Starch-Grafted Polypropylene: Synthesis and Characterization

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ABSTRACT: Graft copolymerization of starch has been carried out onto preirradiated polypropylene (PP) in an aqueous medium using benzoyl peroxide (BPO) as the radical initiator. The maximum percentage of grafting (115%) of starch onto PP was obtained at optimum conditions of BPO concentration, 1.239×10^{-3} moles; temperature, 65°C; in 120 min. using 30 mL of water. Swelling studies were carried out in pure, binary, ternary and quaternary solvent systems comprising of water, ethanol (EtOH), dimethylsulphoxide (DMSO), and *N,N*-dimethylformamide (DMF) in different ratios. Maximum swelling is observed in DMSO and DMF, followed by EtOH and least in water for true graft. Water retention studies of pristine PP and PP-*g*-Starch (both composite and true graft) were investigated at different time periods, temperature and pH. The composite contains grafted PP, unreacted starch and unreacted PP whereas true graft is the product from which both unreacted polymers have been removed. Maximum % water retention of PP-*g*-Starch (composite) (110%) was observed in 8 h at 50°C in neutral medium (pH = 7). The graft copolymers were characterized by FTIR, DTG, DTA, TGA, and SEM. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 602–612, 2011

Key words: polypropylene; starch; graft copolymerization; TGA; swelling; water retention

INTRODUCTION

Although PP is an industrialized polymer and has been widely used as a textile and packaging material due to its inherence properties such as durability, hydrophobicity, chemical inertness toward chemicals and biological attack, etc. To improve properties such as hydrophilicity, swellibility, solubility, chemical inertness, etc. of PP to broaden its applications in dying of fibers, printing of films, paintability, adhesion, agricultural mulches, agricultural planting containers, etc. modification of PP has been attempted by different groups of workers.

Graft copolymerization of styrene onto PP fibers has been studied by simultaneous irradiation method using a 10 MeV electron beam. Samples were irradiated in an environment of N_2 gas.[1] Copolymers of vinylimidazole (VI) and acrylic acid (AA) have been grafted onto PP films using γ-radiations. The effect of the comonomer composition on the percent graft was also investigated.[2] Picchioni et al.[3] carried out the grafting of vinyl monomers onto isotactic polypropyl-

ene (IPP) in the solid state. Wettability and antibacterial assessment of chitosan-containing radiation-induced graft nonwoven fabric of PP-*g*-Acrylic acid was studied by Yang et al.[4] Graft copolymerization of styrene onto poly(vinyl chloride) (PVC) and PP was carried out in a supercritical CO_2 medium using azoisobisacrylamide (AIBN) as a free radical initiator. The thermal stability of grafted copolymer of PVC was better than that of PVC, while grafted copolymer of PP had poorer thermal stability than PP.[5] Graft copolymerization of methacrylic acid onto PP fibers by simultaneous-gamma ray irradiation technique was carried out. The effect of various solvents on grafting was studied. The results have been presented in terms of swelling behavior of PP fiber and the extent of homopolymerization.[6] Effect of solvents on γ–radiation induced graft copolymerization of methyl methacrylate (MMA) onto PP has been studied by Nesser et al.[7] The *tert*-butoxy radical initiated graft copolymerization of MMA and several other monomers onto commercial PP pellets and PP fiber has been investigated in heterogeneous conditions by Dokolas et al.[8] Cation-exchange adsorbent based on a nonwoven PP fabric carrying sulfonate functional groups was synthesized by a one-step graft copolymerization of sodium styrenesulfonate and acrylic acid monomers from binary monomer mixtures using the electron beam preirradiation method in air.[9]

From the literature survey it is therefore inferred that the modification of PP through grafting is being

successfully pursued. However, modification of PP by grafting a polymer through intercrosslinking has not been reported. Starch is a natural polymer found in a variety of plants such as potato, corn and cassava. It is composed of two glucan chains, amylase, and amylopectin. These polymers have the same basic monomer but differ in their length and degree of branching, which ultimately affect their physicochemical properties.[10] Amylopectin consists of granules that are more crystalline, denser and more resistant to penetration by water and to enzymatic action than amylose.[11,12] Starch is frequently used as natural, renewable, and biodegradable filler in polyethylene to enhance its biodegradability.[13,14] Therefore, in the present manuscript we report on the grafting of starch onto preirradiated PP powder through intercrosslinking.

EXPERIMENTAL

Materials

Commercial polypropylene was obtained from Thukral Trading (Delhi, India). The PP beads were recrystallized from 1,4-dimethyl benzene (p-xylene) and precipitated by the addition of methanol, a nonsolvent. The polymer soluble starch, (Merck) and the initiator benzoyl peroxide (Merck) were used as received.

Irradiation of polypropylene

Irradiation of the polymer was carried from Co^{60} source housed in Gamma Chamber–900 (BARC Trombay, India). A definite amount of PP in a known volume of water was irradiated at a constant dose rate of 3.40 kGy/h in order to introduce hydroperoxide groups. These groups offer sites for grafting or attachment of the polymer.

Methods

Graft copolymerization

Preirradiated, dried, and weighed PP (0.200 g) was suspended in known volume of water (0–25 mL) in a flask placed in a water bath maintained at constant temperature (45–75°C), under constant stirring. To this added a definite amount of the polymer starch (0.100–0.250 g) to dissolved in a known volume of water (0–25 mL) and a definite amount of the initiator, BPO (0.100–0.300 g). A continuous flow of nitrogen gas free from oxygen was passed through the reaction medium over the period of reaction time (60–210 min). After the stipulated time period, the flask was removed from the water bath and the contents filtered. The residue contains grafted PP, unreacted starch, unreacted PP, and some amount of BPO. The residue was washed with benzene to remove unreacted BPO. The left over product was dried at 45°C till constant weight was obtained. The product is

referred to as the "Composite." Apparent percentage of grafting of the composite was calculated from initial increase in the weight of 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 original PP and composite, respectively.

The composite was then stirred with water for 2 h at 60°C to remove ungrafted starch. The reaction mixture was filtered and the residue was dried at 45°C and weighed till constant weight was obtained. Percentage of grafting i.e., the percent increase in weight of PP upon grafting after complete removal of the to be grafted polymer starch.

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

where, W_0 and W_g are weights of pristine PP and the graft copolymer, i.e., PP-g-Starch after the complete removal of the ungrafted starch, respectively.

To determine the extent of formation of true graft i.e., the portion of the PP backbone and portion of the to be grafted polymer starch involved in the formation of the graft copolymer, the graft copolymer was further stirred for 2 h at 60–70°C with p-xylene to remove unreacted backbone polymer, i.e., PP. The reaction mixture was filtered, residue was dried at 45°C weighed till constant weight was obtained. The product is the "True graft" and the percentage of true graft 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 washing, respectively removing both unreacted starch and unreacted PP and W_0' is the weight of PP obtained after hydrolysis.

True graft was hydrolyzed with 6 N HCl for 4 h. This results in the hydrolysis of grafted starch leaving the backbone polymer, PP. The solution was filtered and residue i.e., PP was dried and weighed.

Graft copolymerization of starch onto PP was carried out as a function of different reaction variables such as time of reaction, concentration of BPO, amount of water, temperature, and amount of to be grafted polymer the optimum conditions were thus evaluated for achieving the maximum percentage of grafting. The optimum conditions were used to study the effect of amount of starch on % apparent grafting, % grafting and % true grafting measurements.

Characterization of PP-grafted samples

Physical characterization of PP and PP-grafted samples has been done by FTIR spectroscopy, thermal analysis,

and scanning electron microscopy (SEM). The FTIR spectra were recorded on KBr disc using a Thermo-5700 Spectrophotometer (HPU Shimla, India). Thermal analysis of pristine PP and PP-*g*-Starch was carried out in nitrogen (200 mL/min) atmosphere at a rate of 10°C/min. on Perkin Elmer (Pyris Diamond, IIT Roorkee, India). The samples weights were kept within 5–8 mg. Scanning electron microscopy of pristine PP, pristine starch and PP-*g*-Starch at magnification (1000×, EHT = 15.00 Kv) have been taken on LEO vp 435 instrument (IIT Roorkee, India).

Swelling and solubility behavior

Swelling behavior of pristine PP and PP-*g*-Starch (both composite and true graft) was studied in different polar solvents. Samples (0.10 g) each of pristine PP, PP-*g*-Starch composite, and true graft were separately suspended in total of 10 mL of the pure (H_2O, EtOH, DMSO, DMF), binary (H_2O:EtOH), ternary (H_2O:EtOH:DMSO), and quaternary (H_2O: EtOH:DMSO:DMF) solvent systems in different ratios at room temperature (25°C). The samples were filtered after 24 and 48 h. The adhered solvent(s) was dried by gentle pressing between the folds of filter paper and weighed immediately. The increase in the weight of the sample indicates the amount of solvent(s) that the sample can hold i.e., swelling when suspended in solvent(s) for a particular time at a particular temperature. The percent swelling was determined from the increase in the weight of the original sample as follows:

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

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

The swollen sample was dried in an oven (50°C) till constant weight is obtained. The loss in the weight of the sample measures the extent of solubility in the solvent(s) and the percent solubility was calculated from the following equation:

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

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

Water retention studies

To study the property to retain water over a period of time, water retention studies of pristine PP and PP-*g*-Starch (both composite and true graft) were carried out. Swelling of pristine PP (0.50 g), PP-*g*-Starch (composite and true graft; 0.50 g), was carried out in water (30 mL) 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). After the stipulated time period the samples were filtered. The surplus surface water was removed by gentle press-

ing between the folds of filter paper and weighed immediately. The percent swelling was calculated as above.

The swollen sample was allowed to dry in open at room temperature. The samples were weighed after 2 h followed by weighing after an interval of 1 h till constant weight was obtained. Percent weight loss due to loss of moisture from the swollen with time was calculated as follows:

$$\% \text{ Moisture loss} = \frac{W_{st} - W_0}{W_0} \times 100$$

where W_{st} is the weight of swollen polymer at respective time period and W_0 is the weight of original polymer. The amount of water retained after the loss of moisture/water over a particular time is the water retention of the polymer at that period of time.
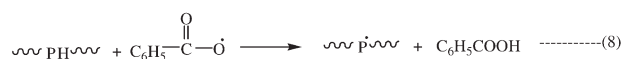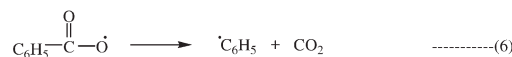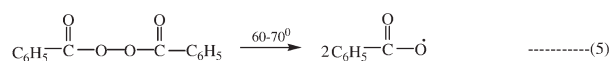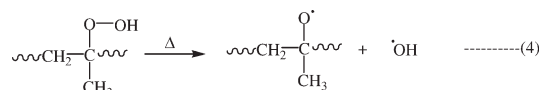
RESULTS AND DISCUSSION

Irradiation of PP in air leads to the formation of hydroperoxide groups on the tertiary carbon of the polymer i.e., backbone where grafting of the to be grafted polymer, starch, occurred in the presence of BPO. Following mechanism is proposed to explain the process of graft copolymerization of PH onto PP.
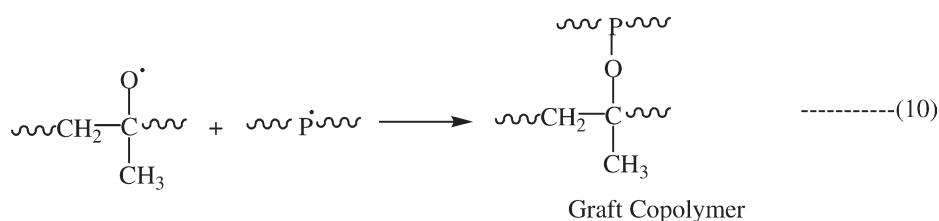
Irradiation of PP
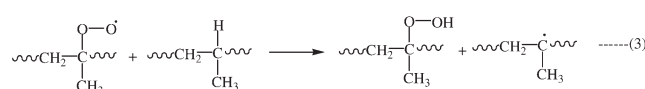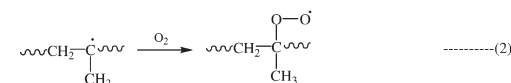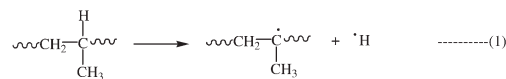
Initiation

where, PH is starch.

The generation of the active sites on the two polymer PP and PH occurs via steps 4, 7, 8, and 9 which unite intermolecularity to give the required graft polymer (Step 10).

Termination/Intercrosslinking

Graft Copolymer

$$---------- (10)$$

Optimum conditions pertaining to maximum percentage of grafting were evaluated and are presented in Figures 1–5.

Optimum conditions of PP-*g*-Starch

Effect of [BPO]

The effect of variation in the concentration of BPO as initiator on percentage of grafting of starch onto PP is presented in Figure 1. It is observed from the figure that % grafting increases with the increase in BPO concentration giving maximum (100%) at BPO concentration $= 1.239 \times 10^{-3}$ moles. With further increase in the BPO concentration, % grafting becomes constant and decreases thereafter. Initial increase in the percent grafting of starch onto PP is due to increase in the number of free radicals due to increasing BPO concentration, which generate active sites on starch (Steps 8 and 9) through chain transfer reactions and terminate via Step 10 to produce graft copolymer. The decrease in percent grafting beyond the optimum BPO concentration is due to the reason that at higher concentrations BPO undergoes induced decomposition, leading to decrease in the initiator concentration and hence lowers the radical concentrations that subsequently decrease the graft copolymer formation.

Effect of temperature

Percentage of grafting of starch onto PP has been studied as a function of temperature and the results are presented in Figure 2. It is observed from the figure that % grafting of starch onto PP increases steadily with the increase in temperature and affords maximum grafting (110%) at 65°. Further increase in the temperature leads to decrease in % grafting. At higher temperature, various chain transfer reactions are accelerated and the decomposition of BPO may be affected.[15]

Effect of water

Graft copolymerization of starch onto PP has been studied as a function of amount of water both during irradiation and graft copolymerization reaction and results are presented in Figure 3. In the first set of reactions, irradiation of PP was carried out in constant volume of water i.e., 20 mL and variation in the amount of water added during the graft copolymerization reaction was studied. It is observed from the figure that percentage of grafting increases with the increasing amount of water giving maximum (115%) when additional 10 mL of water was added. Further, increase in the amount of water decreases % grafting to 40%.

During second set of reactions, variation of amount of water is studied during irradiation of PP. It is observed from the figure that percentage of grafting shows an irregular pattern. When irradiation of PP is carried out in the absence of water and using only 5 mL of water good % grafting (100%, 115%, respectively) is observed beyond which it decreases. However, when irradiation was carried using higher amount of water, percent grafting further increases giving maximum grafting in 20 mL of water. The irregular pattern of grafting is due to the reason that variation in water during irradiation produce different radicals. Radiolysis of water ($H_2O \overset{\gamma-rays}{\longrightarrow} H^\bullet + {}^\bullet OH$) produce excess ˙OH radicals with increasing amount of water which abstract tertiary hydrogen from the backbone to generate free radicals in addition to those generated by direct interaction with γ-rays [eq. (1)]. This helps to increase the number of active sites to give higher grafting. The unreacted ˙OH radicals also terminate the growing polymeric or grafted chain leading to decrease in grafting. Thus variation in water during irradiation gives irregular pattern of grafting.

Thus, combining the total amount of water used during irradiation of PP followed by grafting of starch onto PP, maximum grafting (115%) is attained in total of 15 mL water (BPO concentration = 1.239 $\times 10^{-3}$ moles). The decrease in % grafting may be due to the reason that in excess of water, the interaction between the polymer backbone and macroradicals decreases.

Effect of time

Percent grafting of starch onto PP was studied as a function of time and results are presented in Figure 4. It is observed from the figure that % grafting increases with the increase in time, giving maximum
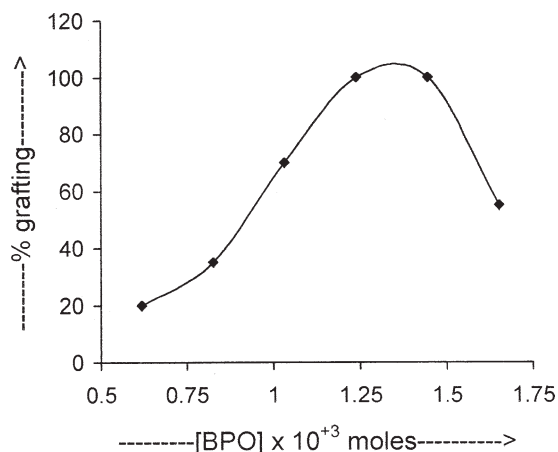
Figure 1 Effect of [BPO] on % grafting. PP, 0.200 g; Starch, 0.150 g; temperature, 60°C; time, 120 min; water, 20(10) mL; optimum [BPO], 1.239×10^{-3} moles.

grafting (115%) in 120 min. Further increase in time leads to decrease in percentage of grafting. This may be due to the increase in the induced decomposition of BPO and may also be due to the killing of the radical sites on the polymeric backbone through abstraction process.

Effect of starch

The effect of the amount of starch on % apparent grafting, % grafting, and % true grafting onto PP was studied using the optimum conditions evaluated for obtaining maximum grafting percentage of starch onto PP and the results are presented in Figure 5. It is observed from the figure that with increasing amount of starch, % apparent grafting and % grafting increases giving maximum 130 and 125%, respectively using 0.200 g of starch and decreases thereafter while maximum % true grafting (66.60%) is obtained using 0.150 g of starch.
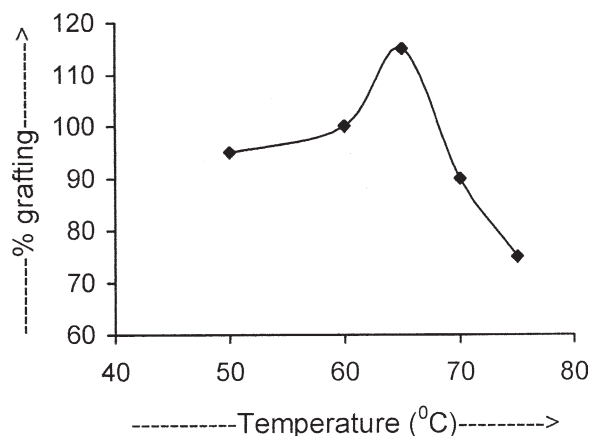

Figure 2 Effect of temperature on % grafting. PP, 0.200 g; starch, 0.150 g; [BPO], 1.239×10^{-3} moles; time, 120 min.; water, 20(10) mL; optimum temperature, 65°C.
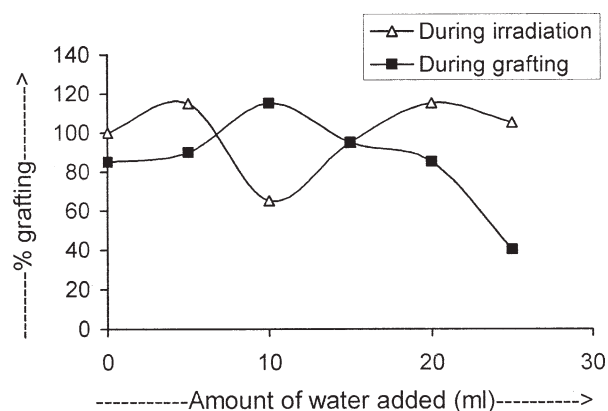

Figure 3 Effect of amount of water on % grafting. PP, 0.200 g; starch, 0.150 g; time, 120 min.; temperature, 65°C; optimum amount of water during irradiation(during reaction), 5(10) mL; [BPO], 1.239×10^{-3} moles.

FTIR analysis

Evidence of grafting is provided by comparison of the FTIR spectra of pristine PP and PP-*g*-Starch presented in Figures 6 and 6b, respectively. The FTIR spectrum of PP shows characteristic peaks at 2921.7 due to —CH$_2$ (asymmetric stretching), 2966.6 cm^{-1} due to —CH$_3$ (asymmetric stretching), 1377.9 cm^{-1} due to —CH$_3$ (symmetric bending), 1458.6 cm^{-1} due to —CH$_3$ (asymmetric bending), 1166.4 cm^{-1} due to another characteristic peak for —CHCH$_3$ and 998.7 cm^{-1} due to helix chain of PP. Apart from the above observed peaks for PP new peak for —COC— (ether linkage between PP and starch sample) appears between 1225.7 and 1081.9 cm^{-1}, and broad spectrum for —OH (polymeric association of hydroxy groups) at 3400–3200 cm^{-1} in the IR spectra of PP-*g*-Starch.

Thermal analysis

The differential thermal gravimetry (DTG), differential thermal analysis (DTA), and thermal gravimetric
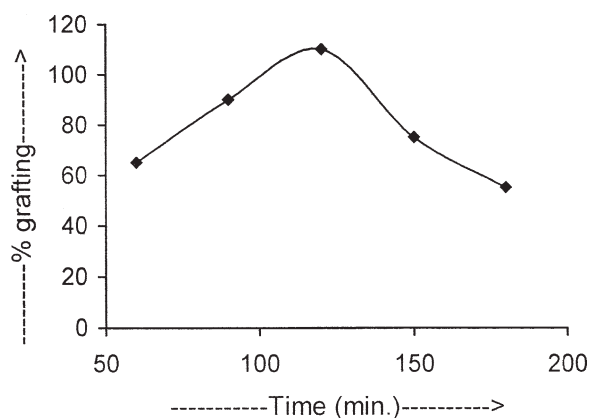

Figure 4 Effect of time on % grafting. PP, 0.200 g; starch, 0.150 g; [BPO], 1.239×10^{-3} moles; temperature, 65°C; water, 5(10) mL; optimum time, 120 min.
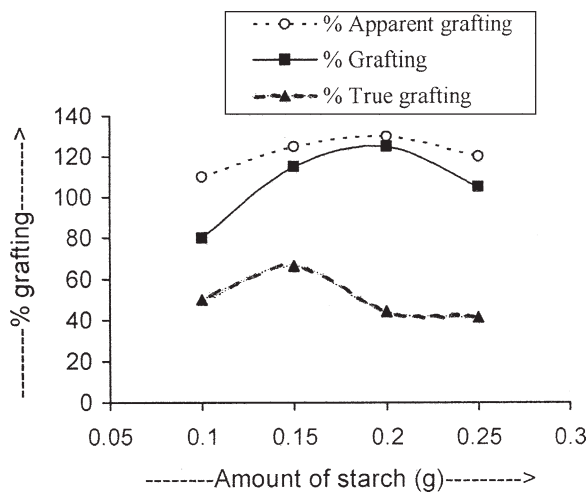
Figure 5 Effect of amount of starch on different grafting parameters.

analysis (TGA) thermograms of pristine PP and PP-*g*-Starch is presented in Figures 7(a–c) and 8(a–c), respectively.

It is observed from the DTG, DTA and TGA curves of PP that decomposition of PP takes in single stage and at a fast rate. A single peak at 448°C is observed with a decomposition rate of 1.816 mg/min. in the DTG curve. The energy required for this decomposition between the temperature 400 and 474°C with maximum endothermic peak at 451°C as depicted in the DTA curve is 129 mJ/mg. Another endothermic peak appearing at 161°C consuming 103 mJ/mg of energy refers to the melting peak. The TGA thermogram corroborates the information depicted by DTG/DTA curves. The decomposition range between the start and the end of the peak in
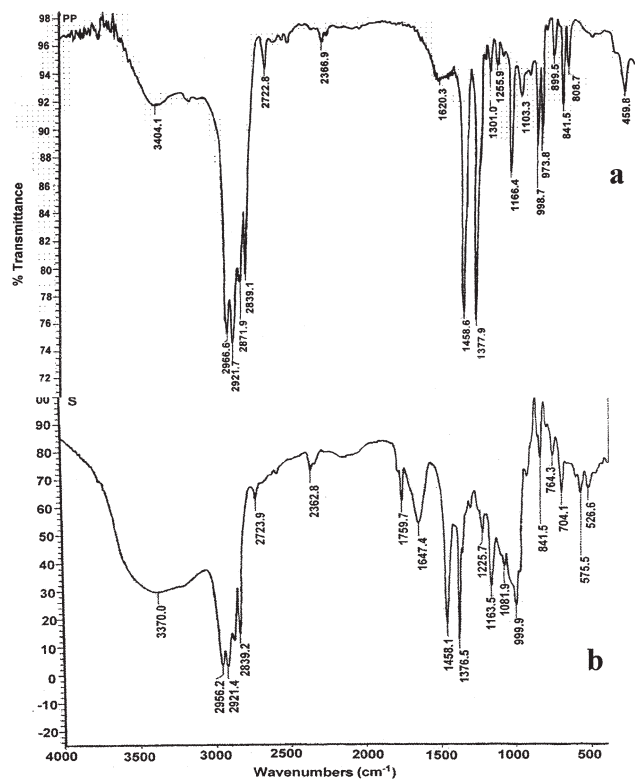
Figure 6 FTIR spectrums of (a) pristine PP and (b) PP-*g*-Starch.

DTG or the endothermic peak of the DTA is in the line with the initial decomposition temperature (IDT; 425°C) and the final decomposition temperature (FDT; 460°C) on the TGA thermogram. The fast rate of decomposition of PP, as depicted by a small temperature difference (35°C) between FDT and IDT is further subsisted by a steep line showing
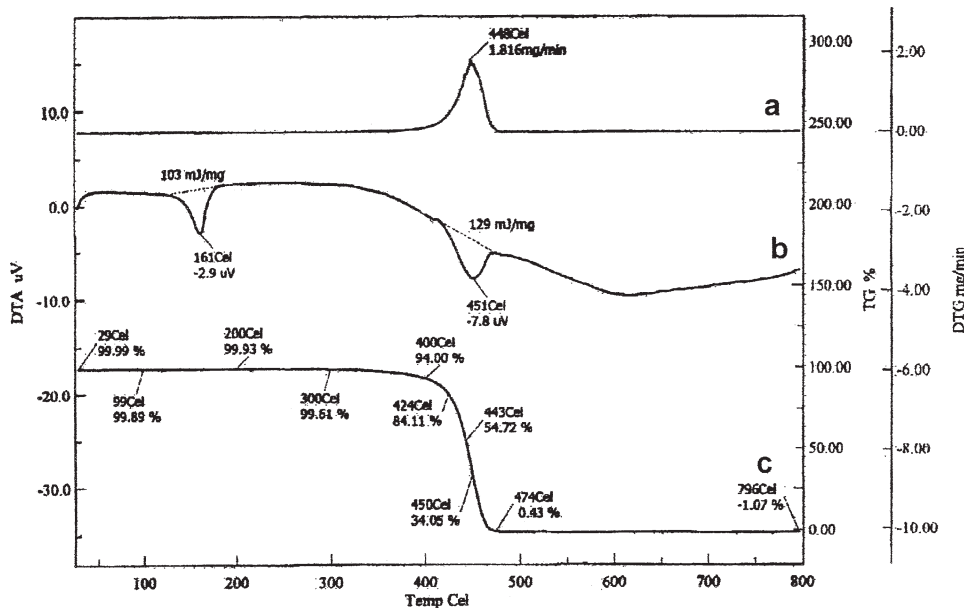

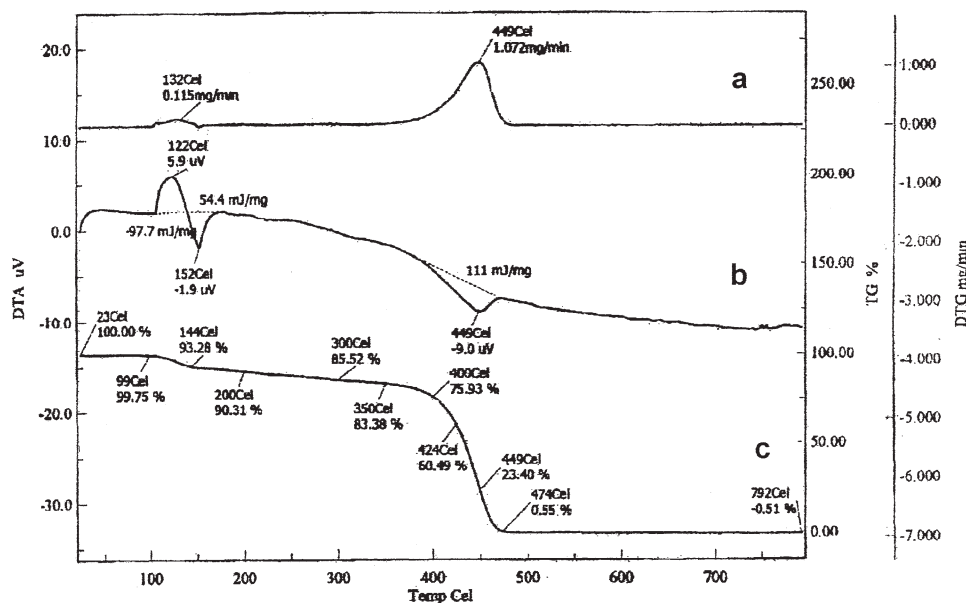**Figure 7** DTG, DTA, and TGA of pristine PP.

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

decomposition with a narrow temperature difference between DT values at each 10% wt. loss.

The DTA and TGA curves of PP grafted with starch also show a single stage of decomposition. However DTG curves shows a split in the peak with the initial decomposition with a fast rising wavering curve with small peak maxima at 432°C at a decomposition rate of 1.035 mg/min. The decomposition further goes giving another maximum at 447°C with an increasing rate of decomposition i.e., 1.067 mg/min. is observed. The decomposition region traversed by the grafted PP in DTA curve shows an endothermic peak indicates a continuous decomposition instead of a sharp peak absorbing less energy (89.5 mJ/mg) as compared to that absorbed by pristine PP. The melting endothermic peak also starts at 60°C and gives a sharp peak at 151°C with 169 mJ/mg of energy absorbs. On perusal of the TGA curve, the decomposition of PP-*g*-Starch is single stage decomposition with IDT and FDT almost coinciding with those of the pristine PP. However the % wt. loss of the grafted polymer is higher than that observed for pristine PP at corresponding temperatures. The temperature difference between every 10% wt. loss of pristine PP is very low indicating fast rate of decomposition. The DT values at every 10% wt. loss of the starch-grafted PP goes parallel to those of pristine PP although toward a little lower side upto 90% wt. loss. The temperature difference between the consecutive DT values of 10% wt. loss for PP-*g*-Starch is 46°C between first 10–20% wt. loss which decreases to 4°C for 50–60% wt. loss and continues to decompose with a small temperature difference between 80 and 90% wt. loss indicating a fast rate of decomposition.

From the DTA and TG data of starch-grafted PP, it is evident that the grafting of starch onto PP changes the thermal behavior of PP. The shifting of melting peak from 161°C of the pristine PP to 151°C in the graft, broad endothermic peak in DTA curve, a splitted DTG peak and higher % wt. loss at corresponding temperature of the grafted PP indicates that some disturbances in the molecular structure of the PP takes place upon grafting. However, when we compare the TG and DTG curve of pristine starch, it is observed the starch is also not very stable to thermal variations. The initial decomposition and final decomposition temperature (300.72 and 331.74°C, respectively) of starch and are also the decomposition temperature at every 10% wt. loss much lower than those of pristine PP. The temperature difference between the first 10% wt. loss is very high (186°C) which decreases to 1°C for 40–50% wt. loss beyond 50% wt. loss this difference increases again and
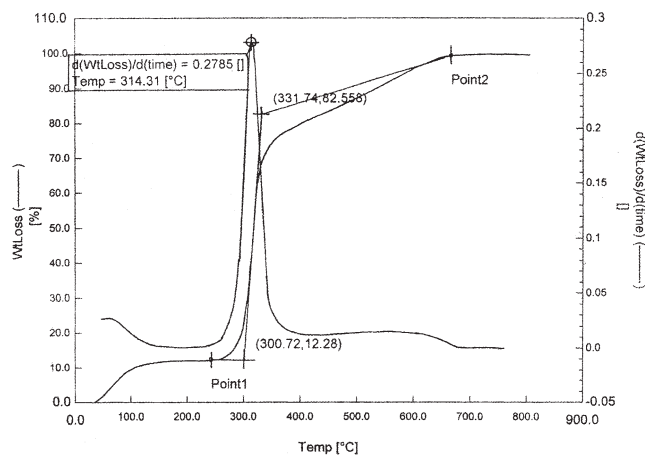

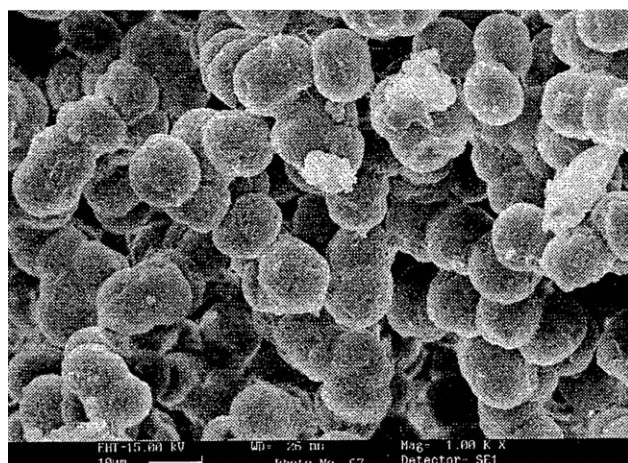**Figure 9** DTG and TGA of pristine starch.

Figure 10 SEM of pristine PP (magnification 1.00KX).

Figure 12 SEM of PP-*g*-Starch (magnification 1.00KX).

attains a value of 129°C between 80 and 90% wt. loss with 0% residue left. Thus, w.r.t. wt. loss with increasing temperature, the decomposition of starch is not fast as compared to pristine PP. The DTG curve (Fig. 9) of pristine starch shows a maximum decomposition temperature at 314.31°C with absorption of 0.2785 mJ/mg of energy. The grafting of starch therefore was not affect the thermal behavior of PP. Pure starch shows a two-step characteristic thermogram, wherein the major weight loss (75%) takes place in the second step within the temperature range of 233–368°C, the temperature for a maximum decomposition was 308°C.[16]

From the thermal data it is thus evident the grafting of starch has successfully being carried out but with no general improvement in the thermal behavior of the backbone i.e., PP.

Scanning electron microscopy

Scanning electron microscopy of pristine PP, starch and PP-*g*-Starch at magnification (1000×, EHT = 15.00 Kv) have been taken on LEO vp 435 instru-
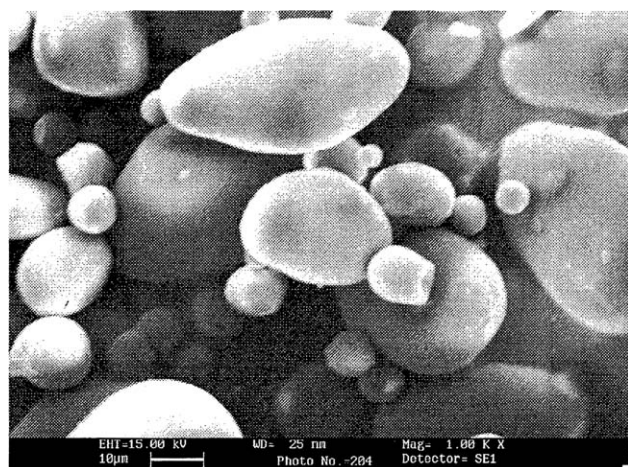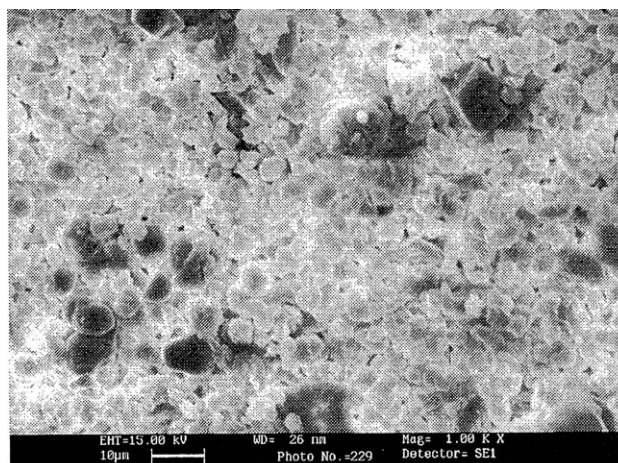

Figure 11 SEM of starch (magnification 1.00KX).

ment and presented in Figures 10, 11, and 12, respectively. The comparison of the scanning electron microscopy of the grafted PP with that of pristine PP shows clearly the change in the topology of the PP surface. Grafting of starch onto PP opens up its matrix and shows deposition of starch on the surface of backbone polymer.

Swelling and solubility behavior

The % swelling and % solubility of PP and PP-*g*-Starch has been studied in pure, binary, ternary, and quaternary polar solvent systems. The results are presented in Tables I and II. It is observed from Table I that PP being a hydrophobic hydrocarbon shows neither swelling nor solubility in the water. However, in polar solvents a high swelling percentage 220 and 240% in ethanol and 190 and 270% in DMF in 24 and 48 h, respectively was observed. The % swelling for PP, however, goes on decreasing with the increasing amount of water in the binary solvent and also in the quaternary solvent system along with the addition of DMSO and DMF. In pure DMSO, both percent swelling and percent solubility (10%) in 48 h is found to be quite low.

However, when the solvent system is shifted to the mixture of water, ethanol and DMSO, maximum swelling percent (220 and 270%) in 24 and 48 h is observed in 3 : 2 : 5 (H$_2$O : EtOH : DMSO) v/v ratio. Further increase in the amount of water and ethanol to DMSO decreases % swelling. In the quaternary solvent system, addition of water, ethanol and DMSO to DMF decreases percent swelling than that observed in pure DMF. The higher swelling percent of PP attributed to the fact that the reprecipitated PP (from beads) offers a fluffy powder which holds the solvents within the empty spaces. PP, however, remain insoluble in all the solvent systems. Similar studies when carried out on PP-*g*-Starch (both

TABLE I
% Swelling and % Solubility Behavior of
PP in Polar Solvents

H$_2$O : EtOH	% Swelling (PP)		% Solubility (PP)	
	24 h	48 h	24 h	48 h
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$_2$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$_2$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	170	0	0

composite and the true graft), different observations were made. Percent swelling of grafted PP was found to be lower than that observed for PP and the grafted samples were found to be soluble to some extent. Decrease in percent swelling in the grafted samples is attributed to the reasons that (i) the empty spaces in the fluffy nature of PP are reduced along with the change in the fluffy structure in grafted PP and (ii) some of the material goes into the bulk of solution thereby affecting the swelling percentage.

These observations were further substantiated from the swelling/solubility data of the starch-grafted PP composite and true grafts. In all the solvent systems, the true graft which lacks both unreacted PP and starch shows higher swelling per-

centage while the composite which contains both unreacted PP and starch shows higher solubility percentage. Maximum swelling percentage (200% in 48 h) of PP-g-Starch (true graft) in binary, ternary and quaternary solvent system and maximum solubility (30% in 48 h) for composite was observed in quaternary solvent system comprising of H$_2$O, EtOH, DMSO, and DMF in ratio 2 : 2 : 3 : 3. It is interesting to note that in pure DMSO, the grafted PP (both composite and true graft) shows much higher swelling (80%, 220%) respectively as compared to PP (10%).

When swelling studies were carried out in binary, ternary, and quaternary solvent system percent swelling of PP decreased from the maximum swelling (270%) in pure DMF in all the solvent systems. But when swelling behavior of grafted PP (true graft) was studied it is observed that percent swelling increases to maximum (200% in 48 h) in 5 : 5/7 : 3 water-ethanol system respectively as compared to (140%) in pure ethanol. In case of ternary and quaternary solvent systems also the percent swelling of true graft is 200 and 195% in 48 h in H$_2$O : EtOH : DMSO (2 : 1 : 7/3 : 2 : 5) and H$_2$O : EtOH : DMSO : DMF (1 : 1 : 4 : 4) ternary and quaternary solvent systems, respectively.

Both composite and true graft show good solubility in all the solvent mixture combinations as compared to zero percent solubility of pristine PP.

Following order of these solvents for giving maximum % swelling of PP is observed

$$DMF(270\%) > EtOH(240\%) > DMSO(10\%) > H_2O(0\%)$$

While the order of the solvents in case of PP-g-Starch is as follows:

TABLE II
% Swelling and % Solubility Behavior of PP-g-Starch Samples in Polar Solvents

H$_2$O : EtOH	% Swelling				% Solubility			
	PP-g-Starch (composite)		PP-g-Starch (true graft)		PP-g-Starch (composite)		PP-g-Starch (true graft)	
	24 h	48 h	24 h	48 h	24 h	48 h	24 h	48 h
0 : 10	160	210	130	140	10	0	0	0
3 : 7	200	200	140	170	0	0	10	20
5 : 5	150	140	170	200	0	10	10	20
7 : 3	25	30	150	200	0	20	10	20
10 : 0	0	10	0	30	0	5	10	20
H$_2$O : EtOH : DMSO								
0 : 0 : 10	80	80	100	220	10	10	0	20
2 : 1 : 7	70	40	170	200	10	20	10	20
3 : 2 : 5	60	50	190	200	10	20	10	20
4 : 3 : 3	30	70	170	140	10	20	10	20
H$_2$O : EtOH : DMSO : DMF								
0 : 0 : 0 : 10	160	180	160	190	20	30	10	10
1 : 1 : 4 : 4	110	110	150	195	10	10	10	10
2 : 2 : 3 : 3	90	50	150	180	10	30	10	10

Samples	% Water swelling								
	Time (h) (temp. = 30°C, pH = 7)			Temp. (°C) (time = 8 h, pH = 7)			pH (time = 8 h, temp. = 50°C)		
	4	8	16	30	40	50	4.0	7.0	9.2
PP	0	0	2	0	2	10	3	10	7
PP-*g*-Starch (composite)	46	58	32	58	84	110	40	110	60
PP-*g*-Starch (true graft)	40	46	44	46	56	88	36	88	44

Composite : EtOH(210%) > DMF(180%)

> DMSO(80%) > H_2O(10%)

True graft : DMSO(220%) > DMF(190%)

> EtOH(140%) > H_2O(30%)

These results are explained by considering the dielectric constant (Є) and polarity index (PI) of these solvents. Water has the maximum Є and PI value (80; 10.3 respectively) followed by DMSO (47.2; 7.2), DMF (38.3; 6.4) and least value of Є is observed for ethanol (24.3; PI not available). PP being a hydrocarbon lacks polarity and therefore shows maximum swelling in DMF with least polarity index. As the value of PI increases % swelling of pristine PP decreases with zero % swelling in water. When PP is graft copolymerized with starch, a polyhydroxy compound, with pendant hydroxyl groups, the trend of swelling behavior shifts. Maximum swelling is observed in DMSO and DMF, followed by EtOH and least in water for true graft. An interesting observation is made during swelling studies that the grafted polymers when suspended in water are found to float on its surface. However, in the presence of DMSO, DMF, and EtOH or in their mixture with water, these polymers move into the bulk of the solvent system and completely get solvated. This might be the reason for least swelling of the grafted samples in water where there is no interaction with water and hence no proper solvation takes place.

Thus, from the swelling studies it is inferred that grafting of starch onto PP, makes the modified polymer soluble in pure solvents or different solvent systems along with swelling due to the pendant polar hydroxyl groups of the grafted starch.

Water retention studies

The results of swelling percentage and water retention studies of PP-grafted samples as a function of temperature, time and pH are presented in Table III and IV, respectively. It is observed from Table III that PP and the grafted samples (both composite

and true graft) show maximum swelling (10, 110, and 88%, respectively) at 50°C in aqueous solution with normal pH (7.0) in 8 h.

The influence of solution pH (4.0, 7.0, and 9.2) on the % swelling of synthesized graft copolymer in distilled water is shown in Table III. It is observed that % swelling of PP-grafted copolymers was found to increase with pH (4–7). When the pH of the external solution increases beyond 5.0, the ionization of the hydroxyl groups in the grafted copolymer also increases. This sudden increase in swelling is due to increased ion osmotic swelling pressure as well as chain relaxation resulting from the electrostatic repulsion among hydroxylate groups inside the copolymer.[17] In addition, the extent of swelling is found more at pH 7, this may be due to the complete dissociation of hydroxyl groups of starch upto this pH value. At high pH values, the concentration of anionic groups in the polymer network increases.[18] With further increase in pH, the ion swelling pressure begins to drop again. Because of the increase in ionic strength of the swelling medium, the ion osmotic swelling pressure decreases, and ultimately reduces the equilibrium swelling capacity of the absorbent polymer.[19] Also the effect of the ionic strength on the water absorbency can be expressed by Flory's equation.[20] According to this equation when the ionic strength of the solution increases, the water absorbency decreases.

We anticipated that under acidic conditions, the graft copolymer network shrinks significantly due to protonation of the hydroxyl groups of starch. In general, starch can be hydrolyzed in acidic solution. For the present study, it is possible that some portion of the PP-*g*-Starch samples could be hydrolyzed to give the shorter grafted chains. The shorter grafted chains can reduce the extent of water absorption.

It is observed from Table IV that swollen PP sample did not show any loss of moisture with time. In case of composite, % moisture loss from each of the swollen sample (prepared as a function of time, temperature, and pH) shows a continuous rise after a period of every one hour. After attaining a particular value no further loss of water is observed. The loss of water has been found to be consistent as observed for the different composite samples.

TABLE IV
% Water Retention (% Moisture Loss) as a Function of Time of PP and PP-g-Starch

	% Water retention (% moisture loss)								
	Time (h) (temp. = 30°C, pH = 7)			Temp. (°C) (time = 8 h, pH = 7)			pH (time = 8 h, temp. = 50°C)		
Time (h)	4	8	16	30	40	50	4.0	7.0	9.2
PP									
2	0	0	0	0	0	0	0	0	0
PP-g-starch (composite)									
2	14 (32)	28 (30)	2 (30)	28 (30)	52 (32)	84 (26)	8 (32)	84 (26)	31 (29)
3	0	0	0	0	22 (62)	60 (50)	0	60 (50)	6 (54)
4	0	0	0	0	0	30 (80)	0	30 (80)	0
5	0	0	0	0	0	2 (108)	0	2 (108)	0
6	0	0	0	0	0	0	0	0	0
PP-g-starch (true graft)									
2	12 (28)	16 (30)	16 (28)	16 (30)	26 (30)	58 (30)	6 (30)	58 (30)	21 (23)
3	0	0	0	0	0	34 (54)	0	34 (54)	0
4	0	0	0	0	0	8 (80)	0	8 (80)	0
5	0	0	0	0	0	0	0	0	0

Thus from the data it is revealed that the starch-grafted PP (composite) swollen in water can retain water maximum upto 5 h beyond which no water loss is observed. This property can be useful for release of water over a period of time in arid region where scarcity of water is a problem.

CONCLUSIONS

The present study thus reveals that starch, a natural polymer, has been successfully grafted onto PP using BPO as a radical initiator. The effects of various reaction conditions on the graft copolymerization were investigated and gives maximum percentage of grafting 115% of starch onto PP at BPO concentration of 1.239×10^{-3} moles in 120 min. at 70°C using 15 mL of water. The structural characterizations by FTIR and SEM have indicated the presence of starch units in the products. The incorporation of starch as graft onto PP does not much affect the thermal behavior. Grafting also changes the chemical interaction of PP-g-Starch with the solvents. Better swelling and solubility of the grafted PP in solvent mixture in comparison to pristine PP has been observed. Water retention studies manifest the use of starch-grafted PP in arid regions.

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