irradiation method was used to initiate grafting of poly(acrylic acid) onto the blend.

acid using the mutual irradiation grafting on the susceptibility of the blend to nonaqueous oily soiling. It is obvious that attachment of polyacrylic acid to the backbone of the blend components via grafting exerts a considerable influence on the soiling properties of the blend. The degree of soiling of the grafted blend is lower than that of the control (untreated polyester/cotton blend). There is also a tendency that the degree of soiling decreases as the extent of grafting increases. A similar situation is encountered when the blend was grafted with methacrylic acid using the $Fe^{2+}-H_2O_2$ redox system (Table IV). This indicates that the introduction of carboxyl-containing polymers in the blend structure accentuates the ionization properties of the blend, and, as a result, a considerable resistance to the soil is imparted to the blend.

However, a close examination of the data of Tables III and IV would reveal that, at approximately the same extent of grafting, the resistance to nonaqueous oily soil obtained with blend graft copolymers induced by chemical initiation is higher than those induced by irradiation; in contrast with hundred percent cotton.³ This reflects differences in the distribution of the graft within the blend

TABLE IV

Nonaqueous Oily Soiling and Nonaqueous Oily Soil Release Properties of Polyester/Cotton Blend Fabric Grafted with Poly(methacrylic Acid) before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L)^a

Add-on (meq COOH/ 100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	1.306	87.2	1.306	88.9	1.473	60.9
29.83	0.752	49.5	0.935	91.4	1.089	78.2
35.19	0.572	31.5	0.917	94.1	1.060	70.9
52.90	0.522	29.5	1.060	91.9	1.089	70.5
99.95	0.530	30.8	0.917	88.9	1.075	69.0
111.00	0.575	30.0	0.998	88.7	1.025	63.5

^a The $Fe^{2+}-H_2O_2$ redox system method was used to initiate grafting of poly(methacrylic acid) onto the blend.

components, molecular weight, molecular weight distribution, frequency of branching, and site of attachment as well as location of the grafted polymer. In case of chemical initiation, it is likely that only the cotton component is amenable to grafting since 100% polyester was not susceptible to grafting under the chemical initiation conditions used. On the contrary, both cotton and polyester could be grafted with acrylic acid using the mutual irradiation method. Hence it can be assumed that in grafting of the polyester/cotton blend using the chemical initiation method, grafting is confined to the cotton component in the blend whereas grafting occurs on both components when the mutual irradiation method was used. With this in mind, it is apparent that the magnitude of physical changes in the blend components occurring during grafting are greater in case of irradiation than in case of the chemical initiation. That is, the ability of the irradiation-induced blend graft copolymers to swell and, therefore, to accommodate soil is more than its mate induced by the chemical means. Nevertheless, the contribution of the methyl groups in the acrylic acid molecule in case of poly(methacrylic acid)-blend graft copolymers in differences in resistance to nonaqueous oily soil cannot be ruled out.

Table III and IV show that the situation is reversed after treatment of the grafted blend samples with DMDEU and $MgCl_2 \cdot 6H_2O$ in the absence and presence of the nonionic softener. A slight improvement in resistance to nonaqueous oily soiling is observed with blend graft copolymers induced by irradiation after these copolymers have been crosslinked in absence of softeners. On the other hand, blend graft copolymers induced by the chemical method show decreased resistance to nonaqueous oily soiling after crosslinking under similar conditions. This suggests that the advantageous effect of chemically initiated grafting on cotton component in the blend is offset by crosslinking whereas irradiation-induced grafting on both blend components permits the grafted polymer on the polyester component to function as a soil-resistant agent. It is understandable that the crosslinking reaction is confined to the cotton component. This is even observed after crosslinking in the presence of softener. Despite the fact that the latter enhances soiling significantly irrespective of the substrate used, yet blend graft copolymers induced by irradiation show the lowest degree of soiling. At any event, however, the enhancement of soiling by the presence of softener could be associated with accentuation of the area of contact between the soil particles and the blend fabric; a soft fiber surface enables soil particles to get embedded in.

Oily Soil Release

Table III shows that grafting of the polyester/cotton blend with poly(acrylic acid) causes substantial improvement in the ease of soil removal provided that the add-on is low. Higher add-ons tend to reduce this improvement and, indeed, blend samples with higher add-ons acquire soil release characteristics comparable with those of the control. At lower add-on, graft chains seem to lie flat on the dry surface of the blend fiber, resulting in protection to the fiber, masking the strong adsorption forces between the fiber and oily soil. On putting in water, these side chains spread away from fiber being mobile and thus assist in soil removal. That assistance of soil removal by the graft is diminished and/or offset at high add-ons suggest that mobility of the grafted chains decreases as the graft

yield (add-on) increases; blend graft copolymers with higher add-ons within the range studied ought to lead to tightness of the blend structure. It is rather possible that, at lower add-on, the grafted blend acquires a balance between hydrophilicity and oleophobicity and this balance is disturbed by increasing the amount of graft (add-on).

Crosslinking of the blend samples grafted with poly(acrylic acid) using a crosslinking formulation consisting of DMDEU and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ causes further improvements in the soil release properties of blend graft copolymers having relatively low add-ons and accentuates those of higher add-ons, though the sample with the highest graft add-on shows comparable percent soil removal with the crosslinked control (Table III). Indication of this is that crosslinking of the grafted blend improves the balance between hydrophilicity and oleophobicity of the grafted blend. The incorporation of nonionic softener in the crosslinking formulation decreases the soil release characteristics of the crosslinked grafted blend fabrics. Nevertheless, the latter acquire much higher soil release properties irrespective of their add-ons as compared with the control treated under similar conditions, but the effect of increasing the magnitude of grafting on lowering the ease of soil removal still persists.

Table IV shows the oily soil release properties of blend samples grafted with poly(methacrylic acid) to different add-ons using Fe^{2+} - H_2O_2 redox system. It is clear that the grafted samples acquire a lower percent soil removal than the untreated blend. Furthermore, the percent soil removal decreases as the add-on increases, unlike grafting with poly(acrylic acid) using the mutual irradiation method. Since, as already indicated, grafting occurs essentially on the cotton component in the blend in case of grafting with poly(methacrylic acid) using the Fe^{2+} - H_2O_2 redox system, it is reasonable to assume that the balance of hydrophilicity and oleophobicity is significantly disturbed. As a result, difficulty in soil removal is encountered. This is not the case with mutual irradiation grafting, where the graft is formed on both blend components, i.e., on cotton and polyester as mentioned above.

Crosslinking of blend-poly(methacrylic acid) graft copolymers using a crosslinking formulation consisting of DMDEU and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ enhances significantly the percent soil removal of the grafted blend samples (Table IV). This implies that the hydrophilicity of the cotton component in the blend decreases by crosslinking and a balance between hydrophilicity and oleophobicity is conferred on the grafted blend fabric. Incorporation of nonionic softener in the crosslinking formulation decreases considerably the ability of the grafted blend samples to release the oily soil. However, the soil release properties of the grafted samples are still better than the control sample crosslinked under similar conditions.

It should be emphasized that the adverse effect of the nonionic softener was observed when 100% cotton was grafted with poly(acrylic acid) and poly(methacrylic acid) using the mutual irradiation and the Fe^{2+} - H_2O_2 redox system methods, respectively.³ In the case of similar grafting of poly(methacrylic acid) to the polyester/cotton blend fabric where grafting occurs exclusively on the cotton component, the same adverse effect of the softener is significant. On the other hand, with blend-poly(acrylic acid) graft copolymers, in which grafting occurs on both cotton and polyester, the effect of the softener is not significant. This necessitates consideration of the influence of the occurrence of the graft

on the entire blend component, the molecular weight and molecular weight distribution, and site and frequency of branching as well as the changes in the blend surface brought about by mutual irradiation grafting on the nonionic softener. Good distribution of the graft throughout the entire blend surface seems to compensate for the adverse effect of nonionic softener.

Some Properties Of Poly(methacrylic Acid)-Blend Copolymers before and after Crosslinking

Table V shows the effect of grafting of polyester/cotton blend fabric with poly(methacrylic acid) on some properties of the fabric before and after durable press treatment. It is seen that the water transport and drop disappearance decrease while moisture regain and water of imbibition increase by grafting poly(methacrylic acid) to the blend fabric. The decrement in water transport and drop disappearance suggests that the copolymer swells spontaneously, and, as a result, water transport and drop disappearance are impeded. This is not the case with water regain and water of imbibition, where enough time is given for the water to penetrate into the grafted copolymer. Indeed, the enhancement in water regain and water of imbibition by increasing the magnitude of grafting substantiates this.

The crease recovery of the blend fabric decreases by grafting the latter with poly(methacrylic acid), indicating that the introduction of the graft into the cotton component of the blend reduces the ability of the blend to recover. The graft adversely affects stabilization of the blend structure by virtue of its amorphous nature since no tension is applied during grafting. Indeed the observed decrease in wash and wear rating as well as enhancement in elongation at break (Table V) support this. Moreover, the tensile strength remains almost intact after grafting, a point which reflects the significant enhancement in elongation at break. The elongation at break of the cotton component becomes close to that of the polyester component after grafting. As a result the expected lower tensile strength of grafted cotton component is not observed since it is compensated for by the improved elongation at break.

Table V shows that durable press treatment exerts a considerable influence on the aforementioned properties with certainly that the onset of grafting on these properties still persists. Durable press treatment enhances the water transport and decreases drop disappearance, moisture regain, and water of imbibition. The decrements in the latter properties is unequivocally due to the decreased accessibility of the cotton component of the blend by the durable press (crosslinking) treatment. On the other hand, the enhancement in water transport by crosslinking of the polyester/cotton blend before and after being grafted could be explained as follows.¹⁹ Water transport phenomenon would be expected to rely on (a) capillary or porosity of the fiber and (b) the interaction of water molecules with the molecular structure of the fiber; these can be termed capillary hydrophilicity and intrinsic hydrophilicity, respectively. Water rises rapidly in the capillary of the fiber if the latter acquires little intrinsic hydrophilicity. In the noncrosslinked blend fabric, water goes up along the capillary and also interacts with the hydroxyl groups of the cotton component through hydrogen bonding.²⁰ As a result of this interaction, the movement of water is retarded,

TABLE V
Effect of Grafting of Polyester/Cotton Blend Fabric with Poly(methacrylic Acid) on Some Properties of the Fabric before and after Crosslinking with DMDEU (120 g/L) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (20 g/L)^a

Treatment	Add-on (meq COOH/ 100 g blend)	Water trans- port (s)	Drop disap- pearance (s)	Moisture regain (%)	Water imbibition (%)	Crease recovery (warp + filling) (°)	Rating	Warp tensile strength (kg)	Elongation at break (%)
Before	—	15	5	3	11	257	3	59	11.9
cross- linking	29.83	14	8	3.7	13.2	230	3	60	20.0
	52.90	13	6	4.5	20.2	222	2.5	61	19.5
	111.00	13	6	4.7	24.2	224	2.0	59	22.0
After	—	10	7	2.2	9.8	310	4.5	56	8.5
cross- linking	29.83	10	9	3.6	12.0	294	4.5	52	18.0
	52.90	12	7	4.4	14.8	278	4.1	52	18.0
	111.00	12	7	4.5	17.0	274	4.0	51	20.5

^a The Fe^{2+} - H_2O_2 redox system method was used to initiate grafting of poly(methacrylic acid) onto the blend.

and hence the rise of water in case of noncrosslinked fabric takes longer than in the case of crosslinked fabric.

As expected, durable press treatment brings about significant improvement in crease recovery and durable press rating while decreasing the tensile strength and elongation at break (Table V). This is observed with the grafted and non-grafted blends. However, the improvement in crease recovery and wash and wear rating is lower with grafted than the nongrafted blend, indicating a lower degree of crosslinking with the grafted blend. The presence of the graft seems to impede reaction of DMDEU with the cotton cellulose component of the blend by blocking some of the cellulose hydroxyls.

Tensile strength of the grafted blend is also lower than the nongrafted blend after crosslinking. This suggests that the grafted cotton of the blend undergoes more molecular degradation during the durable press treatment under the effect of catalyst and heat of curing than the nongrafted cotton since, as already pointed out, the grafted cotton acquires less crosslinks than the nongrafted cotton of the blend. It is well established that strength losses are due to crosslinking and factors associated with as well as molecular degradation of cotton.^{21,22} With respect to elongation at break (Table V), it is observed that crosslinking causes a substantial reduction in elongation at break. This is rather a direct consequence of the rigidity conferred on the cotton and grafted cotton component of the blend by crosslinking. Nevertheless, still persistent is the finding that the grafted blend samples acquire higher elongation at break than the nongrafted blend sample.

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