Vinyl Graft Polymerization-Induced Modification of Some Properties of Poly(ethylene Terephthalate) Fabric

A. HEBEISH, S. E. SHALABY, and A. M. BAYAZEED, *National Research Centre, Dokki, Cairo, Egypt*

Synopsis

Polymerization of glycidyl methacrylate (GMA), methyl methacrylate (MMA), and acrylic acid (AA)/styrene (St) mixtures with poly(ethylene terephthalate) (PET) fabric to different polymer add-ons was performed. Moisture regain, dyeability, and soiling properties of the modified PET were examined. It was found that introduction of poly(GMA) in PET structure brings about (a) improved moisture regain, (b) enhanced dyeing with disperse dyes, (c) affinity and possible dyeing with acid, direct, and reactive dyes, (d) improved aqueous and nonaqueous oily soil resistance, and (e) decreased ease of soil removal. The magnitude of moisture regain, dyeability, and soiling properties are dependent upon the percent of polymer add-on. Polymerization of MMA with PET improved the dyeability of the latter with the disperse dye as well as its resistance to nonaqueous oily soil while decreasing the resistance to aqueous soiling and ease of both aqueous and nonaqueous soil removal. In the case of PET polymerized with poly(AA/St), there was a considerable enhancement in moisture regain, dyeing with the disperse dye, and resistance to aqueous and non-aqueous oily soiling. On the other hand, both aqueous and nonaqueous soil characteristics of PET were imparted by polymerization of the latter with AA/St mixtures.

INTRODUCTION

Graft copolymerization of vinyl monomers on poly(ethylene terephthalate) (PET) fibers has gained importance in incorporating desirable properties, and a lot of work has been done on such grafting.[1-10] In previous papers,[11-14] factors affecting polymerization of methyl methacrylate (MMA), acrylic acid (AA), glycidyl methacrylate (GMA), and acrylic acid/styrene (AA/St) mixture with PET and the general kinetics of the reactions involved have been reported.

The present work was undertaken with a view of studying the effect of polymerization of GMA, MMA, and AA/St mixture with PET fabric on some properties of the latter. Properties examined include (a) moisture regain, (b) dyeability, and (c) soiling and soil release.

EXPERIMENTAL

The parent PET fabrics and the grafted fabrics were the same as reported in previous papers.[11-14] Procedures for polymerization of various vinyl monomers with PET fabrics were based essentially on those described in Refs. 11–14.

Four different dyestuffs, namely, Polar Brilliant Red 3BN (C.I. Acid Red 131), Congo Red (C.I. Direct Red 28), Procion Brilliant Red M2B (C.I. Reactive Red 1) and Samaron Blue H3R (C.I. Disperse Blue 152), were used without purification.

Determination of Moisture Regain

The dry samples were conditioned at 65% relative humidity, at 30°C, and weighed. They were then oven dried at 105°C for 4 h and weighed again:

$$\text{Moisture regain \%} = \frac{(\text{wt conditioned sample}) - (\text{wt dry sample})}{\text{wt dry sample}} \times 100$$

Aqueous Soil

Aqueous soil prepared as follows[15]: 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 shaken 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 an aqueous soil mixture consisting of aqueous stock soil mixture: water 1:99.

Nonaqueous Oily Soil

Nonaqueous oily soil was prepared as follows[15]: 10 g of carbon black and 90 g of motor oil were ground in a mortar with a hand pestle until the materials 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 an oily stock soil mixture:carbon tetrachloride 1:99.

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.[15]

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 France) at a material-to-liquor ratio of 1:100. Three washing cycles, 5 min each, were given, followed by three water rinses in the same machine.[15]

Soiling and Soil Removal Measurements[16]

A Beckman Spectrophotometer Model 26 with an integrating sphere, adjusted normally to a 1-mm opening slit at a 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 had essentially equal initial reflectance before soiling, it was decided to use the re-

flectance value as the means of estimating the soil content after soiling and the extent of soil removal after laundering as follows[17,18]:

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

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

Dyeing Procedures

Acid dye: Fabric samples were immersed in a dye bath prepared to give 2% shade in presence of Glauber salt (3%). The pH of the dye bath was adjusted to 2.5 by sulphuric acid. The dyeing was carried out at 80°C for 1 h using a material-to-liquor ratio of 1:200. The dyed fabrics were treated with boiled water for 15 min, then soaped for 15 min at 100°C in a bath containing 2% soap.

Direct dye: Fabric samples were immersed in a dye bath which was prepared to give 3% shade in presence of Glauber salt (3%). The dyeing was carried out at 100°C for 1 h using a material-to-liquor ratio 1:200. The dyed fabrics were treated with boiled water for 15 min, and then soaped for 15 min at 100°C in a bath containing 2% soap.

Reactive dye: Fabric samples were immersed in a dye bath prepared to give shade 4% in presence of glauber salt (3%). The dyeing was carried at 25°C for 90 min using a material-to-liquor ratio of 1:200. The dyed fabrics were treated with boiled water for 15 min, and then soaped for 15 min at 100°C in a bath containing 2% soap.

Disperse dye: Fabric samples were immersed in a dye bath prepared to give shade 5% in presence of Irgasol DA Gran (Ciba-Geigy) as a dispersing agent and Remol P as a carrier. The dyeing was carried at 95°C for 30 min using a material-to-liquor ratio of 1:200. The dyed fabrics were washed with water at the boil for 30 min, and then soaped for 30 min at 100°C in a bath containing 2% soap.

Color Measurement

Color strength, expressed as K/S, was calculated from reflectance measurements and the Kubelka–Munk equation.[18] A Beckman Spectrophctometer, Model 26, integrating sphere system, UV-visible analytical system was used. Color strength values were calculated as follows:

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

where R is the reflectance and K and S are the absorption and scattering coefficients, respectively.

RESULTS AND DISCUSSION

Moisture Regain

Table I shows the moisture regain of PET fibers before and after polymerization with GMA, AA, St, and AA/St mixture (60:40). It is seen that there is a substantial improvement in moisture regain after polymerization with GMA, AA, and AA/St. This could be associated with hydrophilization of the PET by the polymer-containing carboxylic groups, and the epoxy group itself or the epoxy ring which has been opened in part during washing[13] via the addition of H_2O molecules to the free epoxy ring. Besides this, propping apart of surfaces of the PET elementary fibrils by the grafted polymer would lead to a more open structure, thereby facilitating accommodation of water. This is rather substantiated by the findings that PET polymerized with poly(styrene) aquires higher moisture regain than PET despite the hydrophobic nature of polystyrene and that the moisture regain increases with increasing the percent polymer add-on in the case of acrylic acid/styrene mixture.

Dyeability

The behavior of PET fabric samples polymerized with various vinyl monomers towards different dyestuffs were examined. Table II shows the ability of PET polymerized with poly(GMA) to dye with acid, direct, reactive, and disperse dyes. It is seen that (a) regardless of the dye used, the color strength (expressed in K/S) is greater with the PET fabric polymerized with poly(GMA) than with the untreated PET fabric, (b) the color strength increases by increasing the percent polymer add-on, and (c) the nature of dye determines the magnitude of color strength.

It is understandable that acid, direct, and reactive dyes cannot dye PET fabric. The slight coloration obtained with untreated PET fabric upon application of these dyes is regarded as only staining. However, when PET fabric was poly-

TABLE I

Effect of Polymerization of Glycidyl Methacrylate, Acrylic Acid, Styrene, and Acrylic Acid/ Styrene Mixture with PET Fabrics on Moisture Regain

Sample	Polymer add-on (%)	Moisture regain (%)
Untreated PET	—	0.30
Glycidyl methacrylate grafted	9.50	0.40
	16.00	0.76
	28.00	1.15
	46.10	1.95
	149.80	2.04
Acrylic acid grafted	1.66	0.45
Styrene grafted	19.20	0.37
Acrylic acid/styrene mixture (60:40) grafted	3.60	0.35
	4.40	0.57
	14.80	0.93
	28.00	1.01
	60.00	1.18
	101.14	1.66

TABLE II
Ability of PET Fabric Polymerized with Poly(GMA) to Dyeing with Acid, Direct, Reactive Dyes, and Disperse Dyes

Polymer add-on (%)	Acid dye[a] K/S	Direct dye[b] K/S	Reactive dye[c] K/S	Disperse dye[d] K/S
Zero (untreated PET)	0.0876	0.1078	0.0741	0.7310
1.5	0.1531	0.1551	0.1005	0.8270
5.2	0.1807	0.5300	0.1189	0.8580
28.6	0.8970	0.5590	0.1876	0.8860

[a] Polar brilliant red 3BN (C.I. Acid Red 131).
[b] Congo red (C.I. Direct Red 28).
[c] Procion brilliant red (C.I. Reactive Red 1).
[d] Samaron blue H3R (C.I. Disperse Blue 152).

merized with poly(GMA), appreciable color could be achieved by virtue of opening up the PET structure together with the presence of the functional epoxide ring in poly(GMA). Ring opening seems to occur under the influence of ionic species, permitting interchange with a proton of the dye substituents. This state of affairs would be expected to depend upon the availability of the epoxide groups which, in turn, depend upon the percent polymer add-on. Besides this, other important factors such as ability of the dye to compete with water in opening the ring of the epoxide groups under the conditions of dyeing will influence the magnitude of color strength. This would explain differences in color strength of acid, direct and reactive dyes on PET fabric polymerized with poly(GMA) as well as the enhancement in color strength by increasing the percent polymer add-on (Table II).

Table II (last column) shows that polymerization of PET fabric with GMA prior to dyeing with the disperse dye enhances the color strength substantially. It is well known that disperse dyes are the proper dyestuffs for dyeing of PET fabric. It is also likely that the poly(GMA) is present in an amorphous state because no tension is applied during polymerization. Hence easier dyeing of this polymer, which is distributed in the entire PET fibers, would be expected.

Table III shows the effect of polymerization of MMA and a mixture of AA/St (60:40) with PET fabric prior to dyeing on the dyeability of the fabric with the disperse dye. As is evident, the dyeability of the fabric improves significantly

TABLE III
Effect of Polymerization of Methylmethacrylate and Acrylic Acid/Styrene Mixture (60:40) with PET Fabric on Behavior of the Latter to the Disperse Dye

Sample	Polymer add-on (%)	K/S
Untreated PET	—	0.7310
Methyl methacrylate grafted	1.6	0.9680
	2.8	1.0390
	12.2	1.0060
	28.7	1.2120
Acrylic acid/styrene mixture (60:40) grafted	29.8	1.6240
	47.3	2.6700
	65.4	4.3700

by polymerization of the said monomers to PET fabric prior to dyeing. Furthermore, the color strength increases as the percent add-on increases. This is rather in conformation with the results discussed above and could be explained on similar lines. Nevertheless, a comparison between the results obtained with GMA, MMA, and AA/St mixtures (Tables II and III) at roughly equal percent polymer add-on would indicate that the color strength follows the order AA/St mixture > MMA > GMA. That is, polymerization of AA/St mixture with PET fabrics prior to dyeing exerts the most favorable influence on the ability of PET to dye with disperse dye while GMA causes the least improvement in dyeability. This reflects differences in swellability (due to opening up of the PET structure) brought about by the introduced polymers. Besides differences in nature of the latter, their molecular weight distribution and frequency of branching on the PET backbone may differ considerably. Current data suggest that such differences play an important role in dyeing the samples with the disperse dye.

Aqueous Soiling

Table IV shows the degree of aqueous soiling of PET fabric polymerized with poly(GMA), poly(MMA), and poly(AA/St). It is seen that polymerization of PET with GMA and AA/St mixture reduced the degree of soiling, being dependent upon the magnitude of the polymer add-on. Increasing the latter is accompanied by a reduction in the ability of PET fabric to pick up the aqueous soil. On the other hand, polymerization of MMA with PET fabric decreases considerably the resistance of PET to aqueous soiling.

Improvements of soil resistance observed with PET polymerized with poly(GMA) or with poly(AA/St) as compared with the untreated PET fabric could be associated with a decrease in the capillary rise between fibers in the yarn or within interyarn spaces in the fabric. The decrease in capillary rise brought about by polymerization would be expected to depend upon the nature, amount, molecular size, molecular weight distribution, and frequency of the introduced polymer on PET backbone. This implies that the affinity of the introduced polymer to the soil and its effect on the surface energy of PET fabric would play an important role in soiling. Indeed, this seems to be the case and will account

TABLE IV
Aqueous Soiling Properties of PET Polymerized with Poly(GMA), Poly(MMA), and Poly(AA/St)

Sample	Polymer add-on (%)	DS	SR (%)
Untreated PET	—	0.49	94.69
Glycidyl methacrylate grafted	1.50	0.40	93.79
	5.20	0.34	90.69
	28.61	0.31	71.95
Methyl methacrylate grafted	1.62	0.66	85.54
	2.80	0.66	87.09
	12.20	0.75	69.88
	28.65	0.50	68.65
Acrylic acid/styrene mixture (60:40) grafted	29.80	0.12	86.47
	47.30	0.20	83.25
	65.40	0.25	80.03

for the differences in ability of PET polymerized with different polyvinyl polymers to pick up the soil. At roughly equal percent polymer add-on, the degree of soiling follows the order PET–poly(AA/St) < PET–poly(GMA) < untreated PET < PET–poly(MMA).

Thus, polymerization of PET with GMA or with AA/St mixture enhances the aqueous soil resistance of PET by decreasing capillary rise as well as decreasing the surface energy of PET during soiling with aqueous soiling by virtue of their hydrophilic character. A different situation was encountered when PET was polymerized with poly(MMA). The latter seems to increase the surface energy of PET during aqueous soiling and offsets the advantages brought about by the decrease in capillary rise.

Aqueous Soil Release

Table IV shows the effect of polymerization of GMA, MMA, and AA/St mixture with PET fabric on ability of the latter to release the aqueous soil. It is seen that (a) polymerization of PET fabric with the said monomers reduces considerably the ease of soil removal and (b) the ease of soil removal decreases as the percent polymer add-on increases in accordance with previous work on polyester/cotton blend fabric.[19] This suggests that PET fabric after polymerization offers an ideal resting place for the soil. Introduction of the vinyl polymer in PET seems to open up the structure of the latter, thereby facilitating penetration of the soil particles and assessing association and formation of larger soil particles, which are difficult to be removed during laundering.

Nonaqueous Soiling

Table V shows the effect of polymerization of GMA, MMA, and AA/St mixture with PET on the susceptibility of the latter to nonaqueous oily soil. It is clear that polymerization of these monomers or the monomer mixture with PET enhances the resistance of PET to nonaqueous oily soiling. Moreover, the resistance to soiling increases by increasing the percent polymer add-on. This is obtained irrespective of the monomer used. However, AA/St mixture proves

TABLE V
Nonaqueous Soiling Properties of PET Polymerized with Poly(GMA), Poly(MMA), and Poly(AA/St)

Sample	Polymer add-on (%)	DS	SR (%)
Untreated PET	—	0.99	89.10
Glycidyl methacrylate grafted	1.50	0.98	82.50
	5.20	0.83	77.60
	28.61	0.63	56.50
Methyl methacrylate grafted	1.62	0.98	66.00
	2.80	0.92	54.90
	12.20	0.73	55.80
	28.65	0.54	56.10
Acrylic acid/styrene mixture (60:40) grafted	29.80	0.30	66.10
	47.30	0.32	65.80
	65.40	0.26	64.70

to be the best since polymerization of PET with this mixture brings about the lowest degree of nonaqueous soiling even at roughly equal polymer add-on. This again reflects differences in nature between the monomer used and its subsequent effect on the mode of interaction of the soil with polymer derived thereof inside the PET structure.

Nonaqueous Soil Release

The effect of polymerization of GMA, MMA, and AA/St mixture with PET fabric on the ability of the latter to release nonaqueous oily soil is shown in Table V. It is seen that (a) polymerization of PET with the monomers in question impairs the ability of PET to release the nonaqueous oily soil, (b) the ease of soil removal decreases considerably by increasing the percent polymer add-on, and (c) the magnitude of soil removal depends upon the nature of monomer used; AA/St mixtures give higher soil removal than the other monomers. This is rather the trend observed with aqueous soil release and could be explained on similar basis.

References

1. A. Hebeish, S. E. Shalaby, and A. M. Bayazeed, *Kolorisztikai Ertesito*, **2**, 74 (1979).

2. R. Tsuzuki and S. Maeta, Jpn. Pat. 71 29,918 (1971); Chem. Abstr., **77**, 50069q (1972).

3. M. V. Mikhailov, L. G. Tokareva, T. D. Bratchenko, V. L. Karpova, and Yu. N. Malinskii, Tr. 2-go (Vtorogo) Vses. Soveshch. Po Radiats. Khim. Akad. Nauk SSSR otd. Khim. Nauk, Moscow, 1960, p. 589 (Pub. 1962); *Chem. Abstr.*, **62**, 13296g (1965).

4. S. E. Shalaby, A. M. Bayazeed, and A. Hebeish, *J. Appl. Polym. Sci.*, **22**, 1359 (1978).

5. A. Hebeish, S. E. Shalaby, and M. F. El-Shahid, *Angew. Makromol. Chem.*, **66** (966), 139 (1978).

6. E. E. Magat and D. Tanner, U.S. Pat. 3,413,378 (1968); *Chem. Abstr.*, **70**, 29994h (1969).

7. W. S. George and G. T. Teddy, U.S. Pat., 3,268,622 (1966); *Chem. Abstr.*, **66**, 11763q (1967).

8. T. Achmatowicz, A. Robalewski, and W. Zielinski, Pol. Pat. 59,529 (1970); *Chem. Abstr.*, **74**, 127401q (1970).

9. K. N. Rao, M. H. Rao, P. N. Moorthy, and A. Charlesby, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 893 (1972).

10. M. F. Blin, R. Candan, G. Gaussens, F. Lemaired, and D. Paoli, Fr. Pat., 2,045, 261 (1971); *Chem. Abstr.*, **76**, 15692v (1972).

11. A. Hebeish, S. Shalaby, and A. Bayazeed., *J. Appl. Polym. Sci.*, **26**, 3253 (1981).

12. A. Hebeish, S. Shalaby, and A. Bayazeed, *J. Appl. Polym. Sci.*, **26**, 3245 (1981).

13. A. Hebeish, S. Shalaby, A. Waly, and A. Bayazeed, *J. Appl. Polym. Sci.*, to appear.

14. A. Hebeish, S. Shalaby, and A. Bayazeed, *J. Appl. Polym. Sci.*, **27**, 197 (1982).

15. C. V. Beninate, E. L. Kelly, G. L. Drake, and W. A. Reeves, *Am. Dyest. Rep.*, **55**(2), 25 (1966).

16. W. H. Rees, *J. Text. Inst.*, **45**, 612 (1954).

17. E. Kissa, *Text. Res. J.*, **41**, 621 (1971).

18. P. Kubelka and F. Munk, *Z. Tech. Phys.*, **12**, 593 (1931).

19. A. Hebeish, Annual Technical Report of Project FG-EG 200, submitted to the United States Department of Agriculture (Jan. 1980–Dec. 1980).