

## ENHANCEMENT OF POLY(ETHYLENE-CO-VINYL ACETATE) TENSILE STRENGTH BY INCLUSION OF PRE-DISPERSED O-MMT AND DESTABILIZED BENTONITE AS HYBRID NANOFILLERS

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**ABSTRACT:** Poly (ethylene-co-vinyl acetate)(PEVA) is a copolymer derived from the synthesis of ethylene (hydrophobic) and vinyl acetate (hydrophilic) monomers. In this research, PEVA copolymer with 18% vinyl acetate content was used as matrix and incorporated with organo-montmorillonite and bentonite as hybrid nanofillers in ratios of 4:1, 3:2, 2:3, 1:4. Before undergo the melt compounding process, an optimization procedure of pre-dispersing (O-MMT) and destabilizing(bentonite) were applied to enhance the exfoliation and dispersion of hybrid nanofillers in PEVA copolymer matrix. The Fourier Transform Infrared Spectroscopy (FTIR) analysis was done to analyze the structure of nanofillers, neat PEVA, PEVA nanocomposites and PEVA hybrid nanocomposites. The mechanical properties of all the samples were evaluated by conducting tensile test. Based on the result achieved, the enhancement in tensile strength obtained when PEVA matrix incorporated with hybrid nanofillers in a ratio of 4:1 (O-MMT:Bentonite). This might be due to an adequate content of hydrophobic (O-MMT) and hydrophilic (bentonite) that brings optimum matrix-nanofiller interactions.

**KEYWORDS:** *Poly(ethylene-co-vinyl acetate); Nanofillers; Organo-montmorillonite; Bentonite; Hybrid Nanocomposites*

### 1.0 INTRODUCTION

A research related to polymer-organoclays nanocomposites is broadly exist, however, the number of research particularly involved with poly ethylene-co-vinyl acetate (PEVA) nanocomposite is relatively modest (Merinska et al., 2013). To comprehend the complex morphology of the PEVA copolymer as the nanocomposite matrix is quite challenging due to the presence of semicrystalline, non-polar polyethylene (PE) and amorphous, polar poly (vinyl acetate) (PVA) structure (Fink, 2010; Merinska et al., 2013). The foremost benefit of PEVA copolymer is by varying the VA content in its composition, a wide range of properties is feasible to be obtain. Consequently, their application from rigid plastic to rubber like/ elastic products is possible to develop. One of the best nanofiller candidates for PEVA is silicate material, as it is abundant, low cost, having high aspect ratio and tailorable surface chemistry. Hence, this project is proposed to study the effect of using more than one type of silicate material as nanofiller in PEVA, to further enhance the mechanical performance of PEVA. In a contrast to conventional composite materials, nanocomposites may produce improvement in dimensional stability, strength and stiffness without losing flexibility (Sandi et al., 2005). According to previous studies, incorporating PEVA copolymer with organically modified montmorillonite (O-MMT) nanofiller can contribute to the development of biomedical materials as their biostability, biocompatibility, mechanical and thermal properties can be further improved (Osman et. al., 2015; Osman et. al., 2016). In determining an enhancement in mechanical, thermal and barrier properties of

the end nanocomposite product, the exfoliation and dispersion of the organo-MMT nanofiller are essential (Osman et al., 2016). The degradation of mechanical properties of host polymer will emerge if the nanoparticle is inadequately dispersed and this has been reported by many researchers (Agubra et al., 2013; Osman et al., 2015). For example, Jumahat et al. (2012) revealed that a decreasing in compressive strength for 1 and 3 wt% of nanoclay was reported due to the high localized stresses created by the intercalation structure of nanoclay in the polymer exhibit in the matrix during the compression that contributes to premature failure. Another research by Boo et al. (2007) reveal that, due to the poorly dispersed nanoplatelet, hence, the crack deflection mechanism that prompt to a tortuous path crack growth were perceived on nanocomposite samples. In this research, an optimization method of pre-dispersed OMMT and destabilisation of bentonite were applied in order to achieve greater exfoliation and dispersion of the OMMT and Bentonite in the PEVA matrix. The PEVA nanocomposite and PEVA nanocomposite were produced by melt compounding method and their mechanical properties were evaluated by tensile test.

## 2.0 EXPERIMENTAL

### 2.1 Material

The PEVA copolymer which commercially known as COSMOTHENE EVA H2181 was supplied by the Polyolefin Company (Singapore) Pte. Ltd. The PEVA consisted of 18 wt% of vinyl acetate (VA) and 82 wt% ethylene with a melt flow rate of 2g/10min (ASTM D 1238). A vicat softening point of this PEVA is 63°C (ASTM D 1525) and brittle point is <-75°C. The organo modified montmorillonite (O-MMT) also known as Nanomer (types 1.44P) by Nanocor, Inc. contains 35-45% of dimethyl dialkyl (C14-C18) amine as an organic surfactant was employed as nanofiller. A bulk density of O-MMT, ranges from 200 to 500 kg/m<sup>3</sup> with an average particle length of ≤ 20 microns. This nanofiller possesses a beige colour powder with the chemical formula of (Na,Ca)<sub>0.33</sub>(Al,Mg)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>·nH<sub>2</sub>O. Natural bentonite was supplied by Multifilla (M) Sdn. Bhd., and purchased via ADV System Technology. A bulk density is in the range of 600-1100 kg/m<sup>3</sup> and with the particle size of ≤ 25micron for bentonite nanofiller.

### 2.2 Preparation of sample

#### 2.2.1 Pre-dispersion process of Organo-Montmorillonite (O-MMT) Nanofiller

First, 100g of O-MMT was added into 100ml of distilled water as a ratio of 1:1 (O-MMT:distilled water). Then, the suspension was stirred for 2 hours by using magnetic stirrer at room temperature and ultrasonicated for 5 minutes by applying Branson Digital Ultrasonic Disruptor/Homogenizer (Model 450 D). After that, the suspension was filtered to remove water and then, placed in the oven at 50 °C for about 48 hours for drying process. Finally, before being characterized by Fourier Transform Infrared (FTIR), the pre-dispersed O-MMT powder was ground and sieved to dwindle agglomerated powder.

#### 2.2.2 Destabilization process of Bentonite Nanofiller (PH Control and Salt Addition)

Firstly, 20g of bentonite nanofiller was added into 100 ml distilled water (20% suspension). Next, it underwent ultrasonication process for about 15 minutes. Next, by dropping HNO<sub>3</sub>, the pH of the suspension was modified until it reached pH 4. The suspension was stirred by ultrasonic probe for 5 minutes. After that, NaCl (0.01M) was added and the mixture was stirred for another 5 minutes. The suspension was filtered prior to drying process in an oven (24 hours at 80°C). Finally, the destabilized bentonite was subjected to grinding and sieving process before being characterized by FTIR.

#### 2.2.4 PEVA Nanocomposites and Hybrid Nanocomposites Sheet Preparation

The PEVA nanocomposites and hybrid nanocomposites were prepared according to formulation displayed in Table 1. All the compounded samples underwent mixing process by applying internal mixer machine (Brabender plasticoder) at 160 °C. Then, to gain sheets form (~ 1mm thick), the compounded samples were compressed by using compression moulding machine (model GT-7014-H30C, by GOTECH Co. ) for 5 minutes pre-heat, 3 minutes pressing and 10 minutes cooling at 130 °C. Lastly the sheet specimen were cut for testing.

Table 1. Nanocomposites and hybrid nanocomposites formulation

Types of samples	Weight %			Acronym
	PEVA	OMMT	Bentonite	
Neat PEVA	100	-	-	PEVA
PEVA/O-MMT	96	4	-	PEVA-O
PEVA/Bentonite	96	-	4	PEVA-B
PEVA hybrid nanocomposite 4:1 (OMMT:Bentonite)	96	3.2	0.8	PEVA-O <sub>4</sub> B <sub>1</sub>
PEVA hybrid nanocomposite 3:2 (OMMT:Bentonite)	96	2.4	1.6	PEVA-O <sub>3</sub> B <sub>2</sub>
PEVA hybrid nanocomposite 2:3 (OMMT:Bentonite)	96	1.6	2.4	PEVA-O <sub>2</sub> B <sub>3</sub>
PEVA hybrid nanocomposite 1:4 (OMMT:Bentonite)	96	0.8	3.2	PEVA-O <sub>1</sub> B <sub>4</sub>

### 2.3 Characterization by Fourier Transform Infrared Spectroscopy Analysis

The chemical functional groups of nanofillers, nanocomposite and hybrid nanocomposites were characterized by FTIR analysis. All the specimens were analyzed by Perkin Elmer Paragon 1000 FTIR spectrometer with Attenuated Total Reflectance (ATR) procedure. The test was carried out for 16 scans, in the range of 4000-650  $\text{cm}^{-1}$  and resolution of 4 $\text{cm}^{-1}$ .

### 2.4 Mechanical Analysis by Tensile Test

Tensile test was performed on neat PEVA, PEVA nanocomposites, and PEVA hybrid nanocomposites, according to the ASTM D638 by using instron machine (Model-5582). A dumbbell shape sample was punched on ASTM D-638-M-5 die. The crosshead speed of 50 mm/min was employed. The mean values of tensile strength were recorded from five replicates.

## 3. Result and Discussion

Figure 1 exhibits the spectrum of FTIR of the origin O-MMT, pre-dispersed O-MMT, pristine bentonite and destabilized bentonite. Based on the data shows, there were no significance different between the spectra of all the silicate materials. Hence, it means that both nanofillers did not go through extensive chemistry/structure alteration upon the pre-dispersing and destabilization process. The peak appear at  $\sim 3626\text{cm}^{-1}$  indicates the structural O-H stretching vibration in the MMT, due to water molecules adsorbtion. It can be seen that at this peak ( $\sim 3626\text{cm}^{-1}$ ), the spectra of bentonite is more intense as compared to the O-MMT. This is due to the polarity of bentonite which possess hydrophilic characteristic (Janice et al., 1994). In addition, due to the presence of methylene group of the organic surfactant, the spectra peak at  $\sim 2923\text{cm}^{-1}$  and  $\sim 2855\text{cm}^{-1}$  only appear in the O-MMT sample. For the nanocomposite system, the spectra peak at  $\sim 3425\text{cm}^{-1}$  appears more intense in the samples that contains bentonite due to stretching and bending of the hydroxyl groups. Thus, this proved the existence of bentonite in the PEVA matrix

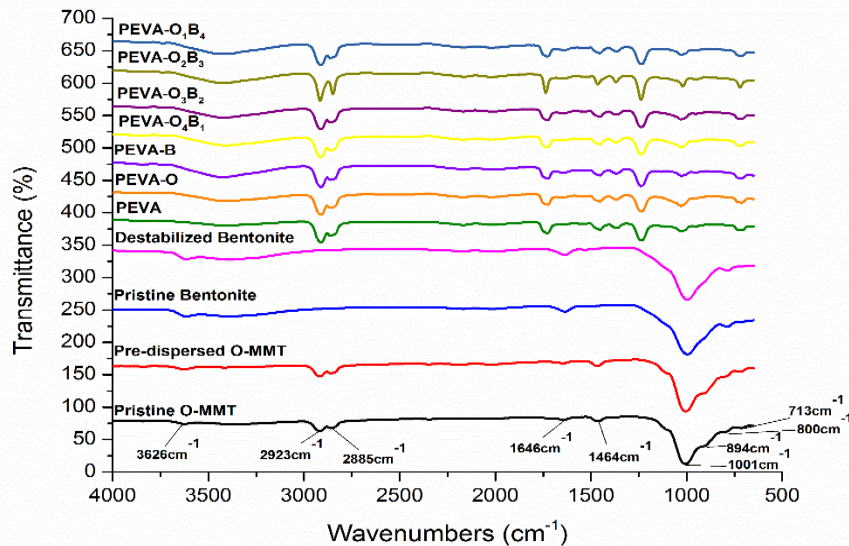


Figure 1: FTIR spectrum of nanofillers (O-MMT/Bentonite), neat PEVA, PEVA nanocomposites and PEVA hybrid nanocomposites.

Figure 2 displays the graph of tensile strength of neat PEVA, PEVA nanocomposites and PEVA hybrid nanocomposites. The results demonstrate the enhancement of tensile strength of the nanocomposites and hybrid nanocomposites in a comparison with neat PEVA. According to previous research, the presence of well dispersed and distributed nanofillers were occurred due to the pre-dispersing and destabilization process. Therefore, for effective reinforcing mechanism, the interaction between copolymer matrix and nanofillers should be ameliorated (Osman et al., 2017; Fauzi et al., 2019). The highest tensile strength value was achieved by PEVA-O<sub>4</sub>B<sub>1</sub>, which exhibit an increment about 36% when benchmarked with neat PEVA. This might occur due to inclusion of well dispersed hybrid nanofiller (O-MMT:Bentonite) into the PEVA copolymer matrix. Furthermore, the balance amount of ethylene (82%) and vinyl acetate (18%) of the PEVA matrix with the ratio of nanofillers, 4:1(O-MMT: Bentonite) also brought the enhancement in the tensile strength of the copolymer. This shows that an adequate content of hydrophobic (O-MMT) and hydrophilic (bentonite) can bring optimum matrix-nanofiller interactions to increase the tensile strength of the resultant nanocomposite.

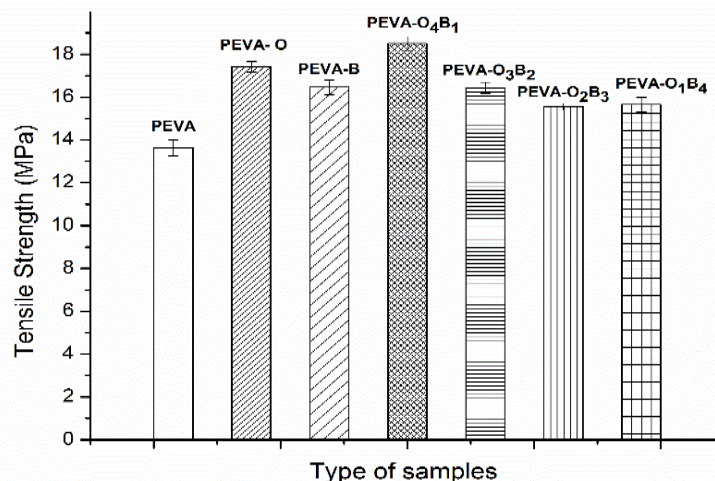


Figure 2: Tensile strength of neat PEVA, PEVA nanocomposites and PEVA hybrid nanocomposites

#### 4.0 CONCLUSION

In summary, hybrid nanofillers in the ratio 4:1 (OMMT:Bentonite) provide enhancement in tensile strength of PEVA copolymer matrix due to adequate amount of matrix and nanofillers composition based on their equivalent in polarity.

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