

# Synthesis and Characterization of Dextrin-Grafted Polypropylene

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**ABSTRACT:** We carried out the graft copolymerization of the water-soluble natural polymer dextrin onto preirradiated polypropylene (PP) in an aqueous medium using benzoyl peroxide (BPO) as the radical initiator. PP was irradiated by  $\gamma$  rays from a  $\text{Co}^{60}$  source at a constant dose rate of 3.40 kGy/h to introduce hydroperoxide linkages, which served as the sites for grafting. The graft copolymerization was studied as a function of different reaction parameters, and the maximum percentage grafting ( $P_g$ ; 55%) of dextrin onto PP was obtained at optimum conditions of  $[\text{BPO}] = 5.165 \times 10^{-2}$  mol/L, temperature = 60°C in 120 min with 15 mL of water. Different grafting parameters, such as the percentage apparent grafting, percentage grafting, and percentage true grafting have been evaluated. The graft copolymers were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy.

Swelling studies were carried out in pure, binary, ternary, and quaternary solvent systems composed of water, ethanol (EtOH), dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF) at different ratios. The maximum swelling percentage PP-*g*-dextrin (both composite and true graft) was observed in pure DMSO and DMF followed by EtOH and water. Water-retention studies of PP and PP-*g*-dextrin (both composite and true graft) were investigated at different time periods, temperatures, and pH values. The maximum percentage water retention of PP-*g*-dextrin (composite, 124%) was observed at 8 h and 50°C in a neutral medium (pH 7). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1090–1101, 2011

**Key words:** graft copolymers; irradiation; poly(propylene) (PP); swelling; thermogravimetric analysis (TGA)

## INTRODUCTION

In the ever-growing plastic era, synthetic polymers such as polyethylene and polypropylene (PP) have almost completely inhabited the modern world. Because of their wide range of properties, including durability; resistance to chemicals, weathering, photodegradation, and biological attack; and hydrophobicity, they are used in diverse applications in various fields. However, the inertness of these polymers excludes their application where chemical affinities or penetration of components is necessary, for example, in the dyeing of fibers, printing of films, paintability, adhesion, agricultural mulches, and agricultural planting containers. To improve these and other properties, such as hydrophilicity, swellability, solubility, and chemical inertness, of PP, the modification of PP has been attempted by different groups of workers.

The graft copolymerization of acrylamide onto a water-insoluble polymer backbone (isotactic PP) and polymerization of acrylamide with a water-insoluble

initiator BPO and a phase-transfer catalyst [tetrabutylammonium bromide ( $\text{Bu}_4\text{N}^+\text{Br}^-$ )] was carried out in a water-xylene binary solvent system.<sup>1</sup> The graft copolymerization of acrylonitrile and its binary mixture with 4-vinyl pyridine onto isotactic PP powder in an aqueous medium with  $\gamma$  rays as an initiator was studied by Kaur et al.<sup>2</sup> PP fibers were grafted with methyl methacrylate (MMA), and the effects of direct and preirradiation methods and monomer concentration on the degree of grafting were investigated by Lopergolo et al.<sup>3</sup> It was found that the direct method was more efficient than the indirect or preirradiation method, and the monomer concentration for the highest degree of grafting was 40% MMA. The mechanical properties (tensile strength) and thermal stability decreased with grafting yield. Water sorbed on porous PP films grafted to various extents by the plasma-graft copolymerization of 2-hydroxyethyl acrylate with acrylic acid or methacrylic acid was examined with differential scanning calorimetry.<sup>4</sup> The graft copolymerization of methacrylic acid onto PP fibers by a simultaneous  $\gamma$ -ray irradiation technique was carried out. The effect of various solvents on grafting was studied. The results were presented in terms of the swelling behavior of PP fiber and the extent of homopolymerization.<sup>5</sup> The *tert*-butoxy radical-facilitated grafting of MMA and

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several other monomers onto commercial PP pellets and fibers was investigated under heterogeneous conditions.<sup>6</sup> A maximum grafting efficiency of over 50% was found. The reaction conditions were altered to favor grafting by the addition of more polymer substrate. The radiation-induced graft copolymerization of comonomer mixtures of acrylic acid and styrene onto PP films by the mutual method was studied by El-Salmawi et al.<sup>7</sup> The graft copolymerization of styrene onto poly(vinyl chloride) (PVC) and PP was carried out in a supercritical CO<sub>2</sub> medium with 2,2'-azobisisobutyronitrile as a free-radical initiator. The thermal stability of the grafted copolymer of PVC was better than that of PVC, whereas the grafted copolymer of PP had a poorer thermal stability than PP.<sup>8</sup> The preirradiation method was also used to graft copolymerize 2,3-epoxypropylmethacrylate onto PP fabric by Nho et al.<sup>9</sup>

From the literature survey, we inferred that the modification of PP through grafting is being successfully pursued with monomers and monomer mixtures. Not much attention has been given to the modification of PP by the grafting of a polymer through intercrosslinking. In this article, therefore, we report on the modification of PP by the grafting of a natural polymer, dextrin, with a chemical method. Dextrin occurs as an intermediate product of starch hydrolysis and is achieved by either enzymatic action or by heating. Dextrin is used as a thickener in textiles and a binder in watercolors and in foundries, food applications, and the manufacturing of adhesives, envelopes, gummed tapes, and postage stamps and bottle labeling.<sup>10</sup> Its water solubility, reactivity, and biodegradability make it a potentially useful material. The grafting of dextrin to PP is likely to introduce hydrophilicity to a hydrocarbon polymer and improve upon the properties of the latter.

## EXPERIMENTAL

### Materials

Commercial PP in the form of beads was obtained from Thukral Trading Co. (Delhi, India). The beads were recrystallized from *p*-xylene, and the powdered PP obtained upon precipitation with methanol was used in all grafting experiments. Irradiation of the polymer was carried from a Co<sup>60</sup> source housed in a Gamma Chamber-900 (BARC, Mumbai, India) at a constant dose rate of 3.40 kGy/h. Dextrin (Merck, Goa, India) and BPO (Merck, Mumbai, India) were used as received.

### Graft copolymerization

To the preirradiated, dried, and weighed PP (0.200 g), suspended in a known volume of water (0–20 mL)

was added a definite amount of dextrin (0.100–0.250 g) dissolved in a known volume of water (0–20 mL) and a definite amount of the initiator BPO (0.100–0.300 g). The reaction flask was placed in a water bath maintained at constant temperature (45–75°C), under constant stirring in a nitrogen atmosphere for a definite interval of time (60–210 min). After the stipulated time period, the flask was removed from the water bath, and the contents were filtered. The residue contained grafted PP, unreacted dextrin, unreacted PP, and some BPO. The residue was washed with benzene to remove unreacted BPO. The leftover product was dried at 50°C until a constant weight was reached, and this was referred to as the composite. The percentage apparent grafting of the composite was calculated from the initial increase in the weight of the original PP as follows:

$$\text{Apparent grafting (\%)} = \frac{W_c - W_0}{W_0} \times 100$$

where  $W_0$  and  $W_c$  are the weights of the PP and the composite, respectively.

The composite was then stirred with water for 2 h at 60°C to remove ungrafted dextrin. The reaction mixture was filtered, and the residue was dried at 50°C and weighed until a constant weight was obtained. The percentage grafting of dextrin onto PP was calculated as follows:

$$\text{Grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where  $W_0$  and  $W_g$  are weights of PP and the graft copolymer, respectively, that is, PP-g-dextrin after the complete removal of the ungrafted dextrin.

The graft copolymer was further stirred for 2 h at 60–70°C with *p*-xylene to remove the unreacted backbone polymer, that is, PP. The reaction mixture was filtered, and the residue was dried at 50°C and weighed until a constant weight was obtained. The product was the true graft, and the true grafting percentage was calculated as follows:

$$\text{True grafting (\%)} = \frac{W_t - W'_0}{W'_0} \times 100$$

where  $W_t$  is the weight of the grafted PP after water and xylene washings and  $W'_0$  is the weight of PP obtained after hydrolysis.

The true graft was hydrolyzed with 6N HCl for 4 h. This resulted in the hydrolysis of grafted dextrin from the polymer backbone and left the backbone polymer, PP. The solution was filtered, and the residue, that is, PP, was dried and weighed ( $W'_0$ ).

The graft copolymerization of dextrin onto PP was carried out as a function of different reaction

variables, such as the time of reaction, concentration of BPO, amount of water, and temperature. The optimum conditions were, thus, evaluated to achieve  $P_g$ .

### Characterization of the PP-grafted samples

Physical characterization of the PP grafted samples was done by Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG), differential thermal analysis (DTA), derivative thermogravimetry (DTG), and scanning electron microscopy (SEM).

### Swelling and solubility behavior

The swelling behavior of PP and PP-g-dextrin (both composite and true graft) was studied in different polar solvents. Samples of each of PP and PP-g-dextrin (composite and true graft) were separately suspended in a total of 10 mL of the neat solvents [water, EtOH, DMSO, and DMF, binary solvent mixture (water–EtOH), ternary solvent mixture (water–EtOH–DMSO), and quaternary solvent mixture (water–EtOH–DMSO–DMF) at different ratios at room temperature (25°C). The samples were filtered after 24 and 48 h. The adhered solvent was dried by gentle pressing between the folds of filter paper and weighed immediately. The percentage swelling was determined from the increase in the weight of the original sample as follows:

$$\text{Swelling (\%)} = \frac{W_s - W_0}{W_0} \times 100$$

where  $W_s$  is the weight of the swollen polymer and  $W_0$  is the weight of the original polymer.

The swollen sample was dried in an oven at 50°C until a constant weight was obtained. The percentage solubility was calculated from the following equation:

$$\text{Solubility (\%)} = \frac{W_0 - W_d}{W_d} \times 100$$

where  $W_0$  is the weight of the original polymer and  $W_d$  is the weight of dried sample after swelling.

### Water-retention studies

The percentage swelling of PP and PP-g-dextrin (both the composite and true graft) in water was determined as a function of variation of time (4, 8, and 16 h), temperature (30, 40, and 50°C), and pH (4, 7, and 9.2). Samples of PP and PP-g-dextrin (composite and true graft) were immersed in water (30 mL) of a known pH maintained at a definite temperature and kept for a predetermined time period. After the stipulated time period, the contents

were filtered. The residue was gently pressed between the folds of filter paper to remove the adhered water and weighed immediately. The percentage swelling was calculated as above.

To determine the water-retention behavior of different samples, the swollen sample was allowed to dry in the open at room temperature, and the samples were weighed initially after 2 h; this was followed by weighing after an interval of 1 h until a constant weight was obtained. The percentage water retention of the samples was calculated as the with respect to percentage weight loss as follows:

$$\text{Weight loss (\%)} = \frac{W_{st} - W_0}{W_0} \times 100$$

where  $W_{st}$  is the weight of swollen polymer at the respective time period and  $W_0$  is the weight of the original polymer.

## RESULTS AND DISCUSSION

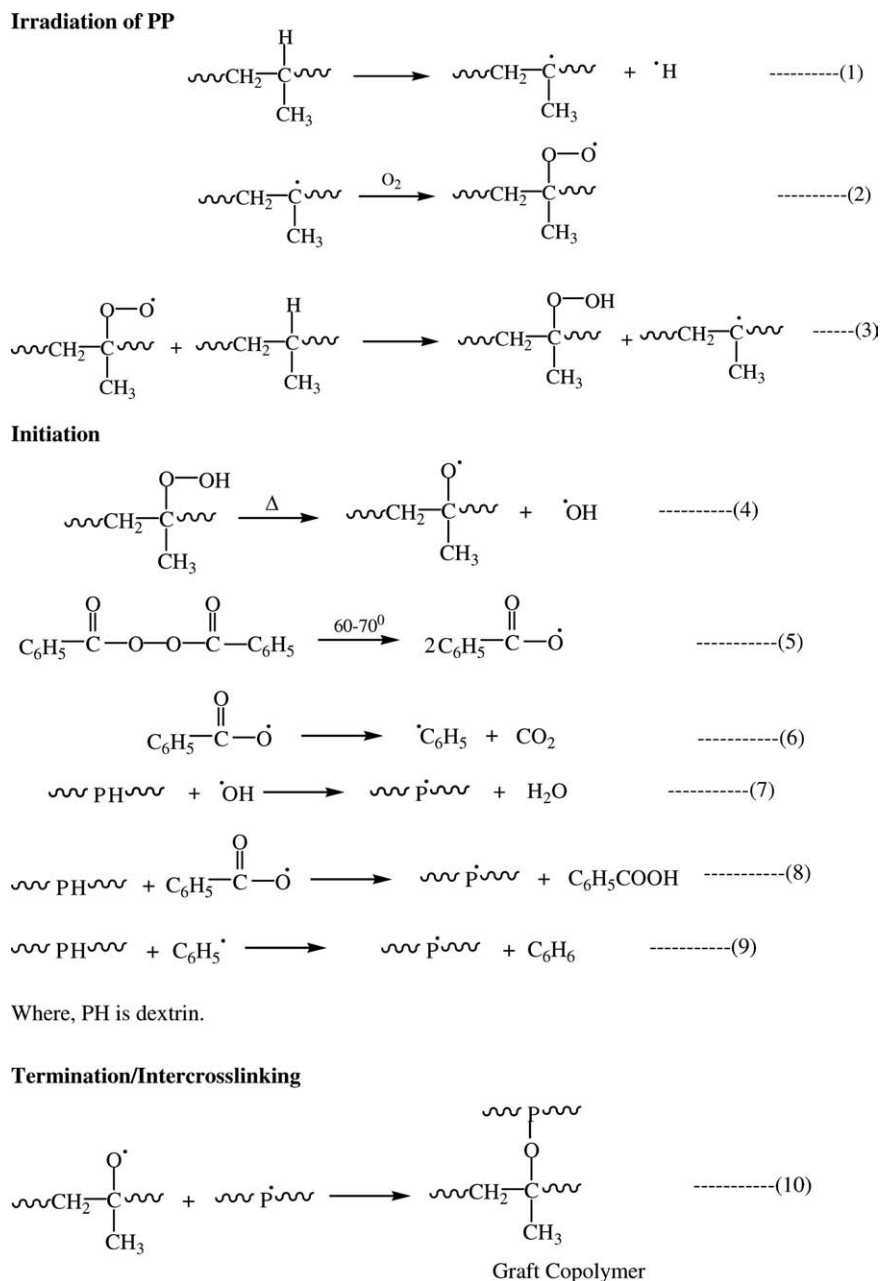
The irradiation of PP led to the formation of hydroperoxide groups onto the polymer backbone where the grafting of dextrin occurred in the presence of BPO. In Scheme 1, a tentative mechanism is proposed to explain the process of the graft copolymerization of dextrin onto PP.

Because the graft copolymer formation took place between the two polymers that is, PP and dextrin, there was, therefore, as such no propagation step. The generation of the active sites on the polymer occurred via steps 4, 7, 8, and 9, and the two polymeric chains united at the active sites to give the required graft polymer (step 10). The purpose of introducing hydroperoxide groups was to have an ether linkage between PP and the grafted polymer that was susceptible to degradation. In case of BPO-initiated grafting onto the unirradiated PP, the direct attachment of the grafted polymer onto the PP took place without any such ether linkages.

Optimum conditions pertaining to  $P_g$  were evaluated, and the results are discussed in the following sections.

### Effect of the BPO concentration

The percentage grafting of dextrin onto PP was studied as a function of the concentration of BPO, and the results are presented in Figure 1. As shown in Figure 1, the percentage grafting increased with increasing concentration of the initiator, giving maximum  $P_g$  (50%) at  $[\text{BPO}] = 6.89 \times 10^{-2} \text{ mol/L}$ ; beyond which, it decreased and attained a constant value thereafter. The increase in the percentage grafting initially was due to the increase in the number of active sites where grafting took place. Beyond



**Scheme 1** Tentative mechanism for the graft copolymerization of dextrin onto PP.

the optimum concentration of the initiator, the percentage grafting decreased, and this may be because the initiator decomposed in the side reaction,<sup>11</sup> such as that shown in Scheme 2. Thus, the decrease in the concentration of the active radicals affected the generation of active sites on the polymeric backbone, and hence, a decrease in the percentage grafting was observed.

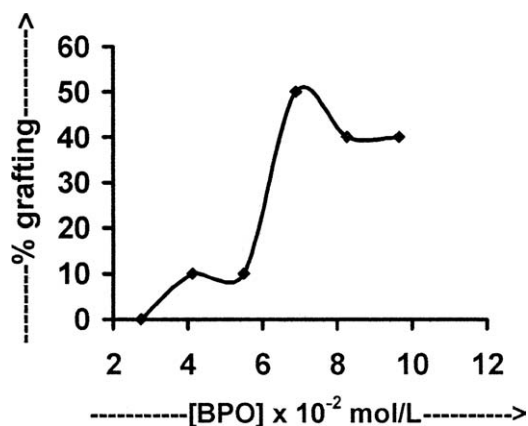
#### Effect of time

The percentage grafting of dextrin onto PP was studied as a function of time, and the results are presented in Figure 2. As shown in Figure 2, the per-

centage grafting increased with increasing reaction time, with the maximum grafting (50%) within 120 min, and decreased thereafter.

#### Effect of the amount of water

The graft copolymerization of dextrin onto PP was studied as a function of the amount of water on the percentage grafting during the irradiation of PP and during the graft copolymerization reaction of PP with dextrin and the results are presented in Figure 3. A steep rise in the percentage grafting was observed on irradiation of PP in the presence of water (5 mL) compared to that in the absence of water. Further



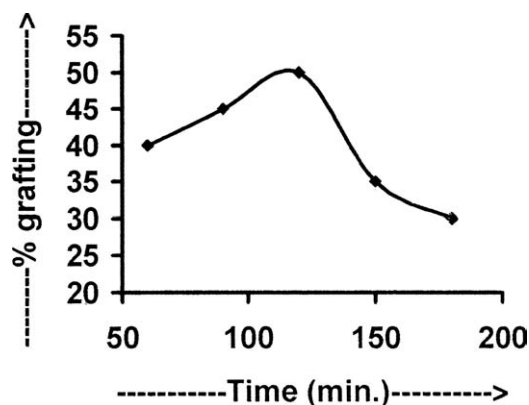
**Figure 1** Effect of the BPO concentration on the grafting percentage (amount of PP = 0.200 g; amount of dextrin = 0.150 g; temperature = 60°C; time = 120 min; volume of water = 5 + 10mL; optimum [BPO] =  $6.89 \times 10^{-2}$  mol/L).

increases in the amount of water increased  $P_g$  with a steady maximum (55%) in 15 mL of water, and the  $P_g$  became constant. With the amount of water fixed at 15 mL during irradiation, the amount of water added during the grafting reaction was varied. A maximum grafting percentage (55%) was obtained when 5 mL of water was added, beyond which, there was a constant decrease in the percentage grafting. The decrease in the grafting percentage beyond the optimum amount of water may have been due to the fact that solvation of dextrin with excess water prevented the formation of active sites and, hence, graft copolymer formation.

#### Effect of the temperature

The effect of the temperature on the percentage grafting of dextrin onto PP is presented in Figure 4. As shown, the percentage grafting rose with increasing temperature to give  $P_g$  (55%) at 60°C, beyond which, the percentage grafting decreased. The maximum number of active radicals was generated because of the initiation by phenyl radicals or hydroxyl radicals at the optimum temperature (60°C), where the formation of the graft took place. Beyond the optimum value, various chain-transfer reactions involving the initiator and solvent were accelerated at higher temperatures; this led to a decrease in the percentage grafting.

The effect of the amount of dextrin on the percentage apparent grafting, percentage grafting, and percentage true grafting onto PP was studied with the optimum conditions evaluated in the preceding var-



**Figure 2** Effect of the time on the grafting percentage (amount of PP = 0.200 g; amount of dextrin = 0.150 g; [BPO] =  $6.89 \times 10^{-2}$  mol/L; temperature = 60°C; volume of water = 5 + 10 mL; optimum time = 120 min).

iations, and the results are presented in Table I. We observed that with increasing amount of dextrin, the percentage apparent grafting, percentage grafting, and percentage true grafting increased, and maximum (65, 55, and 35%, respectively) was obtained with 0.150 g of dextrin.

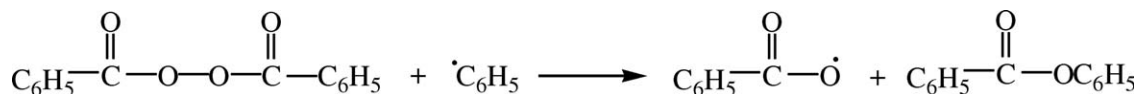
#### Evidence of grafting

##### FTIR analysis

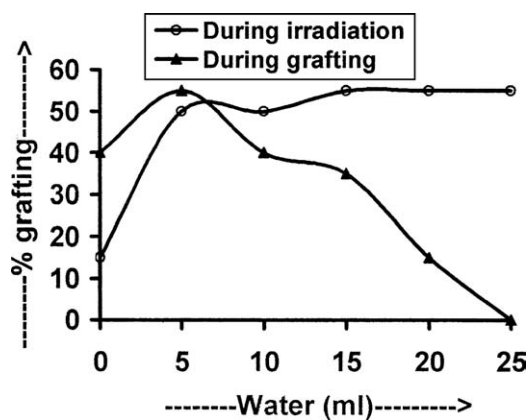
FTIR spectra of PP and PP-g-dextrin were taken on Thermo-5700 spectrophotometer (Nicollet). The FTIR spectrum of PP [Fig. 5(a)] showed characteristic peaks at 2921.7 due to  $-\text{CH}_2$  (asymmetric stretching), 2966.6  $\text{cm}^{-1}$  due to  $-\text{CH}_3$  (asymmetric stretching), 1377.3  $\text{cm}^{-1}$  due to  $-\text{CH}_3$  (symmetric bending), 1459.1  $\text{cm}^{-1}$  due to  $-\text{CH}_3$  (asymmetric bending), 1166.4  $\text{cm}^{-1}$  due to another characteristic peak for  $-\text{CHCH}_3$ , and 998.3  $\text{cm}^{-1}$  due to the helix chain of PP. The FTIR spectra of PP-g-dextrin [Fig. 5(b)], apart from the previously given peaks due to PP, showed a new peak for  $-\text{COC}-$ , which appeared at 1024.2  $\text{cm}^{-1}$ , and also, a broad band for  $-\text{OH}$  (polymeric association of hydroxyl groups) at 3400–3200  $\text{cm}^{-1}$  was observed. The presence of additional peaks in the grafted samples supported the formation of the graft copolymer of PP and dextrin.

##### Thermal analysis

DTG, DTA, and thermogravimetric analysis (TGA) of all of the samples were carried out in a nitrogen (200 mL/min) atmosphere at a heating rate of



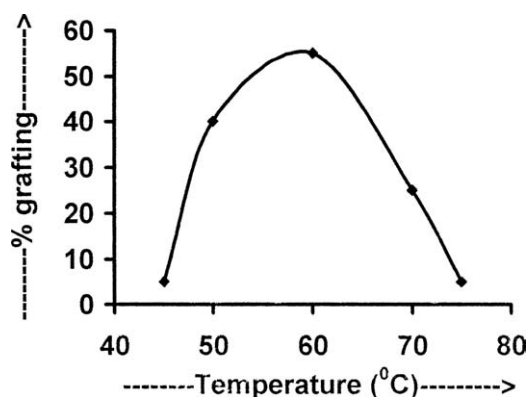
**Scheme 2** Side reaction.



**Figure 3** Effect of the amount of water on the grafting percentage (amount of PP = 0.200 g; amount of dextrin = 0.150 g; time = 120 min; temperature = 60°C; optimum amounts of water during and after preirradiation = 15 and 5 mL, respectively; [BPO] =  $5.165 \times 10^{-2}$  mol/L).

10°C/min on a PerkinElmer Pyris Diamond thermal analyzer (IIT Roorkee). The samples weights were kept within 5–8 mg. The DTG, DTA, and TGA curves of PP, dextrin, and PP-g-dextrin are presented in Figures 6(a–c), 7, and 8(a–c), respectively.

As observed from the DTG, DTA, and TGA curves of PP Figure 6(a–c), the decomposition of PP took place in a single stage and at a fast rate. A single peak at 448°C was observed with a decomposition rate of 1.816 mg/min in the DTG curve. The energy required for this decomposition between the temperatures 400 and 474°C with a maximum endothermic peak at 451°C, as depicted in the DTA curve, was 129 mJ/mg. Another endothermic peak appearing at 161°C and consuming 103 mJ/mg of energy referred to the melting peak. The TGA thermogram corroborated the information depicted by the DTG/DTA curves. The decomposition range between the start and end of the peak in DTG or the endothermic



**Figure 4** Effect of the temperature on the grafting percentage (amount of PP = 0.200 g; amount of dextrin = 0.150 g; [BPO] =  $5.165 \times 10^{-2}$  mol/L; time = 120 min; volumes of water = 15 + 5 mL; optimum temperature = 60°C).

**TABLE I**  
Effect of the Variation of the Amount of Dextrin on Grafting

Amount (mg)	Apparent grafting (%)	Grafting (%)	True grafting (%)
0.100	45	40	20
0.150	65	55	35
0.200	50	50	30
0.250	35	30	30
0.300	30	30	25

Amount of PP = 0.200 g; [BPO] =  $5.165 \times 10^{-2}$  mol/L; time = 120 min; temperature = 60°C; volume of water = 15 + 5 mL (total = 20 mL).

peak of DTA was in line with the initial decomposition temperature (IDT; 425.6°C) and the final decomposition temperature (FDT; 460.5°C) on the TG thermogram. The fast rate of decomposition of PP, as depicted by a small temperature difference (35°C) between FDT and IDT, was further subsisted by a steep line showing decomposition with a narrow temperature difference between the decomposition temperature (DT) values at each 10% weight loss.

The DTG curve of PP-g-dextrin showed two peaks with the initial melting small-peak maxima at 132°C with a melting rate of 0.115 mg/min. The sample remained stable thereafter up to 400°C, where decomposition started and progressed to give a sharp peak at 449°C with a higher rate of decomposition (1.072 mg/min). The DTA and TGA curves of PP grafted with dextrin also showed a double stage of decomposition. In the DTA curve, the melting of the grafted PP showed a unique pattern, with exothermic and endothermic peaks appearing simultaneously at 122°C with a total release of energy of -97.7 mJ/mg and at 152°C, which absorbed 54.4 mJ/mg, respectively. This was in contrast to the sharp endothermic peak of PP at 161°C with an absorption of 103 mJ/mg. The sample further continued to decompose and showed a broad endothermic peak at 449°C with an energy equivalent to 111 mJ/mg.

A perusal of the TGA curve showed that the decomposition of PP-g-dextrin was a double-stage decomposition. A kink in the early stages between 110.50 and 148.7°C with a 7.21 wt % loss of the grafted PP was indicative of the moisture loss. Thereafter, the polymer was stable, and IDT began at 400°C. The decomposition continued with increasing temperature, and final decomposition began at 464.2°C and continued up to 526°C with 0% residue. When we observed the TGA curve of dextrin, we observed that IDT (291.27°C) and FDT (326.49°C) were very low in comparison to either PP or the grafted PP. The DT values at every 10% weight loss of the grafted PP were much higher than those of dextrin and little lower than PP up to 70% weight

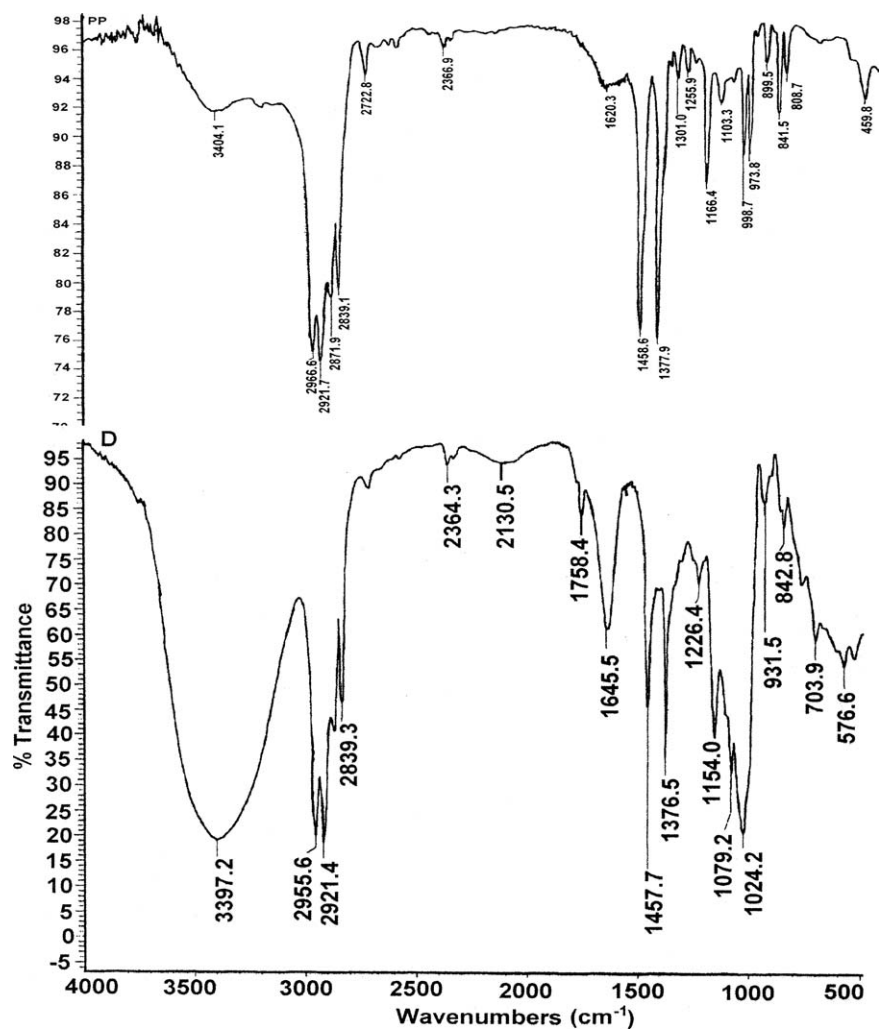


Figure 5 FTIR spectra of PP and PP-g-dextrin.

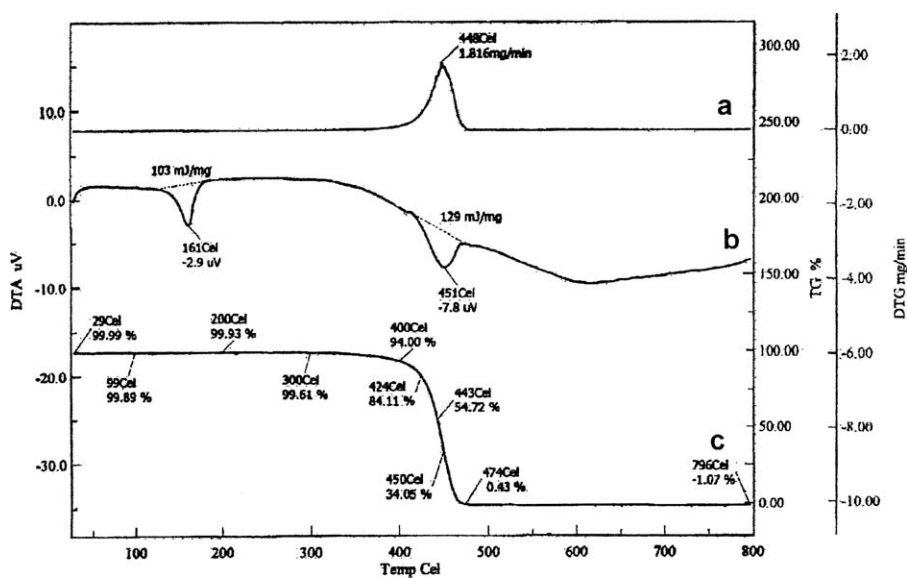


Figure 6 DTG, DTA, and TGA of PP.

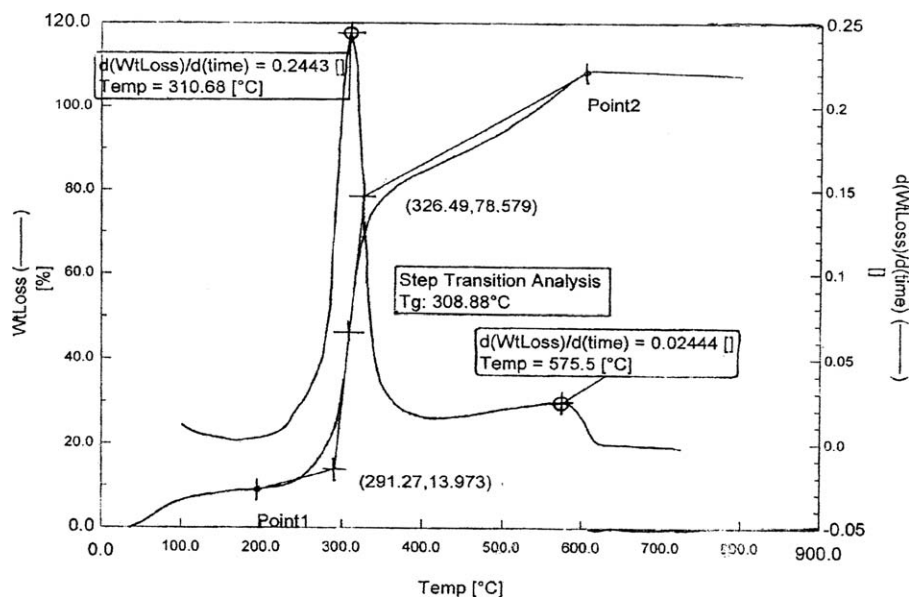


Figure 7 DTA and TGA of dextrin ( $T_g$  = glass-transition temperature).

loss, beyond which these became almost close to those of PP. The temperature differences between each 10% weight loss of the grafted PP from 10 to 20% and 20 to 30% were very high (178 and 29°C, respectively) compared to those of dextrin (57 and 20°C, respectively) and PP (14 and 8°C, respectively), and from 90 to 100%, the temperature difference for all of the substrates was nearly same. This indicated a constant decomposition rate in all three samples.

The thermal data of dextrin, that is, low IDT, FDT, and DT values, showed that dextrin was susceptible to changes in temperature. However, from the DTA and TGA data of dextrin-grafted PP, it was evident

that the grafting of dextrin onto PP did not affect the thermal behavior of PP.

#### SEM

SEM images of PP and PP-g-dextrin at a magnification of 1000 $\times$  were taken on a LEO VP 435 instrument (California) and are presented in Figures 9 and 10, respectively. The comparison of the SEM pictures of the grafted PP with that of PP showed the change in the topology of the PP surface. The grafting of dextrin onto PP opened up its matrix and showed the

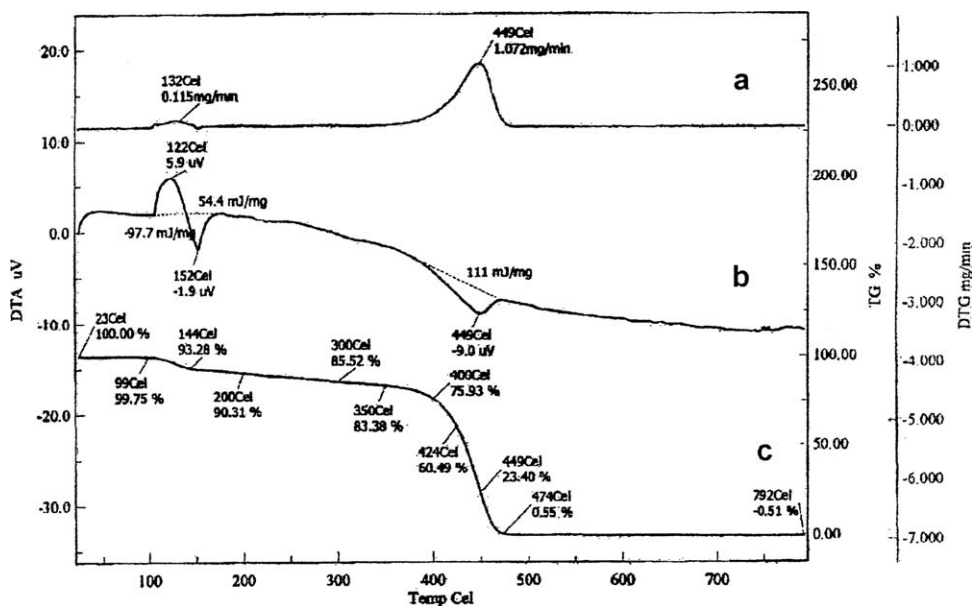


Figure 8 DTG, DTA, and TGA of PP-g-dextrin.



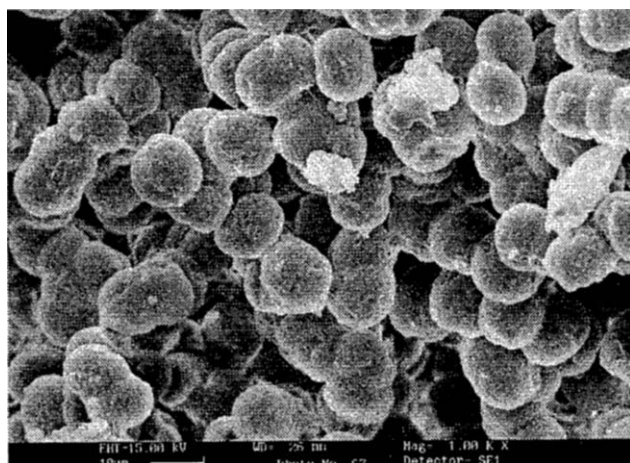


Figure 9 SEM of PP at a magnification of 1000 $\times$ .

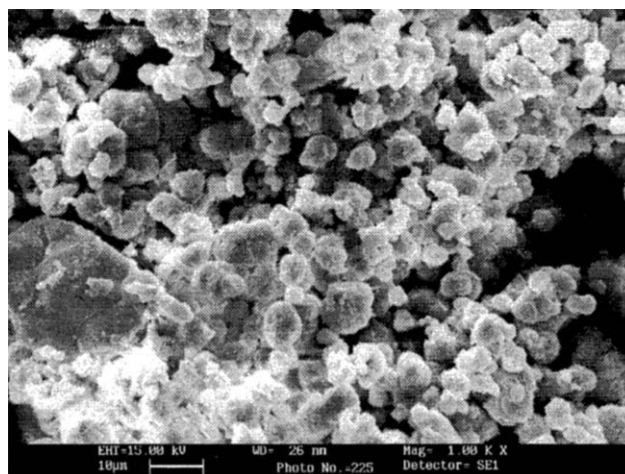


Figure 10 SEM of PP-g-dextrin at a magnification of 1000 $\times$ .

deposition of dextrin on the surface of the backbone polymer.

### Swelling and solubility behavior

The percentage swelling and percentage solubility of PP and PP-g-dextrin were studied in pure, binary, ternary, and quaternary polar solvent systems, and the results are presented in Tables II and III, respectively. As shown in Table II, PP, being hydrophobic, showed neither swelling nor solubility in water. However, in polar solvents, high swelling percentages in EtOH (220 and 240%) and DMF (190 and 270%) at 24 and 48 h, respectively, were observed. In DMSO, however, poor swelling (0 and 10%) at 24 and 48 h, respectively, was observed.

When swelling studies were made in mixed solvent systems, we observed that the percentage swelling of PP obtained in pure solvents continued to decrease with increasing addition of water in the binary solvent and also in the quaternary solvent

system, along with the addition of DMSO and DMF. However, when the solvent system was shifted to the mixture of water, EtOH, and DMSO, the maximum swelling percentages (220 and 270%) in 24 and 48 h, respectively, were observed in 3 : 2 : 5 H<sub>2</sub>O–EtOH–DMSO ratio. Further increases in the amount of water and EtOH decreased the percentage swelling. In the quaternary solvent system, the addition of water, EtOH, and DMSO to DMF decreased the percentage swelling more than that observed in pure DMF. The higher swelling percentage of PP was attributed to the fact that the reprecipitated PP (from beads) offered a fluffy powder, which held the solvents within the empty spaces. PP, however, remained insoluble in all of the solvent systems. Similar studies were carried out on PP-g-dextrin (both the composite and true graft), and different observations were made. The percentage swelling of the grafted PP was found to be lower than that observed for PP, and the grafted samples were found to be soluble to some extent. A decrease in

TABLE II  
Swelling and Solubility Percentage Behavior of PP in Polar Solvents

		Swelling of PP (%)		Solubility of PP (%)	
		24 h	48 h	24 h	48 h
H <sub>2</sub> O–EtOH	0 : 10	220	240	10	10
	3 : 7	200	210	0	0
	5 : 5	170	180	0	0
	7 : 3	150	200	0	0
	10 : 0	0	0	0	0
H <sub>2</sub> O–EtOH–DMSO	0 : 0 : 10	0	10	0	10
	2 : 1 : 7	130	230	0	0
	3 : 2 : 5	220	270	0	0
	4 : 3 : 3	160	210	0	0
H <sub>2</sub> O–EtOH–DMSO–DMF	0 : 0 : 0 : 10	190	270	0	0
	1 : 1 : 4 : 4	180	250	0	0
	2 : 2 : 3 : 3	170	160	0	0

**TABLE III**  
Swelling and Solubility Percentage Behavior of the PP-g-Dextrin Samples in Polar Solvents

		Swelling of PP-g-dextrin (%)				Solubility of PP-g-dextrin (%)			
		Composite		True graft		Composite		True graft	
		24 h	48 h	24 h	48 h	24 h	48 h	24 h	48 h
H <sub>2</sub> O–EtOH	0 : 10	40	90	110	180	30	40	0	0
	3 : 7	80	90	150	230	0	10	0	0
	5 : 5	80	120	220	260	0	10	0	0
	7 : 3	40	40	190	190	0	10	10	10
	10 : 0	0	10	20	30	0	10	10	10
H <sub>2</sub> O–EtOH–DMSO	0 : 0 : 10	180	30	200	150	10	40	20	0
	2 : 1 : 7	90	50	210	230	10	40	10	10
	3 : 2 : 5	90	80	160	190	10	20	10	10
	4 : 3 : 3	90	50	200	220	10	10	20	10
H <sub>2</sub> O–EtOH–DMSO–DMF	0 : 0 : 0 : 10	30	80	200	200	60	20	10	15
	1 : 1 : 4 : 4	30	100	220	300	50	20	20	20
	2 : 2 : 3 : 3	60	170	200	300	50	20	20	20

the percentage swelling in the grafted samples was attributed to the facts that (1) the empty spaces in the fluffy nature of PP were reduced along with the change in the fluffy structure in the grafted PP, and (2) some of the material went into solution, and this affected the swelling percentage.

These observations were further substantiated from the swelling/solubility data of the dextrin-grafted PP composite and true grafts. In all of the solvents studied, the true graft, which lacked both unreacted PP and dextrin, showed higher swelling percentages, whereas the composite, which contained both unreacted PP and dextrin, showed a higher solubility percentage.

The following order of these solvents for the maximum percentage swelling of PP was observed:

DMF (270%) > EtOH (240%) > DMSO (10%)  
> Water (0%)

The order of the solvents for PP-g-dextrin was as follows:

Composite :  
DMSO (180%) > EtOH (90%) > DMF (80%)  
> Water (10%)

True graft :

DMF (200%) = DMSO (200%) > EtOH (180%)  
> Water (30%)

Both the composite and true graft showed good solubility in all of the solvent mixture combinations compared to the zero percentage solubility of PP.

The maximum swelling percentage (300% in 48 h) of PP-g-dextrin (true graft) and the maximum solubility (50% at 24 h) for the composite were observed in the quaternary solvent system composed of H<sub>2</sub>O, EtOH, DMSO, and DMF in the ratio of 1 : 1 : 4 : 4. In pure DMSO, the grafted PP (both the composite and true graft) showed much higher swelling (200%) compared to PP (10%).

When swelling studies were carried out in the binary, ternary, and quaternary solvent systems, the percentage swelling of PP decreased from the maximum swelling (270%) in pure DMF in all of the solvent systems, except in water–EtOH–DMSO in 3 : 2 : 5 ratio, where the percentage swelling was the same (270%). However, when the swelling behavior of grafted PP (both the composite and true graft) was studied, we observed that the percentage swelling of the composite and true graft increased to maximum (120 and 260%, respectively, in 48 h) in the 5 : 5

**TABLE IV**  
Water Swelling Percentage with the Time, Temperature, and pH of the PP and PP-g-Dextrin Samples

Sample	Water swelling (%)								
	Time (h) <sup>a</sup>			Temperature (°C) <sup>b</sup>			pH <sup>c</sup>		
	4	8	16	30	40	50	4.0	7.0	9.2
PP	0	0	2	0	2	10	3	10	7
PP-g-dextrin (composite)	114	100	62	100	110	124	56	124	84
PP-g-dextrin (true graft)	74	36	28	36	46	104	44	104	68

<sup>a</sup> Temperature = 30°C; pH = 7.

<sup>b</sup> Time = 8 h; pH = 7.

<sup>c</sup> Time = 8 h; temperature = 50°C.

**TABLE V**  
**Water Retention and Moisture Loss as Functions of Time for PP and PP-g-Dextrin**

	Water retention (%)/Moisture loss (%)								
	Time (h) <sup>a</sup>			Temperature (°C) <sup>b</sup>			pH <sup>c</sup>		
	4	8	16	30	40	50	4.0	7.0	9.2
PP									
2 h	0	0	0	0	0	0	0	0	0
PP-g-dextrin (composite)									
2 h	82/32	72/28	32/30	72/28	79/31	98/26	26/30	98/26	56/28
3 h	48/66	36/64	4/58	36/64	50/60	71/53	0	71/53	24/60
4 h	18	12/82	0	12/82	22/88	43/81	0	43/81	0
5 h	0	0	0	0	0	12/112	0	12/112	0
6 h	0	0	0	0	0	0	0	0	0
PP-g-dextrin (true graft)									
2 h	48/26	12/24	0	12/24	20/26	81/23	16/28	81/23	42/26
3 h	15/59	0	0	0	0	54/50	0	54/50	12/56
4 h	0	0	0	0	0	24/80	0	24/80	0
5 h	0	0	0	0	0	0	0	0	0

<sup>a</sup> Temperature = 30°C; pH = 7.

<sup>b</sup> Time = 8 h; pH = 7.

<sup>c</sup> Time = 8 h; temperature = 50°C.

water-EtOH system compared to the maximum (90 and 180%, respectively) in EtOH. In the case of the ternary and quaternary solvent systems, the percentage swelling of the true graft also increased, to 230 and 300% in 48 h in the water-EtOH-DMSO (2 : 1 : 7) and H<sub>2</sub>O-EtOH-DMSO-DMF (1 : 1 : 4 : 4 and 2 : 2 : 3 : 3) ternary and quaternary solvent systems, respectively.

These results were explained by considering the dielectric constant ( $\epsilon$ ) and polarity index (PI) of these solvents. Water had the maximum  $\epsilon$  and PI values (80 and 10.3, respectively) followed by DMSO (47.2 and 7.2, respectively) and DMF (38.3 and 6.4, respectively), and the lowest value of  $\epsilon$  was observed for EtOH (24.3; PI not available). PP, being a hydrocarbon, lacked polarity and, therefore, showed maximum swelling in DMF with the lowest PI. As the value of PI increased, the percentage swelling of PP decreased with zero percentage swelling in water. When PP was graft copolymerized with dextrin, a polyhydroxyl compound with pendant hydroxyl groups, the trend of the swelling behavior shifted. Maximum swelling was observed in DMSO and DMF, followed by EtOH, and last, water. An interesting observation was made during the swelling studies: the grafted polymers suspended in these solvents were found to float on the surface of water, whereas in the presence of DMSO, DMF, and EtOH or in their mixture with water, the polymer moved into the bulk of the solvent system and was completely solvated. This might have been the reason for the lowest swelling of the grafted samples in water, where there was no interaction with water, and hence, no proper solvation took place.

Thus, from the swelling studies, we inferred that the grafting of dextrin onto PP made the modified

polymer soluble in pure solvents or different solvent systems along with swelling because of the pendant polar hydroxyl groups of the grafted dextrin.

#### Water-retention studies

The results of the swelling percentage and water-retention studies of PP-grafted samples as a function of the temperature, time, and pH are presented in Tables IV and V, respectively. The maximum percentage swelling of PP (10%) in water was obtained at 16 h at 50°C and neutral pH (7), whereas PP-g-gelatin (the composite and true graft) showed maximum swelling percentages (124 and 104%, respectively) in 8 h at 50°C and neutral pH.

As shown in Table V, the swollen PP sample did not show any loss of moisture with time. For the composite, the percentage moisture loss from each of the swollen samples (prepared as a function of the time, temperature, and pH) showed a continuous rise after every 1 h. After a particular value was attained, no further loss of water was observed. The loss of water was consistent for the different composite samples.

Thus, the data revealed that the dextrin-grafted PP (composite) swollen in water could retain water up to a maximum of 5 h, beyond which no water loss was observed. This property could be useful for the release of water over a period of time in arid regions where the scarcity of water is a problem.

#### CONCLUSIONS

These studies, thus, revealed that dextrin, a natural polymer, was successfully grafted onto PP with BPO as a radical initiator. The effects of various reaction

conditions on the graft copolymerization were investigated and gave  $P_g$  of 55% dextrin onto PP at a BPO concentration of  $5.165 \times 10^{-2}$  mol/L at 120 min at 60°C with 20 mL of water. The structural characterizations by FTIR spectroscopy and SEM indicated the presence of dextrin units in the products. Although the incorporation of dextrin as graft onto PP did not much affect the thermal behavior, it did change the chemical interaction with the solvents. Better swelling and solubility of the grafted PP in the solvent mixture in comparison to PP were observed. The water-retention studies indicated the possibility of the use of dextrin-grafted PP in arid regions.

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