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Mechanical and thermal properties and morphological studies of 10 MeV electron beam irradiated LDPE/hydroxyapatite nano-composite

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HIGHLIGHTS

- LDPE/HAP nano-composite samples were prepared with different wt% of HAP.
- The samples were subjected to irradiation under 10 MeV EB in different doses.
- Mechanical and thermal properties of the samples were investigated and compared.
- The morphology of the nano-composite samples was also studied.
- Mechanical and thermal parameters are strongly dependent on the HAP content.

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ABSTRACT

In this work the nano-composite samples were prepared using the LDPE filled with different weight percentages of hydroxyapatite powder which was synthesized via hydrolysis method. The samples were subjected to irradiation under 10 MeV electron beam in 75–250 kGy doses. Mechanical and thermal properties as well as the morphology of the nano-composite samples were investigated and compared. The hot-set and swelling tests confirmed the radiation crosslinking induced in the polymer matrix especially between the matrix and reinforcement phase. The result indicates that the mechanical and thermal parameters are strongly dependent on the hydroxyapatite content in comparison to radiation.

1. Introduction

The mechanical, thermal, and morphological properties of composites are strongly dependent on the reinforcement and interfacial compatibility of the composite system. This generally involves a hard reinforcement phase within a soft matrix. In all polymer composites, the major problem is the interfacial adhesion between the reinforcement and the matrix. A firm interfacial adhesion between the inorganic fillers and the organic polymer matrix is a key factor to make the composites have good compatibility (Wang et al., 2009).

Bioceramics such as hydroxyapatite (HAP) are the preferred reinforcements because of their stiffness, density, bioactivity, and biocompatibility (Willmann, 1995). Biological applications such as orthopedic materials and parts to repair the damaged bone are amongst the main applications of HAP. The development of composites for this purpose has been investigated with the intention of creating a composite structure that is modeled after the natural bone (Ramakrishna et al., 2001; Cheang and Khor, 2003; Evans and Gregson, 1998). Polyethylene/HAP is one of the composites used as a biomaterial. One of the problems of these composites when used is creation of weak interface between non-polar polyethylene (PE) and polar HAP that will eventually lead to their low mechanical properties.

So far, many researchers have worked on construction techniques and properties of PE/HAP composites. The effect of gamma radiation on the mechanical properties of the composite consisting of PE with 30% of HAP was studied (Smolko and Romero, 2007). The effects of gamma irradiation on PE/HAP composite prepared in decalin solution were studied by other researchers (Carmen et al., 2006). In addition, numerous articles have focused on process mechanism, reinforcement morphology, size and dimensions of

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reinforcement phase, reinforcement percentage, and the polymeric substrate (Wang et al., 1998, 1994; Joseph et al., 2002). The effects of gamma radiation and heat treatment on creep behavior of these composites have also been studied (Suwanprateeb et al., 1998). Radiation processing is one of the inevitable modern technologies which can be utilized for modification of polymers and polymer composites. Irradiation of LDPE/HAP composite causes some physicochemical changes to occur mainly in LDPE, while HAP remains stable. Both crosslinking and degradation by chain scission occur during irradiation, but one of these effects may be predominant in some materials. Crosslinking is the most important effect of radiation in PE because it usually improves the mechanical, thermal and in some cases chemical and environmental properties (Cleland et al., 2003).

In this paper, the effects of high energy electron beam radiation on mechanical and thermal properties, and also the morphology of the LDPE/HAP nano-composite containing different percentages of HAP were investigated and compared.

2. Experimental

2.1. Materials

A commercial low-density polyethylene (LDPE) supplied by Bandar Imam Petrochemical Company LDPE-0075 with a melt flow index of 0.75 g/10 min and a density of 0.92 g/cm^3 was used in this investigation. Synthetic nano-structure HAP was prepared from hydrolysis method according to the reference (Shih et al., 2004).

2.2. Sample preparation

The composite samples consisting of LDPE and HAP powders were melt-mixing in an internal mixer Haake Rheocord 90, 300 ml, made in Germany. They were mixed at 160 °C at 100 rpm for 20 min. The obtained compound was compression molded between polyester sheets at 150 °C using a Dr. Collin warm press instrument to prepare sheets of 2 ± 0.1 mm thickness. The composite samples were made with different HAP wt% of 5, 15 and 30.

2.3. Sample irradiation

The samples were irradiated under the 10 MeV electron beam in doses varying from 75 to 250 kGy at a constant dose rate. The irradiation was performed using the Rhodotron type electron accelerator machine, TT200 model, with a maximum of 8 mA beam current.

2.4. XRD analysis

X-ray diffraction (XRD) analysis was performed by a Philips Analytical X-Ray B.V., with the use of Ni-filtered CuKα radiation (1.5456 Å wavelength), in the 2θ range of 20°–60°. The grain size of the prepared powder product was measured using the Scherer's equation indicated in Eq. (1) as following:

$$t(\mathrm{nm}) = \frac{0.89 \times \lambda(\mathrm{nm})}{B(\mathrm{rad}) \times \mathrm{Cos}\theta} \quad (1)$$

where t is the grain size, λ is the wavelength of X-ray, B is the full width at half maximum of peak in X-ray pattern, and θ is Bragg's angle.

2.5. Microscopic technique

A TEM system EM208S series was utilized to study and determine the size of the nano-particles and morphology of the composite. Tensile fracture and lateral surfaces of the samples were examined using a SEM system, Philips PSEM 500.

2.6. Hot-Set testing

A Heraeus UT 6050HS heating oven was used for determining thermal elongation of the samples. All measurements were carried out with the DIN standard (DIN 57472-602, VDE 0472, 1983). The temperature of the oven was 150 °C with a measuring period of 15 min. The testing and the measuring were performed using laser optics. The working formula for calculation of the hot set value was $100 \times (L_1 - L_0)/L_0$ where L_0 and L_1 were the initial and final length, respectively.

2.7. Swelling test

The swelling ratios (Sw) of the samples were measured to determine the radiation induced crosslinking in the samples. This was carried out by extracting the samples in xylene at 90 °C for 12 h. The extracted samples were dried and weighed. The swelling ratio was calculated as:

$$\mathrm{Sw}(\%) = \frac{w_t - w_0}{w_0} \times 100 \quad (2)$$

where w_0 and w_t were the sample weights before and after the extraction, respectively.

2.8. Thermal analysis

A MDSC apparatus made in TA Company, USA, was used to determine the thermal properties of the samples. The samples were sealed in aluminum pans and the MDSC was carried out in a temperature range between −50 °C up to 250 °C at a heating rate of 10 °C/min. The degree of crystallinity using data obtained from these devices could be calculated by the following equation:

$$X_C(\%) = \frac{\Delta H}{\Delta H_C} \times 100 \quad (3)$$

where ΔH and ΔH_C were the melting enthalpies of unknown and standard (completely crystalline, 290 J/g) polyethylene samples, respectively (ASTM D3418, 2008).

2.9. Mechanical testing

Tensile properties of the samples were measured at room temperature using an Instron-4411 universal testing machine at a test speed of 50 mm/min according to the standard (ASTM D638, 2010).

3. Result and discussion

3.1. Reinforcement phase characterization

Fig. 1 shows the XRD patterns of the standard and synthesized HAP samples. These figures show that the observed peaks in the XRD patterns of synthesized samples are in accordance with the hydroxyapatite phase, in comparison to the standard sample. The average particle sizes of the samples were calculated using Eq. (1) and the data extracted from the diffraction patterns. These calculations were done via fitting the Gaussian function to each single peak and calculating their overlap, with respect to the position and width of the main peaks of the HAP. The average particle sizes estimated were 20–50 nm. TEM micrographs of the synthesized HAP samples are demonstrated in Fig. 2. The existence of nano-size particles in the synthesized HAP samples are obvious in TEM and confirms the results obtained from Eq. (1).