Dyeing Properties of Poly(Methyl Vinyl Pyridine)-Poly(Ethylene Terephthalate) Graft Copolymers

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Synopsis

Grafting of poly(ethylene terephthalate) fibers (PET) with 2-methyl-5-vinylpyridine (MVP) was carried out using γ rays and benzoyl peroxide independently for the initiation of grafting. The poly(MVP)-PET graft copolymers were analyzed for density, moisture regain, and dyeability. Radiation-induced grafting yielded copolymers with densities and moisture regain appreciably higher than those produced by benzoyl peroxide. The same results occurred when acid dyes were used. The behavior of (MVP)-PET graft copolymers towards some reactive dyes was also studied. The extent and rate of dyeing were dependent of pH of the dye bath, nature of the dye and the magnitude of grafting. Dyeing occurs through formation of salt linkages between the pyridine moieties and the solubilizing groups (usually sulfonate groups) in the dye molecule.

INTRODUCTION

Fabric made of poly(ethylene terephthalate) (PET) fibers have many excellent properties the most outstanding of which is crease resistance. However, PET fibers suffer from the drawback of poor antistatic and difficult dyeability because they are highly crystalline, markedly hydrophobic, and do not contain chemically reactive groups. Attempts have been made to eliminate these handicaps by chemical modification of PET fibers through grafting with vinyl monomers having functional groups.[1-7]

Vinyl graft polymerization onto PET fibers can be achieved either by radiation or by chemical means. PET macroradicals capable of initiating grafting could be brought about by subjecting the PET fibers to γ rays from Co-60 (refs. 8–10) or to high-energy electrons from accelerators.[11-14] Grafting can be accomplished using either the mutual or the post irradiation techniques. In the first, both fiber and monomer are irradiated together; in the second the fiber is first irradiated to create the radical sites before the monomer is added. Similar PET macroradicals can be formed under the influence of free-radical initiators. The PET can be oxidized to hydroperoxide[15-21] at several points along the chain in a random manner. It is then allowed to decompose into the active form in the presence of monomer either by heat or by a redox system.

In this work the effect of grafting of PET fibers with 2-methyl-5-vinylpyridine (MVP) on moisture regain, density, and dyeability was investigated. The graft copolymerization reaction was induced by both radiation and chemical methods.

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EXPERIMENTAL

Materials

Poly(ethylene terephthalate) (PET) fibers, Trevira-Hoechst, 1.2 den/40 mm (cotton type) were purified through a mild cleaning treatment with sulphonated fatty alcohol (2 g/liter) at 65°C for 30 min. The fibers were then rinsed with hot and cold water, dried at room temperature, and finally extracted with alcohol for 24 hr.

2-Methyl-5-vinyl pyridine (MVP) was freshly distilled (75°C/13 Torr) before use.

Benzoyl peroxide (BP) was freshly prepared according to Vanino and Harzer.[22]

High-energy rays were provided by the 8000 ci Co-60 radiation source of the Middle Eastern Regional Radioisotope Center. The dose rate of this source is 0.36 Mrad/hr.

Acid and reactive dyes were used. The acid dyes included Erio Rouge Solid GS Conc (not available in the color index) and Xylene Blue AS (acid blue 7, C.I. 42080), whereas the reactive dyes used were Procion Brilliant Orange (reactive orange 1, C.I. 17907), Procion Brilliant Red M2B (reactive red 1, C.I. 18158), Remazole Brilliant Blue R (reactive blue 19, C.I. 61200), and Remazole Golden Yellow (reactive yellow 17, C.I. 18852).

Grafting Using γ Rays

The PET fiber (0.5 g) was irradiated in air to the required dose by γ rays. The graft copolymerization was carried out in a 100-ml stoppered flask. The irradiated sample was introduced into a 50-ml aqueous solution containing the monomer and 2 ml of emulsifying agent (Emulsogen DG-Hoechst). The flask was thermostatically heated to the required temperature before adding the irradiated sample. The reaction was allowed to proceed for different periods of time. The product was washed with distilled water and Soxhlet extracted with methanol and dried. Extraction with alcohol and drying were repeated until a constant weight was attained. The percent increase in weight, based on dry weight of the original sample, was designated as percent graft yield.

Grafting Using Benzoyl Peroxide (ref. 19)

Graft copolymerization was carried out in a 100 ml stoppered conical flask. The PET sample (0.5 g) was introduced into a 50 ml aqueous solution containing the monomer and 2 ml of emulsifying agent (Emulsogen DG-Hoechst). The flask was immediately stoppered and placed in a thermostated water bath for a certain period until the required temperature was reached. The initiator was then added. The reaction was allowed to proceed for different periods of time. The product was washed with distilled water and Soxhlet extracted with methyl alcohol and dried.

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 hr and weighed again:

$$\text{moisture regain \%} = \frac{\text{weight of conditioned sample} - \text{weight of dry sample}}{\text{weight of dry sample}} \times 100$$

Determination of Density

The density of the samples was determined by the density gradient column. The liquids used to prepare the column were nitrobenzene (density 1.2 g/cm^3) and carbon tetrachloride (density 1.595 g/cm^3).

Dyeing

Acid dye: The sample was immersed in a dye bath containing 0.1 g/liter dye, 3% Glauber salt and acetic acid at 80°C using material to liquor ratio 1:200.

Reactive Dyes

(a) Procion dyes: The sample was immersed in a dye bath containing 0.2 g/liter dye and 3% Glauber salt at room temperature using a liquor ratio of 1:200 at specific pH and dyeing was carried out for varying duration.

(b) Remazole dyes: Dye solution was prepared containing 0.1 g/liter dye and 5% Glauber salt. After adjusting the pH, the dye solution was heated for 20 min at 60°C before commencing dyeing. The fiber was immersed into the dyeing bath (material to liquor ratio 1:200) and dyeing was allowed to proceed while stirring for varying lengths of time.

In each case aliquots were withdrawn from the dye bath at different intervals for determination of the percent exhaustion:

% exhaustion

$$= \frac{\text{weight of dye in original dye solution} - \text{weight of dye in the dye solution after certain time of dyeing}}{\text{weight of dye in original dye solution}} \times 100.$$

RESULTS AND DISCUSSION

Density

Figure 1 shows variation of density with graft yields obtained when MVP was grafted to PET fibers using radiation and chemical methods for inducing grafting. The density increases with increasing graft yields up to ca. 10% and ca. 15%, respectively, when the radiation and chemical methods were used. It appears that at relatively low graft yields, the grafted polymer chains were efficiently packed in the PET fibers. At higher graft yields, on the other hand, the packing of polymer and of the PET chains became progressively less efficient. Consequently, the density of the fiber decreased.
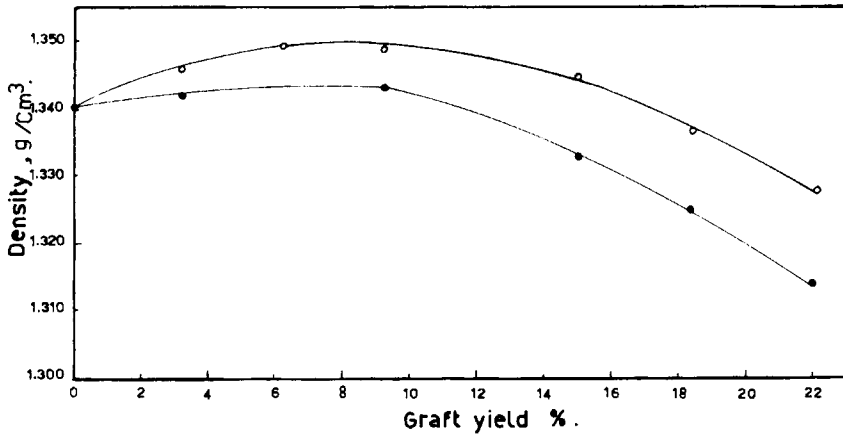
Fig. 1. Variation of density with percent graft. (O) grafting induced by γ ray; (●) grafting induced by benzoyl peroxide.

An interesting feature is that at the same grafting levels, the density of poly(MVP)-PET graft copolymers obtained by the radiation method are higher than those of the chemical method. This reflects differences in packing of the graft polymer in PET fibers. Current work suggests that packing of the poly(MVP) in PET fibers is greater in case of the radiation method than in case of the chemical method. However, differences in molecular weight distribution and frequency of the graft can not be ruled out.

Moisture Regain

Figure 2 shows the effect of grafting of MVP to PET fibers on moisture regain. The moisture regain increases with the increase of graft yield and the increase is more pronounced in samples grafted by the irradiation method than in samples
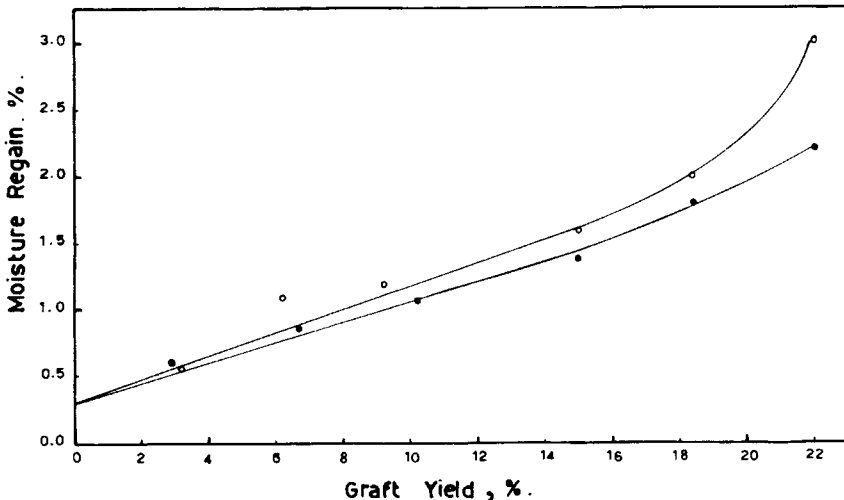

Fig. 2. Variation of moisture regain with percent graft. (O) grafting induced by γ rays; (●) grafting induced by benzoyl peroxide.

grafted by the chemical method, particularly at graft yields higher than 20%. This is in agreement with the density results discussed above.

The improvement in moisture regain is associated with opening up the PET structure. The grafted polymer opens up the structure of PET, decreases tightness of chain packing and allows for more water accommodation. The drawback of poor antistatic can be avoided by increasing the moisture regain of PET.[23]

Dyeability

Acid Dyes

Dyeing of PET fibers, after grafting with MVP, using both the radiation and chemical methods with an acid dye, viz., Xylene Blue AS was carried out at 100°C for varying lengths of time. Figure 3 shows percent of dye exhaustion versus duration of dyeing. There is no dye absorption on the ungrafted PET fibers since dye exhaustion is very poor even after a duration of 1 hr. With the grafted samples, on the other hand, dyeing proceeds very fast initially, slows down with time and then levels off. This is observed regardless of the graft yield and method of grafting. The higher the graft yield, the greater the percent exhaustion. For a given graft yield, samples prepared by irradiation grafting show much more percent dye exhaustion than the corresponding samples obtained by the chemical method. This is once again in agreement with the moisture regain and density and supports the earlier statement that the nature of the graft induced by irradiation differs from that induced by the chemical method.

The enhanced dyeing at higher graft yields is expected since more pyridine moieties would be available. The pyridine moieties are essential for formation of salt linkages between the dye and graft product. Poly(MVP)-PET graft copolymers (Fig. 4) prepared by the chemical method and dyed with another acid dye, viz., acid Erio Rouge Solid GS Conc support this thesis.[23,24]

A comparison of the dyeing rate curves for Xylene Blue AS (Fig. 3) with those for Erio Rouge Solid GS Conc (Fig. 4) on poly(MVP)-PET graft copolymers
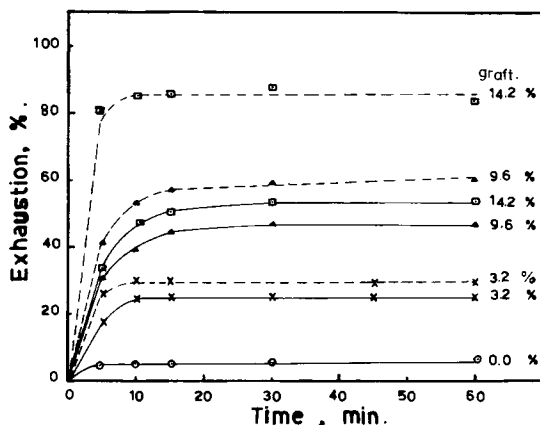

Fig. 3. Effect of methods of graft initiation on dyeing of poly(MVP)-(PET) graft copolymer with xylene Blue AS.   (- - -) grafting induced by γ rays; (—) grafting induced by benzoyl peroxide.
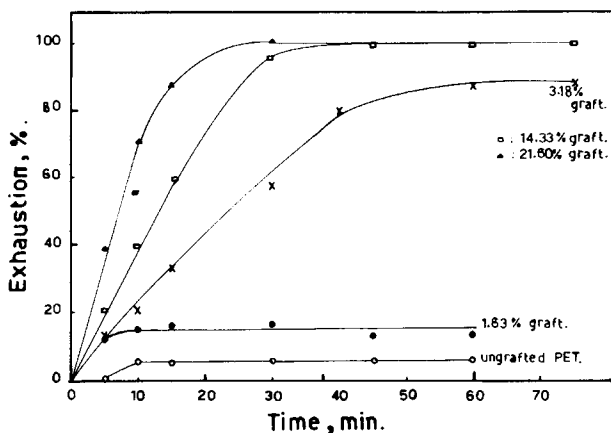
Fig. 4. Dyeing rate curves for Erio rouge solid GS Conc on poly(MVP-PET) graft copolymer having different graft yields.

indicate that the latter dye shows more exhaustion than the former. This is due to differences in the nature of the dye.

Dyeing with Reactive Dyes

Dyeing of poly(MVP)-PET graft copolymers with four reactive dyes, viz., Procion Brilliant Orange MG, Procion Brilliant Red M2B, Remazole Brilliant Blue R, and Remazole Golden Yellow G were carried over a wide range of pH from 1 to 10. It was observed that appreciable dye exhaustion occurs up to pH 3. Above this, the dye exhaustion curves all level off.

Figure 5 shows the dyeing rate curves at different pH's for Procion Brilliant Orange MG and Procion Brilliant Red M2B on grafted PET having 31.5% graft. Figure 6 shows similar curves for Remazole Brilliant Blue R and Remazole Golden Yellow G on poly(MVP)-PET graft copolymer having 15.9% graft. It is clear that both figures show one common feature, i.e., the extent and rate of
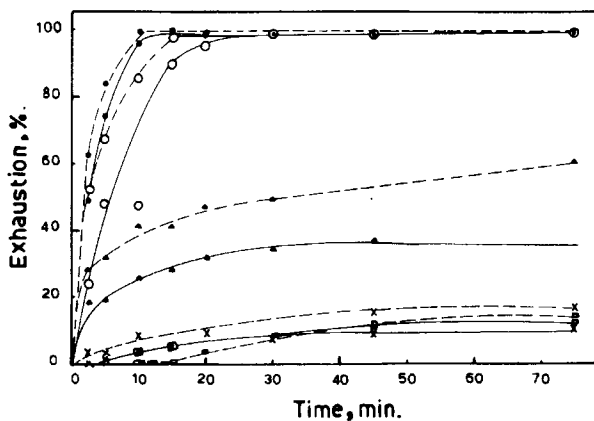

Fig. 5. Dyeing rate curves of Procion dyes at different pH's on poly(MVP)-(PET) graft copolymer having 31.5% graft. (- - -) Procion Brilliant Orange MG; (—) Procion Brillant Red M2B. pH: (●) 1.4; (O) 2.0; (▲) 3.0; (X) 7.0; (□) 10.0.
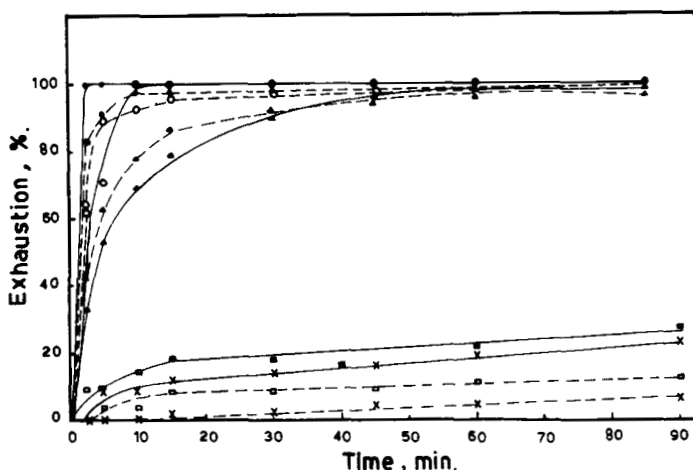
Fig. 6. Dyeing rate curves of Remazole dyes at different pH's on poly (MVP)-(PET) graft co-polymer having 15.9% graft. pH: (●) 1.4; (○) 2.0; (▲) 3.0; (×) 7.0; (□) 10.0. (—) Remazole Brilliant Blue R; (- - -) Remazole Golden yellow G.

dyeing are much more visible in the acidic medium (pH 1.4–3) than neutral and alkaline media. For instance, full dye exhaustion occurs at pH 2 regardless of the dye used. At pH 7 or 10, on the other hand, maximum exhaustion never exceeds 30%.

The enhanced dyeing at low pH can be attributed to the conversion of the solubilizing group (usually sodium or potassium sulfonate) in the dye to the H form. Once this occurred, formation of salt linkage between the dye and pyridine moieties of the graft would be possible.

Figure 7 shows the dyeing rate curves for Procion Brilliant Red M2B and Procion Brilliant Orange MG on grafted PET having different graft yields. Similar curves are shown for Remazole Brilliant Blue R and Remazole Golden Yellow G (Fig. 8). As can be seen in both figures, there is an increase in the extent
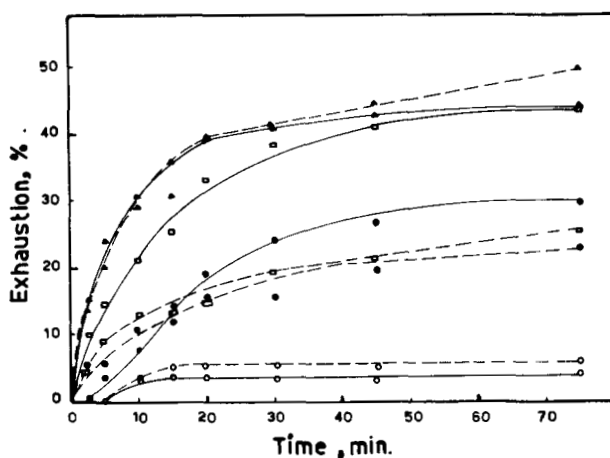

Fig. 7. Dyeing rate curves at pH: 3 for Procion dyes on poly(MVP)-(PET) graft copolymer having different graft yields. (○) ungrafted PET, (●) 1.63 % graft, (□) 14.33% graft, (▲) 21.60% graft. (—) Procion Brilliant Red M2B; (- - -) Procion Brilliant Orange MG.
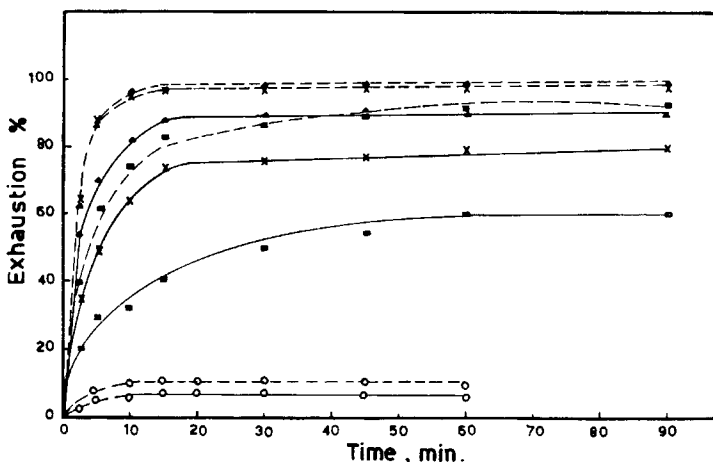
Fig. 8. Dyeing rate curves at pH: 3 for Remazole dyes on poly(MVP)-(PET) graft copolymer having different graft yields. (O) ungrafted PET; (□) 5.7%; (X) 17.0%; (▲) 23.6%. (—) Remazole Brilliant Blue R; (- - -) Remazole Golden Yellow G.

and rate of dyeing as the graft increases; similar to acid dyes. The effect of differences in nature of the dye on the extent and rate of dyeing is also quite apparent (Figs. 7 and 8).

The effects of the grafting on other properties, e.g., mechanical, thermal, and high resistance, are still under investigation.

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