

# Synthesis and Characterization of Biodegradable Polyethylene by Graft Copolymerization of Starch Using Glucose–Ce(IV) Redox System

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**ABSTRACT:** Graft copolymerization of low-density polyethylene (LDPE) onto starch was carried out with glucose–cerium(IV) redox initiator in an aqueous sulfuric acid medium under nitrogen atmosphere. The graft yield was influenced by various parameters like reaction time, temperature, and concentrations of acid, glucose, polyethylene (PE), starch, and initiator. A maximum graft yield of 85.66% was obtained at a temperature of 50°C and at higher concentration of starch. Effect of grafting on crystallinity, morphology, and thermal

properties of modified PE has been evaluated using X-ray diffraction, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA/DTA). Biodegradability of starch-grafted PE has been tested applying soil-burial test. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3229–3239, 2006

**Key words:** graft copolymerization; X-ray diffraction; thermogravimetric analysis (TGA); biodegradable PE

## INTRODUCTION

Today, pollution indices have become an integral part of news. Various kinds of pollutions are known nowadays, among which environmental pollution has become a major problem. Environmental pollution by synthetic polymers is increasing day by day in developing and developed countries because of their non-biodegradable nature. There are a number of biodegradable synthetic polymers, like PCL, PHB, PHBV, PLA, etc., which possess the required properties of a plastic but they are not widely used because of their high cost. So, a number of research scientists are trying to solve this problem by synthesizing biodegradable polymers for the last three decades<sup>1–7</sup> and to develop low-cost biodegradable polymers for various applications like biomedical,<sup>8,9</sup> pharmaceutical<sup>10,11</sup> agricultural, and environmental.<sup>12–15</sup>

Many reports are available for structural modification of gelatin, starch, wool, and other natural polymers by the process of graft copolymerization,<sup>16–19</sup> and varieties of grafted polyethylene (PE) copolymers have been prepared for potential applications in various fields like biomedical applications and packaging of food.<sup>20–24</sup> A great deal of work has been reported for the preparation of biodegradable polyethylene us-

ing various methods.<sup>25–29</sup> However, very little information is available on grafting of naturally occurring biodegradable polymers like starch and gelatin, on commonly used synthetic polymers like PVC and PE.<sup>30–32</sup>

Chemical grafting is a useful technique for carrying out modifications of polymers easily and inexpensively with very thin stable coatings that outlast and outperform the expensive conventional methods. Thus, efforts have been made to solve the problem of pollution by inducing biodegradability in synthetic polymers, like PVC, PE, PS, PP, etc., using chemical method of graft copolymerization. X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal analysis were used to characterize the grafted samples. Soil-burial test was applied to study the biodegradability of grafted polyethylene.

## EXPERIMENTAL

### Materials

Low density polyethylene (LDPE) granules of grade 24FS040, density 0.923 g/cm<sup>3</sup>, and melt-flow index 0.44 g/10 min were obtained from Indian Petrochemicals (Vadodara, India), and used for graft copolymerization of the starch by dissolving it in toluene (5% w/v). Soluble potato starch was supplied by Qualigens Fine Chemicals (Mumbai, India), and used as received. Ceric ammonium sulfate, sulfuric acid, and glucose were supplied by s.d. Fine-Chemicals (Mumbai, India), and used without any further purification.

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**TABLE I**  
Effect of Experimental Conditions on Grafting of Starch on Polyethylene

Sample no.	Initial weights (g)		Concentration of reactants (mL <sup>-1</sup> )			Time (h)	Temperature (°C)	Graft yield (%)
	PE	Starch	H <sub>2</sub> SO <sub>4</sub>	Ce(IV)	Glucose			
1	1.0	1.0	0.25	0.025	0.025	2	50	24.42
2	1.0	1.0	0.25	0.025	0.025	2	40	76.70
3	1.0	1.0	0.25	0.025	0.025	2	45	80.62
4	1.0	1.0	0.25	0.025	0.025	2	55	20.56
5	1.0	1.0	0.25	0.025	0.025	2	60	01.07
6	1.0	1.0	0.25	0.025	0.025	3	50	10.13
7	1.0	1.0	0.25	0.025	0.025	4	50	01.80
8	1.0	1.0	0.25	0.025	0.030	2	50	20.60
9	1.0	1.0	0.25	0.025	0.040	2	50	16.83
10	1.0	1.0	0.25	0.025	0.050	2	50	05.21
11	1.0	1.0	0.25	0.030	0.025	2	50	37.11
12	1.0	1.0	0.25	0.040	0.025	2	50	44.27
13	1.0	1.0	0.25	0.050	0.025	2	50	61.50
14	1.0	1.0	0.30	0.025	0.025	2	50	30.40
15	1.0	1.0	0.40	0.025	0.025	2	50	32.24
16	1.0	1.0	0.50	0.025	0.025	2	50	41.37
17	1.0	1.5	0.25	0.025	0.025	2	50	85.66
18	1.0	2.0	0.25	0.025	0.025	2	50	46.83
19	1.5	1.0	0.25	0.025	0.025	2	50	15.50
20	2.0	1.0	0.25	0.025	0.025	2	50	04.37

The concentration of ceric(IV) ions in the reaction mixture was estimated using standard solution of ferrous sulfate. All solutions were prepared in double distilled water obtained using alkaline KMnO<sub>4</sub>.

### Grafting procedure

The graft copolymerization was carried out under nitrogen atmosphere in a three-necked round-bottomed flask fitted with glass inlet and outlet tubes. Requisite amount of starch and solution of PE (5% w/v) were taken in three-necked round-bottomed flask. The solutions of glucose and sulfuric acid were added in the reaction flask, and the volume was maintained to 100 mL by adding conductivity water. The reaction mixture so prepared was deaerated by bubbling purified nitrogen for half an hour before initiating the reaction; then, calculated volume of stock solution of Ce(IV) ions was poured into the reaction vessel and thermostated to desired temperature. After the required time period, ranging from 2 to 4 h, the reaction was arrested by pouring the reaction mixture into a beaker containing 200 mL methanol. The precipitated crude was filtered and washed thoroughly with hot and cold water to remove ungrafted starch, glucose, and other impurities coprecipitated along with grafted polyethylene. Thereafter, the purified sample was dried in vacuum oven till constant weight. The graft yield was calculated as percent increase in the weight of PE after grafting in comparison with the initial weight of polyethylene taken for graft copolymerization.<sup>33</sup> In this

investigation, we have used the Fanta's formula for calculating the graft yield percentage as given below:

$$\begin{aligned} \text{Percent age of GY} &= \frac{\text{Polymer in graft}}{\text{wt of substrate}} \times 100 \\ &= \frac{\text{wt of Grafted LDPE} - \text{wt of ungrafted LDPE}}{\text{wt of ungrafted LDPE}} \times 100 \end{aligned}$$

### Characterization

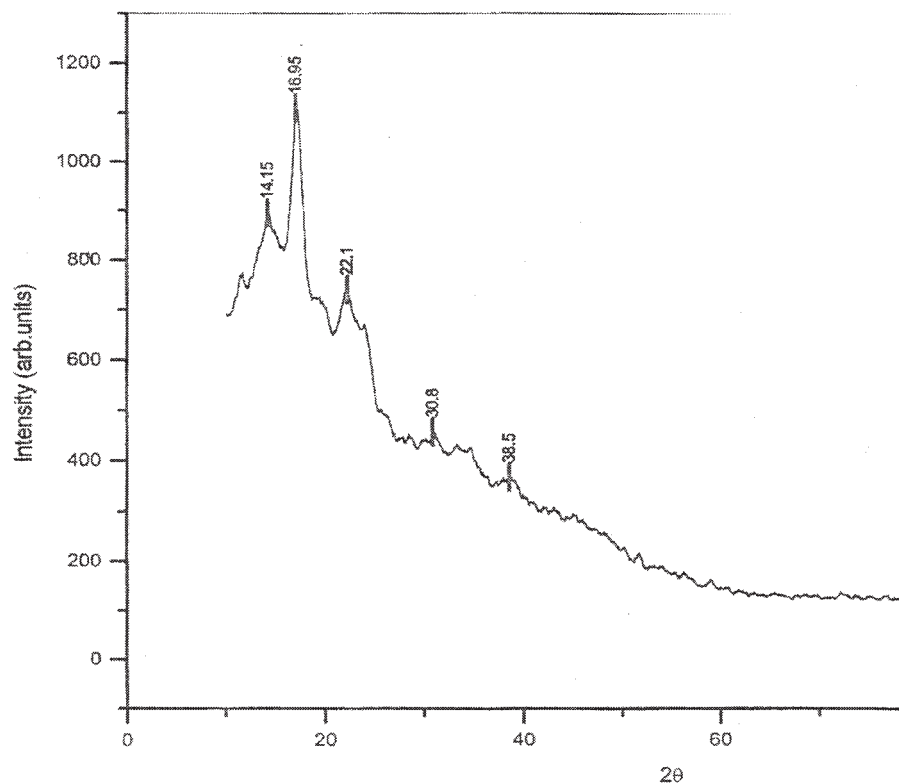
The grafted samples were characterized by applying different methods as given here.

#### X-ray diffraction study

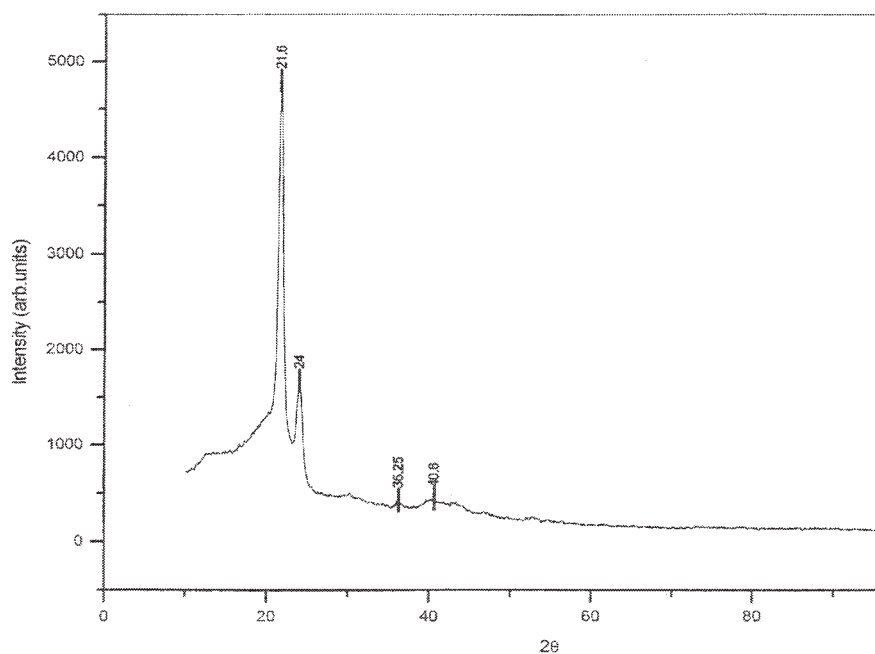
The wide-angle X-ray scattering patterns of starch-grafted PE (PE-g-starch) samples were obtained with PW 1710 Phillips X-ray diffractometer (Holland) using Ni-filtered Cu K $\alpha$  as source of radiation.

#### Scanning electron microscopy

Micrographs of starch-grafted polymer samples were obtained with JOEL-JSM-5800 Scanning Electron Microscope (Japan) at 20 kV. The specimens were coated with 50-nm thick gold films in an automatic sputter coater (Polaron) to avoid surface charging under electron beam.



(a)



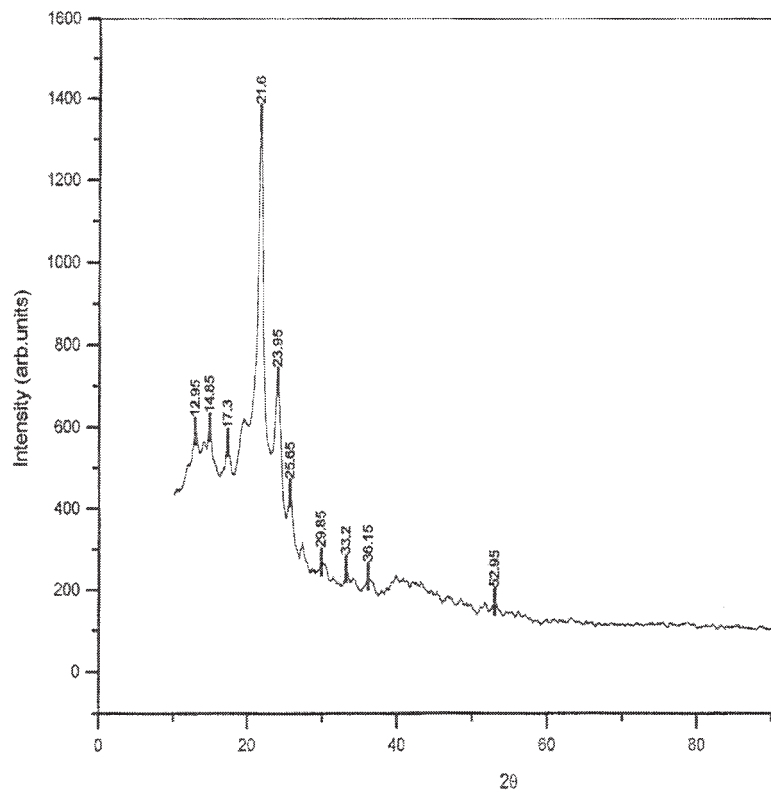
(b)

**Figure 1** X-ray diffraction studies for (a) pure starch, (b) virgin LDPF, (c) PE-g-starch (61.5%), and (d) PE-g-starch (80.68%).

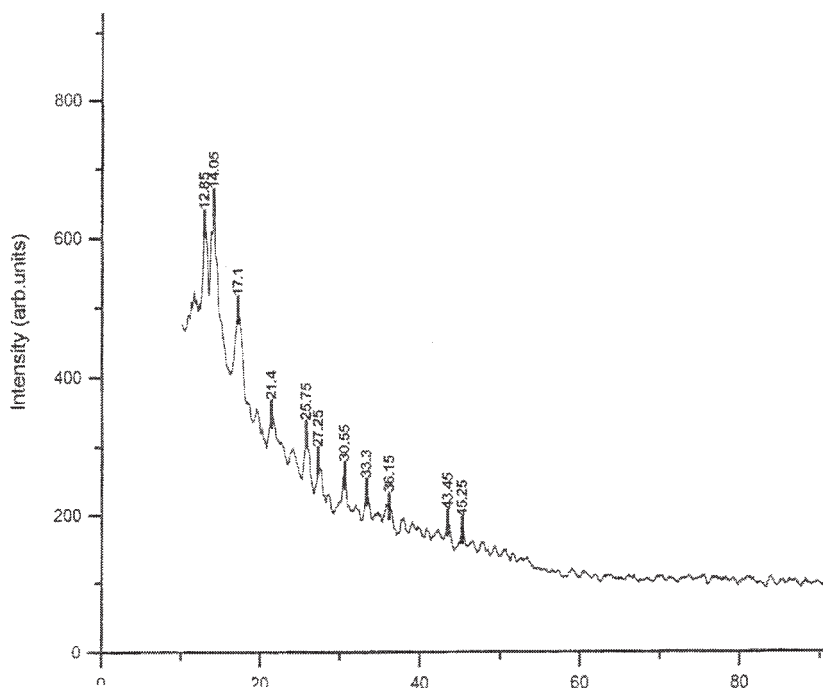
#### Thermal analysis

Differential scanning calorimetry (DSC) thermograms were recorded using a PYRIS Diamond DSC (Perkin-Elmer) thermo analyzer at a heating rate of 100°C/min

under nitrogen within the temperature range of 400–2000°C. TGA/DTA curves of selected samples were recorded using DT-30 Shimadzu Thermal Analyzer at a heating rate of 15°C/min in nitrogen atmosphere.



(c)



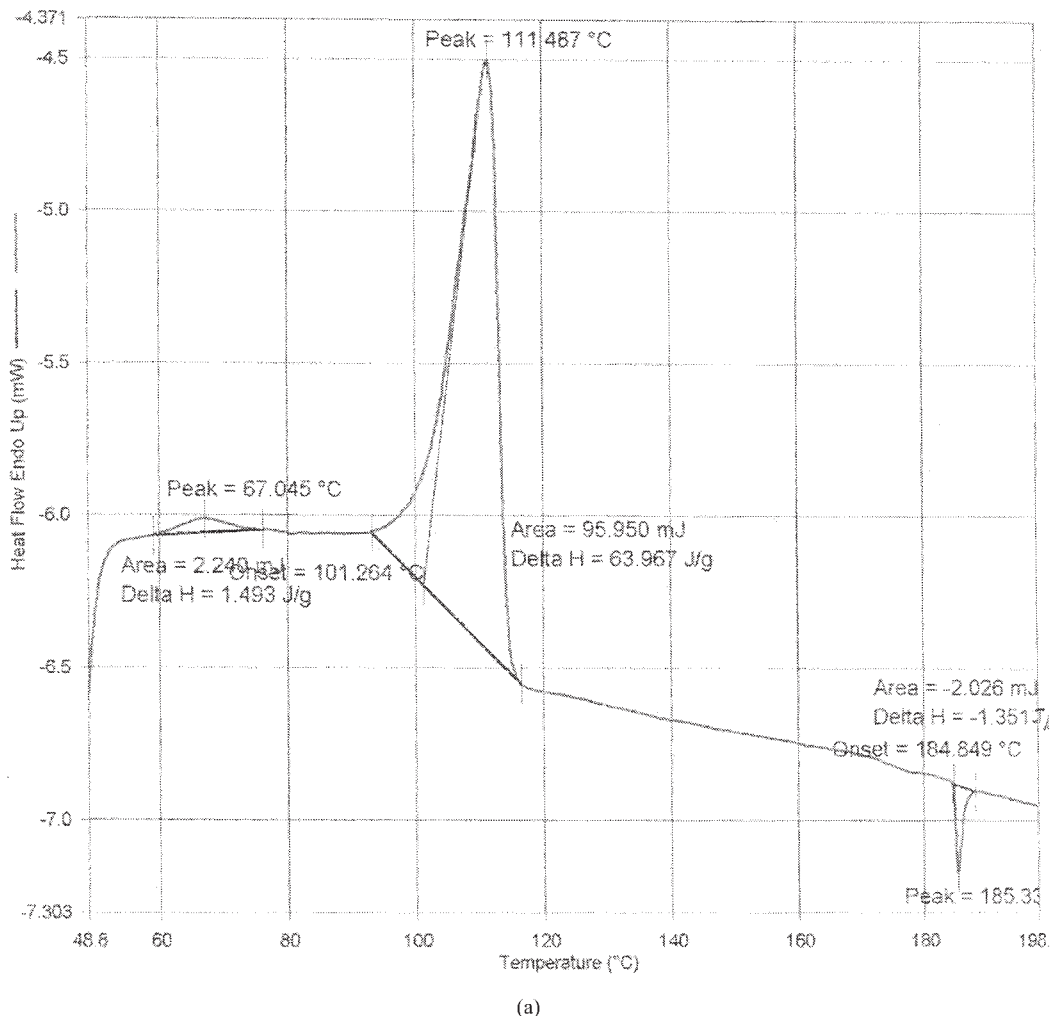
(d)

Figure 1 (Continued from the previous page)

#### Preparation of film by casting method

A 15% solution of PE-g-starch was prepared using toluene as a solvent. The solution was stirred vigor-

ously with magnetic stirrer for homogeneous mixing of samples for about 1 h. Then, PE film was cast by pouring solution onto a clear and dry glass plate. The



**Figure 2** Differential scanning calorimetry thermograms for (a) virgin LDPE, (b) PE-g-starch (61.5%), and (c) PE-g-starch (80.68%).

glass plate was shaken back and forth to spread the solution uniformly, and then it was dried for about an hour in an oven maintained within the temperature range of 30–45°C.

**Biodegradability study**

PE-g-starch films of various graft yields were taken to test the biodegradability of the films. The biodegradability test was carried out by soil-burial test.<sup>34</sup>

**Soil burial test**

The soil for the soil-burial test was obtained from a fertile land. The soil was made free from large clumps, plant debris, etc., and was kept in several earthen pots. In the entire study, the films were not maintained uniform in size but were of uniform thickness of about 0.5 mm. Thin film samples of known weight were buried in these pots at a depth of about 10 cm. The soil

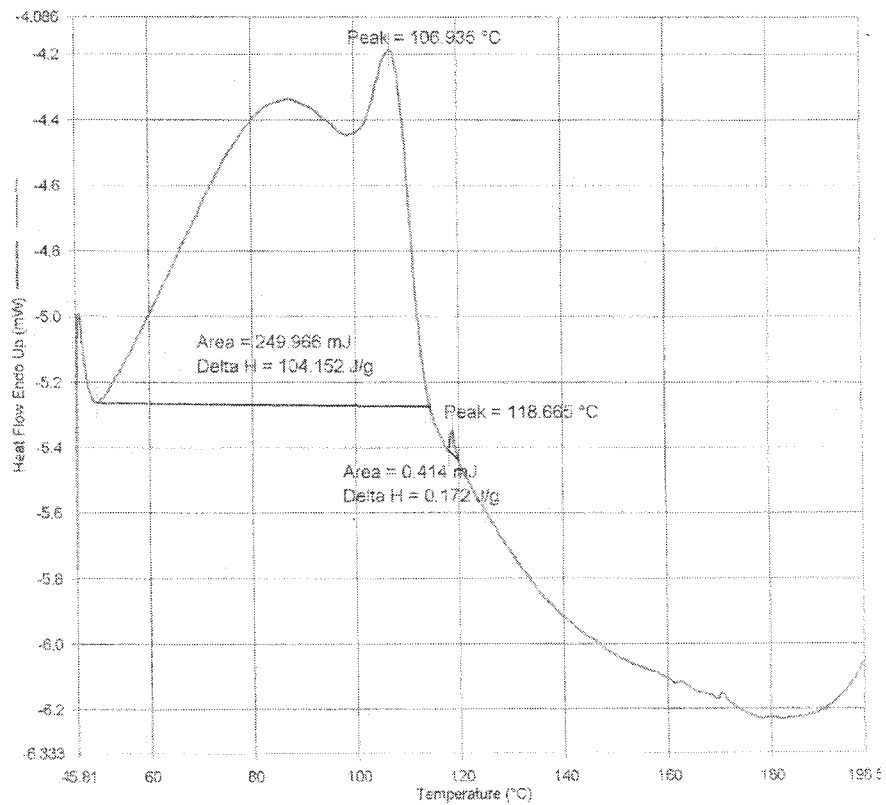
containing the samples was watered daily. The samples were removed periodically after a fixed time interval, washed thoroughly with water, and then the samples were dried within the temperature range of 40–45°C in a vacuum oven for 24 h. The weight of the film was recorded and used to calculate the extent of biodegradation of the samples. The percentage of biodegradation was calculated by using the formula as given below:

Percent age of biodegradation

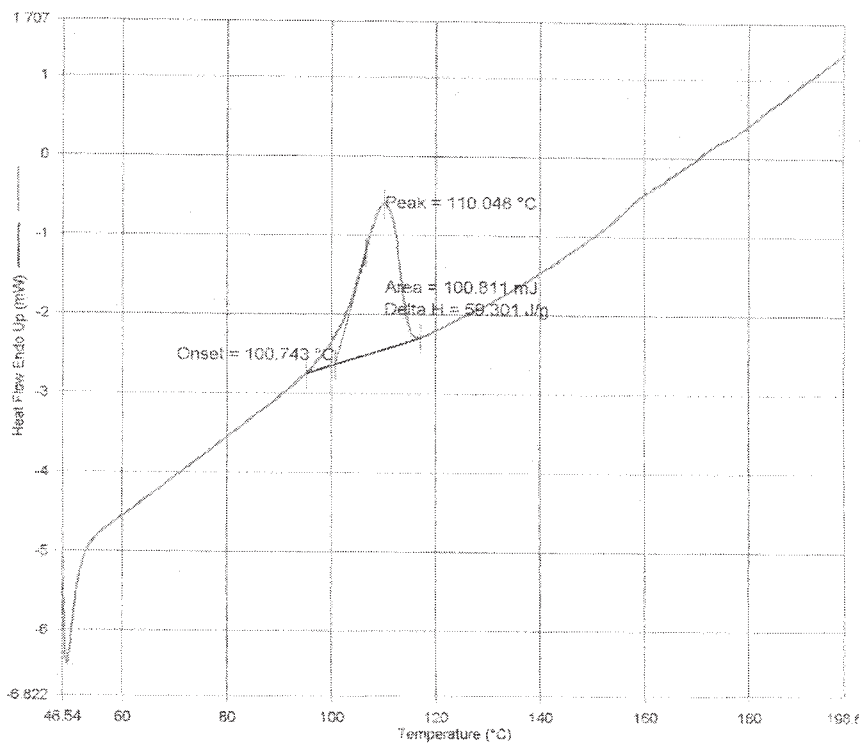
$$= \frac{\text{Original wt of film} - \text{wt of film after } X \text{ days}}{\text{Original wt of film}} \times 100$$

**RESULTS AND DISCUSSION**

The effect of various parameters on grafting of starch onto PE has been studied and used to optimize the conditions of maximum graft yields. The results ob-



(b)



(c)

**Figure 2** (Continued from the previous page)

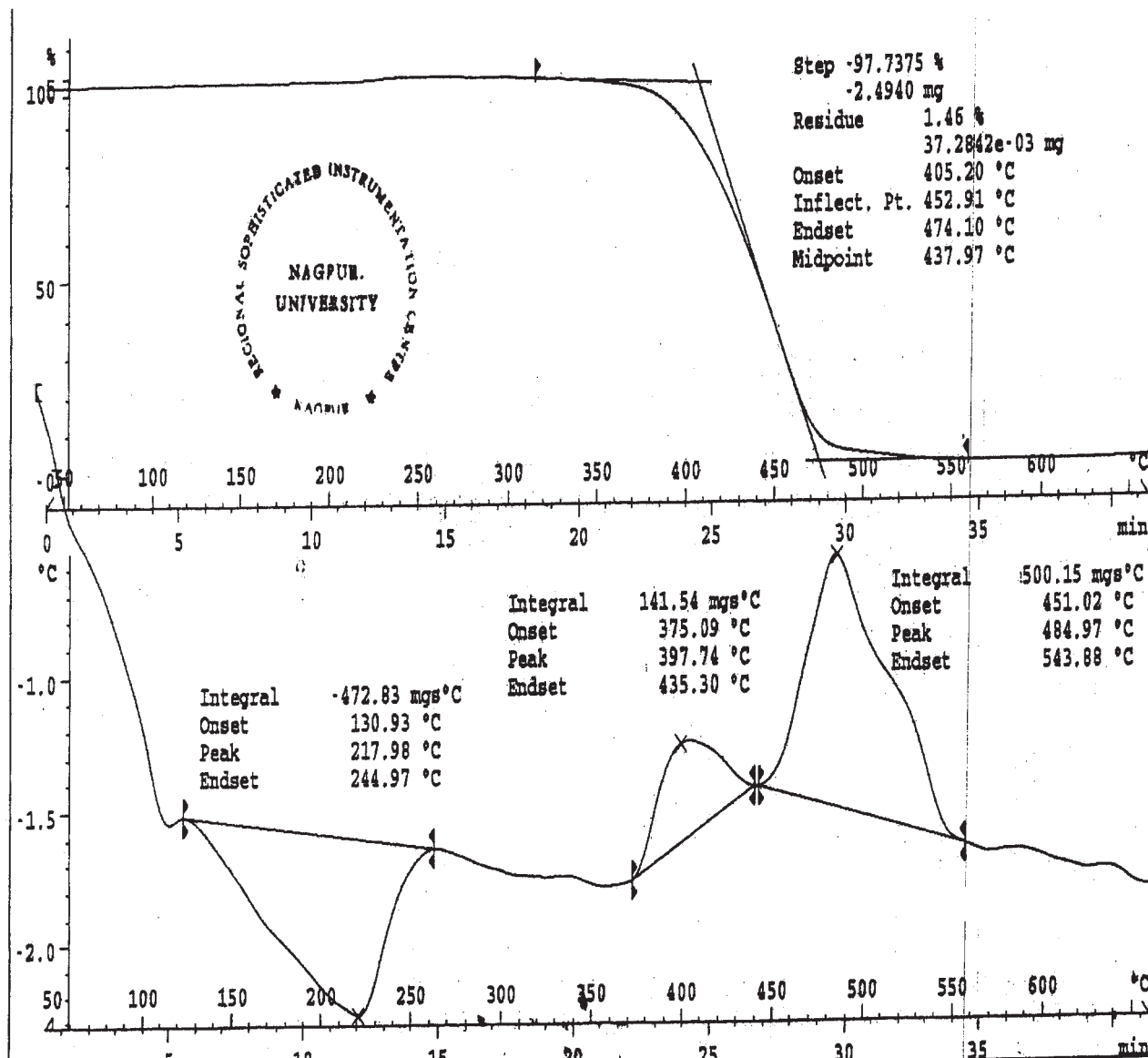


Figure 3 TG and DTA of (a) virgin LDPE and (b) PE-g-starch (41.37%).

tained under different experimental conditions are summarized in Table I.

**Effect of Ce(IV) ion concentration on graft yields**

The effect of Ce(IV) ion concentration on graft copolymerization of starch onto PE has been studied, and the results given in Table I have suggested that graft yields has increased on increasing the Ce(IV) ion concentration from 0.025 to 0.05M. A possible explanation for such observation is that an intermediate complex of Ce(IV)-PE might be formed at the start, which dissociated to give PE macroradicals. The macroradicals so formed react with starch to form graft copolymer. By increasing the concentration of Ce(IV) ions, there was an increase in the concentration of the active

sites on starch and PE; hence, the graft yield was increased on increasing the concentration of Ce(IV) ions in the solution.

**Effect of acid concentration on graft yield**

The role of sulfuric acid on grafting of starch on PE can be drawn from the results shown in Table I. It is observed that with the increase in concentration of the acid from 0.25 to 0.5M, the graft yield has increased. This is attributed to the fact that at higher concentration of sulfuric acid, the swellability of ethylene has increased, which made starch more accessible to the active sites on PE for grafting in comparison with low concentration of the acid.

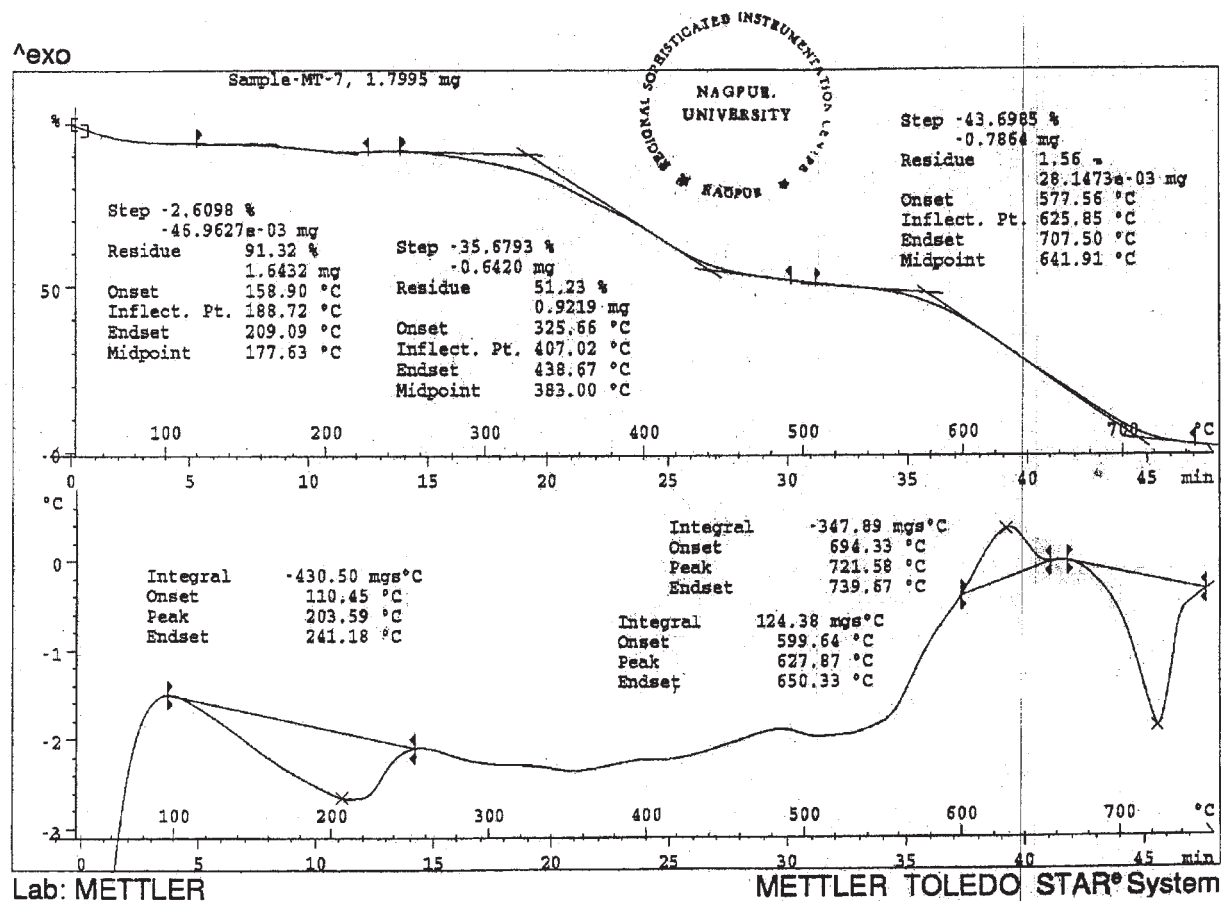


Figure 3 (Continued from the previous page)

### Effect of temperature on graft yields

The graft copolymerization was carried out within the temperature range of 40–60°C, keeping the concentrations of all other reagents constant. The results given in Table I have made it clear that, with the rise in temperature from 40 to 45°C, the graft yield has increased; but, on further increasing the temperature beyond 60°C, the grafting has shown a decreasing trend. This is due to enhancement of the solubility of the starch, and the swellability of PE also has increased the adsorption of starch on the PE backbone because of a high rate of diffusion of starch from the solution, within the studied range of temperature from 40 to 45°C. But, with further increase in temperature, the interactions of PE macroradicals with Ce(IV) ions destroy the activity of the initiating species, hence decreased the graft yields at high temperature.

### Effect of reaction time on graft yields

Results given in Table I have shown the effect of reaction time on graft yields. Graft copolymerization has shown a decreasing trend with the increase in

reaction time from 2 to 4 h. This is mainly due to the destruction of initiating species with increasing time period.<sup>35</sup>

### Effect of glucose concentration on graft yields

Effect of glucose concentration on graft yield was observed by keeping all other reagents constant. The increase in concentration of glucose from 0.025 to 0.05M has decreased the percentage graft yield, because of the formation of radical scavenger and the increase in the rate of termination of growing chains.<sup>19</sup>

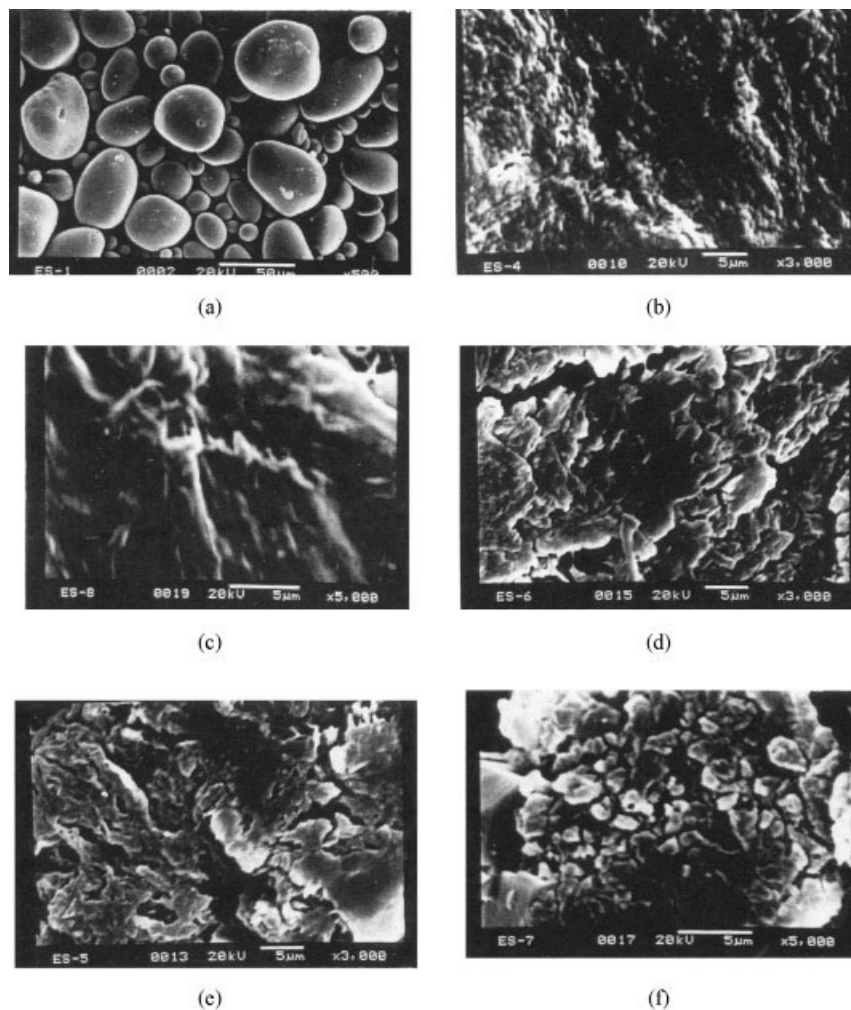
### Effect of concentration of polyethylene on graft yields

An increase in concentration of PE has decreased the percent graft yields, which is due to increase in viscosity of the reaction mixture that hindered the rate of initiation and chain propagation.

### Effect of concentration of starch on graft yields

The effect of starch concentration on grafting was investigated by varying the concentration of starch at





**Figure 4** Scanning electron micrographs of (a) pure starch, (b) Virgin LDPE, (c) PE-g-starch (46.83%), (d) PE-g-starch (61.5%), (e) PE-g-starch (76.7%), and (f) PE-g-starch (80.68%).

constant concentrations of all other reagents. The results of this experiment are shown in Table I. The results have indicated that the percentage graft yield has increased on increasing the concentration of the starch up to a certain limit; and thereafter, it has shown a decreasing effect. This can be explained by assuming that at higher concentration of starch, the concentration of starch macroradicals has increased, and the rate of their combination and disproportion has become faster than the rate of their combination with PE molecules. Another reason for the decrease in graft yields is that the rate of starch diffusion was progressively affected by the polymer deposited on the surface of the PE, which hindered the further grafting of starch.

#### X-ray diffraction study

X-ray diffractograms of virgin and grafted LDPE samples [Fig. 1(a-d)] have shown that there has been a

clear decrease in percent crystallinity with the increase in percent graft yields of starch from 61.5 to 80.68%. This can be attributed to the formation of crosslinks by starch molecules on the backbone of PE.<sup>36</sup> It is also envisaged that, in addition to the decrease in percent crystallinity of PE, there is trapped amorphous starch between the PE chains, which also has contributed toward the decrease in percent crystallinity of the modified PE. The decrease in crystallinity of PE has been due to the disruption of crystallites and the dilution of inherent crystallinity of PE.<sup>20</sup>

The percentage of crystallinity is determined by using the formula as given below:

$$X_c (\%) = \frac{A_c}{A_a + A_c} \times 100 (\%)$$

where,  $A_c$  = area of crystalline phase,  $A_a$  = area of amorphous phase, and  $X_c$  = percentage of crystallinity.

TABLE II  
Data for Biodegradation of Virgin and Starch-Grafted Polyethylene

Sample no.	Graft-on (%)	Original weight of film (g)	Remaining weight of film (g)				
			30 days	60 days	90 days	120 days	150 days
I	00.00	0.1620	0.1620	0.1620	0.1620	0.1620	0.1620
II	41.37	0.1371	0.1217	0.1129	0.1032	0.0891	0.0722
III	44.27	0.2062	0.1780	0.1672	0.1537	0.1342	0.1046
IV	46.83	0.0878	0.0738	0.0694	0.0644	0.0538	0.0437
V	76.70	0.0473	0.0361	0.0226	0.0154	0.0099	0.0059

### Thermal analysis

The study of thermal behavior of starch, virgin PE, and PE-g-starch has been carried out to understand the thermal changes that might occur and to correlate the effect of grafting on thermal transitions occurred in virgin starch and PE. The DSC thermograms of starch, virgin PE, and PE-g-starch [Fig. 2(a–c)] have shown that both area and intensity of the peaks have decreased significantly with increase in the extent of grafting onto PE. The heat of fusion, as obtained from the area under the thermo gram, has also decreased considerably with increase in the degree of grafting,<sup>20</sup> which has indicated that grafted PE is less stable in comparison with the virgin PE. TGA/DTA thermograms of PE and PE-g-starch are presented in Figure 3(a,b). The TGA thermograms of grafted membranes have shown multi-step degradation of PE backbone and grafted starch.<sup>37</sup>

### Scanning electron microscope study

SEM micrographs [Fig. 4(a–f)] have shown that virgin starch is neither uniform in size nor uniform in shape. However, SEM micrographs have indicated for planar but nonuniform surface structures with virgin PE. But, the grafted samples have shown neither planar nor uniform surface. With the increase in percentage of grafting, the planarity and uniformity of the surface have decreased. And, also with the increase in percentage of grafting, some ungrafted starch granules have remained associated

with the grafted sample. On the whole, SEM micrographs have provided substantial morphological evidences in favor of grafting of starch onto PE as reported elsewhere.<sup>32</sup>

### Test of biodegradability of grafted polyethylene

The data given in Tables II and III have clearly demonstrated that grafting of starch on PE has induced biodegradability in PE; otherwise PE has shown almost zero weight loss within the studied time intervals of 150 days. The data given in Table III have also indicated that the extent of biodegradation of PE has increased on increasing the percent graft onto the PE.

## CONCLUSIONS

The extent of grafting could be controlled by controlling the concentration of initiator, sulfuric acid, glucose, and synthetic polymer, grafted unit polymer, and also by reaction time and temperature so as not to alter very much the desirable properties of backbone polymer. Crystallinity of PE has decreased on grafting, as is clear from the XRD study. Morphological studies of grafted samples by SEM have given evidence in favor of surface grafting of starch on PE backbone. Grafting of biodegradable starch moieties on synthetic polymers has also induced biodegradability, and the percentage of biodegradation has increased with the increase in percentage graft yields of starch on PE.

TABLE III  
Percent Biodegradation of Virgin and Starch-Grafted Polyethylene

Sample no.	Graft yields (%)	Biodegradation (%)				
		30 days	60 days	90 days	120 days	150 days
I	0	0	0	0	0	0
II	41.37	11.26	17.64	24.73	35.01	47.32
III	44.27	13.7	18.92	25.46	34.91	49.28
IV	46.83	16.36	20.93	26.65	38.70	50.23
V	76.7	23.65	52.30	67.53	78.26	87.45

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