Thermal Properties of 2-Hydroxyethyl Methacrylate Grafted Polypropylene

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SYNOPSIS

2-Hydroxyethyl methacrylate (HEMA) was graft-copolymerized onto polypropylene using ultraviolet radiation in the presence of benzoin ethyl ether as photoinitiator. The parameters of grafting were optimized for getting maximum graft add-on. The thermal properties of the grafted samples were investigated using differential thermal analysis, thermogravimetric analysis and differential scanning calorimetry. The results have been discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene holds promising future as a textile fiber, although associated with certain drawbacks like buildup of static electricity, low softening and melting points, inability to get dyed, etc. Attempts have been made to modify polypropylene to improve its characteristics. Vinyl monomer grafting constitutes a major step in such direction. However, during such conversion of a linear polymer into a graft copolymer with the help of a different chemical moiety, polypropylene undergoes changes in properties, the degree of change being obviously dependent on the graft level.

The use of low energy UV radiation for graft-copolymerization process has been widely pursued for modifying fiber properties[1-5] because of its least deteriorating effect. Photografting of polypropylene has been shown to improve some of its properties.[6,7]

Many researchers carried out grafting of polypropylene in order to improve its moisture regain, dyeability, etc.[8-14] However, little work has been reported on improving the thermal stability of polypropylene. Sundardi and others[15-17] tried to improve the thermal stability of polypropylene using different vinyl monomers. Similarly, flame proofing of polypropylene by grafting phosphorus-containing vinyl monomers has also been tried.[18,19] Graft copolymer-ization of 2-hydroxyethyl methacrylate (HEMA) has been found to improve the thermal stability of fibers like cotton and silk.[20,21]

In the present study, UV radiation-induced grafting of isotactic polypropylene fibers with 2-hydroxethyl methacrylate using a photoinitiator benzoin ethyl ether was carried out by optimizing various parameters. The thermal properties of the grafted and ungrafted fibers were determined using differential thermal analysis, thermogravimetric analysis, and the differential scanning calorimetry.

EXPERIMENTAL

Materials

Substrates

Isotactic polypropylene staple fibers, "Proplan," supplied by M/s Neomer Ltd., India, were Soxhlet-extracted with acetone for 12 h in order to remove surface impurities and spin finishes.[22,23] The fiber free from all the impurities was considered as "control" for all the thermal analyses and was also used in the grafting experiments.

Chemicals

2-Hydroxyethyl methacrylate (HEMA) supplied by Aldrich Chemical Co. was used without further purification. An organic initiator, benzoin ethyl ether (BEE), was used for graft copolymerization. Meth-

anol and other solvents used were of "chemically pure" grade.

Thermal Analysis

The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) were carried out in nitrogen atmosphere using a Stanton Redcroft thermal analyzer, STA 780. It simultaneously records weight vs. time or temperature for TGA and temperature vs. time curves for DTA. The sample was cut to approximately 1–2 mm length and 20 ± 5 mg sample was taken for each analysis. The analysis was carried out from room temperature (30°C) to 500°C at a heating rate of 10°C/min and with a chart speed of 200 mm/h.

The differential scanning calorimetry (DSC) was carried out on a Perkin Elmer DSC 7 thermal analysis controller TAC 7/DX with T graphics plotter-8. It records the differential power signal, which is the power input required to maintain sample and reference at a same programmed temperature. A sample (10 ± 2 mg cut) was taken for each analysis. The analysis was carried out from 50 to 450°C in a nitrogen atmosphere at a heating rate of 20°C/min.

Graft Copolymerization

Philips 125 W low pressure mercury vapor lamp was used as a source of UV radiation for the process of graft copolymerization. One gram of polypropylene fiber was immersed in 100 mL of grafting solution containing monomer and initiator in a quartz tube. BEE is insoluble in water and needs the presence of at least a small quantity of methanol in the aqueous bath for its dissolution. It was, therefore, dissolved in a previously optimized methanol : water (2.5 : 97.5) mixture. The temperature of reaction was maintained by using a thermostatically controlled glycerine bath. The time of reaction was studied by irradiating the substrate under UV for different time intervals varying from 1 to 6 h. All the parameters of grafting, viz., time and temperature of reaction as well as the initiator and monomer concentrations, were optimized in order to obtain the 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 till constant weight to remove the homopolymer formed.[24] The extracted sample was washed with methanol and then with water, followed by air-drying. The graft add-on and graft yield were determined using standard formulae.[5]

Infrared Spectral Analysis

Infrared spectra were recorded on Perkin Elmer 391 infrared spectrophotometer. Two milligrams of finely cut fibers were mixed with 198 mg of KBr and pellet was prepared. Scanning was carried out from 4000 to 400 cm^{-1} at a slow speed.

RESULTS AND DISCUSSION

Optimization of Parameters of HEMA Grafting

The concentration of BEE was first varied between 0.1 and 0.4% (w/v) keeping the HEMA concentration at 3% (w/v) at 50°C for 3 h. The reaction time was then optimized at 3 h by varying it between 1 and 6 h using optimized concentration of BEE as 0.325% (w/v) at 50°C and 3% (w/v) HEMA. A temperature of 50°C was found to give maximum graft add-on. Finally, when the HEMA concentration was varied from 1 to 5% (w/v), it was found that the graft add-on increased gradually with the increase in HEMA concentration. The maximum graft add-on obtained under these conditions was 10.68%.

Infrared Spectra of the Grafted Fibers

The infrared spectra for the control and grafted polypropylene fibers are shown in Figure 1. It shows an additional peak at 1700 cm^{-1} for the grafted polypropylene sample, confirming the introduction of ester carbonyl groups belonging to the graft in the polypropylene structure.[25] Also, the spectra of grafted fibers showed a characteristic band 3300–3500 cm^{-1}, corresponding to the —OH groups of the HEMA graft chains, which is absent in the IR spectra of the ungrafted polypropylene.

Differential Thermal Analysis

The differential thermal analysis detects the thermal effects accompanying physical/chemical changes in the sample as its temperature is varied through a region of transition.[26] Figure 2 shows the DTA curves of polypropylene, ungrafted and grafted with HEMA. An endotherm is observed at around 167°C which corresponds to the melting point of polypropylene. This is in agreement with the crystalline melting point of isotactic polypropylene, which is quoted at around 167°C.[27] The major exothermic reaction was observed to start at 394°C with a peak at around 399°C in the case of ungrafted polypropylene, which showed total decomposition at 428°C.
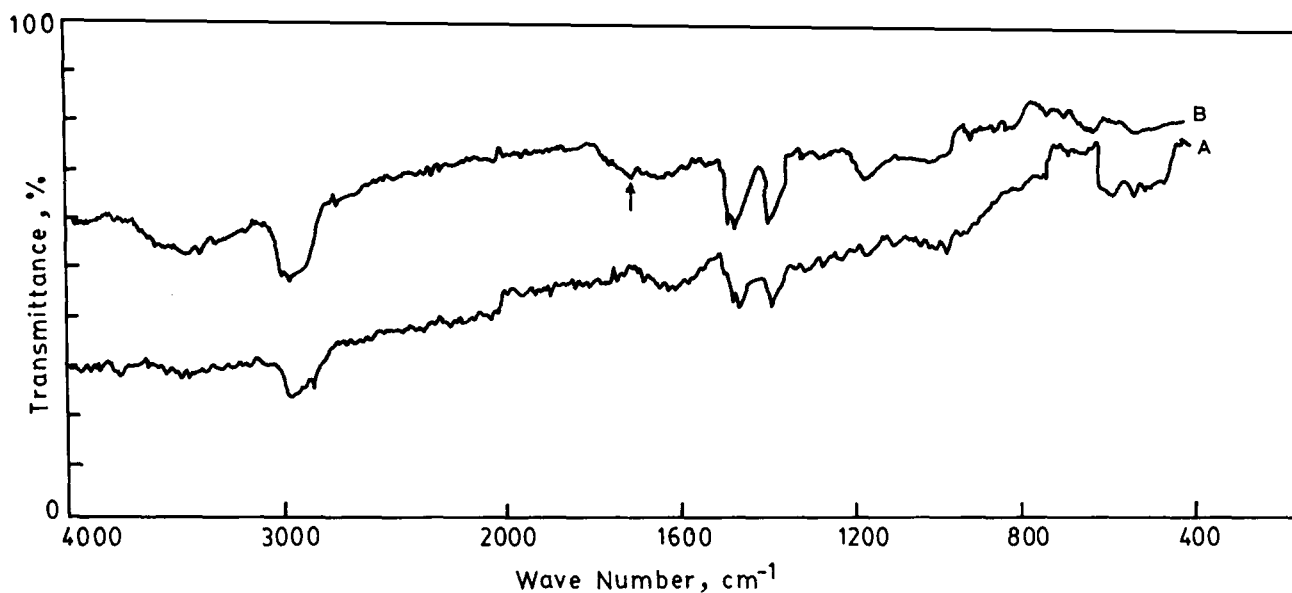
Figure 1 Infrared spectra of polypropylene: (A) ungrafted polypropylene; (B) HEMA-grafted polypropylene.

The peak for the melting point remained unchanged on grafting. This may be due to the fact that the low level of grafting takes place mainly on the sur-

face of polypropylene fibers leaving the internal crystalline structure intact, which accounts for the melting point of polymer. However, for grafted
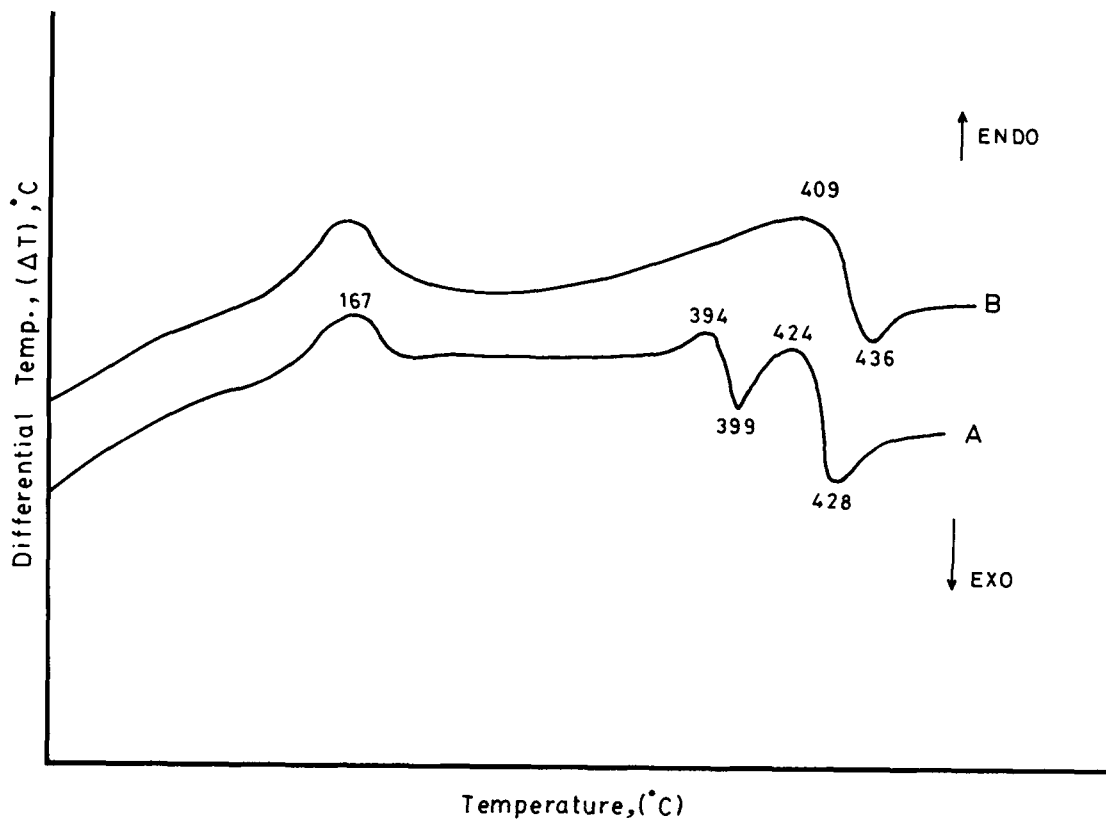
Figure 2 DTA curves of polypropylene: (A) ungrafted polypropylene; (B) HEMA-grafted polypropylene.

polypropylene, the exothermic peak corresponding to polymer degradation shifted to 436 from 428°C.

Thermogravimetric Analysis

The thermogravimetric method is widely used to investigate the thermal decomposition of polymers, which can indicate the behavior of polymer towards the thermal stability. The thermal stability of any polymeric material is usually determined by the strength of the covalent bond between the atoms inside the polymer molecules. Table I shows the values of various bond strengths and bond lengths.[15] From these values, the average complete dissociation

Table I Bond Strength and Length

Bond	Length (Å)	Dissociation Energy (kcal/mol)
C—H	1.07	98
C—C	1.54	81
C—O	1.42	87
C=O	1.21	174
O—H	0.96	110

values for the polymers can be calculated. For polypropylene the calculated value is about 91.2 kcal/mol and for poly-HEMA it is 95.76 kcal/mol. The
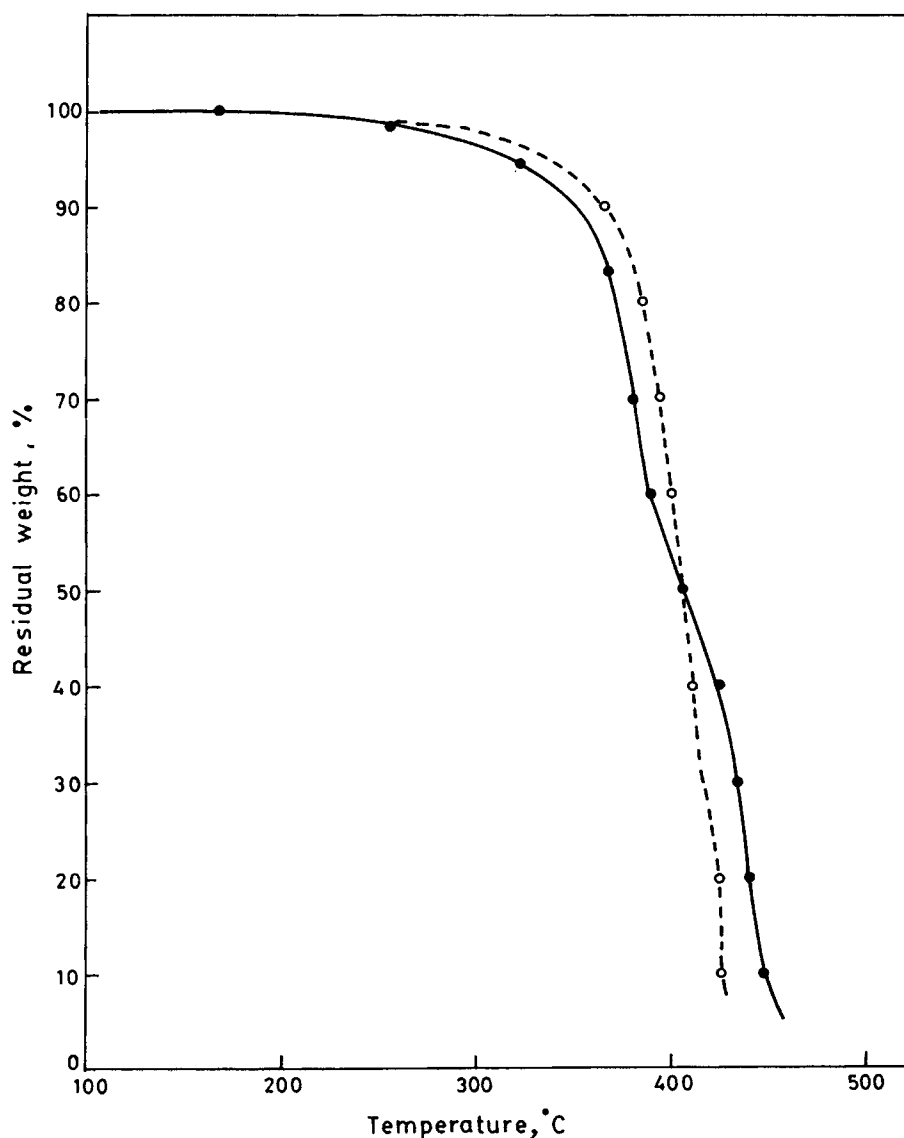
Figure 3 TGA curves of polypropylene: (– – – –) ungrafted polypropylene; (———) HEMA-grafted polypropylene.

comparatively lower dissociation energy for poly-propylene fibers is due to the lack of $C=O$ and $C=C$ bonds, whereas, for poly-HEMA, the higher value is due to the presence of $C=O$ as well as the $C-O$ and $O-H$ bonds. Thus, from these theoretical calculations it can be predicted that the grafting of HEMA onto polypropylene would increase the overall dissociation energy, and, therefore, it is likely that the thermal stability of grafted fibers may improve, although slightly due to considerably low level of HEMA graft add-on.

The results on TGA were obtained by determining the decomposition temperature (T_D) at different weight losses of ungrafted and HEMA grafted polypropylene. From Figure 3, it can be seen that up to a weight loss of 50%, the HEMA-grafted polypropylene shows relatively lower thermal decomposition, which increases beyond 50% weight loss.

Differential Scanning Calorimetry

DSC provides a measure of heat capacity. The signal received from DSC is proportional to the difference of heat capacities between the sample and the reference. Thus, the DSC measurements were carried out to analyze the changes in the thermal properties of the polypropylene fibers before and after grafting with HEMA. Figure 4 shows the DSC thermograms.

It can be seen from that figure that an endothermic peak appears at the temperature of 163°C, which corresponds to the melting point of the polypropylene. Similar peak is obtained in the HEMA-grafted polypropylene wherein the instrument has given a value of 164°C. Sundardi[28] has observed that the grafting of hydrophilic monomers onto polypropylene increases the melting point of fiber. The DSC studied in the present investigation did not show any noticeable improvement in the melting point of polypropylene on grafting, although there is no decrease either. This suggests that the low level of graft add-on achieved is unable either to decrease the crystallinity or to improve significantly the melting point of polypropylene fiber. An exothermic peak appearing at around 390°C in the ungrafted polypropylene shifts to 396°C for the HEMA-grafted polypropylene. Since there are no positive indica-
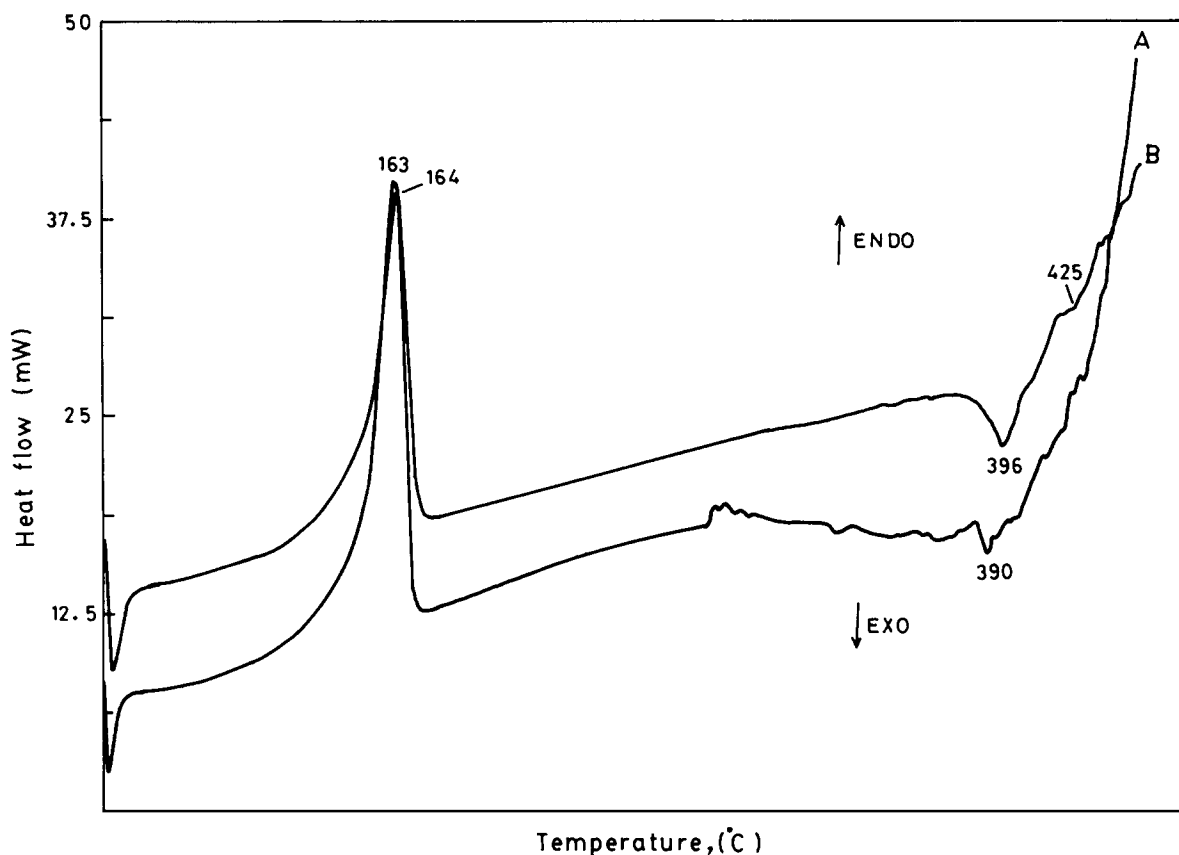
Figure 4 DSC thermograms of polypropylene: (A) ungrafted polypropylene; (B) HEMA-grafted polypropylene.

tions of improvement due to grafting in the thermal stability of polypropylene fibers in the low temperature range up to the melting point of polypropylene, this shift in the exothermic peak at a very high temperature of 390°C may be taken as another indication of the changes taking place in the thermal behavior of polypropylene fibers. The presence of a slight endothermic peak at around 425°C may be due to the thermal decomposition of poly-HEMA.[20]

The thermal stability improves, owing both to the abstraction of labile hydrogen from the tertiary carbon atom followed by grafting at that site and to the crystallization process taking place during the course of heating, involving poly-HEMA moieties. The level of thermal stability imparted in the present case is very poor since it depends on the nature of monomer grafted as well as the amount of graft add-on, which is considerably low.

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