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Optimization of mechanical, thermal and hydrolytic degradation properties of Poly (lactic acid)/Poly (ethylene-co-glycidyl methacrylate)/Hexagonal boron nitride blend-composites through electron-beam irradiation

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ABSTRACT

The main objective of this work is to investigate the influence of electron beam irradiation on mechanical, thermal and hydrolytic degradation properties of Poly (lactic acid) (PLA)/Poly (ethylene-co-glycidyl methacrylate) (PEGM)/Hexagonal boron nitride (HBN) blend-composites for optimizing the properties. The previous studies have reported that the blending of PLA and PEGM with weight ratio (PLA: PEGM) (80:20) reduce the brittleness and improve the toughness. However, the heat deflection temperature (HDT) and other tensile properties were found to be reduced. It was found that HDT can be improved with the incorporation of HBN particles. So far, the effect of PLA/PEGM blending on the hydrolytic degradation properties of PLA was not studied. Hence, in the present work, the hydrolytic degradation test on prepared blend and blend-composites was performed. It is observed that blending of PEGM with PLA significantly retards the hydrolytic degradation of PLA. Further reduction in the hydrolytic degradation of PLA was observed in the blend-composites. To analyze the impact of electron beam irradiation, the prepared specimens of pure PLA, PLA/PEGM blend and PLA/PEGM/HBN blend-composites were irradiated to high energy (4.50 MeV) electron beam (E-beam) at different radiation doses. It is observed from the DSC thermograms of irradiated PLA, PLA/PEGM blend and PLA/PEGM/HBN blend-composites; the glass transition temperature (T_g) is shifted to higher temperature with irradiation. This is attributed to the polymer chains scission and crosslinking caused by E-beam irradiation. Interestingly, the E-beam irradiated blend-composites having a high HBN concentration (i.e. 5 phr and 10 phr) showed higher T_g as compared to the other unirradiated and irradiated samples. Further, the notched impact strength and HDT were remarkably improved with E-beam irradiation in the case of 5 phr and 10 phr blend-composites. The improvement in the yield strength and tensile modulus has also been noticed in the case of E-beam irradiated blend-composites as compared to unirradiated blend-composites. The E-beam irradiation of prepared blend and blend-composites also helps to accelerate the hydrolytic degradation. The E-beam irradiated PLA/PEGM/HBN 5 phr blend composite shows high HDT, high notched impact strength, good yield strength, better tensile modulus and also exhibit fast hydrolytic degradation as compared to the other E-beam irradiated blend and blend-composites and unirradiated PLA. Hence, the E-beam can be employed to optimize the mechanical, thermal and degradation properties of the final product as per the desired application.

1. Introduction

Poly (lactic acid) (PLA), based on lactic acid, is a most promising polymer made from renewable resources. Nowadays, PLA has attracted more attention because it is biodegradable, biocompatible and easily processable with most of the commercial processing equipment [1–3]. Apart from these advantages PLA production energy is 25–55% less as compared to petroleum-based polymers. Although PLA has these advantages, it also has some drawbacks i.e. poor toughness, slow degradation rate, lack of reactive chain groups and hydrophobicity which limits its use in commercial and medical applications. The consumer and biomedical applications of PLA depend on its bulk properties (e.g. toughness, degradation rate etc.) and surface properties (hydrophobicity, roughness, and reactive functionalities). The surface modification of PLA has been undertaken by researchers for medical applications [4,5]. The toughness and elongation at break of PLA are being improved for commercial applications and the improvement in the degradation rate has advantages in both consumers as well as

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medical applications. Many authors have attempted to improve the elongation at break and toughness of PLA through blending [6]. The PEGM is a pronounced polymer to improve the toughness and elongation at break of PLA through reactive blending [7,8]. However, the reactive blending of PLA and PEGM leads to decrease in the HDT and other tensile properties of PLA.

Cairns et al. has used the electron beam irradiation to get the controlled degradation of PLA for medical applications [9]. It has been reported that the electron beam can be used to induce the crosslinking among the polymer chains of PLA in the presence of various crosslinking agents to improve the mechanical and thermal properties of PLA [10–13]. Shin et al. has reported, the E-beam irradiation of PLA in the presence of glycidyl methacrylate induce both crosslinking and branching of PLA chains [14]. In the present work, the PLA/PEGM blend has been synthesized to reduce the brittleness and improve the toughness of PLA. The reactive blending of PEGM with PLA leads to decrement in the HDT. Thus, to improve the HDT of PLA/PEGM blend the HBN particles have been added into the blend as part per hundred i.e. 1 phr, 5 phr and 10 phr. The prepared PLA/PEGM/HBN blend-composites show better HDT as compared to pure PLA and PLA/PEGM blend. Further, to observe the effect of E-beam irradiation on blend and blend-composites, test specimens were prepared and further treated by E-beam with various radiation doses (e.g. 20 kGy, 60 kGy and 100 kGy). It has been noticed that the E-beam irradiation improves the toughness and HDT of PLA/PEGM/HBN blend-composites as compared to the unirradiated PLA/PEGM/HBN blend-composites. The irradiated samples of PLA/PEGM/HBN 5 phr and 10 phr blend-composites reveal the high notched impact strength and HDT as compared to unirradiated and E-beam irradiated PLA, PLA/PEGM blend and PLA/PEGM/HBN 1 phr blend-composite. These improvements with the application of E-beam could be attributed to the introduction of polymer chains scission and polymer chain branching in the PLA/PEGM/HBN blend-composites which enhance the physical interaction of HBN particles with polymer chains asserted by DSC analysis. This also leads to the fine dispersion of the HBN particles in the polymer matrix which in turn uniform phase morphology with good interfacial adhesion asserted by SEM analysis. Further, the hydrolytic degradation studies revealed the blending of PLA with PEGM markedly restricts the hydrolytic degradation of PLA. From the hydrolytic degradation results, it can also be observed that the E-beam irradiation of prepared specimens leads to significant increment in the degradation as compared to unirradiated specimens. Among all compositions, the irradiated PLA/PEGM/HBN 5 phr blend-composite has shown high hydrolytic degradation rate as well as good mechanical and thermal properties which are useful for both commercial and medical applications. Hence, in the present work, the mechanical, thermal and degradation properties of PLA have been optimized with the help of E-beam irradiation.

2. Experimental

2.1. Materials

The Poly (lactic acid), Ingeo 3052D, a commercial grade PLA having melt index 14 g/10 min (210 °C/2.16 kg) and relative viscosity 3.3 (1.0 g/dL in chloroform at 30 °C) was purchased from the Natur-Tec India Pvt. Ltd. Poly (ethylene-co-glycidyl methacrylate) pellets, containing 8 wt% Glycidyl Methacrylate and having a melt index of 5 g/10 min (192 °C/2.16 kg) was procured from Sigma-Aldrich company. The Hexagonal boron nitride (~1 μm particles size) was also purchased from Sigma-Aldrich.

2.2. Preparation method

PLA/PEGM blend and PLA/PEGM/HBN blend-composites were prepared by using twin-screw Micro compounder, X-Plore, DSM, Netherlands. The processing conditions i.e. processing temperature, 210 °C, Mixing time (10 min) and screw speed 80 RPM (rotation per minute) were selected to prepare desired blend and blend-composites. The weight ratio of the blends was fixed at 80:20 (PLA: PEGM) because in general for improvement of toughness of PLA with rubbery polymers the feed ratio of PLA and blend components were usually fixed at 80:20 [15,16]. The multipurpose test specimens-ASTM D638 (150 mm × 12.7 mm × 3.2 mm) of resulting PLA/PEGM blend and PLA/PEGM/HBN blend composites were prepared by injection molding with mold temperature 32 °C. Furthermore, to measure notch impact strength of pure PLA, PLA/PEGMA blend and PLA/PEGM/HBN blend-composites some test Specimens-ASTM D256 (63.5 mm × 12.7 mm × 3.2 mm) were prepared. To compare the mechanical and thermal properties of virgin PLA the test specimens of pure PLA were also prepared by the same preparation method.

2.3. Electron beam irradiation

The prepared specimens of neat PLA, PLA/PEGM blend and PLA/PEGM blend-composites were irradiated to E-beam with beam energy 4.50 MeV and penetration depth 20 mm. It can be assumed that the E-beam irradiation results in homogenous changes through the sample because the sample thickness is less than the penetration depth. Three sets of samples were irradiated to the electron beam with different doses 20 kGy, 60 kGy and 100 kGy respectively by using ILU-EB accelerator at BRIT, BARC, Trombay, Mumbai, India. The E-beam irradiation of all specimens was performed in air. However, all set of samples were packed in polythene cover which is filled with helium gas to avoid the oxidation of pure PLA samples during the irradiation process. The packet of samples was kept on the conveyor belt and its speed was selected as 3.00 m/minute. The distance between the samples and E-beam source is 41.2 cm. The successive passes of the conveyor in radiation zone determine the dose absorbed by the samples. In each pass, the dose absorbed by the samples was 5 kGy as measured by film dosimetry. In this manner, the numbers of passes were selected to achieve the desired dose.

2.4. Characterizations

All unirradiated and E-beam irradiated specimens of pure PLA, PLA/PEGMA blend and PLA/PEGM/HBN blend-composites were mechanically tested by employing Universal Testing Machine (UTM), INSTRON-3382. The tensile properties were measured by using ASTM D638 method with the speed of 10 mm/minute. The Notched Izod impact strength was determined by following ASTM D256 test method with the help of TINIUS OLSEN-515 (USA), impact tester. In each measurement, four specimens were tested for statistical average.

Heat deflection temperature (HDT) of unirradiated and E-beam irradiated specimens was measured by ASTM D256 test method with a load of 1.82 MPa at a heating rate of 2 °C per minute by using GOTECH HV-2000-C3 HDT/VSP testing machine having temperature accuracy ± 0.50 °C.

Differential Scanning Calorimeter (Perkin-Elmer 7) was utilized to perform a thermal analysis of each sample. To estimate the transition temperatures, each sample around 5–10 mg was loaded into the thermal pan and then heated from 40 °C to 200 °C with the scanning rate 10 °C per min.

The unirradiated and E-beam irradiated broken specimens, obtained from notched impact test, were used to execute hydrolytic degradation test. The specimens were immersed in the phosphate buffer solution (PBS) having pH 7.1, at 58 °C. The selected temperature is the standard temperature for biodegradation tests [17,18]. Further, in natural media, the degradation process of PLA stimulates between 25 °C and 58 °C has been reported in the literature [19,20]. The specimens were removed periodically and washed with distilled water and then dried in vacuum oven for 24 h. The weight of specimens before and after hydrolytic degradation test was measured sensitively. The test was