NOTE

Modified Polypropylene Fibers with Enhanced Moisture Absorption and Disperse Dyeability

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INTRODUCTION

Polypropylene (PP) has occupied a prominent place in the textile industry because of the excellent physical properties, chemical resistance, and mechanical properties. However, due to the hydrocarbon nature, as well as the lack of polar sites in the molecular structure, the fiber is not dyeable with existing classes of dyes. Although the mass pigmentation is the most widely accepted method of coloration of the PP fiber, attempts have been made to make the fiber dyeable by chemical treatment, such as bromination of the fiber,[1] blending with another polymer containing polar groups,[2] reactive blending during melt extrusion,[3] or by graft copolymerization of an appropriate monomer into the fiber.[4,5] The graft copolymerization method offers an excellent advantage in terms of the controlled modification of the fiber. As a result, the fiber not only retains most of its inherent physical properties but also acquires additional characteristics through the grafted component. This attractive feature led to several interesting studies on the radiation induced graft copolymerization of vinyl and acrylic monomers into PP fiber with a view to enhance dyeability with different dyes.[5,6]

Sundardi[7] has reported that the grafting of acrylonitrile into PP fiber leads to the disperse dyeability. However, no quantitative determination of the dyeing behavior of the fiber was made. Recently, Gawish et al.[8] have also shown that the preirradiation grafting of 2*N*-morpholino ethylmethacrylate into PP fabric leads to considerable enhancement in the moisture absorption, as well as dyeability with acid dye. In our previous article, we reported the modification of PP fibers by graft copolymerization of acrylonitrile monomer using the preirradiation method, in which the influence of the reaction conditions on the degree of grafting was investigated.[9] In the present study, physical properties such as orientation, crystallinity, and moisture regain, as well as the dyeing behavior of the polypropylene-*g*-polyacrylonitrile (PP-*g*-PAN) fibers with a disperse dye, is described.

EXPERIMENTAL

Materials

Polypropylene, having MFI 16, was supplied by Indian Petrochemicals Corporation Limited, Vadodara, Gujrat. The monofilament was prepared by the melt extrusion of the polymer at 240°C under nitrogen atmosphere on a laboratory-scale, melt-spinning unit. The drawing of the fiber was carried out at 110°C to a draw ratio of 1 : 2.

Acrylonitrile (BDH, India) and dimethylformamide (DMF) were used as received without any further purification. A Co-60 gamma radiation chamber (900 cu-

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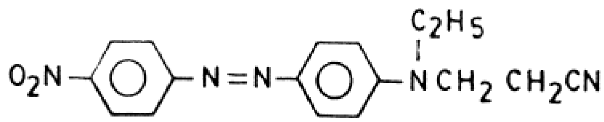
ries) was used for the exposure of fibers. The dose rate of the gamma source was 0.5 kGy/h. Distilled water was used for all experiments. Foron Brilliant Orange E-RL (C.I. Disperse Orange 25) was used as the disperse dye. An anionic dispersing agent was used for the dye bath preparation.



C.I. Disperse Orange 25

Grafting Method

Grafting of acrylonitrile into PP fiber was carried out by the preirradiation method, as reported earlier.[9] The fiber was irradiated with gamma radiation in air and subsequently contacted with acrylonitrile monomer under nitrogen atmosphere in the temperature range of 50–70°C for a desired period. After the grafting reaction, the fiber was Soxhlet-extracted with DMF and dried in vacuum. The degree of grafting was determined as the percentage of increase in the weight of the fiber after the grafting reaction.

$$\text{Degree of grafting } (\%) = [W_g - W_0/W_0] \times 100$$

where W_0 and W_g are the weight of the ungrafted and grafted fibers, respectively.

FTIR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy studies on fibers were carried out on Jasco Micro FTIR. The presence of grafts in the modified fibers was ascertained by monitoring the peak at $\sim 2240\ \text{cm}^{-1}$. Fibers were mounted as a single monofilament, and FTIR were recorded in the absorbance mode.

X-ray Diffraction

The crystallinity of fibers was measured by X-ray diffraction (XRD) on a Phillips X-ray diffractometer in the 2θ range of 10–40° according to the method reported earlier.[10]

Birefringence

Birefringence measurements were carried out on a polarising microscope (Vickers Instruments). Two different principle refractive indices were taken as parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the fiber axis. The refractive index (Δn) was obtained by the following expression:

$$\Delta n = n_{\parallel} - n_{\perp}$$

Moisture Regain

PP-*g*-PAN fibers were dried over P_2O_5 until a constant weight was obtained. Subsequently, fibers were placed at 65% relative humidity (RH) for 1 week. The moisture regain was measured as the percentage of increase in the weight of the dry fiber.[8]

Dyeing

The dyeing of ungrafted and grafted PP (PP-*g*-PAN) fibers containing different amounts of grafted PAN was carried out with Foron Brilliant Orange E-RL on a high-temperature dyeing machine. A 2% shade of the dye was prepared using Lycol 01 as the dispersing agent. The liquor ratio was maintained at 1 : 500. The dyeing was carried out at 100°C for a period of 25 min to 6 h. Dyed fibers were soaped with 2% Lissapol-N detergent at 40°C for 30 min and washed with distilled water. The dye was extracted from the fiber by extraction with DMF, and the dye uptake was measured in terms of the optical density on a spectrophotometer at the wave length of 450 nm.

RESULTS AND DISCUSSION

The grafting of acrylonitrile monomer into PP fibers resulted in the development of PP-*g*-PAN copolymer fibers with different graft levels in the range of 3–11%. Characterization studies were confined to the ungrafted as well as grafted PP fibers with degrees of grafting of 3, 7, and 11%. The presence of grafts in the PP fiber was ascertained by FTIR measurements, as shown in Figure 1. The results show the origin of the absorbance peak at $2243\ \text{cm}^{-1}$ in grafted fibers, while the ungrafted fiber does not show any such peak. This peak is the characteristic of the nitrile group (—C≡N) and suggests the presence of acrylonitrile in the grafted fiber.[11] The intensity of peak at $2243\ \text{cm}^{-1}$ increases with the increase in the degree of grafting, which is essentially due to the higher content of PAN in the fiber

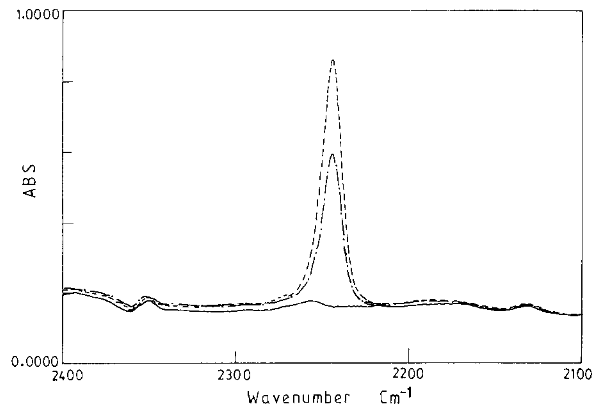


Figure 1 FTIR of ungrafted PP fiber (—) and PP-*g*-PAN fibers containing (–.–.–) 7% and (- - -) 11% graft.

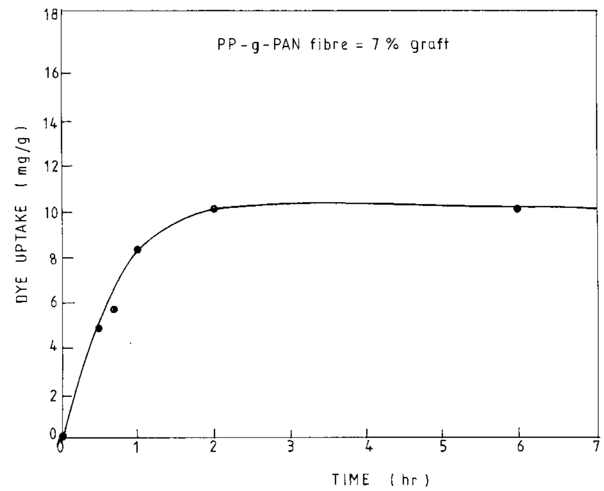


Figure 3 Variation of the dye uptake with the time in PP-*g*-PAN fiber.

at higher degree of grafting. FTIR characterization therefore proves that the fiber is grafted with the acrylonitrile monomer.

The variation of the moisture regain with the degree of grafting is presented in Figure 2. From the results, it is evident that the grafting of acrylonitrile leads to a considerable improvement in the moisture regain of the PP fiber. A maximum moisture regain of 0.9% was observed in the fiber with a graft level of 11%. The enhancement in the moisture regain of the fiber may be attributed to the polar nature of the nitrile group present in the grafted fiber. Our results are in agreement with those of Sundardi,[7] who also found an improvement in the moisture regain of the fiber by acrylonitrile grafting.

The dyeing behavior of a fiber with degree of grafting of 7% is presented in Figure 3. The dye uptake increases with the time of dyeing, and a saturation in the dyeing is attained within 2 h. The variation in the equilibrium dye uptake with the degree of grafting is presented in Figure 4. The equilibrium dye uptake increases with the increase in the degree of grafting but tends to level off beyond the 7% graft level. An increase in the disperse dye uptake of acrylonitrile graft copolymer fibers has been reported by Sundardi as well.[7] However, the author has not carried out any study on the optimization of the dyeing behavior *vis-à-vis* the degree of grafting.

In the disperse dyeing, the ease of penetration of the dye molecule within the fiber is an important aspect that is, in fact, governed by the changes in the physical characteristics of the fiber that arise out of a chemical treatment. One such important factor is the change in

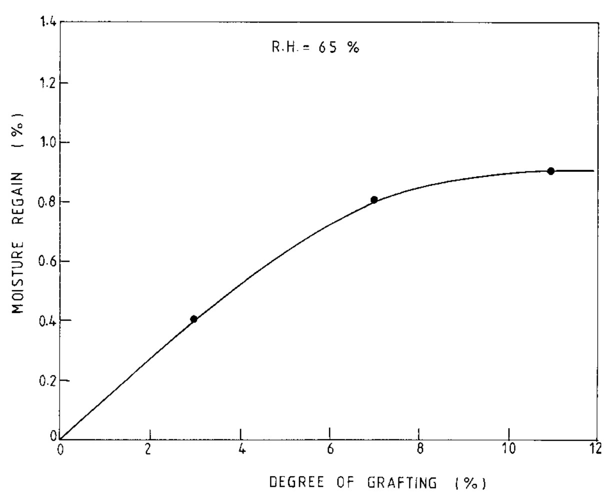


Figure 2 Variation of the moisture regain with the degree of grafting in PP-*g*-PAN fibers.

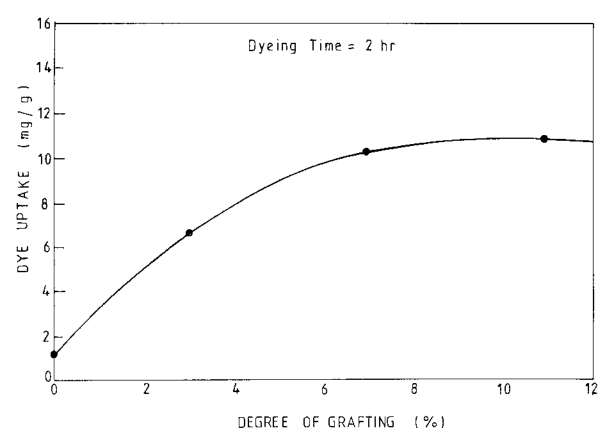


Figure 4 Variation of the dye uptake with the degree of grafting in PP-*g*-PAN fibers.

Table I Percentage of Crystallinity and Birefringence of PP-*g*-PAN Fibers

Fiber	Degree of Grafting (%)	Crystallinity (%)	Birefringence
PP	00	55.8	0.019
PP exposed[a]	00	54.6	0.019
PP-*g*-PAN	3	53.2	0.018
PP-*g*-PAN	7	48.4	0.015
PP-*g*-PAN	11	47.2	0.013

[a] Irradiated with a dose of 20 kGy.

the crystalline-to-amorphous ratio in the fiber. Isotactic PP is a highly crystalline polymer, which leaves very little volume accessible to the dyes. This is the reason that the dye uptake in the unmodified fiber is very low. The grafting of acrylonitrile into PP fiber results in a change in the crystalline-amorphous ratio, as observed in Table I. The irradiation of the fiber with 20 kGy does not cause any significant change in the crystallinity. However, the grafting of acrylonitrile leads to a decrease in the crystallinity of the fiber. The higher the degree of grafting, the lower the crystallinity of the fiber. This feature of decrease in crystallinity due to grafting has also been visualized in the grafting of 2-hydroxyethyl methacrylate into PP fiber and the grafting of styrene into FEP films.[12–14] Moreover, there is a significant change in the orientation of the molecular chains by grafting. The birefringence value of PP fiber decreases with the increase in the graft levels (Table I). This suggests that the disordering of the chains takes place due to the incorporation of PAN grafts in the PP fiber matrix. This is also expected to enhance the dye penetration within the fiber matrix.

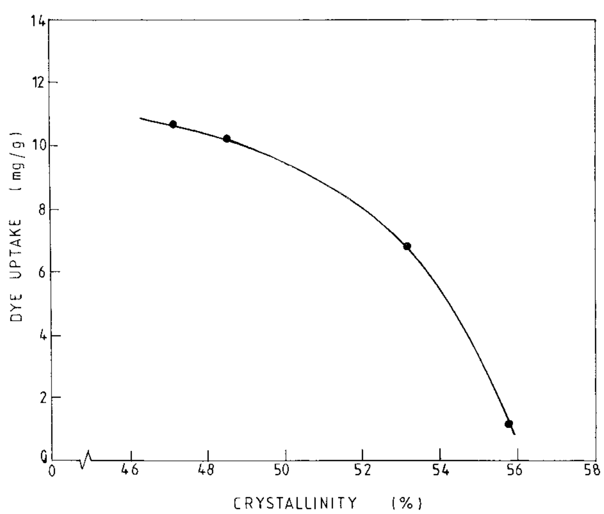


Figure 5 Variation of the dye uptake with the crystallinity in PP-*g*-PAN fibers.

The correlation between the dye uptake and the crystallinity of the fiber, as evident from Figure 5, shows that the dye uptake increases with the decrease in the fiber crystallinity. This is because of the fact that with the decrease in the crystallinity and the disordered structure, the fiber structure becomes more accessible to the dye diffusion. The dye uptake, as a result, increases with the increase in the degree of grafting. In disperse dyeing, no interaction of the dye with sites within the fiber takes place. However, in the present system, the dye molecule contains the nitrile group; hence, the dipolar interaction between the dye and the nitrile groups within the grafted fiber may also be expected to contribute to the enhancement in the dyeability of the fiber. This contribution will be in addition to the contribution of the lowering crystallinity and disordering of chains in enhancing the dye penetration.

CONCLUSION

The radiation grafting of acrylonitrile monomer into PP fiber leads to the enhanced moisture content and excellent dyeability with disperse dye. The moisture regain of the fiber increases from almost 0 to 0.9% for a graft level of 11%. The grafted fibers show excellent dyeability with disperse dyes, which depends on the degree of grafting of the fiber. The increase in the dyeability of the fiber with the increase in the grafting is due to the decrease in the crystallinity and the disordering of the structure of the PP fiber by the grafted PAN component. The dipolar interaction between the polar groups in the dye and the fiber may also contribute to the enhancement in the dye uptake. These results indicate that the radiation-induced grafting of acrylonitrile into PP fiber is an useful method of fiber modification to achieve dyeable PP fiber.

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