

# Synthesis and Characterization of Polypropylene-Grafted Gelatin

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**ABSTRACT:** Modification of polypropylene (PP) has been successfully carried out by graft copolymerization of gelatin, by chemical method using benzoyl peroxide (BPO) as radical initiator. PP was preirradiated by gamma rays at a constant dose rate of 3.40 kGy/h before grafting to introduce hydroperoxide groups. Optimum conditions pertaining to maximum percentage of grafting were evaluated as a function of different reaction parameters. Maximum percentage of grafting of gelatin (115%) was obtained at BPO concentration =  $4.132 \times 10^{-2}$  mol/L in 120 min at 70°C using 30 mL of water. Characterization of PP-g-gelatin was carried out through FTIR, thermogravimetric analysis, and scanning electron microscopy. Swelling studies were carried out in pure, binary, ternary, and quaternary solvent systems comprising distilled water,

ethanol, dimethylsulphoxide (DMSO), and *N,N*-dimethylformamide (DMF) in different ratios. Maximum swelling of PP-g-gelatin (both composite and true graft) was observed in pure solvents that is, DMSO followed by DMF, ethanol, and water and was higher than that observed in the mixed solvent system. Water retention studies of unmodified PP, that is, pristine PP and PP-g-gelatin (both composite and true graft) were investigated at different time periods, temperatures and pH. Maximum % water retention for PP-g-gelatin (composite; 170%) was observed in 8 h at 50°C in neutral medium (pH = 7). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1226–1236, 2010

**Key words:** polypropylene; gelatin; graft copolymerization

## INTRODUCTION

Polypropylene (PP) is hydrophobic, resistant to chemicals at or near ambient temperature and is stable to air and sunlight. This inertness excludes its application where chemical affinities or penetration of components is necessary, for example, 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, modification of PP has been attempted by different groups of workers.

Effect of solvent on  $\gamma$ -radiation-induced graft copolymerization of methylmethacrylate onto PP has been studied by Naser et al.<sup>1</sup> Preirradiation method has been used to graft copolymerize 2,3-epoxypropyl methacrylate onto PP fabric by Chang et al.<sup>2</sup> The grafting of 2-vinyl-4,4-dimethyl azalactone onto electron-beam-activated PP films and fabrics and subsequent reaction of the anchored azalactone groups with various nucleophiles was investigated by Fontaine et al.<sup>3</sup> Picchioni et al.<sup>4</sup> carried out the grafting of vinyl monomers onto isotactic polypropylene

(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.<sup>5</sup> PP films were grafted with acryloyl chloride by  $\gamma$ -irradiation, and the grafted films were reacted with an azo dye.<sup>6</sup> Surface-modified PP films with thermally and photochemically sensitive copolymers consisting of *N*-2-hydroxypropyl methacrylamide (HPMA) and 4-(4-methoxyphenyl-azo) phenyl methacrylate (MPAP), and poly(HPMA-co-MPAP)-g-PP film were prepared by graft copolymerization with plasma postpolymerization technique<sup>7</sup> using Argon. For the purpose of the recovery of urokinase, the PP films were modified by radiation-induced grafting of glycidyl methacrylate (GMA) and subsequent chemical modification of epoxy group of poly-GMA graft chains.<sup>8</sup> Preirradiated IPP powder has been modified by grafting 2-vinyl pyridine and styrene in aqueous medium by Kaur et al.<sup>9</sup>

From the literature studies, it is thus revealed that the modification of PP through grafting has been successfully carried out using either single or binary monomer mixtures. However, a meager data is available where PP has been modified by intercrosslinking it with the preformed polymer either synthetic or natural. In view of the above, we, therefore, report in the present manuscript modification of PP

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by grafting a natural polymer, gelatin, using chemical method.

Gelatin, an animal protein, is a water soluble, biodegradable polymer with extensive industrial, pharmaceutical, and biomedical uses. Its water solubility, reactivity, and biodegradability make it a potentially useful material. Grafting of gelatin onto PP would thus give a product with mixed properties of synthetic and natural polymer, thereby improving upon the inherent properties of PP.

## EXPERIMENTAL

### Materials

Commercial PP was obtained from Thukral Trading, Delhi, India. The beads were recrystallized from 1,4-dimethylbenzene (*p*-xylene), and the powdered PP obtained upon recrystallization with methanol was used in all grafting experiments. Gelatin (Merck) and benzoyl peroxide (BPO; Merck) were used as received. Irradiation of the polymer was carried from Co<sup>60</sup> source housed in Gamma Chamber-900 at a constant dose rate of 3.40 kGy/h to introduce hydroperoxide groups. These groups offer sites for grafting or attachment of the polymer.

## METHODS

### Graft copolymerization

To the preirradiated, dried and weighed PP (0.200 g) suspended in known volume of water (0–25 mL) was added a definite amount of gelatin (0.100–0.350 g) dissolved in a known volume of water (0–25 mL) and a definite amount of the initiator, BPO (0.100–0.350 g). The reaction flask was placed in a water bath maintained at constant temperature (45–75°C) under constant stirring under nitrogen atmosphere for a definite interval of time (30–180 min). After the stipulated time period, the flask was removed from the water bath, and the contents were filtered. The residue contains grafted PP, unreacted gelatin, 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, and this is referred to as the “composite.” Apparent percentage of grafting of the composite was calculated after the complete removal of unreacted BPO by thorough washing with benzene as follows:

$$\% \text{ Apparent grafting} = \frac{W_c - W_o}{W_o} \times 100$$

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

The composite was then stirred with water for definite period of time at 70°C to remove ungrafted

gelatin. The reaction mixture was filtered, and the residue was dried at 45°C and weighed till the constant weight was obtained. Percentage of grafting is the amount of gelatin onto PP after the removal of unreacted gelatin by thorough washing with water and which was calculated as follows:

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

where  $W_o$  and  $W_g$  are weights of pristine PP and the graft copolymer, that is, PP-*g*-gelatin after the complete removal of the ungrafted gelatin, respectively.

The graft copolymer was further stirred for 2 h at 70°C with 1,4-dimethylbenzene to remove unreacted backbone polymer, that is, PP. The reaction mixture was filtered; residue was dried at 45–50°C till constant weight was obtained. The product is the “true graft” from which both unreacted gelatin and PP have been removed, and thus percentage of true grafting was calculated as follows:

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

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

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

Graft copolymerization of gelatin 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 gelatin, and the optimum conditions were thus evaluated for achieving the maximum percentage of grafting.

### Characterization of PP-grafted samples

Physical characterization of PP and PP-grafted samples was done by FTIR spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The FTIR spectra were recorded on KBr disc using a Thermo-5700 Spectrophotometer. Thermogravimetric analysis of pristine PP, gelatin, and PP-*g*-gelatin was carried out under nitrogen (200 mL/min) atmosphere at a rate of 10°C/min on PerkinElmer (Pyris Diamond Thermal Analyzer). The samples weights were kept within 5–8 mg. Scanning electron microscopy of pristine PP and PP-*g*-gelatin at magnification (2.00KX) have been taken on LEO vp 435 instrument.

### Swelling and solubility behavior

Swelling behavior of pristine PP and PP-*g*-gelatin (both composite and true graft) was studied in different polar solvents. Samples (0.10 g) each of pristine PP, PP-*g*-gelatin composite, and true graft were separately suspended in total of 10 mL of the single [water, ethanol, dimethylsulphoxide (DMSO), *N,N*-dimethylformamide (DMF)], binary (water : ethanol), ternary (water : ethanol : DMSO), and quaternary (water : ethanol : DMSO : DMF) solvent systems in different ratios at room temperature (20–25°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 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:

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

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

The swollen sample was dried in an oven (50°C) till the constant weight is obtained. The loss in weight after the sample was suspended in solvent(s) for a particular time, temperature is due to its solubility in solvent(s), and percent solubility was calculated from the following equation:

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

where  $W_o$  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*-gelatin (both composite and true graft) were carried out. Swelling of pristine PP (0.50 g), PP-*g*-gelatin (composite and true graft; 0.50 g) was carried out in water 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 pressing 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 initially after 2 h followed by weighing after an inter-

val of 1 h till the constant weight was obtained. Percent moisture loss due to loss of water from the swollen polymer with time was calculated as follows:

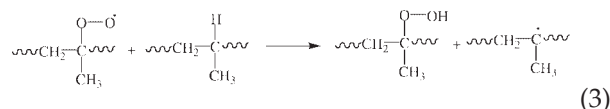
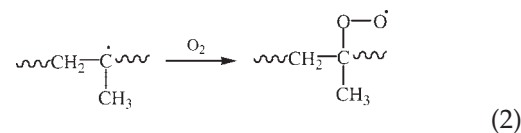
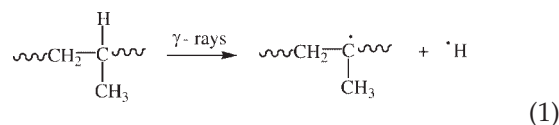
$$\% \text{ Moisture loss} = \frac{W_{st} - W_o}{W_o} \times 100$$

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

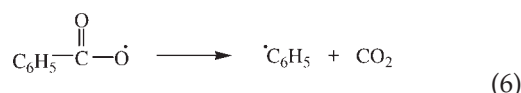
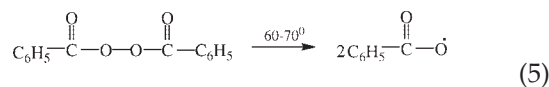
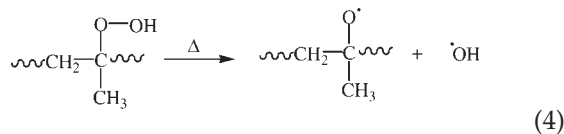
## RESULTS AND DISCUSSION

Irradiation of PP leads to the formation of hydroperoxide groups onto polymer backbone where grafting of gelatin occurred in the presence of BPO. Following mechanism explains the process of graft copolymerization of gelatin onto PP.

### Irradiation of PP



### Initiation



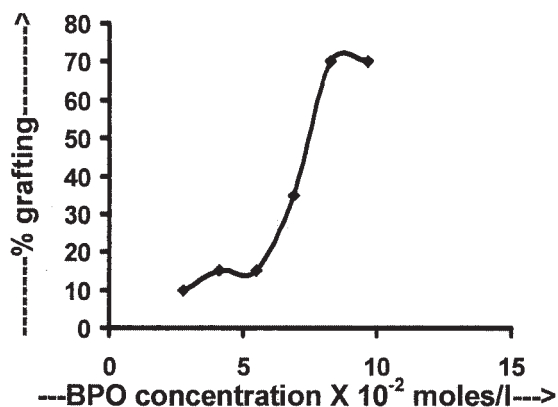
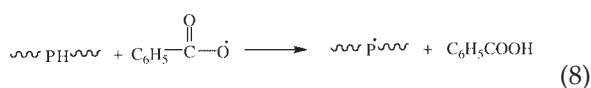
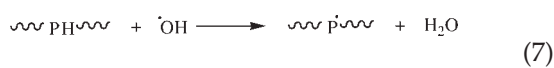
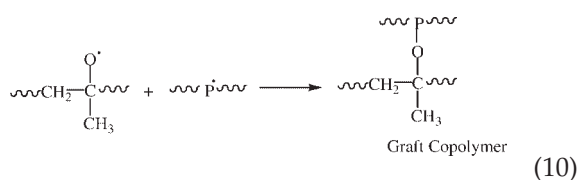


Figure 1 Effect of BPO concentration on % grafting.



where PH is gelatin.

#### Termination/intercrosslinking



Because the graft copolymer formation takes place between the two polymers, that is, PP and gelatin, there is therefore as such no propagation step. The generation of the active sites on the polymer occurs

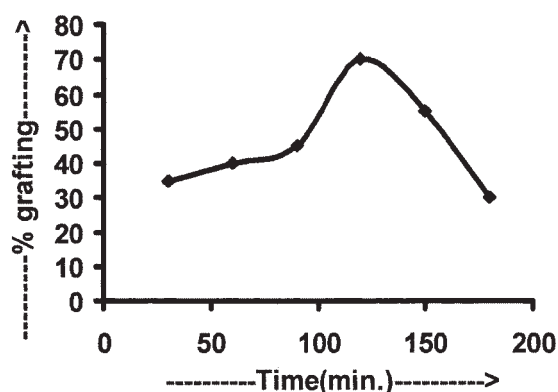


Figure 2 Effect of time on % grafting.

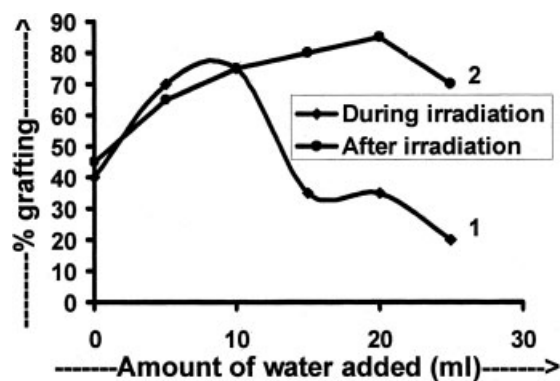


Figure 3 Effect of amount of water on % grafting.

via steps 4, 7, 8, and 9 and the two polymeric chains unite at the active sites to give the required graft polymer (step 10).

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

#### Effect of BPO concentration

Graft copolymerization of gelatin onto PP was studied as a function of BPO concentration, and the results are presented in Figure 1. (PP = 0.200 g, gelatin = 0.200 g, time = 120 min, temperature = 60°C, and water = 5(10)\* = 15 mL; \*amount of water during irradiation of PP (amount of water during grafting reaction of gelatin onto PP). It is observed from the figure that percent grafting of gelatin onto PP increases with increase in BPO concentration giving maximum 70% at BPO concentration =  $8.26 \times 10^{-2}$  mol/L (0.124 mol), in 15 mL of water. With further increase in the concentration of BPO, % grafting remains constant. The initial increase in percent grafting is due to the increase in the number of free radical sites on the gelatin backbone but thereafter the excess BPO is used up either in faster termination of growing polymer chains or killing of the radicals due to the side reactions.<sup>10</sup>

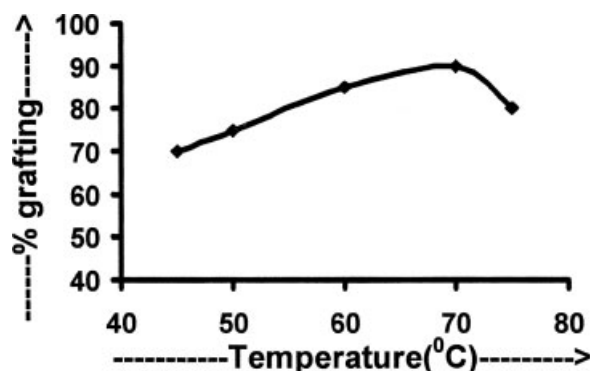
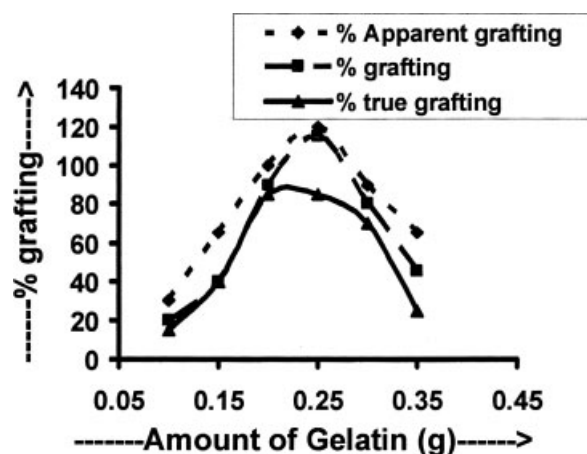


Figure 4 Effect of temperature on % grafting.

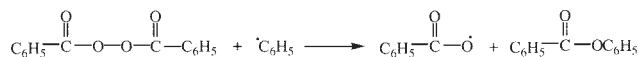


**Figure 5** Effect of amount of gelatin on different grafting parameters.

#### Effect of time

The effect of time on % grafting of gelatin onto PP is presented in Figure 2 (PP = 0.200 g, gelatin = 0.200 g,

BPO concentration =  $8.26 \times 10^{-2}$  mol/L, temp =  $60^{\circ}\text{C}$ , and water =  $5(10) \times \text{mL}$ ). It is noted that % grafting increases initially with the increase in the reaction time giving maximum grafting of 70% for gelatin within 120 min and decreases thereafter. The decrease in grafting may be due to induced decomposition of the initiator with time which decrease the concentration of BPO and hence the overall concentration of the active radicals.



#### Effect of water

Graft copolymerization of gelatin onto PP has been studied as the effect of amount of water on % grafting. [PP = 0.200 g, gelatin = 0.200 g, time = 120 min, temp. =  $60^{\circ}\text{C}$ , and BPO =  $4.132 \times 10^{-2}$  mol/L (in 30 mL of water)]. The variation in the volume of water changes BPO concentration so here the BPO

**TABLE I**  
Effect of [BPO], Time, Temperature, Amount of Water, and Gelatin on Percentage of grafting of Gelatin onto PP

BPO concentration $\times 10^{-2}$ (mol/L)	Time (min)	Volume of water during irradiation (during grafting) (mL)	Temperature ( $^{\circ}\text{C}$ )	Gelatin (g)	% Grafting
2.75	120	5(10)	60	0.200	10
4.13	120	5(10)	60	0.200	15
5.51	120	5(10)	60	0.200	15
6.89	120	5(10)	60	0.200	35
8.26	120	5(10)	60	0.200	70
9.64	120	5(10)	60	0.200	70
8.26	30	5(10)	60	0.200	35
8.26	60	5(10)	60	0.200	40
8.26	90	5(10)	60	0.200	45
8.26	120	5(10)	60	0.200	70
8.26	150	5(10)	60	0.200	55
8.26	180	5(10)	60	0.200	30
2.39	120	0(10)	60	0.200	40
8.26	120	5(10)	60	0.200	70
6.19	120	10(10)	60	0.200	75
4.95	120	15(10)	60	0.200	35
4.13	120	20(10)	60	0.200	35
3.54	120	25(10)	60	0.200	20
2.39	120	10(0)	60	0.200	45
8.26	120	10(5)	60	0.200	65
6.19	120	10(10)	60	0.200	75
4.95	120	10(15)	60	0.200	80
4.13	120	10(20)	60	0.200	85
3.54	120	10(25)	60	0.200	70
4.13	120	10(20)	45	0.200	70
4.13	120	10(20)	50	0.200	75
4.13	120	10(20)	60	0.200	85
4.13	120	10(20)	70	0.200	90
4.13	120	10(20)	75	0.200	80
4.13	120	10(20)	70	0.100	20
4.13	120	10(20)	70	0.150	40
4.13	120	10(20)	70	0.200	90
4.13	120	10(20)	70	0.250	115
4.13	120	10(20)	70	0.300	80

PP = 0.200 g.

concentration changes to  $4.132 \times 10^{-2}$  mol/L (0.124 mol). The variation in the amount of water was studied during irradiation of PP and also during its reaction with gelatin after irradiation.

Figure 3 (curve 1) represents the effect of variation in the amount of water (0–25 mL) during irradiation. After irradiation, a solution of gelatin (10 mL) was added along with the initiator and graft copolymerization was carried out. It is observed from the figure that PP irradiated in the absence of water produces % grafting only (40%), while maximum grafting (75%) was obtained when PP was irradiated in 10 mL of water.

In another set of variation of water, PP was irradiated in 10 mL (optimum value) of water and variation in the amount of water (0–25 mL) was carried out during the graft copolymerization reaction. The results are presented in Figure 3 (curve 2). It is observed from the figure that % grafting increases with the increasing amount of water giving maximum (85%) when 20 mL of water was added during grafting reaction. Furthermore, increase in the amount of water decreases % grafting to 60% in 25 mL.

Thus, maximum grafting (85%) was obtained in total optimum amount of 30 mL beyond which it decreases. The decrease in % grafting due to the reason that, in excess of water, the interaction between the polymer backbone and macroradicals decreases since the later, that is, gelatin imbibes excess amount of water which may hinder the interaction.

### Effect of temperature

The effect of temperature on % grafting of gelatin onto PP was studied, and the results are presented in Figure 4 (PP = 0.200 g, gelatin = 0.200 g, BPO concentration =  $4.132 \times 10^{-2}$  mol/L, time = 120 min, water = 10(20) mL). It is observed from the figure that % grafting increases with the increase in temperature giving maximum (90%) at 70°C. Further increase in the temperature decreases percentage of grafting. Increase in % grafting with increasing temperature is due to the increase in the decomposition of the initiator leading to the formation of more free radicals and generation of active sites on the polymeric backbone. Decrease in % grafting beyond optimum temperature is attributed to premature termination of the growing polymeric chains and due to the occurrence of chain transfer and other reactions.

### Effect of amount of gelatin

The effect of the amount of gelatin on % apparent grafting, % grafting, and % true grafting onto PP was studied using the optimum conditions evaluated in the preceding variations, and the results are presented in Figure 5. It is observed that with

increasing amount of gelatin, % apparent grafting, % grafting, and % true grafting increases giving maximum 120%, 115% using 0.250 g and 85% using 0.200 g, respectively, and decreases thereafter.

### FTIR analysis

Evidence of grafting is provided by the comparison of FTIR spectra of pristine PP and PP-g-gelatin presented in Figure 6(a,b). The FTIR spectrum of PP shows characteristic peaks at 2921.7 due to the  $-\text{CH}_3$  (asymmetric stretching), 2956.6  $\text{cm}^{-1}$  due to the  $-\text{CH}_2$  (asymmetric stretching vibrations), 1166.4  $\text{cm}^{-1}$  due to another characteristic peak for  $-\text{CHCH}_3$  and 998.3  $\text{cm}^{-1}$  due to helix chain of PP. Apart from the above-observed peaks for PP, new peaks at 1167.6–1034.6  $\text{cm}^{-1}$ , 1646.9  $\text{cm}^{-1}$ , and 3400–3200  $\text{cm}^{-1}$  due to  $-\text{COC}-$  (ether linkage between PP and gelatin sample),  $>\text{C}=\text{O}$  of amide group and broad spectrum for  $-\text{NH}_2$  were also found in the IR spectra of PP-g-gelatin.

### Thermogravimetric analysis

The initial decomposition temperature (IDT), final decomposition temperature (FDT), and decomposition temperature (DT) at every 10% weight loss for each sample is presented in Table II.

On perusal of the thermal data (Table II) with respect to IDT and FDT values, it is observed that the IDT of the grafted PP (374°C) is lower than pristine PP (412°C), but the FDT of pristine PP (470°C) is little higher than that grafted PP (463°C), whereas IDT and FDT of grafted PP is higher than the respective values of gelatin (278 and 368°C, respectively). The DT values at every 10% wt loss of the grafted PP goes parallel to those of pristine PP although at little lower side but are much higher than those of gelatin up to 50% wt loss beyond which the DT values of gelatin are much higher than either PP or the grafted PP. It is further observed that the temperature difference between every 10% wt loss of pristine PP is very low, indicating a fast rate of decomposition. The grafted PP, on the other hand, experiences decomposition with higher temperature difference for every 10% wt loss than that of PP up to 40% beyond which the difference becomes same as that of PP. Both PP and grafted PP decomposed without any left over residue.

In case of gelatin, the initial decomposition begins with a very high temperature difference (133°C) between first 10–20% wt loss, which decreases to 24°C up to 30–40% wt loss. Beyond 40%, this difference increases again and attains a value of 110°C between 80 and 90% wt loss with 4% residue left.

Thus, from the thermal data, it is indicated that the grafting of gelatin onto PP improves upon the initial stages of decomposition but attains a similar decomposition pattern as that of PP.

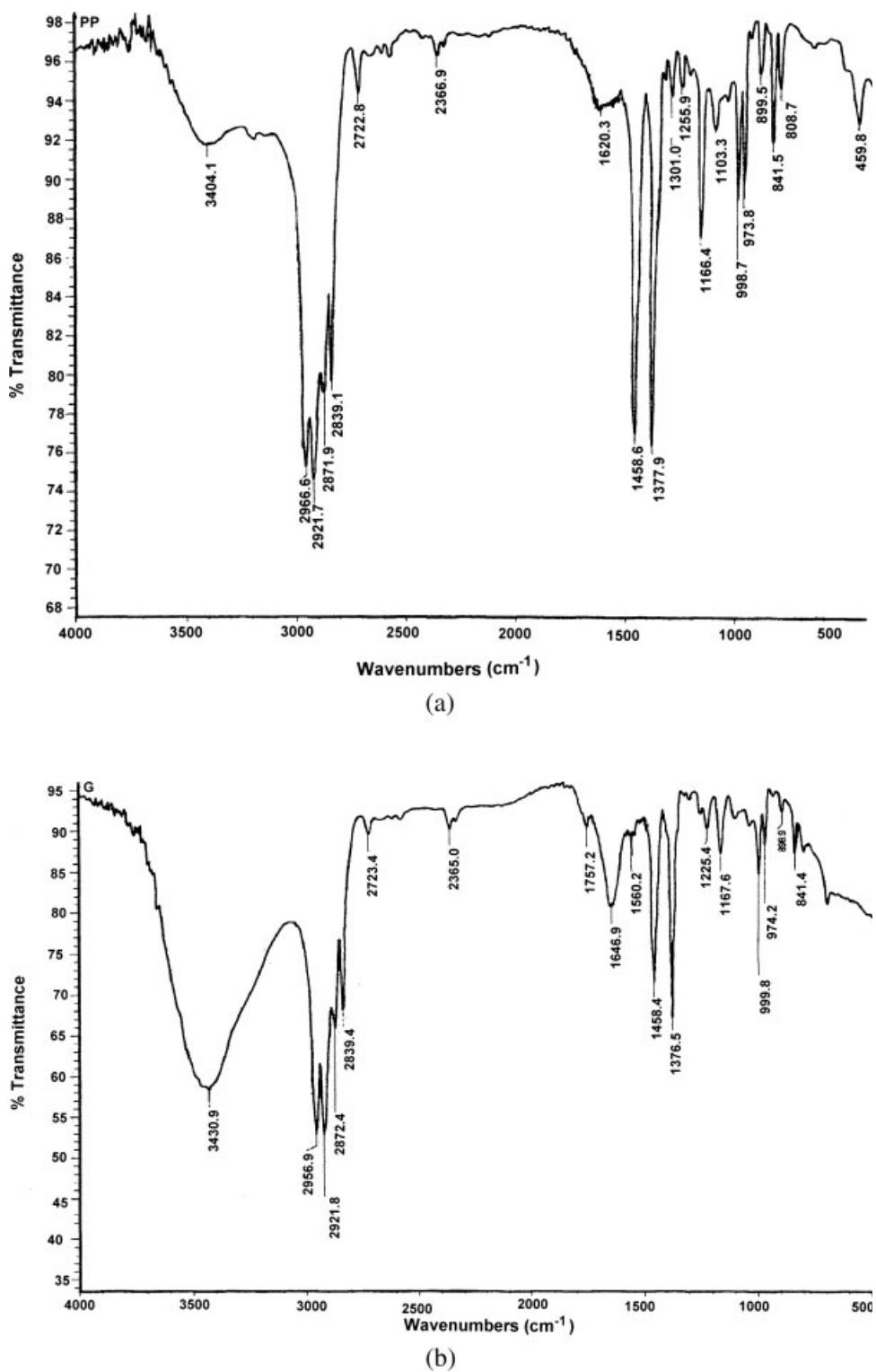


Figure 6 (a) FTIR spectrum of Pristine PP and (b) FTIR spectrum of PP-g-gelatin.

### Scanning electron microscopy

In comparison with the SEM of PP and PP-g-gelatin, it is revealed that gelatin has been successfully grafted on the PP surface. Figure 7 characterizes a

continuous morphology with a homogeneous surface of PP, whereas in Figure 8, incorporation of gelatin as graft onto PP has disturbed the homogeneity of PP surface and has a different surface morphology with uneven distribution.

**TABLE II**  
**Thermogravimetric Analysis of Pristine PP, Gelatin, and PP-g-Gelatin Samples**

Sample	IDT (°C) (at % residue left)	FDT (°C) (at % residue left)	DT (°C) at every 10% wt loss									
			10	20	30	40	50	60	70	80	90	100
PP	412 (99.98)	470 (0)	414	429	436	440	444	447	451	454	459	470
Gelatin	278 (86.42)	368 (47.87)	147	280	314	338	366	423	523	609	719	<sup>a</sup>
PP-g-gelatin	374 (86.51)	463 (0)	321	401	418	427	434	439	444	448	454	463

<sup>a</sup> % residue left, 4.

### Swelling and solubility behavior

Percent swelling and percent solubility of PP and PP-g-gelatin samples was studied in pure, binary, ternary, and quaternary polar solvent systems, and the results are presented in Tables III and IV, respectively. It is observed from Table III that PP being hydrophobic shows no swelling or solubility in water. However, in polar solvents, a high swelling percentage of PP (220 and 240%) in ethanol and (190 and 270%) in DMF in 24 and 48 h respectively, was observed. In DMSO, however, poor swelling (0% and 10%) in 24 and 48 h was observed.

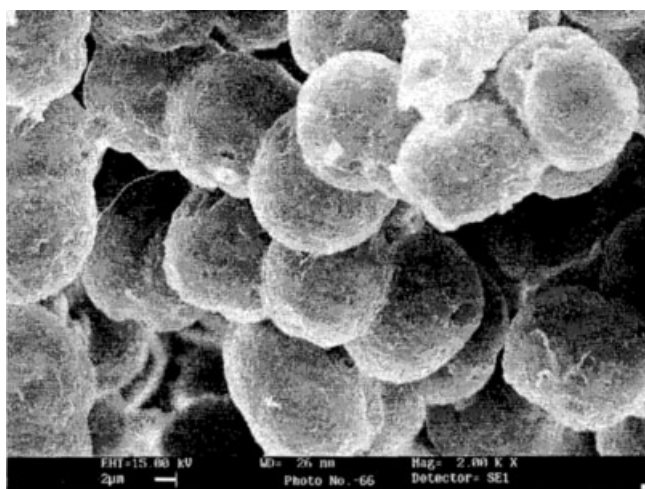
When swelling studies were made in mixed solvent systems, it was observed that percent swelling of PP, obtained in single solvents, goes on decreasing with the increasing addition of water in the binary solvent (H<sub>2</sub>O : EtOH) and also in the quaternary solvent system along with the addition of DMSO and DMF. 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<sub>2</sub>O : EtOH : DMSO) ratio. Further increase in the amount of water and ethanol 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 is attributed to the fact that the recrystallized PP offers a fluffy powder, which holds the solvents within the empty spaces. PP, however, remains insoluble in all the solvent systems.

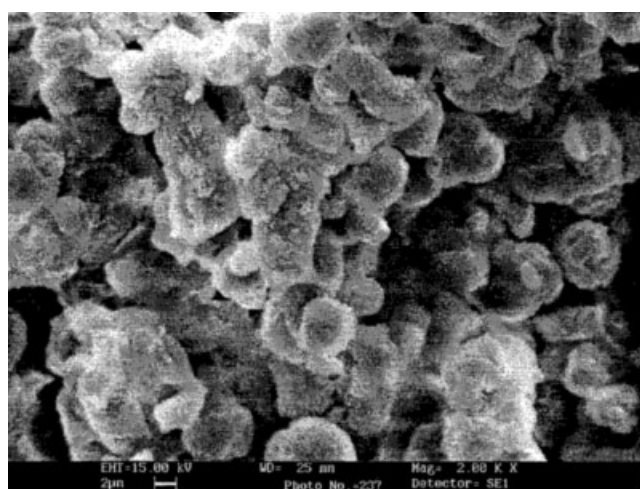
Similar studies when carried out on PP-g-gelatin (both composite and the true graft), different observations were made. Percent swelling of grafted PP was found to be lower than that observed for PP in single solvents, and the grafted samples were found to be soluble to some extent (between 20 and 30%). 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 solution thereby decreasing the swelling percentage.

Following the order of pure solvents toward percentage of swelling of PP and PP-g-gelatin (both composite and true graft) was observed:

PP: DMF (270%) > ethanol (240%) > DMSO (10%) > water (0%)  
 Composite: DMF (110%) > ethanol (80%) > DMSO (60%) > water (30%)  
 True graft: DMF (120%) > ethanol (100%) > DMSO (90%) > water (10%).



**Figure 7** SEM of pristine PP (magnification 2.00KX).



**Figure 8** SEM of PP-g-gelatin (magnification 2.00KX).



**TABLE III**  
% Swelling and % Solubility Behavior  
of PP Organic Solvents

	% Swelling (PP)		% Solubility (PP)	
	24 h	48 h	24 h	48 h
Water : ethanol				
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
Water : ethanol : 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
Water : ethanol : 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

These observations were further substantiated from the swelling/solubility data of the gelatin grafted PP (both composite and true graft). It is observed from Table IV that % swelling of PP-g-gelatin (composite) increases from 80 in (0 : 10) to 100% in (3 : 7 v/v; H<sub>2</sub>O : EtOH) binary solvent system and then decreases to 30% in (10 : 0), that is, pure water in 24 h whereas PP-g-gelatin (true graft) attains optimum swelling in pure ethanol (10 mL) in 24 h, which continuously decreases with the increasing amount of water in the binary H<sub>2</sub>O : EtOH system. Both composite and true graft are soluble up to 20% in 24 and 48 h.

In ternary solvent system comprising water, ethanol, and DMSO, PP-g-gelatin (composite) and (true graft) showed higher % swelling 170% and 130% in 48 h, respectively, in 4 : 3 : 3 v/v ratio of (H<sub>2</sub>O : EtOH : DMSO). Further increase or decrease in any solvent component decreases percent swelling. This can be due to the reason that because of higher amount of water in the solvent mixture, the dielectric constant and polarity index (PI) may be higher, which enhances the interaction of the solvent mixture with the pendent groups of grafted gelatin. Maximum % solubility (30%) was observed in pure DMSO in 24 and 48 h.

In quaternary solvent system (H<sub>2</sub>O : EtOH : DMSO : DMF), it is observed that % swelling and % solubility decrease with the decreasing amount of DMSO and DMF in different ratios. Maximum % swelling (110 and 140%) was observed in 1 : 1 : 4 : 4 ratio in 24 and 48 h for composite and true graft, respectively. Maximum % solubility (30%) of both the composite and the true graft of PP-g-gelatin was observed in 24 and 48 h.

These results are explained by considering the dielectric constant ( $\epsilon$ ) and PI of these solvents. Water has the maximum  $\epsilon$  and PI value (80; 10.3, respectively) followed by DMSO (47.2; 7.2), DMF (38.3; 6.4), and least value of  $\epsilon$  is observed for ethanol (24.3; PI not available). PP being a hydrocarbon lacks polarity and therefore shows maximum swelling in DMF with least PI. As the value of PI increases, % swelling of PP decreases with zero % swelling in water. When PP is graft copolymerized with gelatin, a polyamide, with pendant hydroxyl, amino, and carboxyl groups, the % swelling decreases in DMF

**TABLE IV**  
% Swelling and % Solubility Behavior of PP-g-Gelatin in Organic Solvents

	% Swelling				% Solubility			
	PP-g-gelatin (composite)		PP-g-gelatin (true graft)		PP-g-gelatin (composite)		PP-g-gelatin (true graft)	
	24 h	48 h	24 h	48 h	24 h	48 h	24 h	48 h
Water : ethanol								
0 : 10	80	60	100	90	20	20	20	20
3 : 7	100	90	90	90	20	10	20	10
5 : 5	90	80	80	90	10	10	20	10
7 : 3	60	80	80	20	20	10	20	0
10 : 0	30	20	10	10	10	10	0	0
Water : ethanol : DMSO								
0 : 0 : 10	40	60	90	90	30	30	30	30
2 : 1 : 7	60	70	30	120	20	30	20	10
3 : 2 : 5	90	110	30	120	20	20	10	10
4 : 3 : 3	110	170	30	130	0	10	10	10
Water : ethanol : DMSO : DMF								
0 : 0 : 0 : 10	70	110	90	120	30	20	30	30
1 : 1 : 4 : 4	70	110	80	140	20	20	20	30
2 : 2 : 3 : 3	70	50	60	80	20	10	20	20

**TABLE V**  
**% Water Swelling with Time, Temperature, and pH of PP and PP-g-Gelatin Samples**

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-gelatin (composite)	124	144	80	144	144	170	88	170	124
PP-g-gelatin (true graft)	30	36	46	36	40	60	30	60	16

and ethanol whereas in DMSO and water increases. An interesting observation was made during swelling studies that the grafted polymers suspended in these solvent(s) was found to float on the surface of water, whereas in the presence of DMSO, DMF, and ethanol or in their mixture with water, the polymer moves into the bulk of the solvent system and completely gets solvated. This might be the reason for the least swelling of the grafted samples in water where there is no complete interaction with water, and hence no proper solvation takes place.

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

#### Water retention studies

Swelling percentage and water retention of PP-grafted samples were studied as a function of time, temperature, and pH, and the results are presented

in Tables V and VI, respectively. It is observed from Table V that PP and PP-g-gelatin (both composite and true graft) show maximum swelling (10%, 170%, and 60%, respectively) at 50°C in water with neutral pH (7.0) in 8 h.

The swollen samples were placed at room temperature, and the loss of water with time was evaluated as % moisture loss, and the results are presented in Table VI. Swollen sample of PP did not show any loss of moisture with time. However, in case of the grafted samples, the swollen composite samples (prepared as a function of time, temperature, and pH) show a continuous rise in % moisture loss with every 1 h. After attaining a particular value, no further loss of moisture was observed. It was further observed that the loss of moisture is consistent for different composite samples with 170 and 144% swelling.

In case of true graft samples, % moisture loss is observed only within first 2 h beyond which no further loss of moisture was observed except in the case of the sample with maximum swelling (60%)

**TABLE VI**  
**% Water Retention (% Moisture Loss) as a Function of Time of PP and PP-g-Gelatin Samples**

Time (h)	% 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)		
	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-gelatin (composite)								
2	94 (30)	110 (34)	58 (22)	110 (34)	110 (34)	140 (30)	62 (26)	140 (30)	92 (32)
3	70 (54)	78 (66)	26 (54)	78 (66)	75 (69)	108 (62)	34 (54)	108 (62)	64 (60)
4	34 (90)	42 (102)	0	46 (98)	46 (98)	82 (88)	10 (78)	82 (88)	38 (86)
5	10 (114)	26 (118)	0	26 (118)	24 (120)	60 (110)	0	60 (110)	12 (112)
6	0	2 (142)	0	4 (140)	0	32 (138)	0	32 (138)	0
7	0	0	0	0	0	6 (162)	0	6 (162)	0
8	0	0	0	0	0	0	0	0	0
	PP-g-gelatin (true graft)								
2	2 (28)	4 (32)	12 (34)	4 (32)	10 (30)	34 (26)	4 (26)	34 (26)	2 (18)
3	0	0	0	0	0	8 (52)	0	8 (52)	0
4	0	0	0	0	0	0	0	0	0

where percent moisture loss falls from 26% in 2 h to 52% in the next hour. The low percent moisture loss and hence poor water retention in true grafted samples is due to the fact that (i) percent swelling is low (60%) (ii) true graft constitutes a product of the two polymers, that is, PP and gelatin, which are covalently linked and is different from the composite which other than the true graft contains the unreacted PP and gelatin. These unreacted polymers help the product to swell more and to retain the water for longer period of time.

Thus, from the results, it is revealed that the gelatin grafted PP (composite) swollen in water can retain water maximum up to 6 h beyond which no water loss is observed. This property can be useful for the release of water over a period of time in arid regions where scarcity of water is a problem.

### CONCLUSIONS

The present studies thus reveal that gelatin, a natural polymer, can be successfully grafted onto PP using BPO as a radical initiator. The effects of various reaction conditions on the graft copolymerization were investigated and gave maximum percentage of grafting 115% of gelatin onto PP at BPO concentration of  $4.132 \times 10^{-2}$  mol/L in 120 min

at 70°C using 30 mL of water. Although the incorporation of gelatin as graft onto PP does not much affect the thermal behavior, it however changes the chemical interaction with the solvents. Better swelling and solubility of the grafted PP in solvent mixture in comparison with pristine PP has been observed. Water retention studies manifest the use of gelatin grafted PP in arid regions.

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