Biodegradation and Swelling Studies of Gelatin-Grafted Polyethylene

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ABSTRACT: In this article, we report on biodegradation studies and the swelling/solubility behavior of gelatingrafted polyethylene (PE). The successful synthesis of graft copolymers of PE with gelatin was carried out with benzoyl peroxide as the radical initiator. Biodegradation studies of the grafted PE were carried out via a soil burial test (with and without the addition of urea). Percentage weight loss was studied as a function of time, and we observed that the percentage weight loss increased with time and was higher for urea-enriched soil samples. Microanalysis of the soil containing the samples was carried out after a specified number of days. An increase in the colonies of microorganisms with increasing number of days was observed. This revealed that the microorganisms fed upon the grafted material, which led to an increase in the per-

INTRODUCTION

Although plastics have a number of advantages over other materials, their lack of biodegradability has caused much concern because of their role in causing environmental pollution. Various attempts have, therefore, been made to develop biodegradable plastics. Successful methods of preparation of biodegradable polyethylene (PE) are limited. The use of naturally available and highly hydrophilic biodegradable monomers such as monosaccharides, disaccharides, and oligosaccharides as building blocks for environmentally friendly biodegradable polymers could be an alternative method. The modification of polymers by surface grafting represents a practical and widely used solution for the modification of the surface properties of preformed polymers; this method can be extended for the preparation of biodegradable polyolefins. Huang¹ studied biodegradable polymers and copolymers and reasoned that biodegradable polymers containing both hydrophilic and hydrophobic segments could be used in drug-delivery sys-

WVILEY InterScience® centage weight loss. Hydrolysis of the samples, taken out from the soil after a specified number of days, revealed a continuous loss of weight with increasing number of days. The effect of the degradation of the grafted samples buried in soil and urea-enriched soil on the growth of plants was studied, and we found that the plants grew normally in the soil containing the grafted material. Swelling studies were made in binary and ternary solvent systems comprising water–ethanol and water–ethanol–dimethyl sulfoxide, respectively, to study the maximum swelling and solubility of the grafted PE. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3878–3884, 2008

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tems. Kuwajima et al.² grafted methyl methacrylate onto gelatin by radical initiators and studied these substances in aqueous solution at temperatures between 60 and 80°C. Among the initiators used [peroxysulfates, 9-azobisisobutyronitrile, and benzoyl peroxide (BPO)], potassium peroxysulfate was found to be the most efficient in this particular graft polymerization. Rosa et al.³ studied the thermal properties and enzymatic degradation of blends of poly(Ecaprolactone) with gelatin. Apostolov et al.⁴ worked on biodegradable laminates based on gelatin and observed that a compression-molded gelatin-starch (1 : 1 w/w) blend showed improved mechanical properties compared to neat gelatin. All of the materials prepared were biodegradable, that is, environmentally friendly because they do not pollute nature. Starch-blended biodegradable PE films grafted with vinyl acetate showed better printability performance without affecting biodegradation properties.⁵ Varma et al.⁶ studied the biodegradation behavior of blends of poly(*\varepsilon*-caprolactone) and low-density PE and observed that enzymatic degradation showed an appreciable weight loss, whereas soil and compost burial showed a small weight loss. Enzymatic and fungal degradation studies of crosslinked gelatin grafted with various vinyl monomers were done by Satyanarayana and Chatterji,⁷ who observed that despite extensive grafting, the protein portion was still

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accessible to enzymatic attack. Fungi are known to easily attack amphiphilic systems with low total grafting and higher hydrophilic content. Bhat and Kumar⁸ studied the biodegradability of poly(methyl methacrylate) blends with some cellulose derivatives by the soil burial test and enzymatic degradation. Studies on the biodegradability of common plastics, such as PE, polystyrene, and polyesters were performed by Potts et al.⁹ with a mixture of four species of fungi. Biodegradation was estimated by the density of growth on solid surfaces containing the test material as a sole source of carbon. Studies of the burial of certain plastics were also conducted, and biodegradability was measured by weight loss after a definite period of time.

Microorganisms attack some flexible polymers; this was determined by Feldman and Banu¹⁰ by using the soil burial test method. They demonstrated that highly filled polyolefin elastomer formulations having a significant percentage of postconsumer polyolefins (up to 60% in laboratory conditions) had interesting properties from the biodegradation point of view. The effect of microorganisms' attack after soil burial was evaluated by visual examination, weight loss, water absorption, and changes in the mechanical properties.

In view of this, gelatin has been chosen to modify polymers for the induction of biodegradable behavior. Therefore, in this article, we report on the modification of PE by its graft copolymerization with gelatin with BPO as the radical initiator.

EXPERIMENTAL

Materials and methods

Commercial PE was obtained as beads from Thukral Trading Co. (Delhi, India). PE was dissolved in *p*-xy-lene and was precipitated with the addition of methanol. PE was irradiated from a Co^{60} source housed in a Gamma Chamber-900 (BARC, Trombay, Mumbai, India) at a constant dose rate of 3.40 kGy/h. Gelatin and BPO (S.D. Fine Chemicals, Mumbai, India) were used as received. Water, ethanol, and dimethyl sulfoxide (DMSO) were used as solvents for the swelling studies and were distilled before use.

Gelatin was grafted onto preirradiated PE with BPO as the radical initiator. Optimum conditions pertaining to the maximum percentage of grafting were evaluated. Maximum grafting percentage (112.5%) was obtained at [BPO] = 3.4×10^{-2} mol/L, amount of water = 30 mL, temperature = 60° C, and time = 120 min, with 0.200 g of PE, 0.250 g of gelatin, and 0.150 g of BPO.

The grafted PE containing both unreacted PE and gelatin is referred to as the PE-*g*-gelatin composite, whereas the graft from which the unreacted gelatin and PE were removed by washing with water and xylene, respectively, is referred to as the true graft.

The percentage grafting of gelatin onto PE was calculated as follows:

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

where W_0 and W_g are the weights of the original PE and the graft copolymer, that is, PE-g-gelatin, after the complete removal of the ungrafted gelatin, respectively.

Biodegradation studies

Biodegradation behavior of PE and the PE composite and true graft was studied by determination of the loss in weight during the soil burial test.

Soil burial method

Soil (1200 g) was placed in different pots. A weighed amount (1 g) of each of the samples, that is, pure PE and PE-g-gelatin (composite and true graft separately), wrapped in synthetic net was placed separately in each pot. Care was taken that the samples were completely covered with the soil. The pots were covered with aluminum foil and kept at room temperature. The weights of all of the samples, PE and grafted PE, were measured at regular intervals of time (10 days).

The weight loss percentage as a function of the number of days was determined as

Weight loss % = $\frac{\text{Initial weight at the beginning} - \text{Final weight after 10 days}}{\text{Initial weight at the beginning}} \times 100$ Weight loss% (after every 10 days) = $\frac{\text{Initial weight before 10 days} - \text{Final weight after 10 days}}{\text{Initial weight before 10 days}} \times 100$

To study the effect of nitrogenous compounds on the degradation behavior of the samples, similar studies were also made with samples in ureaenriched soil (6 g of urea/kg of soil).

Microanalysis

To corroborate degradation, an assay of the soil containing samples was studied in nutrient agar medium and CzepeckDox medium. The growth of microorganisms such as bacteria and fungi was checked at definite intervals of time. Samples of the soil (1%) containing PE and PE-g-gelatin (composite and true graft) were separately mixed well with 10 mL of normal saline. This was diluted through a serial dilution method. To tube number 1 was added 1 mL of supernatant (from the saline solution containing soil samples), and this was thoroughly mixed. From this tube (number 1), 1 mL each was transferred to the second tube and so on to make the further dilutions.

Hydrolysis studies

For the hydrolysis studies, a definite weight (0.500 g) of different samples of pristine PE and PE-*g*-gelatin (composite and true graft) separately wrapped in synthetic net was buried in soil. The samples were taken out after a definite interval of time (10 days), washed with water to remove the adhered soil, and dried. The dried sample was weighed and hydrolyzed with 20 mL of 6N HCl for 4 h. After the hydrolysis, the residue was dried and weighed.

Growth of plants

Whether or not the degradation products from the polymer samples affected the growth of the plants, the growth of soybean plants and wheat plants was checked from the germination stage. The soybean seeds and wheat seeds were placed uniformly in different pots containing the samples along with a reference pot containing no grafted sample. The plants were allowed to grow in the open for 35 days. The length and height of the roots and shoot, respectively were measured.

Swelling and solubility behavior

The swelling behavior of the pristine PE, composite, and true graft in different polar solvents was studied. Samples each of the pristine PE, PE composite, and PE true graft were separately suspended in 10 mL of the solvent and kept at 40°C. The samples were filtered after 24 h. The adhered water was dried by gentle pressing between the folds of filter paper, and the sample was weighed immediately. The percentage swelling was determined from the increase in the weight of the original sample as follows¹¹:

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 until a constant weight was obtained, and the percentage solubility was calculated from the following equation:

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

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

Dried samples were again placed for swelling study in the solvent for another 24 h at the same temperature. The swelling and solubility percentages were calculated as follows:

Swelling %
$$= \frac{W_{d'} - W_d}{W_d} \times 100$$

Solubility % $= \frac{W_d - W_{d''}}{W_d} \times 100$

where W_d is the weight of the polymer after 24 h, $W_{d'}$ is the weight of the swollen sample after 48 h, and $W_{d''}$ is the weight of the dried sample after 48 h.

RESULTS AND DISCUSSION

Biodegradation studies

Soil burial studies

Biodegradation is the chemical decomposition of materials brought about by living organisms (bacteria, fungi, etc.) or their secretion products or takes place through the action of enzymes. The main attacking agents in biodegradation are microorganisms, such as actinomycetes fungi and bacteria.

Gelatin, a polyamide protein, is a biodegradable polymer and was grafted onto PE. On grafting, the crystallinity of both of the polymers was affected. This disturbance in the crystallinity and the presence of the biodegradable polymer was expected to induce degradability in the PE chain.

The biodegradation of different grafted samples buried in the soil was monitored as a function of number of days, and the results are presented in Figure 1. As shown in the figure, we observed that the percentage weight loss of the samples increased continuously with increasing number of days; this indicated that the samples continuously degraded with increasing length of time. Percentage weight loss was determined by subtraction of the weight of the sample taken out on a particular day (i.e., after every

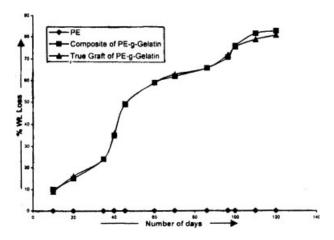


Figure 1 Weight loss (%) as a function of the number of days in simple soil ([BPO] = 4.4×10^{-2} mol/L, temperature = 60° C, time = 120 min, volume of water = 35 mL).

10 days) from the initial weight, that is, the weight of the sample at the start of the degradation study each time. For the composite sample, the weight loss percentage was 83%, and for the true graft sample, it was 81% in simple soil.

In another setup, the percentage weight loss of the sample was measured every 10 days. The percentage weight loss of the sample was taken as the weight of the sample on each 10th day minus the preceding weight of the sample before 10 days, and the results are presented in Figure 2. As shown in the figure, in the first 10 days, about 10% of the weight was lost; this further decreased to 6–7% in the next 10 days. Beyond this, an increase in the percentage weight loss was observed for the next 30 days. Thereafter, it again showed a decrease and an increase in the percentage weight loss. The decrease in the percentage

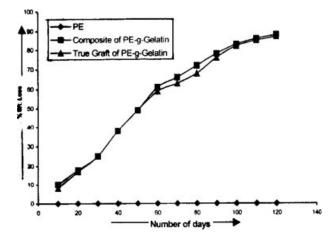


Figure 3 Weight loss (%) as a function of the number of days in urea-enriched soil ([BPO] = 4.4×10^{-2} mol/L, temperature = 60° C, time = 120 min, volume of water = 35 mL).

weight loss was due to the invasion of microorganisms into the substrate and the absorption of the moisture. These microorganisms feed upon the substrate, thereby increasing the percentage weight loss of the sample. Beyond 90 days, a continuous decrease in the percentage weight loss was observed.

Similar studies were carried out in urea-enriched soil, and the results are presented in Figures 3 and 4. For the composite sample, the weight loss percentage was 88%, and for the true graft sample, the weight loss percentage was 87% in urea-enriched soil. As shown in the figures, the degradation for all of the samples in urea-enriched soil was faster than for the samples in soil without urea. This was attributed to the fact that the growth of the microorganisms acting upon the polymer surfaces was enhanced in the presence of nitrogenous urea, which helped in better degradation of the polymer.

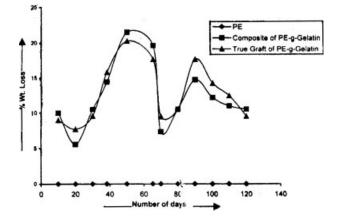


Figure 2 Weight loss (%) as a function of the number of days in soil (weight loss for every 10-day interval; [BPO] = 4.4×10^{-2} mol/L, temperature = 60° C, time = 120 min, volume of water = 35 mL).

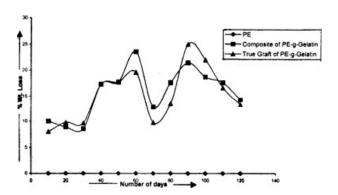


Figure 4 Weight loss (%) as a function of the number of days in urea-enriched soil (weight loss for every 10-day interval; [BPO] = 4.4×10^{-2} /L, temperature = 60° C, time = 120 min, volume of water = 35 mL).

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TABLE I Growth of Microorganisms as a Function of the Number of Days in the CzapekDox Medium

		Total number of colonies				
Days	Dilution	PE	PE-g-gelatin (composite)	PE-g-gelatin (true graft)		
10	10^{-2}	60	190	202		
	10^{-4}	5	165	168		
20	10^{-2}	70	172	185		
	10^{-4}	35	138	115		
30	10^{-2}	88	210	235		
	10^{-4}	30	190	220		
45	10^{-2}	17	290	310		
	10^{-4}	10	272	302		
60	10^{-2}	26	280	360		
	10^{-4}	6	265	320		
75	10^{-2}	58	188	290		
	10^{-4}	12	156	298		
90	10^{-2}	12	230	350		
	10^{-4}	8	160	310		
120	10^{-2}	16	190	210		
	10^{-4}	4	90	170		

Microanalysis

Pure gelatin was found to be completely degradable within 10–20 days. PE-containing soil and the original soil samples showed a very small growth of bacteria, whereas the composite material and the true graft of PE exhibited a rich growth of bacteria. The growth of microorganisms as a function of the number of days in CzapekDox media and agar media is presented in Tables I and II, respectively. Careful perusal of the table reveals that the growth (total count of all of the colonies) of the microorganisms on CzapekDox and nutrient agar media was high on the first 10th day. Beyond this, a decrease in the growth

TABLE II Growth of Microorganisms as a Function of the Number of Days in the Nutrient Agar Medium

		Total number of colonies					
Days	Dilution	PE	PE-g-gelatin (composite)	PE-g-gelatin (true graft)			
10	10^{-2}	2	207	228			
	10^{-4}	1	56	88			
20	10^{-2}	23	158	90			
	10^{-4}	16	34	67			
30	10^{-2}	32	165	135			
	10^{-4}	22	40	120			
45	10^{-2}	25	210	186			
	10^{-4}	18	190	150			
60	10^{-2}	27	190	210			
	10^{-4}	22	180	165			
75	10^{-2}	29	155	160			
	10^{-4}	7	130	130			
90	10^{-2}	22	240	248			
	10^{-4}	15	170	188			
120	10^{-2}	8	198	142			
	10^{-4}	4	135	128			

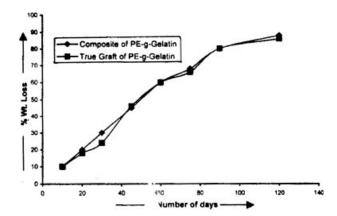


Figure 5 Weight loss (%) as a function of the number of days: with respect to hydrolysis studies.

was observed up to 30 days; growth then increased. Maximum growth was observed between 45 and 50 days; growth decreased until 75 days and increased further in 90 days. As illustrated when the growth in the colonies of bacteria/fungi (Tables I and II) are compared with the weight loss Figure 2, the increase and decrease in percentage weight loss paralleled the increase/decrease in the growth of microorganisms. The growth of the bacteria in the soil containing the PE-g-gelatin (composite and true graft) was attributed to the fact that the bacteria abided by the samples and continuously fed on them, thus degrading the sample and increasing their numbers simultaneously. Thus, gelatin, itself a biodegradable natural polymer, induced this behavior into these polymers, which are otherwise resistant to degradation.

Hydrolysis studies

The results of the hydrolysis of the PE-g-gelatin composite and PE-g-gelatin true graft placed for degradation in the soil are shown in Figure 5. The percentage weight loss increased with increasing number of days. The percentage weight loss was comparable to the percentage weight loss presented as a function of the

TABLE III							
Growth Measurements of Soybean Plants in the Soil							
Containing PE and Grafted PE Samples							

	Simp	ole soil	Urea-enriched soil		
	Length of root (cm)	Length of shoot (cm)	Length of root (cm)	Length of shoot (cm)	
Reference plant	- 0	4.1	-	1.0	
without sample PE-g-gelatin	5.2	4.1	5.6	4.9	
(composite) PE-g-gelatin	5.4	4.2	5.6	4.8	
(true graft)	5.4	4.3	5.6	4.8	
PE	5.1	4.2	5.5	4.8	

Grafted PE Samples								
	Simp	le soil	Urea-enriched soil					
	Average length of root (cm)	Average length of shoot (cm)	Average length of root (cm)	Average length of shoot (cm)				
Reference plant without								
sample	6.1	6.8	6.6	7.2				
PE-g-gelatin (composite)	6.2	6.9	6.8	7.4				
PE-g-gelatin (true graft)	6.0	6.7	6.5	7.2				
PE	6.0	6.7	6.7	7.2				

TABLE IV Growth Measurements of Wheat Plants in the Soil Containing PE and Grafted PE Samples

number of days (Fig. 1). This substantiated the observed degradation. Hydrolysis of the sample left behind PE, the amount of which decreased continuously with increasing number of days.

The hydrolysis studies thus confirmed that the degradation, which started at the degradable grafted polymer, that is, gelatin, induced the same into the PE.

Effect of the degradation of the grafted samples on the growth of plants

The lengths of the roots and shoots of soybean and wheat plants were measured after 35 days; the results are presented in Tables III and IV, respectively. The growth of the plants was much better in urea-enriched soil. For soil containing the grafted samples, the lengths of the roots and shoots showed a slight increase, whereas in urea-enriched soil, not much variation in the lengths of the roots and shoots was observed.

These observations indicate that the degradation products were not harmful to the growth of the plants.

Swelling studies

The results of the swelling behavior of the PE, PE composite, and PE true graft in binary and ternary

solvent systems are presented in Tables V and VI, respectively. As shown in Table V, it is clear that percentage swelling of PE increased with increasing amount of ethanol in the water–ethanol solvent system, both in 24 and 48 h. A maximum swelling percentage of 50% was observed in 3 : 7 v/v water–ethanol and neat ethanol (10 mL). PE was totally insoluble in this solvent system.

The gelatin-grafted PE sample (composite) experienced an increase in percentage swelling from 60 and 142.85% in water to maxima of 260 and 533.33% in the 5 : 5 v/v water–ethanol solvent system in 24 and 48 h, respectively. With further increase in the amount of alcohol in the solvent mixture and pure ethanol medium, percentage swelling was found to decrease. A maximum solubility of 50% of the composite was obtained in 48 h in the 5 : 5 water–ethanol medium.

Similar observations were made for the PE-*g*-gelatin true graft. A maximum swelling percentage of 510% and a maximum percentage solubility of 37.75% were observed in the 5:5 v/v water–ethanol solvent system in 48 h. Higher values of percentage swelling and percentage solubility for the composite were due to the presence of unreacted hydrophilic gelatin.

Swelling studies were also carried out with a ternary system comprising water-ethanol-DMSO. As shown in Table VI, it is clear that the percentage

 TABLE V

 Swelling (%) and Solubility (%) of PE, PE-g-Gelatin (Composite), and PE-g-Gelatin (True Graft) in a Water–Ethanol System

Sample	Time (h)	Percentage	10 : 0 (mL)	7:3 (v/v)	5:5(v/v)	3:7(v/v)	0:10 (mL)
PE	24	l Swelling	20	20	30	30	40
		Solubility	0	0	0	0	0
	48	Swelling	30	30	40	50	50
		Solubility	0	0	0	0	0
PE-g-gelatin composite	24	Swelling	60	140	260	240	210
00 1		Solubility	30	30	40	30	20
	48	Swelling	142.85	271.42	533.33	414.28	312.5
		Solubility	37.75	37.75	50	37.75	25
PE-g-gelatin true graft	24	Swelling	50	130	220	210	180
0000		Solubility	20	20	30	20	10
	48	Swelling	130	250	510	400	290
		Solubility	25	25	37.75	24	25

Sample	Time (h)	Percentage	0:0:10 (mL)	1:2:7 (v/v)	2:3:5(v/v)	3:4:3 (v/v)
PE	24	Swelling	50	40	30	20
		Solubility	0	0	0	0
	48	Swelling	60	50	50	40
		Solubility	0	0	0	0
PE-g-gelatin composite	24	Swelling	130	240	270	280
		Solubility	10	20	20	30
	48	Swelling	277.77	350	425	457.14
		Solubility	11.11	12.5	14.3	25
PE-g-gelatin true graft	24	Swelling	110	200	250	280
0000		Solubility	10	10	20	20
	48	Swelling	250	320	370	420
		Solubility	11.11	11.11	11.11	11.11

 TABLE VI

 Swelling (%) and Solubility (%) of PE, PE-g-Gelatin (Composite), and PE-g-Gelatin (True Graft) in a Water–Ethanol–DMSO System

swelling of PE decreased with decreasing amount of DMSO in the water–ethanol–DMSO system in both 24 and 48 h. A maximum swelling percentage of 60% was observed in neat DMSO in 48 h. However, PE was totally insoluble in the ternary solvent system.

The PE-*g*-gelatin composite sample experienced increases in percentage swelling from 130 and 277.77% in neat DMSO to maxima of 280 and 457.14% in the 3:4:3 v/v water–ethanol: DMSO solvent system in 24 and 48 h, respectively. The maximum percentage solubility was found to increase with decreasing amount of DMSO in the ternary system in both 24 and 48 h.

For PE-*g*-gelatin, the true graft percentage swelling increased from 110 and 250% in neat DMSO to 280 and 420% in the 3:4:3 v/v water–ethanol–DMSO solvent system in 24 and 48 h, respectively. The percentage solubility remained same in 48 h.

Thus, we observed that the composite and the true graft sample showed good swelling behavior in 24 and 48 h, which indicates that when buried in soil, they are able to take up moisture from the soil and then swell. Both of these factors would help in the exposure of the material to microorganisms, the attack of which will thus be facilitated.

CONCLUSIONS

By the specific functionalization of PE, new products are continuously being developed that find increasing use in a wide variety of industrial applications and lead to a significant value addition. The grafting of the biodegradable polymer gelatin onto PE successfully induced biodegradable behavior into the otherwise resistant PE. The use of such modified biodegradable polymers could eventually replace packaging materials. Thus, this would promote the use of biodegradable PE without the risk of environmental pollution.

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