Modification of Polypropylene Fiber by Radiation-Induced Graft Copolymerization of Acrylonitrile Monomer

CLARA PLESSIER,[1] BHUVANESH GUPTA,[1] ADOLPHE CHAPIRO[2]

[1] Department of Textile Technology, Indian Institute of Technology, New Delhi 110016, India

[2] CNRS, F-94320, Thiais, France

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ABSTRACT: Modification of polypropylene fiber was carried out by graft copolymerization of acrylonitrile monomer using the preirradiation method. The influence of synthesis conditions (preirradiation dose, monomer concentration, temperature, draw ratio, and storage) on the degree of grafting was investigated. For all preirradiation doses, the degree of grafting was found to increase with the reaction time. The higher the preirradiation dose, the higher the degree of grafting was. The dilution of monomer with DMF showed peak maxima for the degree of grafting at 80% monomer concentration. Both the initial rate of grafting and the final degree of grafting were found to increase with an increase in the reaction temperature. An activation energy of 31.2 kJ/mol was found for the grafting reaction. The degree of grafting in the drawn fiber showed different behavior as compared to the undrawn fiber. The storage of the irradiated fiber at −4°C prior to the grafting showed a decrease in the degree of grafting initially for a period of 8 days, beyond which the degree of grafting remained constant. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1343–1348, 1998

Key words: polypropylene; acrylonitrile; fiber; radiation; graft copolymerization

INTRODUCTION

Polypropylene (PP) fiber is a hydrocarbon structure of the lowest specific gravity among the fiber forming polymers. The fiber has good mechanical properties and is resistant to most chemicals, which makes it attractive for a large number of textile applications. The major requirements for the textile related applications of a fiber are dyeability with conventional techniques and ironing. However, due to its hydrophobic nature and lack of polar sites, this fiber is difficult to dye with the existing classes of dyes. At the same time, the high crystallinity restricts the penetration of disperse dyes within the fiber structure. This is the reason that mass pigmentation is the only widely used method of coloring the fiber.[1]

Efforts have been made to modify PP fiber by introducing dye receptor sites by adding additives during the melt spinning process[2,3] or by graft copolymerization of an appropriate monomer to introduce reactive or polar sites into the fiber structure that may be used as the dye sites.[4] Radiation grafting has proved to be a very effective technique to impart desirable properties into a polymer without any consideration of the shape of the material.[5] The attractive feature of radiation grafting is that the size of the grafted component can be easily controlled by proper selection of the irradiation dose and its intensity.[5,6]

Grafting studies have been carried out to achieve a PP fiber with optimum moisture regain and excellent dyeability with different classes of dyes.[7–13] The grafting of methacrylic acid into PP fiber was found to introduce dyeability with both

Correspondence to: B. Gupta.

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the basic and disperse dyes. The moisture regain also improved from 0 to 3.2% for a graft level of 50%.[11] Sundardi[7] also reported that the fiber could be dyed with different dyes, depending on the chemical nature of the monomer grafted into the fiber. Although a few studies[9,14,15] have been reported on the graft copolymerization of acrylonitrile monomer into PP fibers, a systematic evaluation of the grafting conditions for an optimum degree of grafting has not been reported so far.

In the present investigation the grafting of acrylonitrile monomer into PP fiber was carried out by the preirradiation technique. The influence of synthesis conditions on the degree of grafting is investigated. The variation of the physical properties and the dyeability of modified fibers will be communicated subsequently.[16]

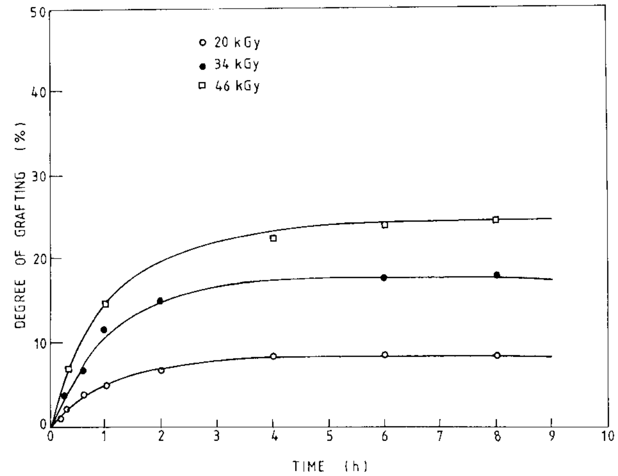

Figure 1 Variation of the degree of grafting with the time at different preirradiation doses. Grafting temperature 60°C.

EXPERIMENTAL

Materials

PP (manufactured by IPCL, India) was used for the present study. The fiber was prepared by melt spinning of PP at 240°C on a lab-scale spinning unit. The drawing of the fiber was carried out at 110°C to a draw ratio of 1 : 2. The average diameter of the fiber was 0.99 mm. Acrylonitrile monomer (BDH, India) was used as received without any further purification. DMF was used as received. Distilled water was used for all experiments.

Irradiation

PP fibers were irradiated in air by γ rays from a ^{60}Co γ irradiation source (900 Ci). The dose rate of radiation was 0.5 kGy/h. After the irradiation, fibers were kept at −4°C in air prior to the grafting experiments.

Grafting Experiments

Grafting was carried out in glass ampoules of 2 × 16 cm^2 size. The fiber was placed in an ampoule containing the required amount of the monomer. Nitrogen was purged into the ampoule to remove air from the grafting solution. Subsequently, the ampoule was placed in a water bath maintained at a constant temperature. After the desired period, the ampoule was taken out and the polyacrylonitrile (PAN) homopolymer adhering to the fiber surface was removed by extraction with DMF. Finally, the fiber was dried in an air oven and weighed.

The degree of grafting into the fiber was calculated according to the following equation[11]:

$$\text{degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

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

The grafting efficiency was obtained as follows[11]:

$$\text{grafting efficiency (\%)} = \frac{\text{weight of grafted PAN}}{\text{weight of grafted PAN} + \text{weight of PAN homopolymer}} \times 100$$

RESULTS AND DISCUSSION

The grafting of acrylonitrile into PP fiber was carried out to establish a correlation between the degree of grafting and the reaction conditions such as monomer concentration, radiation dose, time of grafting, additives, fiber draw ratio, and the storage of the irradiated fiber prior to the grafting. The basic concept of using unpurified acrylonitrile monomer was to reduce the step of monomer purification to make the whole process more economical on an industrial scale.

Influence of Preirradiation Dose

The influence of the preirradiation dose on the degree of grafting is presented in Figure 1. The de-

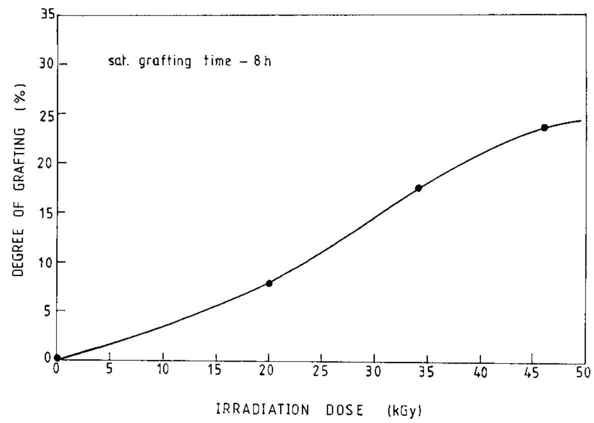

Figure 2 Variation of the final degree of grafting with the preirradiation dose. Grafting conditions are the same as in Figure 1.

gree of grafting increases with time but levels off beyond a period of 2 h. From the results it may be seen that the saturation in the grafting is achieved between 4 and 6 h of grafting time. The trend in the degree of grafting versus time remains almost identical for all three preirradiation doses. The variation in the final degree of grafting (taken as grafting at 8 h) with preirradiation dose is presented in Figure 2. The higher the preirradiation dose, the higher is the degree of grafting. Such behavior is essentially due to the generation of a higher number of radicals within the fiber that are available for the grafting reaction with the monomer. Similar observations have been made in the grafting of acrylic acid into polyethylene.[17]

The variation in the grafting efficiency with the time of grafting is presented in Figure 3. The decrease in the grafting efficiency with the increase in the grafting time is due to the higher rate of homopolymerization as compared to the rate of grafting reaction, a feature that is evident in the

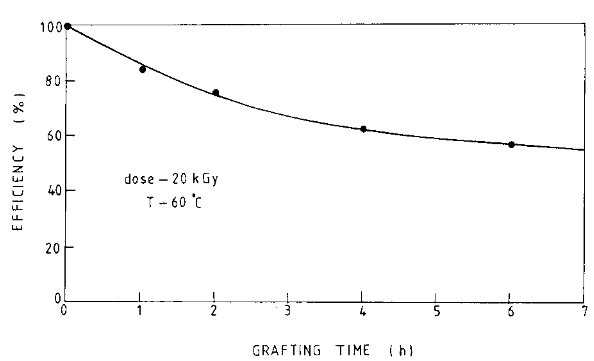

Figure 3 Variation of the grafting efficiency with the time of grafting.

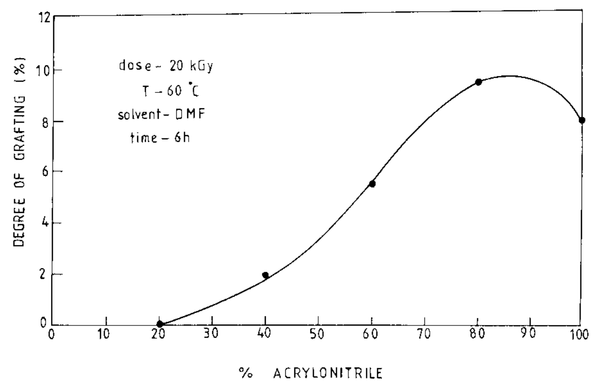

Figure 4 Variation of the degree of grafting with the monomer concentration.

diffusion controlled grafting system as discussed later. In such systems, the monomer availability to the grafting sites within the fiber is considerably reduced, which eventually leads to the quick growing chain termination. This is not the case during the homopolymerization that proceeds without any diffusion-induced constraints in the grafting medium.

Influence of Monomer Concentration

The grafting of acrylonitrile monomer was carried out in DMF as the solvent medium at a temperature of 60°C. Figure 4 shows the variation in the degree of grafting with acrylonitrile concentration. Grafting increases with the acrylonitrile concentration up to 80%, beyond which it tends to decrease. The origin of maxima at 80% seems to be the result of the complexity due to the diffusion-controlled mechanism in the grafting system as observed in other systems.[18–20] In such cases, the initial grafting takes place at the film surface only. These grafted layers swell in the grafting medium and the further grafting proceeds deep into the middle by progressive diffusion of the monomer through these swollen layers. This was also proved in the polyethylene-acrylonitrile system.[21] Because the DMF acts as the solvent for PAN, the grafted zones in the fiber are swollen in the grafting medium comprising the monomer and DMF. Therefore, the monomer diffuses within the fiber through these grafted layers and is controlled by the instantaneous swelling of the grafted layer at a particular time of the reaction. Hence, as long as the DMF is present in the grafting mixture, the monomer availability to the grafting sites is regulated properly, leading to the higher degree of grafting with increasing mono-

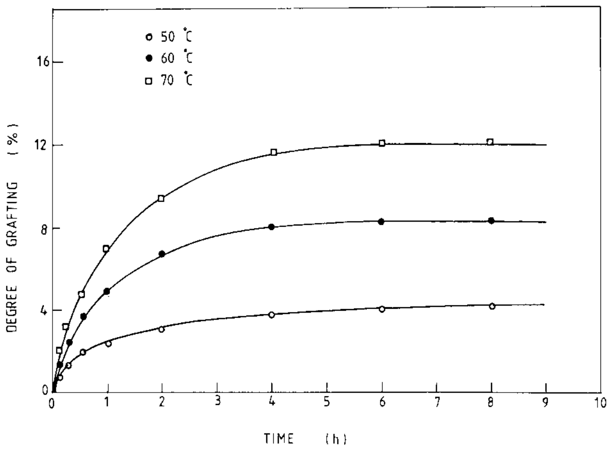

Figure 5 Variation of the degree of grafting with the reaction temperature. Pre-irradiation dose 20 kGy.

mer concentration. The lowering of the degree of grafting for 100% monomer is because the acrylonitrile monomer acts as the nonsolvent for PAN chains. The swelling of the grafted zone is therefore markedly lowered. The diffusion of monomer through the grafted zone and hence the accessibility of the monomer to the grafting sites is reduced, which is reflected in the lowering of the degree of grafting.

Influence of Reaction Temperature

The variation of the degree of grafting with the reaction temperature is presented in Figure 5. From the slope of three plots, one can state that the rate of grafting increases with the increase in the reaction temperature. The higher level of the final degree of grafting is achieved at a higher temperature. Such behavior may be attributed to two factors:

1. At higher temperature, the diffusion of monomer within the fiber should be enhanced. As a result, the availability of the monomer to the grafting sites is increased, leading to the higher rate of propagation.
2. The higher temperature results in the higher reactivity of radicals toward the monomer, leading to the higher degree of grafting.

Although the termination of primary radicals ($P^\bullet$) by mutual recombination would also increase at a higher temperature (step 1), it seems that this deactivation is negligible as compared to the propagation reaction (step 3) leading to the higher graft levels.

1. $P^\bullet + P^\bullet \rightarrow P - P$ deactivation
2. $P^\bullet + M \rightarrow P - M^\bullet$ initiation
3. $P - M^\bullet + nM \rightarrow P - Mn{+}1^\bullet$ propagation

The Arrhenius plot of the rate of grafting is presented in Figure 6. The activation energy of the grafting reaction was found to be 31.2 kJ/mol. Mori et al.[21] reported the activation energy of 60 kJ/mol for the polyethylene-*g*-acrylonitrile system. The lower value of the activation energy in our system may be due to the ease of the diffusion of the monomer affected by the lower crystallinity as compared to the polyethylene films (and hence a lower temperature coefficient).

Influence of Draw Ratio

The variation in the degree of grafting with the time of reaction for undrawn and drawn fibers is presented in Figure 7. The drawn fiber shows a lower initial rate of grafting as compared to the undrawn fiber. However, the final degree of grafting is higher in the drawn fiber. As discussed in the earlier section, it is the monomer diffusion through grafted layers that plays an important role in the grafting reaction. Because the PP fiber

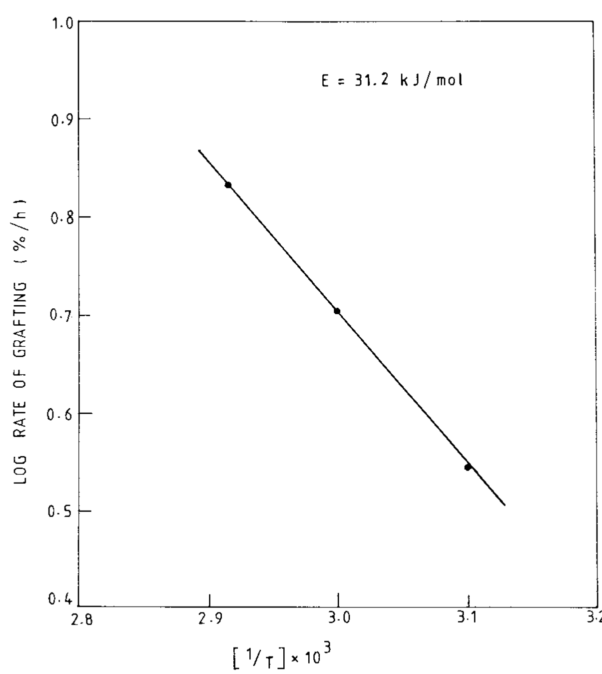

Figure 6 Arrhenius plot of rate of grafting versus [1/*T*]. Grafting conditions are the same as in Figure 5.

is semicrystalline in nature, it is the amorphous fraction of the fiber that is available for the monomer diffusion. The drawing of the fiber leads to the higher crystallinity as measured by the X-ray diffraction (crystallinity of undrawn fiber 50.1%, drawn fiber 55.8%). It may therefore be assumed that the higher crystallinity in the drawn fiber leads to the lower rate of monomer diffusion within the fiber.[21,22] As a result, the propagation step slows down and the initial rate of grafting decreases.

The higher value of the final degree of grafting in the drawn fiber may be understood from the availability of more free radicals for the grafting reaction within the fiber. The irradiation leads to the generation of radicals in the crystalline and amorphous regions. In the drawn fiber the radicals that are produced in the crystalline regions are still active due to the immobility of the molecular chains. These active radicals may eventually diffuse out at the crystallite surface and initiate the grafting. This would lead to the higher degree of grafting.[22] One of the factors that contributes to the lower degree of grafting in undrawn fiber is the high mobility of chains in the amorphous region due to the low glass transition temperature of the PP fiber. In the undrawn fiber, due to the relatively large amorphous fraction, a large number of generated radicals may undergo deactivation by recombination during irradiation. The degree of grafting decreases as a result.

Influence of Pregrafting Storage Time

The fibers after irradiation were stored at −4°C in a refrigerator. The variation of the degree of grafting with the storage time is presented in Figure 8. The degree of grafting decreases quickly up to 8 days of storage and remains almost unchanged there after up to 4 weeks. These results indicate that the fiber becomes stabilized within a week of the storage time. Similar observations were made earlier for the grafting of acrylic acid into polyethylene films.[17] Sundardi[7] has also shown that the storage of irradiated fibers at room temperature leads to a continuous decrease in the degree of grafting similar to the observation in our system. However, the author studied the storage only up to 1 week.

The initial decrease in the degree of grafting in our system may be attributed to the postirradiation deactivation of some active centers in the fibers. This may be in the form of crosslinking and chain scission along the polymer backbone. At the same time, the trapped polymeric radicals ($P^{\bullet}$) may react with other centers to produce stable structures (deactivation), thereby decreasing the amount of radicals available for the grafting. From our results, we can state that this deactivation of radicals is completed within 1 week of the storage period under experimental conditions.

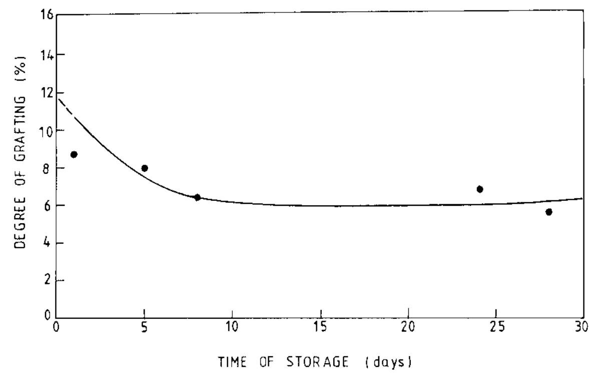

Figure 8 Variation of the degree of grafting with the storage of preirradiated fiber. Grafting conditions: monomer concentration, 100%; temperature, 60°C. Preirradiation dose 20 kGy.

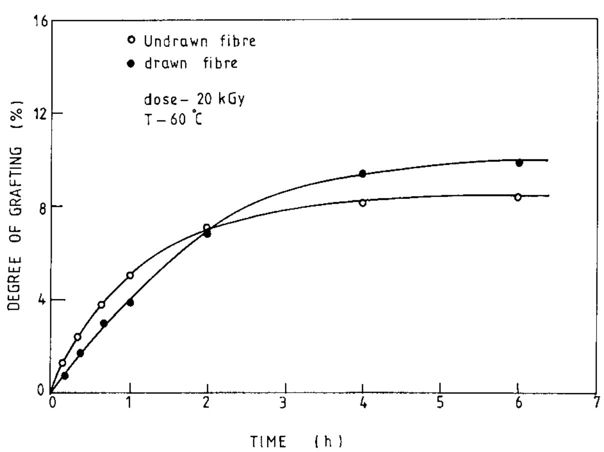

Figure 7 Variation of the degree of grafting with time for undrawn and drawn fibers.

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