Ultraviolet Radiation-Induced Graft Copolymerization of 2-Hydroxyethyl Methacrylate onto Polypropylene

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SYNOPSIS

Polypropylene staple fibers were grafted with 2-hydroxyethyl methacrylate (HEMA) using ultraviolet radiation in the presence of three different photoinitiators, uranyl nitrate (UN), ceric ammonium nitrate (CAN), and benzoin ethyl ether (BEE), separately. The parameters of grafting were optimized for obtaining maximum graft add-on. BEE appeared to be a better photoinitiator than the other two, giving maximum possible graft add-on. CAN, as a chemical initiator, did not show significant improvement in grafting. The moisture regain of the grafted polypropylene increased in proportion with the graft add-on. Dyeing with reactive dye could give only light color to the grafted fiber. Possible explanations have been given. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Graft copolymerization, as a process, involves polymerization of a monomer in the form of side chains onto a backbone polymer, such as a textile fiber. The advantage of grafting textile fibers is that the properties of the graft copolymer remain, principally, those of the backbone polymer along with the properties added due to the graft. Of the two techniques of grafting, the chemical initiation involves either thermal dissociation of oxidizing agents or chemical reactions to generate free radicals, whereas, during photoinitiation, the radical sites are produced on the backbone polymer by hydrogen abstraction.

The use of low-energy UV radiation for the graft-copolymerization process has been widely pursued for modifying fiber properties[1-5] because of its least deteriorating effect.

Polypropylene fibers, though possessing excellent chemical and thermal resistance, find limited use as an apparel fiber because of buildup of static electricity, low softening, and melting points, inability to become dyed, etc. On subjecting polypropylene to radiations of either high or low energy, however, it yields reactive sites for chemical reaction. Armstrong and Walsh[6] grafted polypropylene with various vinyl monomers using γ-radiation that improved moisture regain, dyeability, melting point, etc., without significantly altering the strength. Tazuke and Kimura[7] as well as Nito et al.[8] grafted polypropylene film with acrylonitrile using benzophenone as the photoinitiator, and the wettability of the film was shown to improve. Using the same photoinitiators, Zhang and Ranby[9] grafted acrylic acid and acrylamide onto polypropylene. Use of different initiators has been made by different workers[10-13] to graft copolymerize polypropylene with vinyl monomers.

2-Hydroxyethyl methacrylate (HEMA) is a hydrophilic monomer that is also widely used in the enzyme immobilization technique.[14] In the present study, therefore, UV radiation-induced grafting of polypropylene staple fibers with HEMA using uranyl nitrate, ceric ammonium nitrate, and benzoin ethyl ether separately as photoinitiators was carried out by optimizing the time and temperature of the reaction as well as the concentrations of various initiators and HEMA in order to obtain maximum possible grafting. Ceric ammonium nitrate was also used for the chemical initiation technique of grafting for comparison. As a measure of hydrophilicity imparted, the moisture regain of the grafted samples was determined. Also, the grafted fibers were subjected to dyeing with dyes of a reactive and a disperse class to observe the coloration of polypropylene.

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Journal of Applied Polymer Science, Vol. 51, 1567–1574 (1994)
 CCC 0021-8995/94/091567-08

EXPERIMENTAL

Materials

Substrates

Isotactic polypropylene staple fibers, "Proplan," supplied by Neomer Ltd., India, were Soxhlet-extracted with acetone for 12 h to remove surface impurities and spin finishes.[15,16]

Chemicals

2-Hydroxyethyl methacrylate (HEMA) supplied by Aldrich Chemical Co. was used without further purification. Two inorganic initiators, namely, uranyl nitrate (UN) and ceric ammonium nitrate (CAN), and one organic initiator, benzoin ethyl ether (BEE), were used for the graft copolymerization. Methanol and other solvents used were of "chemically pure" grade.

Dyes

A reactive dye, Reactofix Brilliant Red HE 3BL (C.I. Reactive Red 120) supplied by Atic Ind., and a disperse dye, Dispersol Red D 2B (C.I. Disperse Red 92) supplied by Jaysinth Dye Chem., were used for the dyeing of polypropylene.

Graft Copolymerization Using UV Radiation

One gram of polypropylene fibers was immersed in 100 mL of the grafting solution containing monomer and initiator in a quartz tube. The photoinitiators UN and CAN were soluble in water, whereas BEE was soluble either in pure methanol or in a methanol: water mixture. BEE, therefore, was used in the grafting baths comprising different methanol:water compositions varying between 0 and 100 to determine the suitable bath composition in which BEE was soluble and, also, the graft level maximum. The other two initiators, UN and CAN, were used in pure aqueous grafting baths only. A Philips HPW 125 W mercury vapor lamp fit in wooden chamber was used as a source of UV radiation. Different constant temperatures of reaction were maintained by using a thermostatically controlled glycerine bath. The substrate, placed in a quartz flask containing the grafting solution, was irradiated for different time intervals varying from 1 to 6 h in an enclosed wooden chamber containing the UV lamp, the distance between the lamp and the substrate being about 12 cm. The flasks were intermittently shaken. All the parameters of grafting, viz., time and temperature of reaction as well as the initiator and monomer concentrations, were optimized by varying the values of one parameter at a time in order to obtain maximum possible graft add-on.

After completion of the grafting reaction, the sample was removed, washed with methanol, and extracted with a boiling methanol:water (50 : 50) mixture for 7 h until constant weight to remove the homopolymer formed.[17] The extracted sample was washed with methanol and then with water followed by air-drying. The whole procedure was repeated until the homopolymer was removed completely as indicated by the constant weight of the grafted sample. The graft add-on and graft yield were determined using standard formulae as follows:

$$\text{Graft add-on, \%} = \frac{W_2 - W_1}{W_1} \times 100$$

and

$$\text{Graft yield, \%} = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1 is the weight of the original sample; W_2, the weight of the grafted sample; and W_3, the weight of the monomer taken initially.

Graft Copolymerization Using Chemical Initiation

CAN was also used in the absence of UV radiation as a chemical initiator for grafting polypropylene fibers with HEMA. The fibers were immersed in an aqueous grafting solution containing varying amounts of HEMA and CAN placed in an Erlenmeyer flask kept in the thermostatically controlled glycerine bath at different temperatures for varying lengths of time. Various parameters of grafting were optimized in this case also. The grafted sample was extracted free of homopolymer, as described above, followed by air-drying. The graft add-on and the graft yield were then calculated.

Dyeing with Disperse Dye

One gram each of the control and the HEMA-grafted polypropylene fibers were subjected to dyeing in an aqueous bath using a disperse dye, Dispersol Red D 2B (10 g/L), keeping a liquor ratio of 50. Lyocol OI [Sandoz (I) Ltd.], 1 g/L, was used as a dispersing agent and the pH was maintained at 4.5–5.5 using acetic acid. The temperature was raised from 40 to 130°C at a rate of 1°C/min in a "high-temperature beaker dyeing machine." In this machine, the fiber and the dye liquor along with the additives are placed

in the stainless-steel beakers and tightly closed with stainless-steel lids and these beakers are rotated in a revolving assembly placed in an outer stainless-steel closed vessel containing glycerine. The glycerine in the outer vessel is heated electrically to high temperature. After dyeing, samples were given a treatment with 2 g/L caustic soda and 2 g/L sodium hydrosulfite at 70°C for 15 min with subsequent washing to remove the dye attached to the fiber surface. The dye bath liquor was tested for the percent exhaustion by measuring the optical density on a Pye Unicam-SP8-400 UV/vis spectrophotometer at a wavelength of 517 nm, corresponding to the λ_{max} of the dye used.

Dyeing with Reactive Dye

One gram each of the polypropylene fibers, both ungrafted and grafted, were subjected to dyeing with a reactive dye, Reactofix Brilliant Red HE 3BL (20 g/L), in a "open bath beaker dyeing machine," keeping the liquor ratio of 50. In this machine, the stainless-steel beakers are open and the fiber mass is agitated up and down in the dye liquor to achieve uniform dyeing. Glauber's salt (70 g/L) was used for exhaustion and sodium carbonate (20 g/L) was used for dye fixation. The temperature was raised to 90°C and dyeing was carried out for 1 h. The samples were soaped, washed, and dried. The dye uptake by the fibers was determined from the dye bath exhaustion values as described above at a wavelength of 542 nm, which corresponds to the λ_{max} value of the dye used.

Determination of Moisture Regain

The moisture regain of the control and grafted polypropylene was determined by the oven-drying method.[18] The fibers were kept initially in a P_2O_5 desiccator for 4 h to reduce the moisture below the regain value. The samples were then placed in a desiccator containing saturated ammonium nitrate (65% RH, 30°C) for more than 72 h. The conditioned samples were then weighed accurately and dried in an oven at 110°C for 3 h. After cooling in a P_2O_5 desiccator, the samples were weighed. The procedure of oven-drying and weighing was repeated until constant weight was obtained.

Table I Effect of Methanolic Bath Composition on Grafting of HEMA onto Polypropylene Using BEE Photoinitiation

Methanol : Water	Graft Add-on (%)
100 : 0	0.00
50 : 50	0.00
25 : 75	2.17
10 : 90	5.92
5 : 95	7.56
2.5 : 97.5	8.24
0 : 100	0.00

RESULTS AND DISCUSSION

The graft-copolymerization reaction onto textile fibers takes place through generation of free-radical sites on the backbone polymer, which can be accomplished in a number of ways. The chemical initiation technique and the use of radiation of low energy inevitably needs initiators for this purpose. The initiators decompose either on heating or in presence of radiation into free radicals that are capable of abstracting the H atom from the backbone polymer, creating site for the growth of a graft chain.

In the present work, polypropylene fibers were grafted with HEMA using three different photoinitiators, UN, CAN, and BEE, separately, of which CAN alone also acts as a chemical initiator. The monomer HEMA and the initiators UN and CAN were soluble in water as well as in methanol, whereas BEE was insoluble in water and needed the presence of at least a small quantity of methanol in the aqueous bath for its dissolution. To obtain maximum graft add-on, the parameters of graft-copolymerization reaction, viz., the time and temperature of the reaction as well as concentrations of each of the initiators and HEMA, were optimized.

It was observed that the use of a pure methanolic bath for photoinduced grafting of HEMA under UV radiation in the presence of any of the three photoinitiators, UN, CAN, and BEE, did not produce any grafting. The aqueous grafting bath was, therefore, used for the reactions incorporating UN and CAN initiators. For grafting using BEE, different compositions of the methanol:water mixed bath were tried. These results are given in Table I, which clearly indicate that a methanol:water mixed grafting bath having the composition 2.5 : 97.5 gave the maximum graft add-on under the given conditions of time (3 h), temperature (50°C), HEMA concentration [3% (w/v)], and BEE concentration [0.30% (w/v)]. This composition of the methanol:water bath was, therefore, used in all the grafting reactions incorporating BEE as the photoinitiator.

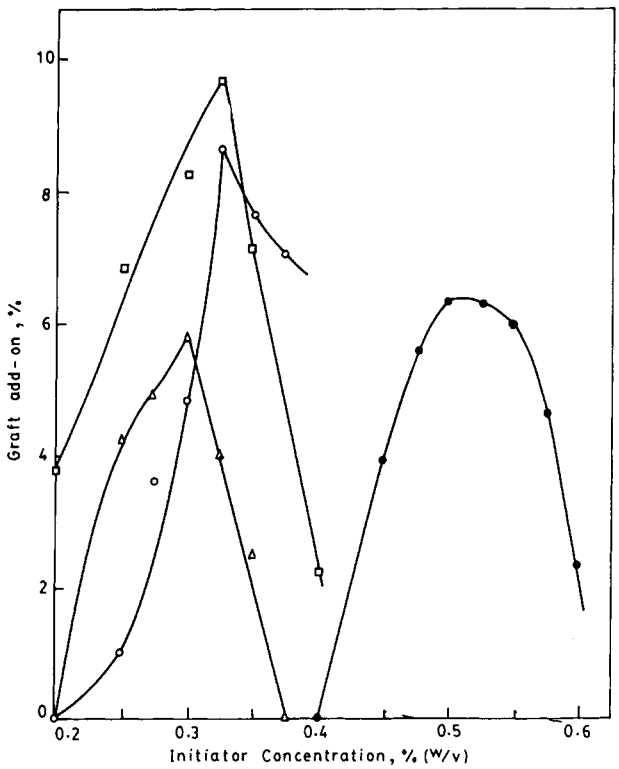

Figure 1 Effect of initiator concentration on the grafting of HEMA onto polypropylene: (○) UN initiation; (□) BEE initiation; (△) CAN initiation; (●) CAN-chemical initiation.

Effect of Initiator Concentration

To study the effect of initiator concentration on photoinduced grafting of HEMA onto polypropylene, the concentrations of UN, CAN, and BEE were varied from 0.10 to 0.40% (w/v), keeping the HEMA concentration at 3% (w/v) and carrying out grafting at 50°C for 3 h. CAN, as a chemical initiator, was used in the range of 0.40–0.70% (w/v). Figure 1 shows these results. Accordingly, up to a specific initiator concentration in each case, the graft add-on increased due to an increased number of sites generated for grafting. Beyond these specific concentrations, however, the values of graft add-on decreased. In the presence of excess initiator, the growing polymeric side chains of HEMA terminate rapidly, thereby decreasing the graft add-on. A similar effect of increasing photoinitiator concentration has been reported earlier for cellulose grafting.[19,20]

In comparing the role of CAN as a photoinitiator in the presence of UV radiation and as a chemical initiator in the absence of UV radiation, it was observed that in the latter case the quantity of CAN required for grafting was higher along with the higher reaction temperature of 80°C at almost equivalent levels of graft add-on.

Among the three different initiators, the UV radiation-induced grafting using the BEE photoinitiator gave somewhat higher values of graft add-on.

Effect of Reaction Time

Figure 2 shows the effect of the time of reaction on the graft add-on. In the case of chemical initiation using CAN, the HEMA graft add-on increased with time of grafting from 1 to 4 h and leveled off thereafter. In the photoinitiation technique, however, the graft add-on increased with the time of reaction up to 3 h using CAN and BEE and up to 4 h using the UN photoinitiator, beyond which it decreased. The attainment of increased graft add-on with the time of reaction was probably due to the increasing extent of initiation and propagation of the graft-copolymerization reaction. The decrease in grafting after a particular time period, in the case of the photoinduced reaction, was due to the detrimental effect of

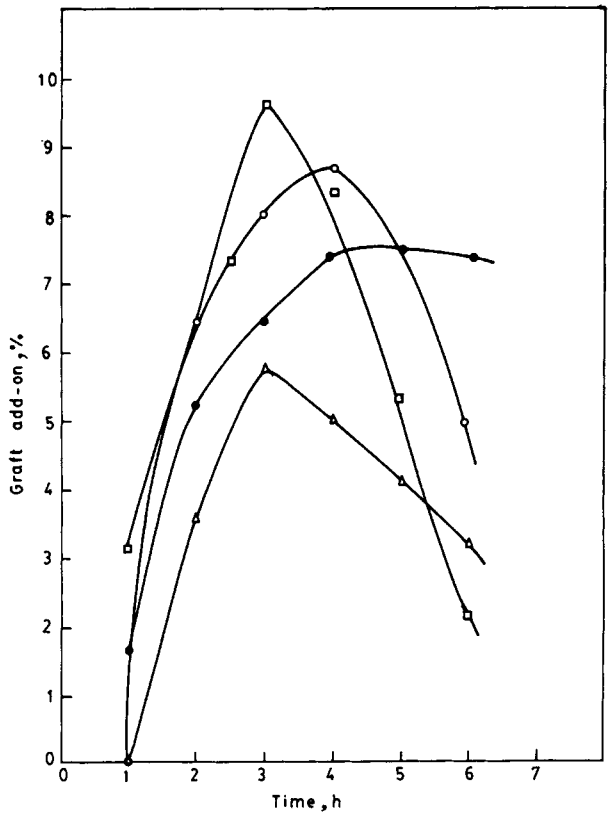

Figure 2 Effect of time of reaction on the grafting of HEMA onto polypropylene: (○) UN initiation; (□) BEE initiation; (△) CAN initiation; (●) CAN-chemical initiation.

UV radiation onto the grafted side chains of HEMA at longer irradiation times in the presence of a photoinitiator. Such a decrease in the graft add-on with increased time of photoinduced grafting has been observed earlier by Herold and Fouassier.[21] In the case of chemically initiated graft copolymerization, such detrimental effects are absent and, hence, the graft add-on does not decrease with further reaction time.

Effect of Reaction Temperature

Figure 3 shows the effect of reaction temperature on the graft add-on. The graft add-on in the presence of UV radiation increased with increasing temperature up to 50°C and thereafter decreased. Chemical initiation using the CAN initiator did not show any grafting up to a temperature of 40°C. With further increase in temperature, maximum graft add-on was obtained at 80°C and then it decreased. With increase in temperature, more and more free radicals are formed, which enhance the grafting. A higher temperature beyond a specific one, however, causes an increased extent of radical termination, decreasing the free radical availability, thereby reducing the graft level.

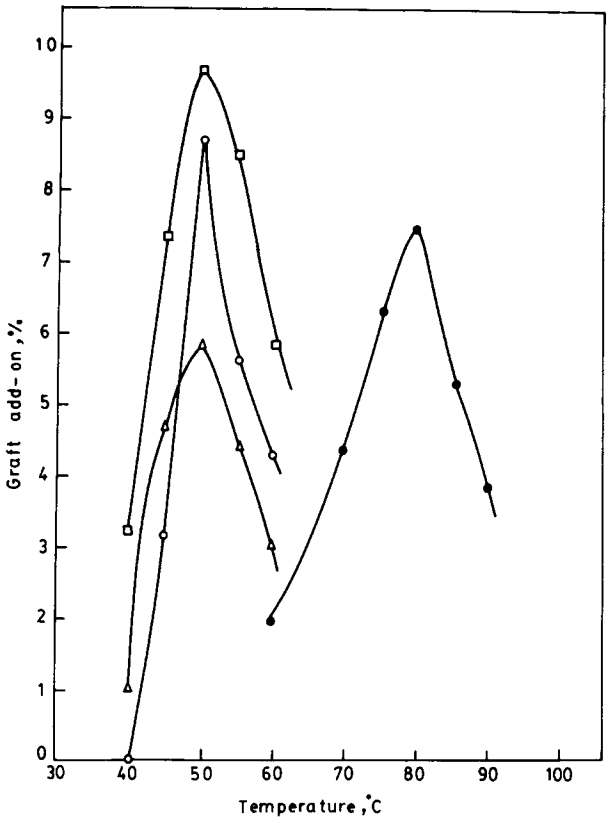

Figure 3 Effect of temperature of reaction on the grafting of HEMA onto polypropylene: (○) UN initiation; (□) BEE initiation; (△) CAN initiation; (●) CAN-chemical initiation.

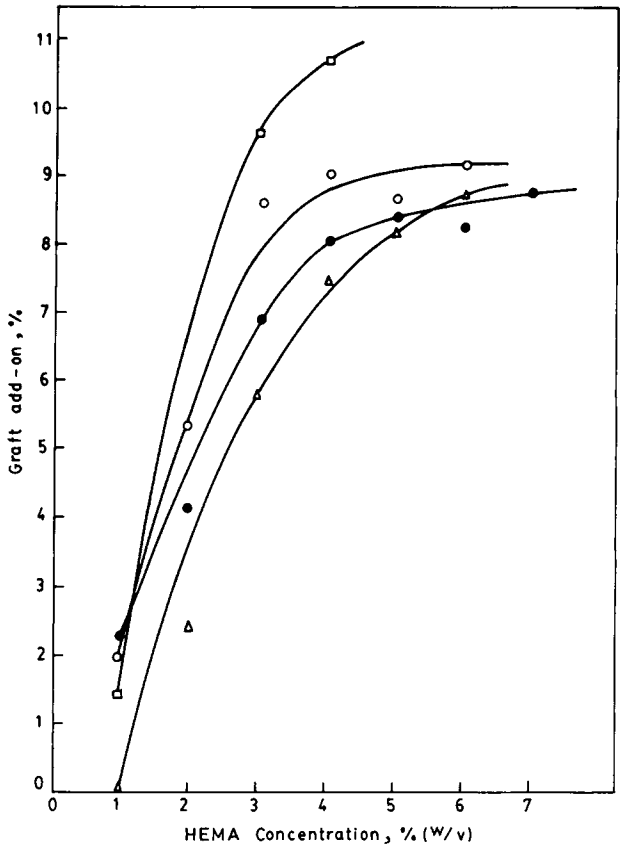

Figure 4 Effect of concentration of HEMA on the graft add-on onto polypropylene: (○) UN initiation; (□) BEE initiation; (△) CAN initiation; (●) CAN-chemical initiation.

Effect of Monomer Concentration

The effect of increasing the concentration of HEMA from 1 to 6% (w/v) on graft add-on and graft yield is shown in Figures 4 and 5, respectively. Figure 4 shows that the graft add-on increased with increase in HEMA concentration and ultimately leveled off. The increase in graft add-on was obviously due to the increased availability of the monomer for the grafting reaction. The maximum graft yield was observed at 3% (w/v) HEMA concentration (Fig. 5) in all cases, suggesting that the utilization of HEMA is better only at this concentration as compared to that at any other concentration used. Although grafting increased beyond 3% (w/v) HEMA concentration, the corresponding homopolymer for-

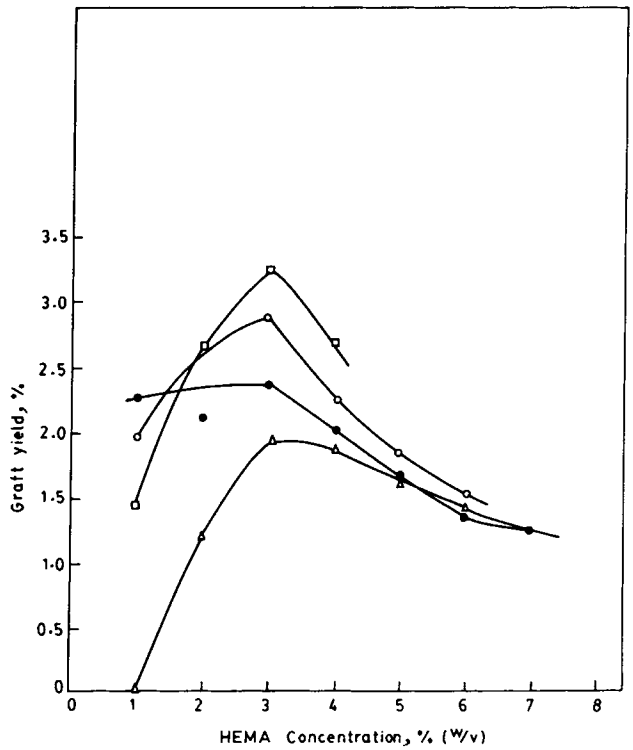

Figure 5 Effect of concentration of HEMA on graft yield of polypropylene: (○) UN initiation; (□) BEE initiation; (△) CAN initiation; (●) CAN-chemical initiation.

mation also increased, leading to lowering of the graft yield at higher HEMA concentrations. Thus, a maximum graft add-on of 10.68% was obtained onto polypropylene fibers by UV radiation-induced grafting using a bath containing 4% (w/v) HEMA and 0.325% (w/v) BEE, the time and temperature of the reaction being 3 h and 50°C, respectively. Increasing the HEMA concentration beyond 4% (w/v) led to a high level of homopolymerization that was difficult to extract from the grafted sample. The graft level, as such, has remained considerably low, attributable to the highly compact structure of polypropylene fibers that hinders even slight penetration of the bulky HEMA molecules inside the substrate to produce efficient grafting.

Moisture Regain of Grafted Fibers

HEMA is a hydrophilic monomer and, hence, the effect of HEMA grafting on moisture regain of the extremely hydrophobic polypropylene fibers was studied. Figure 6 shows that the moisture regain increased with corresponding increase in HEMA graft add-on. The absorption of moisture by a substrate depends on atmospheric humidity, the accessible nature of the substrate, and the presence and availability of groups in the substrate capable of absorbing moisture. When polypropylene fibers were grafted with HEMA, the hydrophilicity increased because of the —OH groups of HEMA that take part in the formation of hydrogen bonds with moisture. As the graft add-on increases, the number of available —OH groups from HEMA graft chains increases.

Dyeability of Grafted Fibers

The coloration of textile fibers is of great importance for its apparel uses. None of the conventional dyestuffs/dyeing methods can color this fiber satisfactorily because of its inert olefinic nature as well as highly compact fiber structure. Polypropylene can be colored only in its dope state by mixing the molten mass with pigments followed by extrusion of the colored filaments.

A disperse dye penetrates the synthetic textile fiber and imparts color even in absence of any polar groups. The dye strength in the fiber is governed

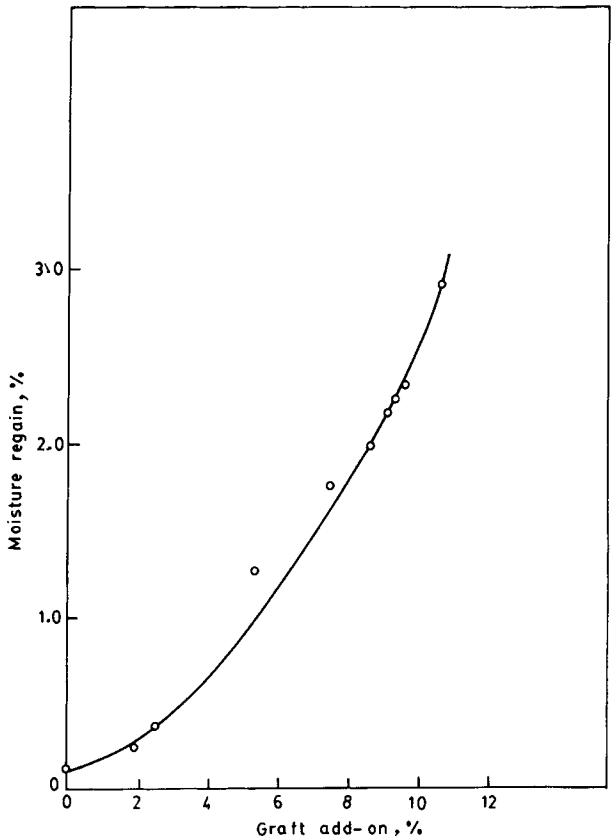

Figure 6 Effect of HEMA-graft add-on on moisture regain of polypropylene.

mainly by the openness of the fiber structure, which can generally be enhanced by the use of chemicals or higher temperature, as in the case of poly(ethylene terephthalate) fibers.

On dyeing HEMA-grafted polypropylene with a disperse dye at 130°, no significant change in the dye bath exhaustion was noticed, suggesting, thereby, that at the level of grafting obtained in the present work there is no appreciable change in the fiber structure as far as its opening up is concerned. For any polymeric substrate, a chemical reaction takes place mainly in the amorphous region followed by that in the semicrystalline region, the extent depending upon the severity of the reaction conditions as well as the nature of the reaction. Graft copolymerization in case of polypropylene fibers also depends on these factors, and since polypropylene is highly crystalline and compact, the limited amount of grafted chains of poly(HEMA) as well as their bulky nature (due to bulky HEMA molecules) are unable to open up the polypropylene fiber structure. The disperse dye uptake, therefore, did not show any remarkable variation between the ungrafted and HEMA-grafted fibers.

The molecules of HEMA possess —OH groups. A reactive dye can react with these groups to form a strong covalent bond. For this reaction to take place, alkaline conditions are essential. As in any other conventional dyeing, a larger amount of dye must first exhaust onto the fiber from the dye bath before any reaction between the dye and the fiber takes place. In the case of HEMA-grafted polypropylene, the graft chains cannot penetrate the highly compact fiber structure due to the bulkiness of HEMA, and, hence, it was assumed that most of the —OH groups of the grafted poly(HEMA) chains will be available for the reaction with the reactive dye. Thus, the reactive dye could impart color to the HEMA-grafted fibers, which was totally absent in the case of ungrafted fibers. However, it was observed that even in this dyeing the dye on the fiber was extremely low, and from the textile use point of view, it was not a deep dyeing, but only a light color.

The reactive dye uptake as well as the moisture sorption depends on the available —OH groups due to HEMA-graft chains in polypropylene. Although the moisture regain of the grafted polypropylene fibers increased, the dyeability with reactive dye did not manifest greatly and only a color tint was observed. Although the absorbance values of the exhausted dye bath were estimated quantitatively on a spectrophotometer, there was hardly any significant difference in values so as to report them.

Under the prevailing conditions of grafting, the highest level of the HEMA graft achieved was only 10.68%, which may not be sufficient enough either to incorporate a large number of —OH groups or to open up the fiber structure for improving its accessibility. A molecule of dye is much more bulkier than that of moisture and, hence, the penetration of the dye molecule itself is greatly hindered by the compact structure of the substrate, as has been confirmed by disperse dyeing. The reactive dye exhausted on the grafted polypropylene fibers was, therefore, only about 5% of the original dye bath. This also indicates that the HEMA-graft chains lie mostly on the fiber surface and the compact structure of polypropylene does not allow bulkier HEMA molecules to penetrate either. The higher HEMA-graft levels will be helpful in imparting color to polypropylene fibers.

CONCLUSION

In conclusion, it may be stated that the UV radiation-induced grafting has been as equally effective as the chemical initiation technique in the present work. For a highly compact and inert fiber like polypropylene, the graft level is considerably low because of the low accessibility of fiber as well as the bulkiness of the monomer HEMA. The moisture regain of the grafted fibers increased; however, the dyeability was not satisfactory, owing also to the bulky nature of the dye molecules.

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Received February 25, 1993
Accepted August 5, 1993