Melt Rheological Behavior of High Density Polyethylene/Poly(Vinyl Alcohol) Fiber Composites Prepared via Melt Compounding Method

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Abstract. In this work, high density polyethylene (HDPE)/poly(vinyl alcohol) (PVA) fiber composites have been fabricated via melt compounding by employing a twin-screw extruder. The resulted composites samples of four different PVA fiber loadings (i.e. 0, 5, 10, and 20 wt\%) were then characterized using an oscillatory rheometer to investigate the effect of PVA loadings on their melt rheological behavior (e.g. storage modulus, loss modulus, complex viscosity). Additionally, the surface morphology of cryo-fractured surface of the composites were also investigated by using a scanning electron microscopy (SEM). The SEM micrographs showed that PVA fibers were perfectly embedded and well blended in HDPE matrix. Additionally, the melt rheological analysis results showed that the complex viscosity of all nanocomposites samples (i.e. PVAC-5, PVAC-10, and PVAC-20) were higher than that of neat PP (i.e. PVAC-0) and increased with the increase of nanoclay concentrations. Moreover, to further study the relationship between the PVA fiber loadings and complex viscosity of the composites, a well-known Carreau-Yasuda equation was employed to model the complex viscosity data from the rheological test. It was found that the equation fitted well the rheological test data.

1. Introduction

It is well-known that plastics have been widely used in the world and become part of our life. It was due to their many advantages (e.g. low density, low price, good mechanical properties, various applications, easily to process into any kind of forms) compared to other materials (e.g. metals, ceramics, wood, etc). High density polyethylene (HDPE) is considered as one of the most widely and frequently used thermoplastic polymers. It has been used in many applications, e.g. packaging, boxes, household goods, piping, etc. It is because HDPE is low cost, low density, good chemical and corrosion resistance, easy to be processed and recycled [1]. Moreover, its properties could be enhanced by blending and filling with reinforcing materials, i.e. micro-/nano-fillers, fibers, etc [2].

In other hand, poly(vinyl) alcohol (PVA) is a biodegradable type of thermoplastic polymers made from vinyl acetate. PVA fibers can be considered as one of fibers that have high reinforcement performance and have demonstrated good results in terms of tensile strain capacity, toughness, and crack bridging properties. Additionally, these fibers also suitable for many applications due to their high resistance to UV, chemicals/alkali, abrasion, and fatigue [3]. Recently, PVA fibers have been widely used in
construction applications, such as in fiber reinforced cementitious composites (FRCC) [4, 5]. The FRCC at least consists of three phases, which are: cement paste/matrix, fiber, and aggregates. The incorporation of fibers in FRCC may increase the energy absorption/toughness, strength, and/or strain of the FRCC [3]. Additionally, PVA fiber can also be used to fabricate polymer/PVA fiber based composites. There have been several literatures about polymer/PVA fiber based composites. Wu et al. [2] studied the preparation and characterization of HDPE/PVA. They found that the mechanical properties of HDPE increased with the addition of PVA fiber. Nevertheless, there have been limited number of literatures that studied PVA fiber filled polymer based composites, and thus it becomes an interesting topic of research.

One of the most preferred and widely used method to fabricate polymer composites is melt compounding. It is because this method is quite simple, low cost, and “green” method since no-solvent is used. Furthermore, this method is very suitable with the plastic industrial machines (i.e. extruder, injection molding), which makes the industrial scale production and commercialization of the polymer composites becomes easier [6, 7]. One of the key factors to fully understand the internal morphology/structure and processability (especially via extrusion/injection molding) of the composites is by studying their melt rheological properties. To the best of our knowledge, the number research studies regarding with the melt rheological studies of HDPE/PVA fiber composites are still limited, and thus it becomes an interesting topic of research. The present work focuses on the fabrication of HDPE/PVA fiber composites and characterization their morphology and melt rheological properties of the prepared nanocomposites.

2. Experimental

2.1. Materials

High density polyethylene (HDPE)/Polyvinyl alcohol (PVA) fiber composites were fabricated by melt compounding HDPE pellets (product name: M-300054, from SABIC, Saudi Arabia) with PVA fibers (product name: RECS15, from Kuraray, Japan). The HDPE has density of 954 kg/m³ and melt flow index (MFI) of 30.0 g/10 min (low melt viscosity). Whereas, the PVA fiber has diameter 0.04 mm, thickness of 15 dtex, cut length of 8 mm, specific gravity of 1.3. Figures 1a and 1b show the appearances of HDPE pellets and PVA fibers, respectively. Whereas, Figure 1c shows a scanning electron microscopy (SEM) image of single of PVA fiber.

![Figure 1](image)

**Figure 1.** a) Photograph of HDPE pellets; b) photograph of PVA fibers; and c) SEM image of a single PVA fiber

2.2. Composites preparation

The melt compounding process was carried out in a twin-screw extruder (TSE) (Farrell FTX-20, UK) at screw speed of 17 rpm and die temperature of 200 °C. The melt composites from the die was then cooled down in waterbath, dried (using air blower), pelletized (by cutting machine), and put in oven for moisture removal. After completely dried, the composites pellets were then molded into ASTM standard samples using an injection molding machine (Super Master, SM120, from Asian Plastic Machinery Co., China). The HDPE/PVA fiber composites were fabricated at four different PVA loadings, i.e. 0, 5, 10,
20 wt%, which correspond to PVAC-0, PVAC-5, PVAC-10, PVAC-20, respectively. Figures 2a and 2b exhibit the appearances of twin-screw extruder (TSE) and injection molding machine used in this work.

2.3. Composites characterization
The surface morphological study was done by using a Scanning Electron Microscopy (SEM), JEOL JSM-6360A, Japan. The samples used for the SEM analysis were cryo-fractured molded bars. Prior to the SEM examination, the cryo-fractured bar samples were coated with a fine layer of gold to minimize the overcharging/overheating of the samples, and also to improve the signal and resolution. The composites samples were examined by the SEM at 15 kV and magnification of 200X. Additionally, the effects of PVA fiber loadings on the melt rheological behavior of HDPE/PVA fiber composites were examined by the use of an oscillatory rheometer ARG2 (from TA Instrument, USA). The melt rheological test was performed under frequency sweep procedure using parallel plates fixture. The testing conditions were as follow: strain of 0.01%; fixed temperature of 150 °C; angular frequency range of 0.05 - 500 rad/s. The samples used in the melt rheological test were disk-like composites samples obtained from the injection molding. Prior to the melt rheological test, the disk-like sample was put in between the parallel plates, and conditioned at fixed temperature of 150 °C until the whole composites sample was completely melted. Before starting the analysis, the excess of samples melt around the parallel plates was removed using a scraper. The data generated from the melt rheological test was complex viscosity $|\eta^*|$ vs angular frequency ($\omega$). Figures 2c and 2d exhibit the appearances of Scanning Electron Microscopy (SEM) and oscillatory rheometer apparatus used in this work.

![Figure 2](image-url)

**Figure 2.** Photograph of a) Twin-screw extruder (TSE); b) Injection molding machine; c) Scanning Electron Microscopy (SEM); d) Oscillatory rheometer

3. Results and discussion
The surface morphology of the HDPE/PVA fiber composites has been examined by a Scanning Electron Microscopy (SEM). Figures 3a and 3b show the SEM images of HDPE/PVA composites, i.e. PVAC-0 and PVAC-10, respectively. The figure shows that the PVA fibers were well blended and embedded in the HDPE matrix (shown by the arrows). It was also observed that the fibers entangled one with the others. Additionally, it seemed that there were less interactions between the HDPE matrix and the PVA fibers (shown by the circle dashed-line). The SEM images of the other samples were similar but not presented in this paper.
Figure 3. SEM images of cryo-fractured surface of HPDE/PVA fiber composites: a) PVAC-0 and b) PVAC-10

Additionally, the melt (state) rheological analysis of the HDPE/PVA fiber composites was carried out under torsion mode in parallel plate geometry using frequency sweep test. This test was performed at a constant temperature of 150 °C; constant strain of 0.1 %, and angular frequency range of 0.05 and 500 rad/s. Figure 4 shows the complex viscosity $|\eta^*|$ as function of angular frequency ($\omega$) of HDPE/PVA fiber composites measured at fixed temperature of 150 °C. As seen in the figure, the complex viscosity of the composites were all higher than the neat HDPE. Furthermore, the improvement of complex viscosity was more significant at higher PVA loadings (i.e. PVAC-10 and PVAC-20) than at the lower one (PVAC-5).

![Complex viscosity graph](image)

Figure 4. Complex viscosity $|\eta^*|$ as function of angular frequency ($\omega$) for HDPE/PVA fiber composites at different PVA fiber loadings

Additionally, several complex viscosities of the composites samples (at several angular frequencies) are given in Table 1 and also plotted in Figure 5. Using these table and figure we could further observe the effect of PVA fiber loadings as well as the angular frequency on the complex viscosity of the HDPE/PVA fiber composites. As shown in Figure 5 and in accordance with Figure 4, the complex viscosity considerably increased with increasing PVA fiber loadings. The increase of complex viscosity $|\eta^*|$ was most likely due to the dispersion of the PVA fiber in the HDPE matrix, as well as the interaction between them, which resulted in the restricted mobility of HDPE molecular chains in the molten state.
Additionally, the rheological properties of composites materials could also be affected by the frictional interaction among the fillers as well as the interaction between the polymer chains and the fillers [8].

Table 1. Representative complex viscosity of HDPE/PVA fiber composites

| Angular Frequency (rad/s) | Complex viscosity of HDPE/PVA fiber composites (Pa.s) |
|---------------------------|-----------------------------------------------------|
|                           | PVAC-0 | PVAC-5 | PVAC-10 | PVAC-20 |
| 0.1                       | 621.1  | 1004   | 10,630  | 1.49E+05|
| 1                         | 592.3  | 882.7  | 5,304   | 47,980  |
| 10                        | 519.4  | 688.7  | 1,725   | 8,235   |
| 100                       | 360.6  | 453.3  | 635.6   | 1,441   |
| 500                       | 225.3  | 276.4  | 374.5   | 693.8   |

Furthermore, the increase of complex viscosity was prominent at lower angular frequencies (i.e. 0.1 – 10 rad/s). For example, at angular 100 rad/s the increases of complex viscosity of the composites were only about 0.26; 0.76; 3 times fold of the neat PP, for PVAC-5, 10, 20, respectively. Whereas, at angular frequency of 1 rad/s, the increases of complex viscosity were about 0.5; 8; 80 times fold of the neat PP, for PVAC-5, 10, 20, respectively. Furthermore, at angular frequency of 0.1 rad/s, the complex viscosity of the composites dramatically increased by 0.6; 16; and 240 times fold of the neat PP, for PVAC-5, 10, 20, respectively. At lower angular frequencies (i.e. 0.1 – 10 rad/s), the movement of HDPE molecular chains were very limited, due to the presence of PVA fiber and the interaction between both of them, and thus the complex viscosity was high. Whereas, when the angular frequency of the test increased, the HDPE molecular chains started to move (i.e. less restricted) regardless the presence of PVA fiber, and thus the complex viscosity started to decreased rapidly. This explanation was in accordance with the curve shape of PVAC-10 and PVAC-20 exhibited in Figure 4. The figure shows rapid decline of complex viscosity for both PVAC-10 and PVAC-20 as the angular frequency increased. This phenomenon was called “high shear-thinning” behavior. In the other hand, PVAC-0 and PVAC-5 showed “low shear-thinning” behavior, because the complex viscosity decrease gradually [8].

![Figure 5. Representative complex viscosity |η*| of HDPE/PVA fiber composites at different angular frequencies](image)

Additionally, to further study the complex viscosity |η*| behavior as function of angular frequency (ω) of the HDPE/PVA fiber composites, we have fitted the complex viscosity |η*| data from the frequency
sweep test results to the Carreau-Yasuda equation [9, 10], as shown in Eq (1). Figure 6 shows the schematic diagram of the Carreau-Yasuda equation.

\[
\eta^*(\omega) = \eta_0 \left[ 1 + (\lambda \omega)^n \right]^{(n-1)/n}
\]  

(1)

Figure 6. Schematic diagram of Carreau-Yasuda model

Where, \( \eta_0 \) is the zero shear viscosity (or complex viscosity, in this study), \( \lambda \) is the time constant (or cross-over time) and the inverse \( 1/\lambda \) is the critical value of shear rate (or angular frequency, in this study) at which the complex viscosity begins to decrease. The slope in the power-law region is given by \( (n-1) \). Equation (1) reduces to the Newtonian fluid behavior for \( n = 1 \) and describes shear-thinning behavior when \( n < 1 \), while \( a \) is the Yasuda parameter which is attributed to the amplitude of the region of transition between \( \eta_0 \) and the power law region [9, 10]. All parameters, \( \eta_0 \), \( \lambda \), \( n \), and \( a \) obtained from fitting complex viscosity data are listed in Table 2. As noticed from Figure 4, Carreau-Yasuda model fitted the complex viscosity data of the composites satisfactorily.

**Table 2.** Parameters with respect to the Carreau-Yasuda model for HDPE/PVA fiber composites

| Sample   | \( \eta_0 \)  | \( \lambda \) | \( n \) | \( A \) |
|----------|---------------|-------------|-------|-------|
| PVAC-0   | 621.1         | 0.02        | 0.61  | 0.64  |
| PVAC-5   | 1,004         | 0.24        | 0.75  | 0.68  |
| PVAC-10  | 10,630        | 4.39        | 0.52  | 11    |
| PVAC-20  | 1.49E+05      | 4.31        | 0.23  | 2.74  |

4. Conclusion

In the present work, HDPE/PVA fiber composites have been prepared via melt compounding method using a co-rotating twin screw extruder. The prepared composites samples were then characterized to study the effect of PVA fiber loadings on morphology and melt rheological properties of the composites. Morphological study revealed that all the composites samples showed that the PVA fibers were well blended and embedded in the HDPE matrix. Though it seemed that there were less interactions between the HDPE and PVA fibers. In the melt rheological analysis, the complex viscosity of all the composites samples increased with increasing PVA fiber contents at all angular frequencies. However, the improvement of \( |\eta^*| \) was more prominent at lower angular frequencies (e.g. 0.1-10 rad/s) than at higher ones (e.g. 100, 500 rad/s). Additionally, composites samples PVAC-10 and PVAC-20 exhibited a “high shear-thinning” behavior as the angular frequency increased. In other hand, the PVAC-0 and PVAC-5 demonstrated a “low shear-thinning” behaviour.
References
[1] Low J H, Andenan N, Abdul Rahman W A, Rusman R, Majid R A 2017 Evaluation of rice straw as atural filler for injection molded high density polyethylene bio-composite materials Chem. Eng. Trans. 56 1081-86
[2] Wu S, Ji G, Shen J 2003 Study on ultraviolet irradiation modification of high-density polyethylene and its effect in the compatibility of HDPE/PVA fibre composites, Mater. Lett. 57 2647-50.
[3] Ahmed S F U, Mihashi H 2011 Strain hardening behavior of lightweight hybrid polyvinyl alcohol (PVA) fiber reinforced cement composites, Mater. Struct. 44 1179-91.
[4] Xu B, Toutanji H.A, Gilbert J 2010 Impact resistance of poly(vinyl alcohol) fiber reinforced high-performance organic aggregate cementitious material, Cement and Concrete Research 40 347-51.
[5] Nematollahi B, Sanjayan J, Ahmed Shaikh FU 2015 Tensile strain hardening behavior of PVA fiber-reinforced engineered geopolymer composite J. Mater. Civil Eng. 27 04015001.
[6] Chafidz A, Latief, F H, Samad U A, Ajbar A, Al-Masry W 2016 Nanoindentation creep, nano-impact, and thermal properties of multiwall carbon nanotubes-polypropylene nanocomposites prepared via melt blending, Polym-Plast Technol. 55 1373-85.
[7] Chafidz A, Rengga W D P, Khan R, Kaavessina M, Almutlaq A M, Almasry W, Ajbar A 2017 Polypropylene/multiwall carbon nanotubes nanocomposites: Nanoindentation, dynamic mechanical, and electrical properties, J Appl. Polym. Sci. 134 45293-316.
[8] Chafidz A, Kaavessina M, Al-Zahrani S, Al-Otaibi, M N 2016 Rheological and mechanical properties of polypropylene/calcium carbonate nanocomposites prepared from masterbatch J. Thermoplast. Compos. 29 593-622.
[9] Choi H J, Kim S G, Hyun Y H, Jhon M S 2001 Preparation and Rheological Characteristics of Solvent-Cast Poly(ethylene oxide)/Montmorillonite Nanocomposites Macromol. Rapid Comm. 22 320-25.
[10] Sorrentino L, Berardini F, Capozzoli, M R, Amitrano S, Iannace S 2009 Nano/micro ternary composites based on PP, nanoclay, and CaCO3, J Appl. Polym. Sci. 113 3360-67.