Tensile Toughness Improvement of Poly(ethylene-co-vinyl acetate)(PEVA) by Incorporation of Hybrid Pre-dispersed O-MMT and Destabilized Bentonite

Tuty Fareyhynn Mohammed Fitrı1, Azlin Fazlina Osman1*, Rahimah Othman1,2, and Khairul Anwar Abdul Halim1

1Center of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, University Malaysia Perlis, 02600, Perlis, Malaysia
2School of Bioprocess, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia

E-mail: Tutyfareyhynn@gmail.com

Abstract. Poly (ethylene-co-vinyl acetate) (PEVA) is a biocompatible copolymer that exhibits flexibility similar to elastomeric materials, yet it can be processed like other thermoplastic. PEVA is biocompatible, offers excellent optical clarity, barrier properties, and stress-crack resistance [1, 2]. However, to be used as implantable biomedical device, further improvement in the PEVA toughness is needed because this property of PEVA is not sufficiently high. Therefore, this project aimed to employ organically modified montmorillonite (OMMT) and nano-bentonites (Bent) with

1. Introduction

Poly (ethylene-co-vinyl acetate)(PEVA) is a copolymer that exhibits flexibility similar to elastomeric materials, yet it can be processed like other thermoplastic. PEVA is biocompatible, offers excellent optical clarity, barrier properties, and stress-crack resistance [1, 2]. However, to be used as implantable biomedical device, further improvement in the PEVA toughness is needed because this property of PEVA is not sufficiently high. Therefore, this project aimed to employ organically modified montmorillonite (OMMT) and nano-bentonites (Bent) with
different surface properties as hybrid nanofillers to reinforce the PEVA, thereby improving its tensile toughness [3]. Hybrid bentonites nanofillers with different polarity (hydrophobic versus hydrophilic) was hypothesized to result in more optimum nanofiller-PEVA interactions, as the PEVA copolymer contains the hydrophobic polyethylene chains and hydrophilic poly(vinyl acetate) chains in its structure [1,2,4]. Enhancement in nanofiller-PVAc interactions would also lead to improvement in overall hybrid PEVA nanocomposite’s mechanical performance as biomaterial [4]. Recent works verified that incorporation of nanoclay into the PEVA copolymer can enhance its mechanical properties if only the nanofiller is well dispersed throughout the matrix [4-6]. In contrast, deterioration of mechanical properties of host polymer will occur if the nanoclay is inadequately dispersed and this has been reported by many researchers [5,7].

To produce plate-like nanoparticles with very high aspect ratio inside the polymer matrix, OMMT in stacking (tactoids) form can be exfoliated or delaminated into nanometer thick layers. Based on previous study, the pre-dispersing process of the OMMT in liquid medium can reduce its tactoid size and more facilitate its exfoliation and dispersion in the PEVA matrix during the melt compounding process [5]. In this research, the best parameters of the pre-dispersing process [6] were applied to prepare the OMMT as nanofiller in the PEVA. It is also worth mentioning that the use of unmodified bentonite as co-nanofiller in the PEVA could be challenging as it contains highly stacked platelets (tactoids) held tightly together by electrostatic forces [4]. Therefore, the destabilization of bentonite by pH control and salt addition was also done to break up these large tactoids. In this paper, the effect of hybrid OMMT/bent silicate nanofillers addition on the tensile toughness of the PEVA was studied. Different ratios of OMMT/Bent were used and the best ratio that resulted in the greatest enhancement in the tensile toughness of the hybrid nanocomposite was reported.

2. Methodology

2.1. Materials

Poly ethylene-co-vinyl acetate (PEVA) copolymer (COSMOTHENE EVA H2181) containing 18 wt% of vinyl acetate (VA) and 82 wt% of ethylene was supplied by the Polyolefin Company (Singapore) Pte.Ltd. Organo modified montmorillonite (organo-MMT), that comprising of 35-45% of dimethyl dialkyl (C14-C18) amine as an organic surfactant was employed. This organo-MMT was manufactured by Nanocore, Inc, and known as Nanomer (types 1.44P). The natural bentonite was supplied by Multifilla (M) Sdn. Bhd. The average particle size of this clay is ≤ 25 micron and density of the clay powder is in the range of 600-1100 kg/m³. For destabilization process of bentonite, nitric acid (HNO₃) (65%) used was supplied by MERCK and sodium chloride (NaCl) used was supplied by Sigma Aldrich. For both nanofillers, dispersing medium used was distilled water.

2.2. Sample Preparation

2.2.1. Preparation of the pre-dispersed OMMT
The pre-dispersing method of the organo-MMT was prepared in water medium (distilled water: OMMT = 1:1). The suspension was stirred by using magnetic stirrer for 2 hours at room temperature. After that, it was ultrasonicated using Branson Digital Ultrasonic Disruptor/Homogenizer (Model 450 D) for 5 minutes. The suspension was placed onto the filter paper to filter out the distilled water and then was inserted into the oven for 48 hours at 50 °C. Lastly, the pre-dispersed OMMT powder was ground and sieved before being characterized by using fourier transform infrared (FTIR).

2.2.2. Preparation of the “destabilized” Bentonite
The bentonite was prepared as 20% suspension in water medium. After that, it was stirred by using ultrasonic probe for 15 minutes. Then, the pH of the suspension was adjusted by dropping HNO₃ until it reached pH 4 and stirred for 5 minutes by using ultrasonic probe. Next, NaCl (0.01M) was added and stirring was continued for 5 minutes. The suspension was filtered and underwent drying process for 24 hours at 80 °C. After that, the suspension was washed with hot water (80°C) and dried for 24 hours at 80°C. Lastly, the ‘destabilized’ bentonite were ground and sieved before being characterized by FTIR.

2.2.3. Preparation of PEVA hybrid nanocomposite samples
The PEVA hybrid nanocomposites were prepared based on the formulation summarized in Table 1. The hybrid nanocomposite samples were prepared by melt compounding the PEVA copolymer with the OMMT/Bent at 160 °C using internal mixer (Brabender plasticoder) machine. The compounded materials were then compressed by using compression moulding machine (model GT-7014-H30C by GOTECH Co.) to obtain sheet form (~1mm thick). 5 minutes of pre-heat, 3 minutes of pressing and 10 minutes of cooling time at 130 °C were employed in this process. Finally, the nanocomposite sheets were cut for testing.

Table 1. Formulation of nanocomposites.

| Types of samples | EVA | Weight % OMMT | Weight % Bentonite | Acronym   |
|------------------|-----|---------------|-------------------|-----------|
| Neat PEVA        | 100 | -             | -                 | PEVA      |
| PEVA/OMMT        | 96  | 4             | -                 | PEVA-O    |
| PEVA/Bentonite   | -   | -             | 4                 | PEVA-B    |
| PEVA hybrid nanocomposite with OMMT/Bent ratio 4:1 | 96  | 3.2           | 0.8               | PEVA-O₂B₁ |
| PEVA hybrid nanocomposite with OMMT/Bent ratio 3:2 | 96  | 2.4           | 1.6               | PEVA-O₂B₂ |
| PEVA hybrid nanocomposite with OMMT/Bent ratio 2:3 | 96  | 1.6           | 2.4               | PEVA-O₃B₃ |
| PEVA hybrid nanocomposite with OMMT/Bent ratio 1:4 | 96  | 0.8           | 3.2               | PEVA-E₀B₄ |

2.3. Characterization of the nanofillers
2.3.1. Fourier transform infrared spectroscopy (FTIR)
Both nanofillers and hybrid nanocomposites samples were analyzed by Perkin Elmer Paragon FTIR spectrometer with Attenuated Total Reflectance (ATR) in the range of 4000-650cm\(^{-1}\) at 32cm\(^{-1}\) resolution and 32 scans.

3. Mechanical testing

3.1. Tensile test
Tensile test was carried out by using Instron machine model-552, on the neat PEVA, PEVA nanocomposite and PEVA hybrid nanocomposites according to the method ASTM D638. The testing was carried out by using dumbells samples punched from an ASTM D-638-M-5 die. The crosshead speed of 50mm/min was used. Tensile toughness was determined by calculating the area under the stress-strain curve. The mean values of tensile toughness was determined based on five replicates tested.

4. Results and Discussion

4.1. Morphology of pre-dispersed OMMT and destabilized Bentonite

Figure 1. FTIR spectra of OMMT and Bentonite nanofillers.

Figure 1 displays the FTIR spectra of the pristine OMMT, pre-dispersed OMMT, pristine bentonite and destabilized bentonite. No significant difference in the feature of FTIR spectra between the pre-dispersed and destabilized nanoclays in comparison with their pristine form. This shows that upon the pre-dispersing and destabilization process, both nanofillers did not undergo significant structure/chemistry modification. At the band between 1464cm\(^{-1}\) to 1646cm\(^{-1}\) and 3626cm\(^{-1}\), the peak of bentonite is broader as compared to the OMMT due to the stretching and bending of hydroxyl group which is more prominent in the hydrophilic (unmodified) bentonite. The spectra peaks of OMMT at ~2855cm\(^{-1}\) and ~2923cm\(^{-1}\) represent the presence of both methylene groups and quartenary ammonium salt of the organic surfactant. In the spectra of Bentonite, these peaks were absent and this shows that the nanofiller was not surface modified with any organic compound [4]. Based on Figure 2, the incorporation of bentonite nanofillers (as single or hybrid form) into the PEVA matrix resulted in more intense spectra peak at ~3425cm\(^{-1}\) as compared to neat PEVA and PEVA-OMMT.
nanocomposite. As mentioned earlier, this was due to the stretching and bending of hydroxyl groups, confirming the presence of bentonite in the PEVA matrix.

Figure 2. FTIR spectra of neat PEVA, PEVA nanocomposites and PEVA hybrid nanocomposites.

Figure 3. Tensile toughness of neat PEVA, PEVA nanocomposites and PEVA hybrid nanocomposites.

Figure 3 shows the comparison of tensile toughness of neat PEVA, PEVA nanocomposites and PEVA hybrid nanocomposites with different ratio of OMMT:Bent nanofillers. Apparently, PEVA-O₂B₁ sample shows the highest tensile toughness value, and reached about 52% increment when benchmarked with the neat PEVA. Other nanocomposites show lower or similar tensile toughness values with the neat PEVA. This suggests that the use of hybrid OMMT/Bent (4:1) nanofiller resulted in better degree of nanoclay exfoliation and dispersion inside the PEVA matrix due to the correct composition of hydrophobic and hydrophilic nanofillers that would interact with the hydrophobic ethylene chains and hydrophilic vinyl acetate chains of the PEVA copolymer. Furthermore, the pre-dispersing process of the O-MMT and destabilization process of the bentonite might facilitate their dispersion throughout the PEVA matrix due to reduced tactoid size of the silicate platelets. As a result, the nanofillers could be better aligned in
the direction of the stress to more efficiently absorbed energy during tensile deformation.

5. Conclusions
In summary, the use of OMMT and Bent nanofillers in hybrid form has provided greater toughening effect to the PEVA copolymer as compared to their single form (OMMT alone or Bent alone). The hybrid pre-dispersed OMMT/destabilized Bent nanofillers have brought the largest increment in the tensile toughness of the PEVA when used in the ratio of 4:1 (PEVA-O₄B₁).

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