Surface Graft Copolymerization of Acrylic Acid onto Corona-Treated Poly(ethylene terephthalate) Fabric

GUO YUHAI,1 ZHANG JIANCHUN,2 SHI MEIWU2

¹ The State Key Laboratory of Polymer Materials Engineering, Sichuan Union University, Chengdu, 610065, People's Republic of China

² The Quartermaster Institute of General Logistic Department, The Chinese People Liberary Army, Beijing, 100010, People's Republic of China

Received 17 June 1998; accepted 16 November 1998

ABSTRACT: Acrylic acid (AA) was grafted onto the surface of poly(ethylene terephthalate) (PET) fabric after having short-time corona-discharge treatment (CDT) in an atmosphere in the presence of the initiator. The effect of N,N-dimethylformamide (DMF) pretreatment time, CDT time, graft copolymerization time and temperature, concentration of AA, and the content of initiator on graft yield of PET fabric was discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1161–1164, 1999

Key words: corona-discharge treatment; graft copolymerization; poly(ethylene terephthalate)

INTRODUCTION

Poly(ethylene terephthalate) (PET) fiber is widely used because of its outstanding stabilities and excellent mechanical properties. It has, however, some drawbacks, such as high hydrophobicity of surface, color absorption, adhesion, and antistatic properties. To overcome these disadvantages of PET, various kinds of means, such as coating,¹ corona-discharge,^{2,3} alkaline treatment,^{4,5} and low temperature plasma,^{6–8} are used. But durability is not sufficient, so a large number of researchers have studied the grafting of vinyl monomers onto PET fibers and fabrics. Grafting onto PET can be achieved by either radiation, such as glow-discharge,^{9,10} ultraviolet (UV),^{11–13} γ -ray,^{14–16} excimer laser,¹⁷ or chemical means^{18–20}; but grafting by chemical is often limited. However, there are serious difficulties in grafting of monomer onto PET because of high crystalline contents, density, and the lack of chemical reactive groups. In this case of irradiation, the very low yield of radicals cannot lead to a high degree of grafting. On the other hand, the drawn fibers absorb very little monomer, and the rate of diffusion into bulk is very small.

Corona-discharge treatment (CDT) is different from other techniques, such as γ -ray, UV, and glow-discharge. Only CDT has an effect on polymer surfaces and does not damage bulk properties. The speed and ease of processing have made CDT to be widely used to the polymers required for printing and painting. However, initiating copolymerization by CDT has not been applied widely; little^{21–23} has been reported on the graft of the monomer onto polymer surfaces.

The purpose of this article is to describe the application of CDT in the presence of initiator to initiate graft copolymerization of acrylic acid (AA) onto PET fabric, to compare with the treatment without an initiator. The PET fabric is corona-treated in air. The subsequence graft of

Correspondence to: G. Yuhai.

Contract grant sponsor: The Quartermaster Institute of General Logistic Department, The Chinese People Liberary Army.

Journal of Applied Polymer Science, Vol. 73, 1161-1164 (1999)

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AA onto fabrics is performed in an aqueous solution of AA under various conditions without degassing.

EXPERIMENTAL

Materials

A plain-weave PET fabric of 52.5 g/m² unfinished, undyed, and unsized was cut into pieces of 3×30 cm. The samples were subjected to a Soxhlet extractor with methanol for 24 h, then dried at atmospheric pressure. The inhibitor in AA was removed by distillation under reduced nitrogen pressure. Ammonium persulfate (APS) and *N*,*N*dimethylformamide (DMF) are of reagent grade.

Sample Preparation

Extracted fabrics were dipped into DMF solvent heated by a temperature-controlled oil bath for predetermined times at 140°C. Excess DMF was removed by blotting with filter paper after treatment, followed by immersion in various concentrations of aqueous solution of APS (weight ratio to samples, with a liquid ratio of 1:10) for 10 min, dried in cool air, then stored in a descciator kept at 25°C and 60% RH for CDT.

CDT

In this experiment, the pretreated samples were placed under the rope wire corona-discharge cell manufactured by the No. 9 Radio Factory of DaLian China, and a 1.5-cm gap was treated in air with ambient temperature. The potential applied was 15 kV.

Graft Copolymerization

To effect graft copolymerization, the pretreated samples treated by CDT were put into glass ampules immediately containing AA of predetermined concentration (1 : 20 liquid ratio), and the ampules were placed in a oil bath adjusted to the reactive temperature. After reaction, homopolymer of AA was removed by washing in boiling water for several hours. The washing water was changed until the weight of samples kept constant. The grafted samples were dried under vacuum at 105°C and weighed to determine the graft yield. The graft yield was calculated as follows:



Figure 1 Effect of CDT time on graft yield: DMF treatment temperature, 140°C, time (from 1 to 4), 0, 5, 10, and 20 min; [APS], 5%; [AA], 20%; T, 70°C; t, 1 h.

Graft yield (%)

$$= \frac{\text{wt of grafted sample (after washing)}}{\text{wt of original sample}} \times 100$$

RESULTS AND DISCUSSION

Effect of DMF Treatment Time

The effect of DMF treatment time on the graft yield with a constant APS concentration, AA concentration, and reactive time was shown in Figure 1. As seen from the figure, the graft yield with CDT increased largely as compared to the yield by means of a chemical way without CDT. The DMF treatment time has significant effect on graft yield. The figure shows that a DMF treatment time of 10 s is sufficient for the chemical way since prolonged treatment time does not lead to a further increase but, rather, goes down in the graft yield. The crystallinic structure changes in the PET fabrics, leading to an increase in AA uptake, then a decrease with longer DMF treatment time is known in earlier literature.²⁴ A different graft law by both means of chemical and CDT could be seen in the figure, which is being further studied.

Effect of Copolymerization Time on Graft Yield

Graft of PET fabrics treated by CDT was carried out at various copolymerization times, as shown in Figure 2. The result may be due to following reasons: (1) peroxide produced on CDT PET fabric



Figure 2 Effect of copolymerization time on the graft yield (DMF treatment temperature and time separately): 140°C, 10 min; [APS], 5%; CDT time, 15 s; [AA], 20%; *T*, 70°C.

surfaces is decomposed to initiate graft copolymerization; (2) the homopolymerization of AA is formed with longer reactive time, which improves the viscosity of reactive solution and, to a greater extent, hinders the diffusion of AA to fabric surfaces. A similar result is reported in graft copolymerization of ethyl acrylate onto corona-treated cellulose film.²¹

Effect of Copolymerization Temperature

Figure 3 shows that the effect of copolymerization temperature from 50-90°C on the grafting of AA onto PET fabrics. It could be seen that the graft yield reached a maximum value when the reactive temperature increases up to 80°C, then declines. A similar result is obtained from the graft



Figure 3 Graft yield versus copolymerization temperature (DMF treatment temperature and time separately): 140°C, 10 min; [APS], 5%; CDT time, 15 s; [AA], 20%; T, 70°C; t, 1 h.



Figure 4 Graft yield versus concentration of AA (DMF treatment temperature and time separately): 140°C, 10 min; [APS], 5%; CDT time, 15 s; *T*, 70°C; *t*, 1 h.

copolymerization of AA onto PET fibers treated by means of γ -ray.²⁵

Effect of Concentration of AA

Figure 4 shows that the graft yield is changed with an aqueous solution of AA under various concentrations. The optimum of graft yield is obtained at around 60% AA concentration. Larger amount of AA concentration could not increase the degree of the graft. The result is consistent with the research on graft copolymerization of styrene onto cellulose by CDT.²⁶

Effect of Concentration of APS

It could be seen from Figure 5 that graft yield increases with an increase of APS concentration



Figure 5 Graft yield versus concentration of APS (DMF treatment temperature and time separately): 140°C, 10 min; CDT time (from 1 to 4), 5, 10, 15, and 20 s; [AA], 20%; T, 70°C; t, 1 h.

with an range of 0-3%, further increase of APS concentration does not enhance grafting except curve 3 at 15 s of CDT time, and a drop of graft yield is observed.

CONCLUSION

All results indicate that it is possible to graft of AA onto PET fabric by corona-discharge treatment, and the graft yield increases in the presence of the APS initiator. The graft yield is improved with a short-time CDT, but drops with a increase of time.

Finally, we would like to emphasize that graft of vinyl monomer onto other polymer treated by CDT in the presence of initiator is perhaps accelerated as compared to the result in the absence of initiator described in the literature earlier.²⁶

This research has been funded by The Quartermaster Institute of General Logistic Dept., The Chinese People Liberary Army.

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