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Sugar end-capped polyethylene: Ceric ammonium nitrate initiated oxidation and melt phase grafting of glucose onto polyethylene and its microbial degradation

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Abstract

Low density polyethylene (LDPE) was modified to introduce biodegradability by grafting highly hydrophilic monomers (which can act as nutrients for microorganisms) such as glucose by a novel melt phase reaction using Brabender plasti-corder in the presence of ceric ammonium nitrate (CAN) to obtain 4-*O*-hydroxymethyl D-arabinose (sugar) end-capped LDPE (Su-*g*-LDPE) at a maximum grafting of 16%. The grafted polymers were characterized by FTIR, thermal analysis, WAXD and mechanical property measurements. The biodegradability of Su-*g*-LDPE was carried out by soil-burial test and by optical density measurements in presence of an aerobic bacterium *Pseudomonas* sp. The degraded polymer shows changes in weight, crystallinity and inherent viscosity. Optical density of the medium registered an increase with degradation. FTIR spectra of the degraded samples showed 70% decrease in the ketone carbonyl index (ν_{1719}/ν_{1465}) of Su-*g*-LDPE indicating microbial degradation of LDPE matrix, which was further confirmed by SEM micrographs. The present data support a microbial oxidation process involving β-oxidation whereby the carbonyl is further oxidized to carboxylic acid and affects cleavage of the LDPE chain at the ends.

Keywords: Low density polyethylene; Glucose; Melt phase grafting; Biodegradation

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1. Introduction

The environmental pollution caused by the nonbiodegradability of synthetic hydrocarbon polymers especially low density polyethylene (LDPE) used in packaging, agriculture and industry has been created and continues to create large concerns all over the world. These polymers are characterized by properties such as high molecular weight, chemical inertness, hydrophobicity, reduced surface area, relative impermeability to oxygen, etc. which make them resistant to microbial attack and at the same time present enormous restrictions in the design and development of biodegradable polymers [1,2]. However, several design techniques have been developed for introducing biodegradability in polyethylene [3–9]. Blending of polyethylene with biodegradable polymers such as starch and cellulose has been practiced as a viable methodology [3–5]. It has, however, been noted that the starch gets enzymatically hydrolyzed in a biologically active environment leaving the polymer in a disintegrated form [1]. A fairly large amount of starch is needed to get a reasonable degradability even at the cost of its mechanical property [6]. Chemical modification or grafting of starch and starch-derived products onto LDPE provides another feasible approach for incorporating starch into the polymer for effecting degradation by microbial consumption of starch followed by chain scission [7–9]. Yet another methodology reported for the development of biodegradable LDPE is the modification of polymer backbone by introducing some weak links such as $-C{=}O$ groups that may permit controlled degradation into low molecular weight oligomers which can then be utilized and consumed by microorganisms [10]. The many inadequacies of the existing

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biodegradable plastics for eco-friendly applications indicate the need for novel approaches for the design of the material.

A combined methodology of in situ oxidative modification of polymer backbone by introducing −C═O groups followed by grafting is expected to yield added advantage. Anchoring of simple sugars such as monosaccharides or disaccharides instead of starch on polyethylene can reduce the negative effects on physical properties observed in the case of polysaccharide grafting. Glucose, a naturally abundant, renewable monosaccharide that can be chemically modified by oxidative ring opening reactions is having great potential as a hydrophilic modifier to induce biodegradation. The utilization of ceric ammonium nitrate (CAN) for chemical modification of polymers by ring opening of glucose is reported [11]. There is no available literature on reactive grafting of glucose on polyethylene in presence of CAN. Hardly any successful research has been done for designing new polymers or affecting minor chemical modifications of polyethylene with attachment of sugar molecules. Recent literature shows novel possibilities for grafting of monomers in a melt phase reaction at high shear conditions when free radicals are generated in situ [12]. Various attempts have been reported in the functionalization of LDPE [13–15]. The use of CAN has not been mentioned in any work on the oxidation of LDPE. As microbial oxidation is reported to be the first step in the biodegradation of LDPE, the use of oxidized LDPE might enhance the microbial oxidation followed by chain scission [16].

In the present work, oxidation of LDPE followed by grafting of glucose by melt phase reaction in Brabender plasti-corder is studied in presence of CAN which is acting as an oxidant as well as an initiator. The grafting of highly hydrophilic sugar molecule, glucose onto polyethylene functionalized by oxidation is expected to make polyethylene more susceptible to microbial attack by increasing the number of active sites and the hydrophilicity of LDPE. The modified LDPE was characterized by spectroscopic, thermal and mechanical evaluation. Biodegradation of grafted LDPE was studied by soil-burial test and in presence of an aerobic bacterium *Pseudomonas* sp. Degradation was followed by weight loss, optical density measurements, thermal evaluation, FTIR spectroscopy, WAXD and changes in surface morphology by SEM.

2. Experimental

2.1. Materials

Film grade polyethylene (Indothene 24FS040; melt flow index 4.0 gm/10 min and density 0.922 gm/cc) was supplied by Indian Petrochemical Corporation Limited, Vadodara. CAN from Aldrich Chemical Company, USA, was used as received. Glucose and toluene (AR grade) were obtained from S.D. Fine-Chem Ltd, Mumbai and were used without further purification. A commercial soil-based compost produced from municipal solid waste was collected from a biotreatment plant at Velappinsala, Kerala, India.

2.2. Synthesis of sugar grafted polyethylene

Sugar grafting onto LDPE by the ring opening of glucose in the presence of CAN was carried out by melt phase reaction in Brabender plasti-corder fitted with a measuring mixer (W-50) preset at 130 °C and a rotor speed of 60 rpm in air. Torque generated during grafting was recorded with time. Twenty-five grams of the LDPE were put into mixer followed by CAN addition. Glucose was added after 10 min only to permit oxidation of LDPE to take place. Reaction continued until the increase of torque after the flux got stabilized. Un-reacted glucose and CAN were removed by dissolving the sample in toluene and washed thoroughly with water using mechanical stirrer. The product was filtered through a sintered glass crucible and dried at 60 °C in vacuum oven to a constant weight. The percentage grafting and grafting efficiency were calculated. Experiment was repeated at different percentages of CAN and glucose and also at different temperature conditions. Su-*g*-LDPE having a maximum grafting of 16% was chosen for all further studies.

Hydroxyl values of the grafted LDPE were analyzed by adding a standard solution of pyridine–acetic anhydride to the toluene solution of the sample and refluxing for 4 h. Excess of acetic acid was back titrated with standard KOH. Hydroxyl value was calculated as the number of milligram of KOH per gram of the sample [17].

Oxidized LDPE (OxiLDPE) was prepared by carrying out oxidation using CAN for 10 min in Brabender plasti-corder. The product was washed thoroughly with toluene and water and dried in vacuum oven at 60 °C to a constant weight. NaOH/EtOH treatment of OxiLDPE was accomplished by stirring the sample in NaOH/EtOH mixture for half an hour [13]. The product was then washed with ethanol and dried in vacuum oven to a constant weight.

2.3. Water absorption

Water absorption test was carried out according to ASTM D750-95. Compression-molded specimens (5 × 5 cm) of Su-*g*-LDPE, OxiLDPE and LDPE were placed in a container of distilled water maintained at 30 °C. The samples were taken out at regular intervals from the water, gently blotted with a tissue paper to remove the excess of water on the surface, weighed immediately, and replaced in the water. The percentage increase in weight during the immersion in water was calculated according to the equation.

$$\%W_f = \left[W_w - W_d/W_d\right] \times 100$$

where W_f is the final increased weight percentage, W_d and W_w are the weights of the samples when dry and after moisture uptake, respectively. Averages of three values were recorded.

2.4. Soil-burial test

Biodegradation was studied by soil-burial method as per ASTM D5338-98. Soil-based compost was taken in three