

Vapor-Phase Grafting of Methyl Acrylate on Fiber Surfaces Treated with Aqueous Dispersions of Metal Oxides

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Synopsis

Textile fabrics of cotton, wool, nylon, polyester, acrylic, and polyolefin pretreated with aqueous dispersions of photosensitive metal oxides (antimony, tin, titanium, and zinc oxide) were exposed to methyl acrylate vapors with simultaneous ultraviolet irradiation ($>3100 \text{ \AA}$) for up to 2 hr. The metal oxides acted either as effective photosensitizers, causing increased polymer grafting on the fiber surface, or as photoabsorbers causing a net decrease in grafting compared to unsensitized photografting. Metal oxide-induced grafting occurred more readily on hydrophilic fibers and was accompanied by less homopolymer formation, in comparison to grafting on more hydrophobic fibers. Antimony and tin oxides were more effective on hydrophilic fibers, while zinc oxide was more effective on hydrophobic fibers. Titanium dioxide was essentially ineffective as a photosensitizer. The sensitized grafting process was studied in relationship to irradiation and monomer flow time, the degree of homopolymer formation accompanying grafting, the nature of the metal oxide and polymer graft on the fiber surface, and the reflectance characteristics of the metal oxide-treated fabrics.

INTRODUCTION

Suspensions of photosensitive metal oxides have been shown to initiate polymerization of vinyl and acrylic monomers in solution when exposed to ultraviolet radiation in the presence of traces of oxygen and water.¹⁻⁵ Although numerous metal oxides are effective photosensitizers,⁵ zinc oxide¹⁻⁴ has received the most attention. Divergent opinions as to the nature of the initiating radicals present in zinc oxide-sensitized polymerization have been presented. However, work by Yamamoto and Oster⁴ has indicated that hydroxyl radicals coming from decomposition of hydrogen peroxide are responsible for initiation of polymerization in this case. In a related area, metal oxides applied to fibers can cause photo-induced oxidative degradation of the fiber⁶⁻⁹ through formation of free-radical species. Since photosensitive metal oxides can cause photosensitized free-radical attack on fibers, and at the same time initiate vinyl or acrylic polymerization, metal oxides should be capable of initiating photosensitized graft polymerization on the surface of fibers.

Requirements for metal oxide-induced graft polymerization would be fulfilled in a system in which aqueous dispersions of metal oxide were applied directly to the fiber surface, followed by irradiation of the treated fiber in the presence of monomer vapors. In this paper, we report the sensitized photopolymerization of methyl acrylate onto the surface of six basic fiber types (cotton, wool, nylon, polyester, acrylic, and polyolefin) using aqueous disper-

sions of antimony oxide, tin(IV) oxide, titanium dioxide, and zinc oxide as photoinitiators.

EXPERIMENTAL

Materials and Reagents

All fabrics except wool used in this study were obtained from Testfabrics, Inc., and washed in 60°C water containing 0.1% sodium lauryl sulfate prior to use. The fabrics were as follows: acrylic, Acrilan Type 156, #955; cotton, 80 × 80 print cloth, #400W; nylon, spun type 200, #358; polyester, Dacron Type 54, #754-W; polypropylene, Herculon Type 40. Wool fabric was obtained from Burlington Industries and was 1 × 1 plain weave worsted. Monomers, wetting agents, and other reagents were Aldrich, Baker, Eastman, or PCR, Inc. chemicals and were used without further purification. Hydroquinone was added to the monomer prior to introduction into the bubbler system. The metal oxide powders were Baker-Analyzed reagents and were used without further purification.

Vapor-Phase Grafting Procedure

Fabric samples (3 × 6 in.) were thoroughly wet out in a 1% aqueous suspension of metal oxide (antimony, tin(IV), titanium (anatase), or zinc oxide) for 1 min. After passage through a laboratory pad to remove excess liquid, the fabric was stapled to a wire screen. The screen was placed in a 4-liter resin kettle equipped in the center with a Pyrex cold finger containing a 200-W Hanovia high-pressure mercury arc. Two gas inlets and outlets were in the top of the reactor.

The distance from the source to the fabric surface under these conditions was 6 cm. Nitrogen was bubbled through the neat monomer and into the reactor from 15 min to 2 hr while the samples were simultaneously irradiated with light. Throughout the irradiation, the temperature in the reactor remained <35°C. The intensity of light at 6 cm remained essentially constant over the photografting study with 102 $\mu\text{W}/\text{cm}^2$ falling on the fabric surface from wavelengths between 300 and 400 nm and 1.6 $\mu\text{W}/\text{cm}^2$ for wavelengths below 300 nm.

After irradiation, the samples were removed from the reactor, washed in 1% aqueous acetic acid, 60°C tap water, and 30°C distilled water, and conditioned prior to weighing to determine total polymer uptake. Homopolymer was extracted from the samples with benzene. Examination of extracted homopolymer by IR revealed that the homopolymers were essentially free of fiber substrate. Reaction conditions for the photografting experiments, the percentage uptake of grafted polymer, and selected properties of the photografted products are listed in Tables I-VI.

Analytical Methods

The tensile properties of warp yarns from control and polymer grafted wools were determined by ASTM procedure D-2256-66T. Color measure-

TABLE I
Grafting on Hydrophilic Fibers^a

Fiber	Metal oxide		% Uptake of poly-(methyl acrylate) ^b		
	Type	% Uptake	Graft	Homo-polymer	Graft/homopolymer
Cotton	—	—	3.2	0.0	—
Cotton	antimony	2.3	9.3	0.6	15.5
Cotton	tin	1.0	10.0	1.8	5.5
Cotton	titanium	1.0	1.9	0.6	3.2
Cotton	zinc	0.6	8.6	1.5	5.7
Wool	—	—	27.6	0.0	—
Wool	antimony	1.7	37.9	0.0	—
Wool	tin	2.3	25.4	0.0	—
Wool	titanium	0.7	21.9	0.0	—
Wool	zinc	1.0	10.9	0.8	16.0
Nylon	—	—	7.5	3.7	2.0
Nylon	antimony	5.2	4.7	1.5	3.1
Nylon	tin	2.4	28.5	4.5	6.3
Nylon	titanium	3.5	1.9	0.8	2.2
Nylon	zinc	4.5	7.2	3.2	2.4

^a All photografting carried out for 2 hr from 6-cm distance using a Pyrex-filtered 200-W mercury arc and a 10 cc/sec flow rate of methyl acrylate vapor into the reactor.

^b Corrected for metal oxide still present on the fiber.

TABLE II
Grafting on Hydrophobic Fibers^a

Fiber	Type	% Uptake	% Uptake of poly-(methyl acrylate) ^b		
			Graft	Homo-polymer	Graft/homopolymer
Acrylic	—	—	0.0	0.0	—
Acrylic	antimony	2.6	1.1	0.1	11.0
Acrylic	tin	2.7	0.0	0.0	—
Acrylic	titanium	0.8	0.2	0.2	1.0
Acrylic	zinc	2.0	1.0	5.1	0.2
Polyester	—	—	0.3	0.0	—
Polyester	antimony	5.4	0.5	0.0	—
Polyester	tin	1.5	2.9	0.0	—
Polyester	titanium	2.5	2.2	0.0	—
Polyester	zinc	3.3	3.4	1.2	2.8
Polyolefin	—	—	0.3	0.0	—
Polyolefin	antimony	2.3	0.0	0.3	—
Polyolefin	tin	1.9	0.3	0.5	0.6
Polyolefin	titanium	1.1	0.0	0.0	—
Polyolefin	zinc	1.8	1.5	4.3	0.3

^a All photografting carried out for 2 hr from 6-cm distance using Pyrex-filtered 200-W mercury arc and a 10 cc/sec flow rate of methyl acrylate vapor carried by nitrogen.

^b Corrected for metal oxide still present on fiber.

TABLE III
Properties of Treated Cottons

Metal oxide		Exposure conditions ^a	% Polymer graft	Flexural rigidity <i>G</i> , mg/cm ²	Tensile Properties of Yarn		
Type	% Uptake				Tensile strength, g	% Elongation at break	Energy to break, g-cm
—	—	—	—	56	300 ± 52	7.2 ± 0.7	77 ± 23
—	—	B	3.2	121	272 ± 45	8.1 ± 1.3	60 ± 16
Tin	1.0	—	—	178	267 ± 54	6.2 ± 1.1	53 ± 19
Tin	1.0	A	—	120	307 ± 36	8.5 ± 1.1	75 ± 14
Tin	1.0	B	10.0	213	279 ± 42	7.5 ± 0.9	63 ± 16
Zinc	0.6	—	—	121	292 ± 54	8.2 ± 1.3	70 ± 19
Zinc	0.6	A	—	115	305 ± 20	8.3 ± 1.1	71 ± 11
Zinc	0.6	B	8.6	128	272 ± 45	8.3 ± 1.6	59 ± 18

^a A, Light only; B, light and monomer.

TABLE IV
Properties of Treated Wools

Metal oxide		Exposure conditions ^a	% Polymer graft	Flexural rigidity <i>G</i> , mg/cm ²	Tensile Properties of Yarn		
Type	% Uptake				Tensile strength, g	% Elongation at break	Energy to break, g-cm
—	—	—	—	95	327 ± 33	29 ± 3	652 ± 164
—	—	B	27.6	291	423 ± 40	42 ± 4	818 ± 127
Tin	2.3	—	—	181	417 ± 44	31 ± 4	641 ± 155
Tin	2.3	A	—	184	443 ± 51	36 ± 4	782 ± 162
Tin	2.3	B	25.4	376	472 ± 58	39 ± 4	929 ± 188
Zinc	1.0	—	—	173	432 ± 41	30 ± 5	690 ± 163
Zinc	1.0	A	—	173	406 ± 33	33 ± 5	654 ± 152
Zinc	1.0	B	10.9	205	456 ± 42	36 ± 5	796 ± 202

^a A, Light only; B, light and monomer.

TABLE V
Properties of Treated Nylons

Metal oxide		Exposure conditions ^a	% Polymer graft	Flexural rigidity <i>G</i> , mg/cm ²	Tensile properties of yarn		
Type	% Uptake				Tensile strength, g	% Elongation at break	Energy to break, g-cm
—	—	—	—	21	779 ± 73	54 ± 5	1823 ± 320
—	—	B	7.5	94	861 ± 106	52 ± 6	1900 ± 381
Tin	2.4	—	—	60	762 ± 112	52 ± 7	1646 ± 505
Tin	2.4	A	—	59	803 ± 82	53 ± 4	1792 ± 349
Tin	2.4	B	28.5	345	774 ± 165	49 ± 4	1624 ± 343
Zinc	4.5	—	—	174	825 ± 84	52 ± 8	1690 ± 389
Zinc	4.5	A	—	56	716 ± 151	54 ± 6	1676 ± 381
Zinc	4.5	B	7.2	101	832 ± 102	52 ± 3	1752 ± 238

^a A, Light only; B, light and monomer.

TABLE VI
Properties of Polyesters, Acrylics, and Polyolefins

Zinc oxide % Uptake	Ex-posure condi- tion ^a	% Polymer graft	Flexural rigidity <i>G</i> , mg/ cm ²	Tensile strength, g	% Elongation at break	Energy to break, g-cm
Polyester						
—	—	—	283	872 ± 144	32 ± 4	1045 ± 275
3.3	—	—	320	864 ± 116	35 ± 3	1046 ± 190
3.3	A	—	308	923 ± 111	37 ± 2	1168 ± 199
3.3	B	3.4	170	870 ± 60	44 ± 2	1183 ± 113
Acrylic						
2.0	—	—	92	778 ± 47	16 ± 1	560 ± 48
2.0	A	—	86	718 ± 76	15 ± 1	526 ± 90
2.0	B	1.0	295	736 ± 61	16 ± 1	530 ± 46
Polyolefin						
—	—	—	412	2079 ± 149	38 ± 2	3471 ± 431
1.8	—	—	313	1937 ± 232	36 ± 4	3321 ± 755
1.8	A	—	372	2103 ± 142	37 ± 4	3404 ± 587
1.8	B	1.5	1722	2133 ± 228	49 ± 4	4574 ± 940

^a A, Light only; B, light and monomer.

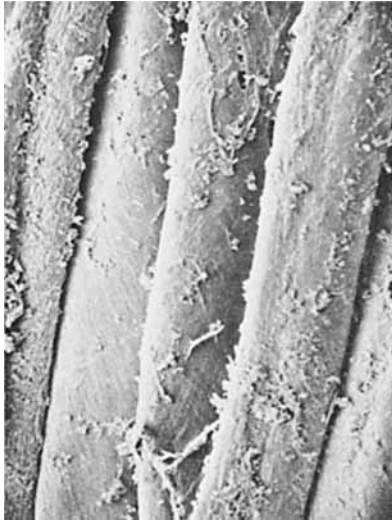
ments were made with a Beckman Ultraviolet-Visible DB Spectrophotometer equipped with a reflectance head over a wavelength range of 300 to 700 nm and with a standardized Gardner XL10 Color Difference Meter with values expressed in Rd, a, b color coordinates. Scanning electron microscopy of samples was determined using a Cambridge Stereoscan Mark II, operated in the secondary mode at 5 kV and magnifications of 580–1230×. The sample specimens were cut from the center of the fabrics, coated on both sides with gold, cemented to the specimen stub with conductive cement, and recoated with gold.

RESULTS AND DISCUSSION

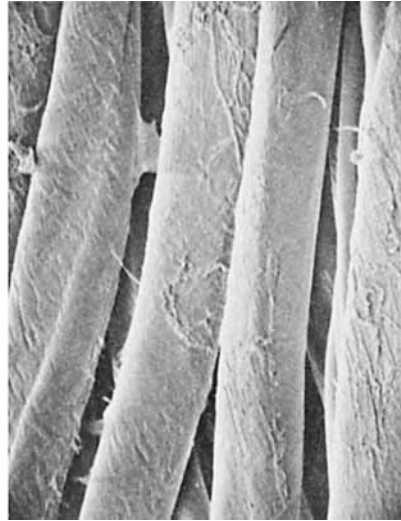
Grafting of Methyl Acrylate—General Considerations

Fabrics treated with aqueous dispersions of metal oxides gave 0–38% grafts of poly(methyl acrylate) (Tables I and II). Untreated fabrics that absorbed significant quanta of light above 3100 Å, and that are readily wet out by water, were found to act as photosensitizers themselves, thereby leading to significant graft uptakes of poly(methyl acrylate) with limited accompanying homopolymerization (Tables I and II). Fiber-sensitized grafting occurs most readily on wool and nylon and slightly on cotton. There was little grafting on the other synthetic fibers, probably due to their inability to be wet and swollen by water.

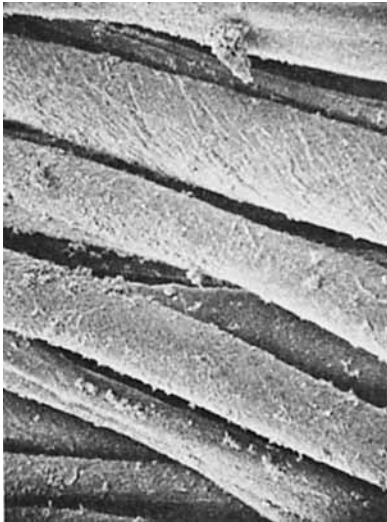
The amount of metal oxide deposited on the fiber surfaces from aqueous dispersion appears to be dependent on the interaction of the particular metal oxide–fiber combination. Nylon (Table I) and polyester (Table II) have the



(a)



(b)



(c)



(d)

Fig. 1 (continued)

highest degree of metal oxide deposition, and antimony was deposited most heavily on the fiber surfaces. Scanning electron micrographs of the metal oxide-coated fibers revealed relatively even distribution of the oxides on the fiber surfaces. Examples of tin and zinc oxide deposition on selected fibers appear in Figure 1. Zinc oxide is removed from cotton as well as the other fibers by the dilute acetic acid wash (Figs. 1a, 1b), whereas the other metal oxides used in the study are not and final grafts had to be corrected for metal oxide content. Both tin and zinc oxide are somewhat irregularly deposited on cotton (Figs. 1a, 1c). They are more evenly deposited on wool, nylon, and

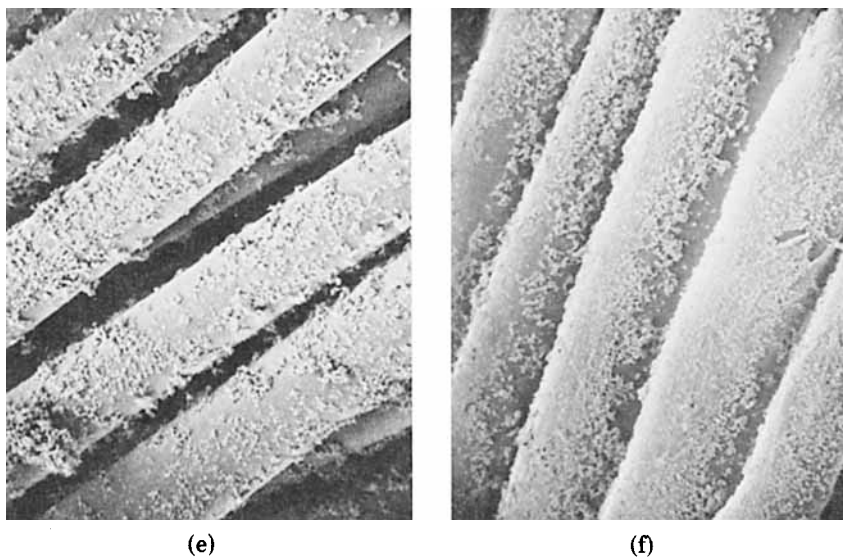


Fig. 1. Scanning electron micrographs of fabric samples treated with 1% aqueous dispersions of metal oxides. (a) Cotton with 0.6% zinc oxide (1210 \times). (b) Sample (a) after washing in dilute acetic acid (1090 \times). (c) Cotton with 1% tin(IV) oxide (1175 \times). (d) Wool with 2.3% tin(IV) oxide (615 \times). (e) Nylon with 4.5% zinc oxide (1230 \times). (f) Polyester with 2.5% tin(IV) oxide (1100 \times).

polyester (Figs. 1d, 1e, 1f), although the undersides of the fibers are not coated in some instances (Fig. 1f).

The metal oxides cause little fiber degradation on the wet fabrics during irradiation up to 2 hr, suggesting poor metal oxide-fiber interaction. However, the metal oxides acted either as effective photosensitizers enhancing vapor-phase grafting of methyl acrylate on the fibers or as photoabsorbers inhibiting grafting on the fibers. The metal oxides tended to effectively photo-initiate some grafting on the hydrophobic fibers studied (acrylic, polyester, and polyolefin), whereas the metal oxides showed more variable sensitizing properties on the hydrophilic fibers (cotton, wool, nylon). Nevertheless, the overall uptake of grafted polymer on hydrophilic fibers always tended to be much greater than on hydrophobic fibers. In most instances, the ratio of grafting to homopolymer formation was >5 . However, zinc oxide tended to lead to extensive homopolymerization compared to the other metal oxides. Comparison of reflectance spectra of untreated and metal oxide-treated fabrics reveals only small significant differences in the reflectance characteristics of these fabrics below 380 nm, and no relationship exists between the relative light absorption of the fabric from 300 to 380 nm and the degree of grafting. Therefore, it appears that photosensitization or photoshielding of the fibers by metal oxide is highly dependent on the fiber-metal oxide combination grafted.

Grafting of Methyl Acrylate on Cotton

The metal oxides with the exception of titanium dioxide caused more extensive grafting of poly(methyl acrylate) on cotton than found when untreated

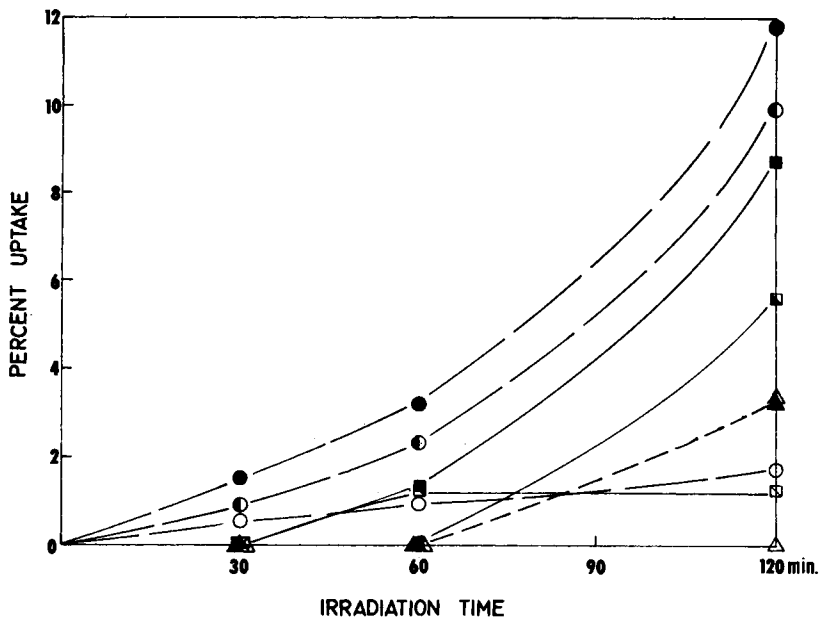


Fig. 2. Effect of irradiation time on the percentage uptake of poly(methyl acrylate) on control and tin(IV) and zinc oxide-treated cotton: (---) control; (—) tin(IV) oxide; (—) zinc oxide; (●, ■, ▲) total polymer uptake; (○, □, △) graft uptake; (○, □, △) homopolymer.

ed cotton was exposed to methyl acrylate vapors (Table I). The presence of metal oxide caused significant homopolymer formation, but the degree of homopolymer formation was much less than grafting in each case. Antimony oxide resulted in a high degree of grafting with less homopolymerization, compared to tin and zinc oxides. However, there was no correlation between the degree of grafting and the amount of oxide on the cotton, or the respective reflectance spectra of the fabrics.

The effect of irradiation time on unsensitized grafting and grafting in the presence of tin oxide and zinc oxide was studied in detail (Fig. 2). Unsensitized grafting of poly(methyl acrylate) on cotton proceeded after a 60-min induction period, with slow grafting occurring without significant accompanying homopolymerization up to the end of the 2-hr irradiation period. In the presence of tin oxide, grafting proceeded without an induction period, and became more rapid with time up to the end of irradiation. Homopolymer formation did not increase markedly after the initial radiation period. With zinc oxide, grafting occurred after an induction period and was accompanied by extensive homopolymer formation. In this study on cotton, the two metal oxides appeared to lower the induction period for photopolymerization, but in the process caused limited homopolymer formation.

Also, the location of grafted polymer was affected by the presence of metal oxide in these photografting processes on cotton (Fig. 3). Unsensitized grafting leads to deposition of polymer without significant change in the appearance of the cotton fiber surface (Fig. 3a). Either very even disposition of polymer on the surface has occurred, or the polymer is deposited under the fiber surface. Metal oxide-treated cotton samples were essentially unaffec-

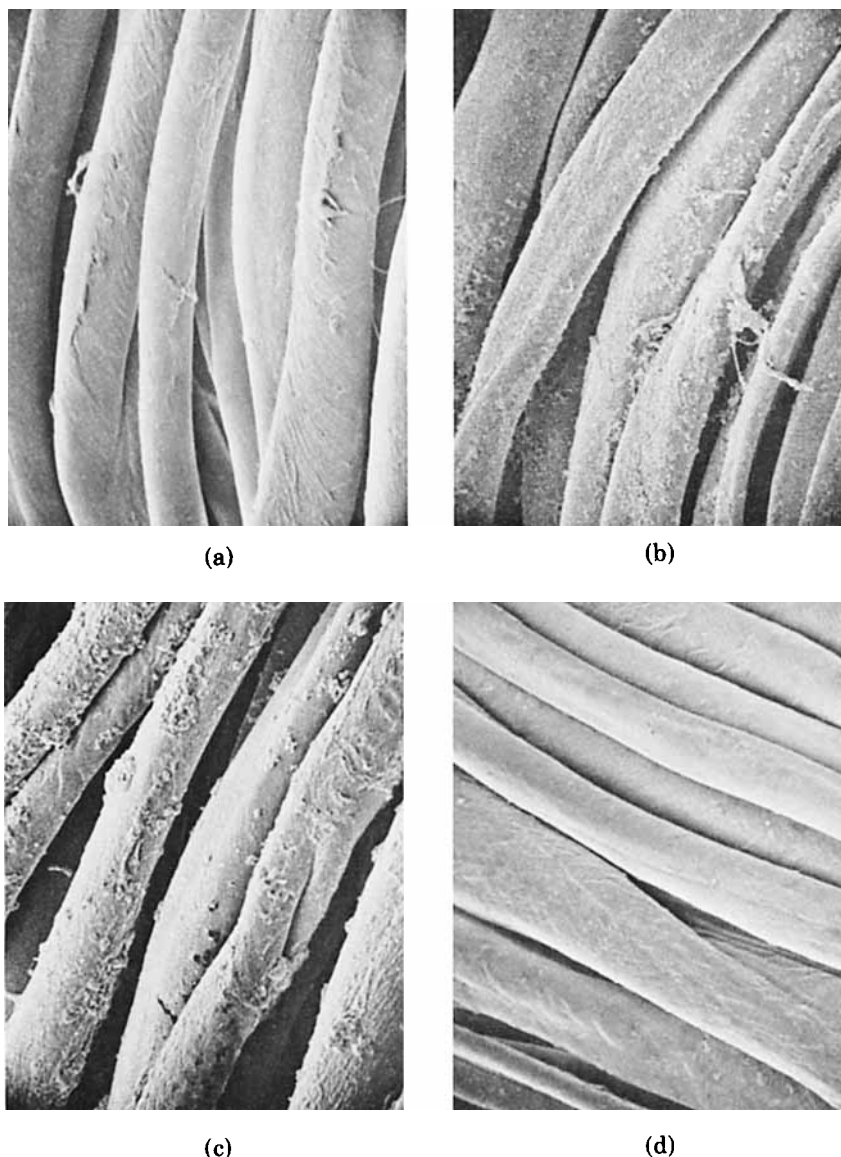


Fig. 3. Scanning electron micrographs of grafted cotton samples. (a) wet-out cotton grafted with 3.2% poly(methyl acrylate) (1060 \times). (b) Tin(IV) oxide-treated cotton grafted with 10.0% poly(methyl acrylate) (1225 \times). (c) Zinc oxide-treated cotton grafted with 7.4% poly(methyl acrylate) (1000 \times).

ed when exposed to light only, although residual metal oxide, such as tin oxide, could still be seen (Fig. 3b). Photolysis in the presence of methyl acrylate vapor yielded a 10.0% irregular graft nucleating from the fiber surface of the tin oxide-treated sample (Fig. 3c), whereas an even graft of 7.4% poly(methyl acrylate) occurred, with essentially no metal oxide remaining, when zinc oxide was used (Fig. 3d). The zinc oxide is removed readily by the dilute acid wash following grafting, since the graft apparently does not encapsulate the zinc oxide particles.

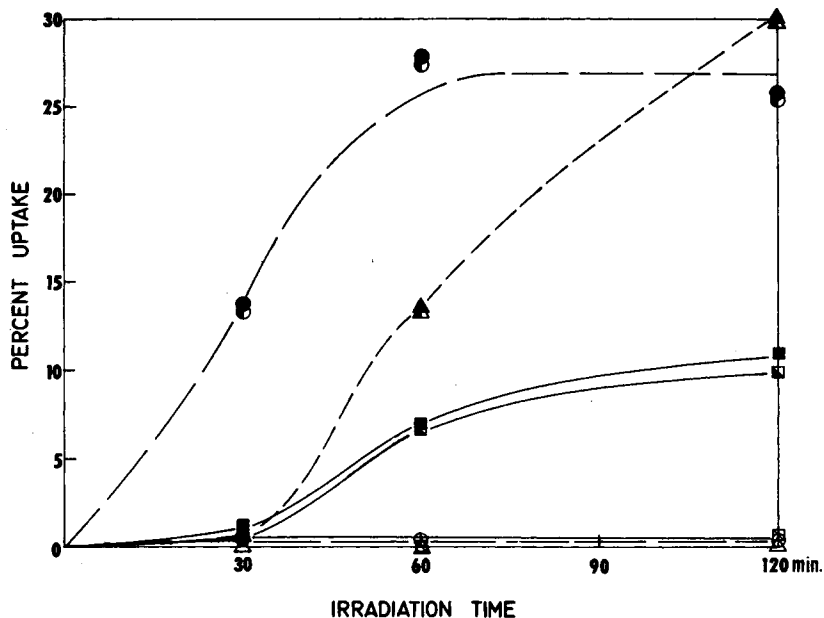


Fig. 4. Effect of irradiation time on the percentage uptake of poly(methyl acrylate) on untreated and tin(IV) and zinc oxide-treated wool: (---) untreated wool; (---) tin(IV) oxide-treated; (—) zinc oxide-treated.

The flexural rigidities and tensile properties of untreated tin and zinc oxide-treated samples before and after grafting and light exposure were examined (Table III). Although treatment with the metal oxides caused the cotton to increase in flexural rigidity, and tin oxide caused possible deterioration of tensile properties, light exposure and subsequent washing of the sample with dilute acid had essentially no effect on these properties for metal oxide-treated samples, other than to return the fabric to properties more nearly like those of untreated cotton. Untreated and zinc oxide-treated cotton grafted samples with essentially no poly(methyl acrylate) nucleating from the fabric surface had lower flexural rigidities than cotton grafted using tin oxide sensitizer in which polymer nucleated from the surface. However, the polymer location had little effect on the overall tensile properties of the cotton.

Grafting of Methyl Acrylate on Wool

Wool was readily photografted with methyl acrylate vapors in the presence or absence of metal oxide, with only antimony oxide providing a higher degree of grafting than found with unsensitized wool (Table I). Zinc oxide was the only metal oxide to cause a significant decrease in the amount of poly(methyl acrylate) grafted to the wool, and was also the only metal oxide that caused significant homopolymer formation.

Study of the effect of irradiation time on grafting for control and tin oxide- and zinc oxide-treated fibers indicated that tin oxide greatly shortened the induction period (Fig. 4). At the same time, tin oxide caused the grafting to

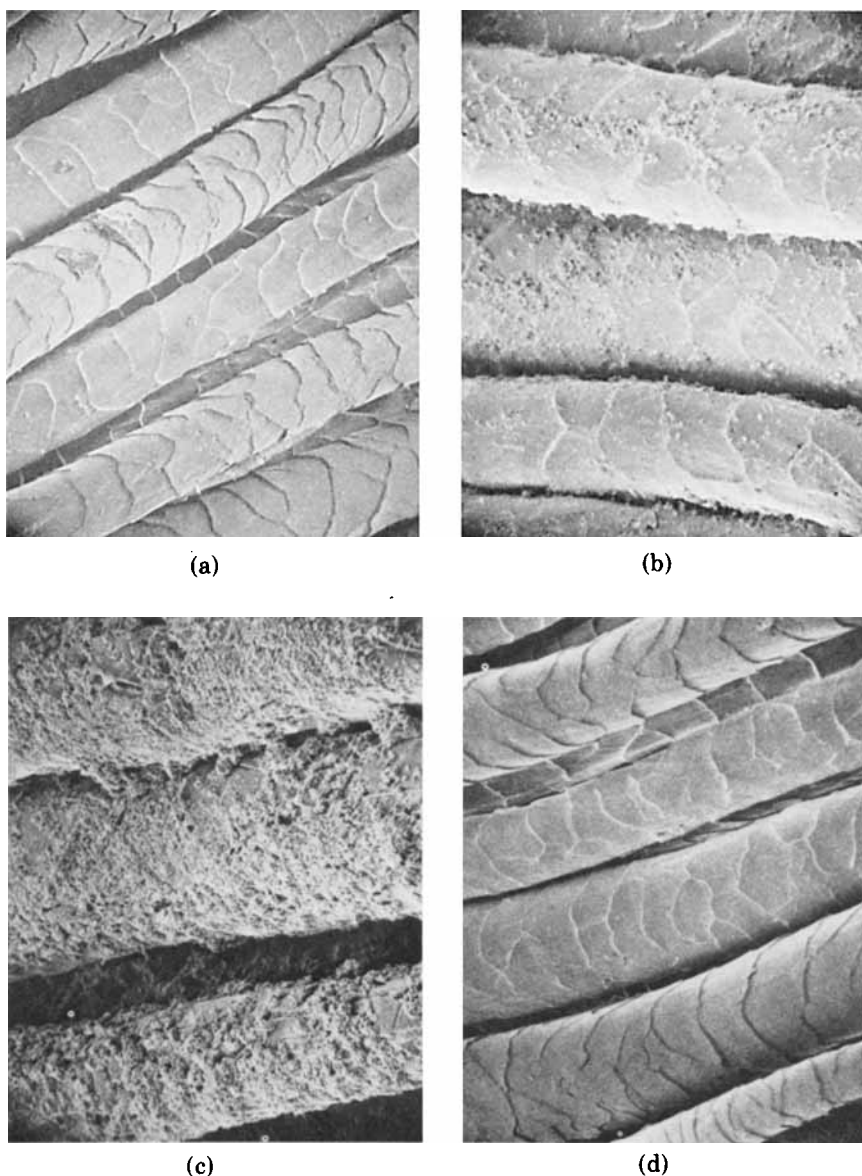


Fig. 5 Scanning electron micrographs of grafted wool samples. (a) Wet-out wool grafted with 27.6% polymer (580 \times). (b) Tin oxide-treated wool exposed to light for 2 hr (1190 \times). (c) Tin oxide-treated wool grafted with 25.4% polymer (640 \times). (d) Zinc oxide-treated wool grafted with 10.0% polymer (580 \times).

level off over the 60-min irradiation period. Zinc oxide-treated wool underwent an induction period similar to that of untreated fabric before grafting occurred. Following the induction period, rate of grafting was much slower for zinc oxide-treated wool, with the rate of grafting leveling off after 60 min. After the initial induction period, untreated wool underwent rapid grafting, and at the end of the 2-hr irradiation time studied, an increasingly rapid rate of grafting was still indicated.

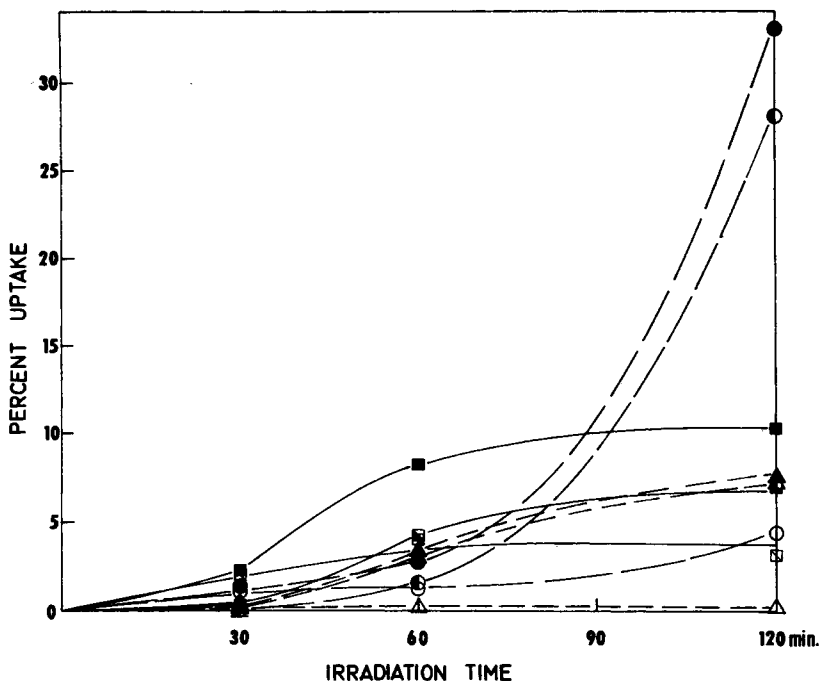


Fig. 6. The effect of irradiation time on the percentage uptake of poly(methyl acrylate) on untreated and tin(IV) and zinc oxide-treated nylon: (---) untreated nylon; (—) tin(IV) oxide-treated; (—) zinc oxide treated.

Examination of scanning electron micrographs of the wool samples indicated the nature of the grafting process on wool (Fig. 5). The surface of wet-out grafted wool (Fig. 5a) is essentially unchanged by the high graft. Although some deposition of polymer was evident on the surface, a majority of the polymer graft resided under the surface of the wool. Whereas irradiation of tin oxide-treated wool has little effect on the wool in the absence of monomer (Fig. 5b), extensive graft polymer formation was evident (Fig. 5c) nucleating from the wool surface with some interfiber bonding between fibers. Tin oxide selectively confined grafting to the fiber surface. No graft is seen on the surface of zinc oxide-treated wool, indicating that the lower graft uptake (Fig. 5d) is due to photoshielding and reduction of the fiber-induced grafting, rather than to zinc oxide-induced grafting.

Untreated grafted wool has a moderate increase in flexural rigidity and some change in tensile properties (Table IV). The wool yarns are stonger, have significantly higher elongations at break, and exhibit higher total energies to break indicating that poly(methyl acrylate) deposited in the wool strengthens the fibers somewhat and causes them to become more elastic. Deposition of poly(methyl acrylate) on the wool surface, using tin oxide, results in a higher flexural rigidity as well as improved tensile properties. Zinc oxide-treated grafted fabrics have a correspondingly smaller effect on the properties of the wool. The presence of metal oxide on the wool surface had only a small effect on the stiffness of the fabric and tensile strength, and there was no particular change on exposure of these treated wools to light.

Grafting of Methyl Acrylate on Nylon

Only tin oxide caused a significant increase in grafting of poly(methyl acrylate) on nylon, compared to untreated nylon (Table I). The other metal oxides either had no effect on the degree of grafting or significantly decreased grafting. Significant homopolymerization occurred on both untreated and metal oxide-treated nylon, with tin oxide having the highest ratio of grafted

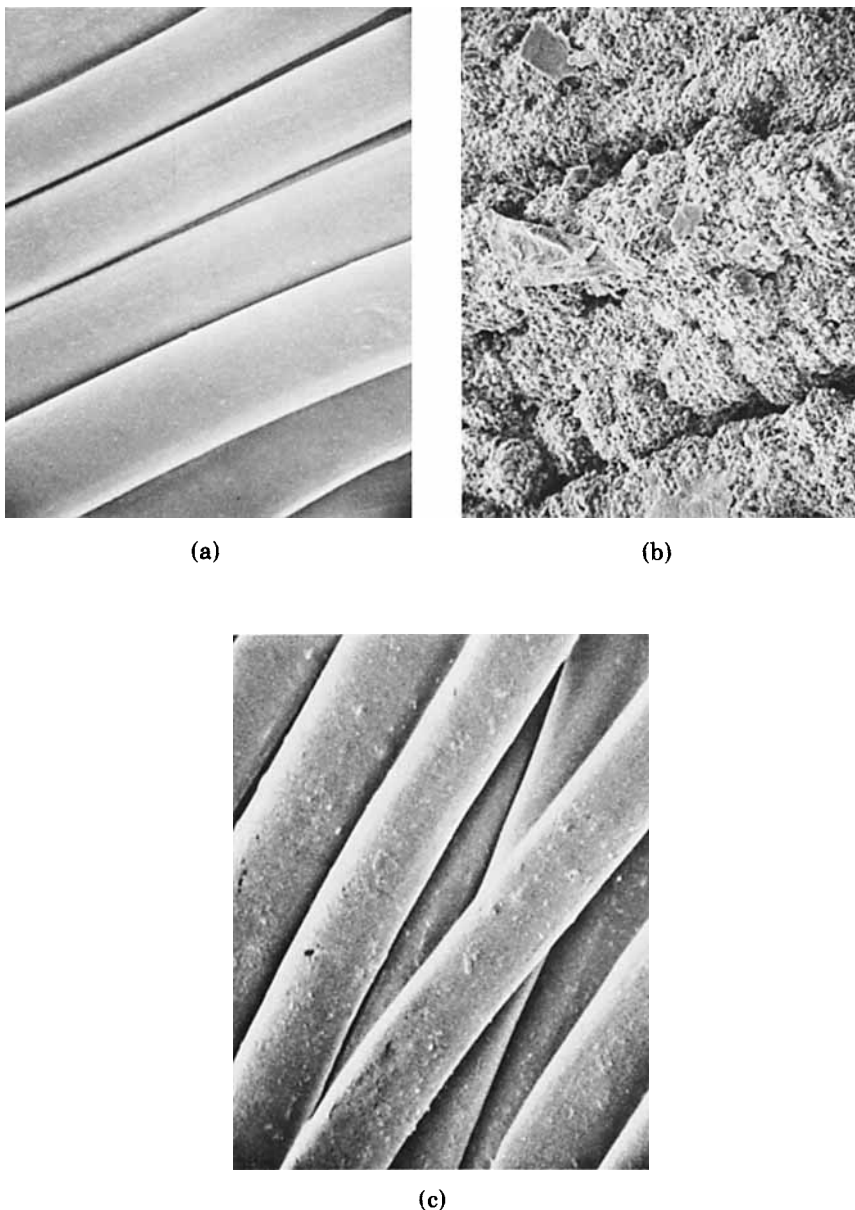
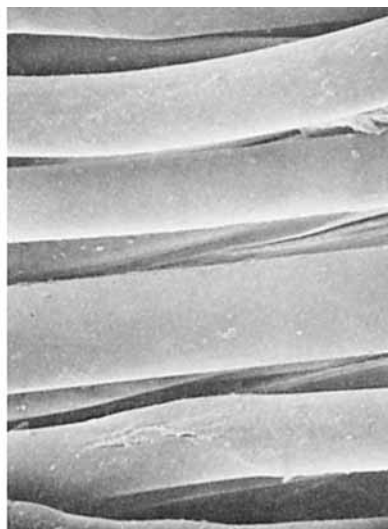


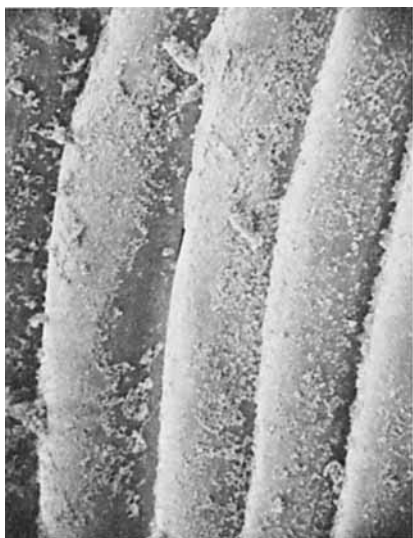
Fig. 7. Scanning electron micrographs of grafted nylon samples. (a) Wet-out nylon grafted with 7.5% polymer (1050 \times). (b) Tin oxide-treated nylon grafted with 28.5% polymer (690 \times). (c) Zinc oxide-treated nylon grafted with 7.2% polymer (1100 \times).



(a)



(b)



(c)



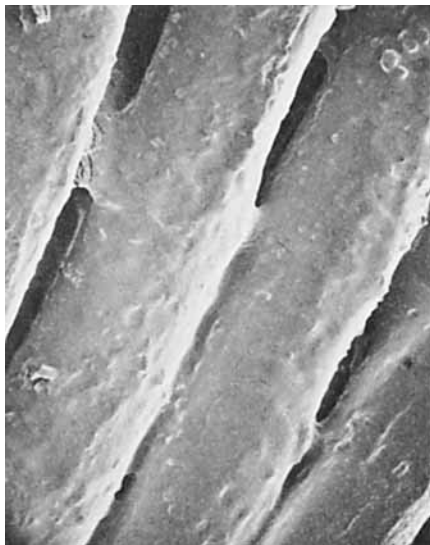
(d)

Fig. 8 (continued)

polymer to homopolymer. The inherent structure of nylon was such that it contributes to initiation of homopolymerization.

Grafting on untreated as well as tin oxide- and zinc oxide-treated samples occurred after an induction period (Fig. 6). With both metal oxide-treated nylons, grafting leveled off quickly after 60 min, whereas the rate of grafting on untreated nylon increased over the 2-hr reaction period studied.

Scanning electron microscopy (Fig. 7) of the untreated grafted nylon indicates even deposition of poly(methyl acrylate) (Fig. 7a) on or under the surface of the nylon. Nylon treated with tin oxide and grafted with 28.5% poly(methyl acrylate) (Fig. 7b) has a rather uneven graft of polymer nucleating



(e)

Fig. 8. Scanning electron micrographs of selected grafted polymer, acrylic, and polyolefin samples. (a) Zinc oxide-treated acrylic grafted with 1.1% polymer (930 \times). (b) Polyester grafted with 0.3% polymer (1000 \times). (c) Tin oxide-treated polyester grafted with 2.9% polymer (1070 \times). (d) Zinc oxide-treated polyester grafted with 3.4% polymer (970 \times). (e) Zinc oxide-treated polyolefin grafted with 1.8% polymer (950 \times).

from the nylon surface with noticeable interfiber bonding where the polymer coating has grown together. In addition, the presence of ungrafted material not removed on extraction is seen on the fiber surface. Grafted zinc oxide-treated nylon has an irregular surface, due to zinc oxide crystals imbedded in the polymer matrix on the fiber surface (Fig. 7c).

The nature and location of the graft on nylons are reflected in the flexural rigidity and tensile properties of the treated samples. Whereas unsensitized, grafted nylon had essentially no increase in flexural rigidity and in yarn tensile properties, surface-grafted nylon initiated with tin(IV) oxide has a 15-fold increase in flexural rigidity and essentially unchanged tensile properties. The zinc oxide-treated grafted sample has properties very much like those of grafted untreated nylon. Also, light exposure alone has little effect on the nylon.

Grafting on Polyester, Acrylic, and Polyolefin

Since this study was made using aqueous dispersions of metal oxides, it would be expected that the more hydrophobic fibers, such as polyester, acrylic, and polyolefin, would be grafted less readily than the more hydrophilic fibers studied, due to the lack of wetting and swelling of hydrophobic fibers by water. A lower degree of grafting of poly(methyl acrylate) was found for untreated polyester, acrylic, and polyolefin fibers than for the hydrophilic fibers studied; however, often the metal oxide markedly increased the degree of grafting on the hydrophobic fibers, although extensive homopolymer was

formed when zinc oxide was used. Polyester was more readily grafted in the presence of metal oxide by this technique than was acrylic or polyolefin.

Scanning electron micrographs of selected grafted hydrophobic fibers (Fig. 8) showed that the grafted poly(methyl acrylate) was essentially confined to the fiber surface. For example, when zinc oxide was used to graft 1.1% poly(methyl acrylate) on acrylic fiber (Fig. 8a), the polymer could be seen on the fiber surface, with thin strands of grafted polymer appearing between fibers. Irregular deposition of polymer was observed on untreated polyester (Fig. 8b). On both tin oxide-treated (Fig. 8c) and zinc oxide-treated (Fig. 8d) polyester, grafted polymer and metal oxide were evident on the fiber surface. The surface deposition of poly(methyl acrylate) on zinc oxide-treated polyolefin (Fig. 8e) was quite evident, with an extensive coating of polymer containing embedded zinc oxide crystals on the polyolefin surface accompanied by extensive interfiber bonding.

The surface deposition of polymer also tended to affect the flexural rigidity and tensile properties of the treated fabrics, as evidenced by the samples from oxide-induced grafting. Although grafted zinc oxide-treated polyester had a decrease in flexural rigidity, a marked increase in the energy to break was noted. With grafted zinc oxide-treated acrylic and polyolefin where interfiber bonding was quite evident, large increases in flexural rigidities were noted. Although the tensile properties of the acrylic samples were essentially unchanged, the grafted polyolefin, having more extensive surface coating and interfiber bonding, had a significant increase in both breaking elongation and energy to break.

CONCLUSIONS

Aqueous dispersions of photosensitive metal oxides present on the surface of textile fibers induce grafting of methyl acrylate vapor on the fibers when they are exposed to ultraviolet irradiation ($>3100 \text{ \AA}$). The degree of grafting and accompanying homopolymerization is dependent on the fiber type and the metal oxide used with, hydrophilic fibers being more readily grafted than hydrophobic fibers. In some instances, where wet-out fibers that absorb into the near ultraviolet are irradiated in the absence of metal oxide, significant grafting on the fiber surface occurs. Also in such cases, application of aqueous metal oxide dispersion often causes a net decrease in photografting, and tends to localize the polymer on the fiber surface. Previous studies of photo-induced reactions in the presence of metal oxides¹⁻⁹ have indicated that the reactions can proceed via chemical or energy transfer mechanisms. Although the exact nature of initiation of grafting with these metal oxides cannot be determined from this study, it is unlikely that grafting proceeds via a simple energy transfer mechanism due to the limited interaction possible between the photo-excited metal oxide crystal and the fiber surface and the semiconducting properties of certain of the metal oxides used. Therefore, there is a strong possibility that initiation occurs *via* photosensitized formation of hydrogen peroxide on the metal oxide surface followed by desorption and subsequent photolysis of hydrogen peroxide to form radicals. Radicals formed by this means could lead to abstraction of hydrogen from the fiber surface and subsequent grafting of poly(methyl acrylate) at these sites.

References

1. M. C. Markham and K. J. Laidler, *J. Phys. Chem.*, **57**, 363 (1953).
2. J. C. Kuriacase and M. C. Markham, *J. Phys. Chem.*, **65**, 2232 (1961).
3. A. Bernas, *J. Phys. Chem.*, **68**, 2047 (1964).
4. M. Yamamoto and G. Oster, *J. Polym. Sci. A-1*, **4**, 1683 (1966).
5. A. A. Kachan and V. A. Shrubovich, *Ukr. Khim. Zh.*, **32**, 105 (1966).
6. G. S. Egerton and K. M. Shah, *Text. Res. J.*, **38**, 130 (1968).
7. H. A. Taylor, W. C. Tincher, and W. F. Hamner, *J. Appl. Polym. Sci.*, **14**, 141 (1970).
8. G. Irick, Jr., *J. Appl. Polym. Sci.*, **16**, 2387 (1972).
9. J. F. Rabek, *Photochem. Photobiol.*, **7**, 5 (1968).

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