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Effects of electron beam irradiation on mechanical properties and nanostructural–morphology of montmorillonite added polyvinyl alcohol composite

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ABSTRACT

This paper is aiming to analyze the effects of electron beam irradiation on the mechanical properties and structural–morphology of nano-sized montmorillonite (MMT) added polyvinyl alcohol (PVOH) composite. MMT particles were added to the PVOH matrix at various loading level that ranges from 0.5 to 4.5 phr MMT and electron beam irradiated with dosages ranging from 6 to 36 kGy. The results showed that tensile strength of MMT added PVOH composites at 1.5 and 2.5 phr MMT were observed marginally higher compare to neat PVOH when irradiation dosages increased to 26 kGy. However, when the concentration of MMT exceeded 2.5 phr, the application of irradiation seems to cause adverse effect to the PVOH–MMT composite. Besides, according to the X-ray diffraction analysis, the application of low irradiation dosage ($\leqslant$16 kGy) has significantly enhanced the intercalation effect of MMT particles at high loading (4.5 phr) in PVOH matrix. This also found to be consistent with the scanning electron microscopy observation where the dispersion of MMT particles in PVOH matrix was noted to be more homogeneous than non-irradiated samples. Further increment in irradiation dosage up to 36 kGy has significantly reduced the crystallinity which indicates the higher radiation energy could rupture the crystallite structures in PVOH matrix.

1. Introduction

Polyvinyl alcohol (PVOH) is a unique hydrophilic polymer which soluble in water [1]. PVOH is widely used in food, adhesives, biomedical scaffolds, and sizing agent for textile industries [2]. PVOH has high degree of crystallinity due to the small sized hydroxyl (–OH) pendant group which able to fit into the lattice structure promotes formation of highly orientated structure. Meanwhile, PVOH can be divided into two categories, namely fully hydrolyzed and partially hydrolyzed PVOH. The fully hydrolyzed PVOH is usually higher crystalline compared to partially hydrolyzed PVOH. The highly crystalline material is usually more desirable in term of stronger mechanical properties as compared to the latter due to the presence of strong hydrogen bonds that holds the chains together [3]. These strong bonds prevent the mobility of the chains within the matrix, causing it to exhibit higher rigidity and strength.

Most of the time, the existing properties of PVOH is insufficient to fulfill the advance application nowadays. In fact, the mechanical properties of PVOH can be further improved with the composite hybrid method by adding of mineral type reinforcing agents. Such reinforcement is very important especially in adhesive and biomedical scaffolding applications. One of the most suitable types of reinforcing agent is using montmorillonite (MMT). Many researches have been reported that the nano-size MMT is an effective and biocompatible reinforcing which shown its reinforcing effect even applied at a very small quantities [4]. This filler has been explored significantly recently years due to its ability to form highly exfoliated composites when added to polymer materials. The end-product, known as polymer/silicate or composite, can form either the exfoliated or intercalated composite. The terms of intercalated and exfoliated are used to describe the two general classes of MMT that can be prepared. The intercalated structures

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are the well ordered multi-layered structures, where the extended polymer chains are embedded into the interlayer space between the individual of MMT layers. The exfoliated structures form when the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations. The interlayer spacing can be on the order of the radius of gyration of the polymer. Therefore, the silicate layer may be considered to well disperse in the organic polymer. The silicate layer of an exfoliated structure may not be as ordered as in intercalated structure. The nanostructures of the MMT can be measured and observed by using X-ray Diffraction measurements. The intercalated and exfoliated nanocomposites shows better mechanical and barrier performances than microcomposites due to its large interfacial surface area and small particle distance of MMT [5].

Commonly, exfoliated composite can be easily obtained compared to intercalated composite because it able to achieve a certain extent of stiffness, strength, and barrier properties as compared to the conventionally filled polymers with small quantity of filler [6]. Nevertheless, studies done by several papers have discovered that intercalated and exfoliated coexist on MMT added polymer nanocomposites [6,7]. This is due to the both intercalation and exfoliation are highly depending on the hydrophilicity and surface energy MMT and type of polymer. Previous study by Strawhecker and Manias [7] found that, the addition of Na^+ MMT into PVOH discovered that MMT has improved the mechanical and thermal properties of the neat PVOH up to a limit before exhibiting inferiority due to agglomeration drawback. In this case, it is expected that further enhancement can be done via the introduction of crosslinking networks. Up to date, many papers reported on the research of PVOH-layered silicate [6–8]. Nevertheless, the studies focused on the characterization of PVOH–MMT composite has not been well explored with application series of electron beam irradiated dosage as the secondary enhancement element on PVOH–MMT compound. Therefore, this paper focuses on the effect of electron beam irradiation on the mechanical properties, thermal properties, as well as the crystallographic structure of the PVOH–MMT composites. Electron beam has been chosen over other forms of irradiation due to its high energy and lower reduction time subsequently produces less embrittlement on the irradiated polymeric compound Almaslow et al. [9].

2. Methodology

2.1. Materials

Fully hydrolyzed polyvinyl alcohol Sekisui Selvol™ polyvinyl alcohol 103 with 4% solution viscosity at 20 °C 4.00 cP and hydrolysis 98.40 mole% manufactured by Sekisui Specialty Chemicals America, LLC. was used in this study. The commercial grade of montmorillonite (MMT), Nanomer 1.3P was purchased from Nanocor, Arlington Height. All these materials were used as received.

2.2. Sample preparation

The samples of PVOH–MMT were prepared with MMT at 0.5, 1.5, 2.5, 3.5 and 4.5 phr. Initially, PVOH was dissolved in distilled water using a water bath at 97 ± 2 °C for 30 min until all PVOH particles have dissolved for one hour. A motor driven stirrer with appropriate speed (300 rpm) was used to stir the mixtures evenly. The stirrer was stopped upon reaching homogenous mixture. The MMT was added into the solution and the stirring was resumed until it completely dissolved. The dissolved solution was the cast onto trays of approximately 1 mm thickness. The cast samples were dried in an oven at 60 °C for two days. The dried cast samples were peeled off from the cast trays and packed in polyethylene bag to keep out from moisture. On the other hand, a portion of cast sample were electron beam irradiated at irradiation voltage of 15 kV, current of 1 mA, and energy of 1 MeV under the EPS-3000 electron beam irradiation machine. The samples were electron beam irradiated at various doses of 6, 16, 26 and 36 kGy with the rate of 2 kGy/pass.

2.3. Samples characterization

2.3.1. Mechanical properties

The cast samples were cut into a rectangular shape of 65.5 mm × 6.0 mm in accordance with ASTM D1882. The cut samples were tested by using Instron tensile machine at crosshead speed of 50 mm/s. The tensile strength, elongation at break and Young modulus were taken as an average of the five specimens.

2.3.2. X-ray Diffractometer (XRD)

The dispersion and crystallinity of MMT in the PVOH matrix were tested by using the XRD-6000 Shimadzu X-ray Diffractometer at 40 kV and 40 mA with the scanning rate of 1°/min. The samples were scanned over a range of 2θ = 0–40°. The d-spacing and inter-chain separation of MMT and MMT added PVOH were calculated with the following formula (Bragg's formula):

$$d = \frac{\lambda}{2\sin\theta} \tag{1}$$

$$R = \frac{5}{8}\left(\frac{\lambda}{\sin\theta}\right) \tag{2}$$

where d = d-spacing, Å; λ = wavelength, nm; θ = Bragg angle, radian; R = inter-chain separation, Å.

The crystallite size of the samples was calculated by using the following formula (Scherrer formula):

$$L = \frac{k\lambda}{b\cos\theta} \tag{3}$$

where L = crystallite size, Å; k = Scherrer constant; b = FWHM, radian.

2.3.3. Scanning Electron Microscopy (SEM)

The surface morphologies of fractured samples were investigated by using a SEM machine of Hitachi S3400N with a voltage of 15 kV. The deformed surface of the samples were observed under the microscopy at magnification of 1000×, 3000× and 10,000×.

2.3.4. Transmission Electron Microscopy (TEM) Test

TEM test was conducted to observe the dispersing and intercalation of MMT particles in polymer matrix. A transmission electron microscope (TEM) with the acceleration voltage of 100 kV was used to study the morphologies of the nano-particles of MMT and the dispersion of MMT in PVOH matrix and its crosslinked constituents. The specimens of samples used for TEM test were in ultrathin form. The ultrathin specimens were sectioned by using a cryogenic ultra-microtome.

3. Results and discussion

3.1. Mechanical properties

Fig. 1 shows the tensile properties of the PVOH–MMT at varying irradiation dosages. Generally, it can be found that when MMT was added at low level <1.5 phr, there is an increment of tensile strength of the composite. This observation is in agreement with the previous observation of various researchers [10] where the intercalation of MMT have occurred that promotes the effective