VIETNAM JOURNAL OF CHEMISTRY VOL. 49(5) 567-572 OCTOBER 2011

STUDY ON THE PROCESSING CONDITIONS, MORPHOLOGY AND THERMAL PROPERTIES OF COMPOSITES BASED ON POLYETHYLENE AND FLY ASH

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Received 10 December 2010

Abstract

The composites based on high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) 75/25 wt.% (abbreviated as PE) and fly ash (FA) were prepared by melt mixing at 85/15 wt.%. In order to improve the dispersion and adhesion of FA into PE matrix, FA was modified with vinyl trimetoxy silane (VTMS). The results showed the suitable conditions to prepare PE/FA composites are mixing temperature 180°C, mixing speed 50 rpm and mixing time 5 minutes. The study on morphology of PE/FA composites exhibited the dispersion, the adhesion and the interaction of modified FA (MFA) with PE matrix are better than those of original FA (OFA). The DTA, TGA curves showed the PE/MFA-OFA composite has low thermo-oxidation degradation rate and weight loss in comparison with those of PE and PE/OFA. That proved the role of MFA-OFA mixture in improving the thermal stability of PE.

1. INTRODUCTION

In the recent years, high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) have been applicated in many different areas because of their high toughness, flexibility, high tensile strength, low gas permeability, ect. In 2007, global capacity of polyethylenes reached to 78 million tons [1].

Fly ash (FA) is an inorganic waste formed by coal combustion process in thermo electrical power plans. Millions of tons of FA have been eliminated each year around the worlds. Only in China, the total amount of FA was accumulated up to 4 billion tons in 2002, which occupied about 4000–5000 hectares. However, an amount approximately 30% of FA is effectively used in some concrete, cement, catalyst, composite products [2]. In Vietnam, there are four biggest electric stations which generated 1.24 million tons of FA in 2009, its 10 wt.% is utilized as admixture of cement and raw material to produce the brick [3]. In order to enlarge the applications, the using of FA particles instead of metakaolin, $CaCO_3$, carbon black to produce polymer composites has been focused in recent years such as PP/FA [4, 5], HDPE/FA, LLDPE/FA [5-8], PVC/FA [9]. The results showed that the mechanical properties of composites exhibited marginal increase in tensile strength, young's modulus, elongation at break and hardness. However, FA is an inorganic material whereas polymers are organic materials, in order to increase the FA – polymer interaction, adhesion, dispersion and mechanical properties of composites, some silanes were used to modify FA such as 3-amino propyl trietoxy silane, Z-6032 [4 - 9].

Owing to the large applications of HDPE and LLDPE as well as researches on polymer/FA materials, in this study, we used HDPE collaborating with LLDPE to combine their advantages. HDPE has little chain, a high proportion of crystals, strong intermolecular forces, which results in higher density, tensile strength, hardness and brittle but less elongation at break than other types of PE. LLDPE structurally differs from HDPE in that the molecular trunk consists of shorter branches. LLDPE has higher flexibility, elongation at break, impact strength but less tensile strength and a proportion of crystals than HDPE. Therefore, the elongation at break and impact strength of HDPE can be improved by adding LLDPE. We tested and found that polymer mixture reached the best machanical properties at a proportion of HDPE/LLDPE 75/25 wt.% (abbreviated as PE). PE and FA modified and unmodifed by vinyl trimethoxy silane (VTMS) were prepared by melt mixing in the Haake Rheomixer. The effects of processing conditions (such as mixing temperature, mixing time, rotor speed) on the mechanical properties of the composites were investigated. In order to understand more detail about the effect of treatment of FA with VTMS, morphological properties of PE/FA composites were observed by field emission scanning electron microscope (FESEM). Thermal properties of composites have also been reported.

2. EXPERIMENTAL

2.1. Materials

High density polyethylene (HDPE) and linear low density polyethylene (LLDPE) produced by Sabic. Co (South Korea) with the corresponding density is 0.96 and 0.93 g/cm^3, respectively. Fly ash (FA) provided by Pha Lai Thermal Power Plant, total weight of SiO_2, Fe_2O_3, Al_2O_3 is approximates 86 wt. %, moisture content is about 0.3 wt. %, particle size of 3 to 10 µm. The organo-silane with chemical named vinyl trimethoxy silane (VTMS) 98 %, HNO_3 65 %, C_2H_5OH 95 % and CH_3COOH obtained from China.

2.2. Preparation of composites

Mixture of polymers which consists of 75 wt.% HDPE and 25 wt.% LLDPE is denoted as PE. FAs include OFA (original fly ash), MFA (fly ash was modified by VTMS, we reported in our previous paper [10]) and MFA/OFA (30/70 wt.%) mixture). The composites based on PE and FAs (85/15 wt.%) were melt mixed in the Haake Rheomixer (Germany) in the processing conditions as mixing temperature 175 - 190°C, mixing time 3 - 6 minutes, rotor speed 45 - 60 rpm.

2.3. Measurements

Imitation of the relative melt viscosity in mixing process was carried out by Haake Rheomixer. Determination of mechanical properties was performed according to ASTM D 638 by using Zwick 2.5 tensile tester. The tests were conducted at crosshead speed of 10 mm/min at room temperature. Field emission scanning electron microscope (FESEM, S-4500, Hitachi, Japan) was employed to examine structural morphology of the surface of the composites, and also to investigate the dispersion of FA in the PE matrix. The themal properties were studied by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) using DTG-60H and DSC-60 thermogravimetric analyzer of Shimadzu. Co (Japan) under air atmosphere at a heating rate of 10 °C/min, the temperature range from room temperature to 600°C.

3. RESULTS AND DISCUSSION

3.1. Rheological studies of PE/MFA-OFA composites with varying processing conditions

The torque measurements have been successfully used to obtain qualitative information concerning relative melt viscosity and mixing process of the composites. In order to investigate the rheology of PE/MFA-OFA composites, we carried out mixing process with different conditions such as mixing temperature, mixing time and rotor speed in a Haake intermixer. Fig. 1 presents the relationship between torque and time of mixing for PE/MFA-OFA composites.

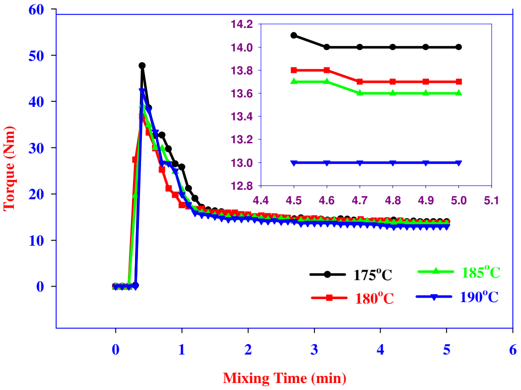

Fig. 1: Plots of torque versus time of mixing for PE/MFA-OFA composites in different mixing temperatures

It is apparent from the Fig. 1 that processing conditions have a serious effect on the rheological properties when adding the same weight of MFA/OFA into mixture. From Fig. 1, the plots of torque versus time of mixing for PE/MFA-OFA composites in different temperatures at 175, 180, 185 and 190°C, respectively, decrease with increasing mixing temperature. Similarly, when increasing rotor speed or decreasing mixing time, the melt viscosity of mixture enhances (table 1). The smaller the torque of the composites (or viscosity of the composites) is, the easier producing composites will be.

3.2. Determination of suitable processing conditions

In the fabrication of composites, processing conditions including mixing temperature, mixing time, mixing speed influenced strongly on the properties and the structure of the composites [11, 12].

3.2.1. Mixing temperature

Tensile strength and elongation at break properties of PE/MFA-OFA composites which were prepared at different mixing temperature are shown in Figs. 2 and 3. It is clear that the mixing temperature affected significantly on tensile strength and elongation at break.

Table 1: Stability torque of PE/MFA-OFA composites at different processing conditions

Mixing temperature (°C)	Stability torque (Nm)	Mixing Speed (rpm)	Stability torque (Nm)	Mixing time (min)	Stability torque (Nm)
175	14.02	45	13.17	3	14.32
180	13.73	50	13.73	4	13.81
185	13.65	55	13.91	5	13.73
190	13.00	60	14.17	6	13.54

The tensile strength versus mixing temperature and elongation at break versus mixing temperature curves of the composites show the maximum values at 180°C. It is obvious that the mixture of PE and MFA/OFA at temperature lower than 180°C, MFA/OFA could not disperse in PE matrix due to high melt viscosity of mixture. At temperature higher than 180°C, the increase in viscosity - flow of polymer supports dispersibility of MFA/OFA in PE matrix. However, the mixture at high temperature can lead to the degradation of PE chains, therefore, the mechanical properties of composites reduce. In this case, 180°C is expected as a most suitable temperature for processing the composites.

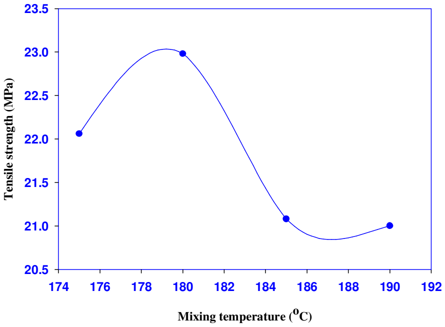

Fig. 2: The effect of mixing temperature on tensile strength of PE/MFA-OFA composites

3.2.2. Mixing time

The effect of mixing time on tensile strength and elongation at break properties is shown in Table 2. Results in table 2 show mechanical properties of PE/MFA-OFA composites in which the highest reached values at mixing time of 5 minute. When the mixing time is less than 5 minutes, it may be not enough to disperse MFA-OFA uniformly in the matrix. However, if mixing time is longer than 5 minutes, PE molecules can be degraded by thermo-oxidation. Therefore, mixing process performing for 5 minutes is most appropriate to examine the effect of other factors in the research composites.

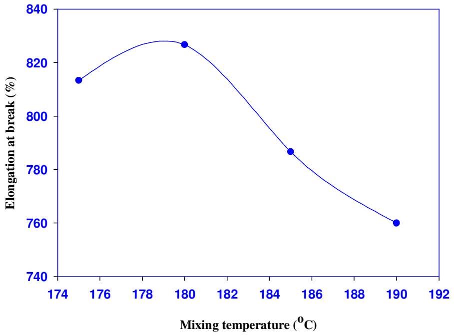

Fig. 3: The effect of mixing temperature on elongation at break of PE/MFA-OFA composites

Table 2: Effect of mixing time on the mechanical properties of PE/MFA-OFA composites

Time, min	3	4	5	6
Tensile strength, MPa	20.99	21.19	22.98	21.57
Elongation at break, %	760.00	766.67	826.67	780.00

3.2.3. Mixing speed

Table 3 reflects the effect of mixing speed on the tensile strength and elongation at break of PE/MFA-OFA composites. The data in Table 3 indicates that the mechanical properties of PE/MFA-OFA composites reached highest values at mixing speed of 50 rpm. When mixing speed is less than 50 rpm, MFA-OFA can not disperse uniformly in PE matrix as well as interact weakly with PE. Besides, when mixing speed is more than 50 rpm, the oxidative decomposition can reduce the mechanical properties of the composites due to high friction heat and shear stress of rotors during mixing process. Over all, some concludes can be suggested such as mixing temperature at 180°C, mixing speed of 50 rpm and mixing time of 5 minutes. These conditions will be applied to produce the composites for mechanical testing and morphology observation.

Table 3: Effect of mixing speed on the mechanical properties of PE/MFA-OFA composites

Speed, rpm	45	50	55	60
Tensile strength, MPa	20.40	22.98	21.58	21.50
Elongation at break, %	730.00	826.67	766.67	760.00

3.3. Morphology

The morphology of the PE/FA composites is presented in Fig. 4. It clearly shows a two-phase structure of composites consisting of matrix phase (PE) and dispersed FA particles. OFA particles disperse well in the polymer matrix but interact weakly with polymer that are observed as bright part in Fig. 4 a. After treating FA particles by using VTMS, MFA are not only good dispersion but also better adhesion and interaction with PE matrix (Fig. 4 b,c,d). The organic part in MFA acts linking OFA with PE matrix, so, adhesion and interaction of mixture of OFA and MFA with PE matrix are improved significantly (Fig. 4 b,d). Therefore, modifying FA is very necessary to improve morphological and mechanical properties of the composites [6, 8].

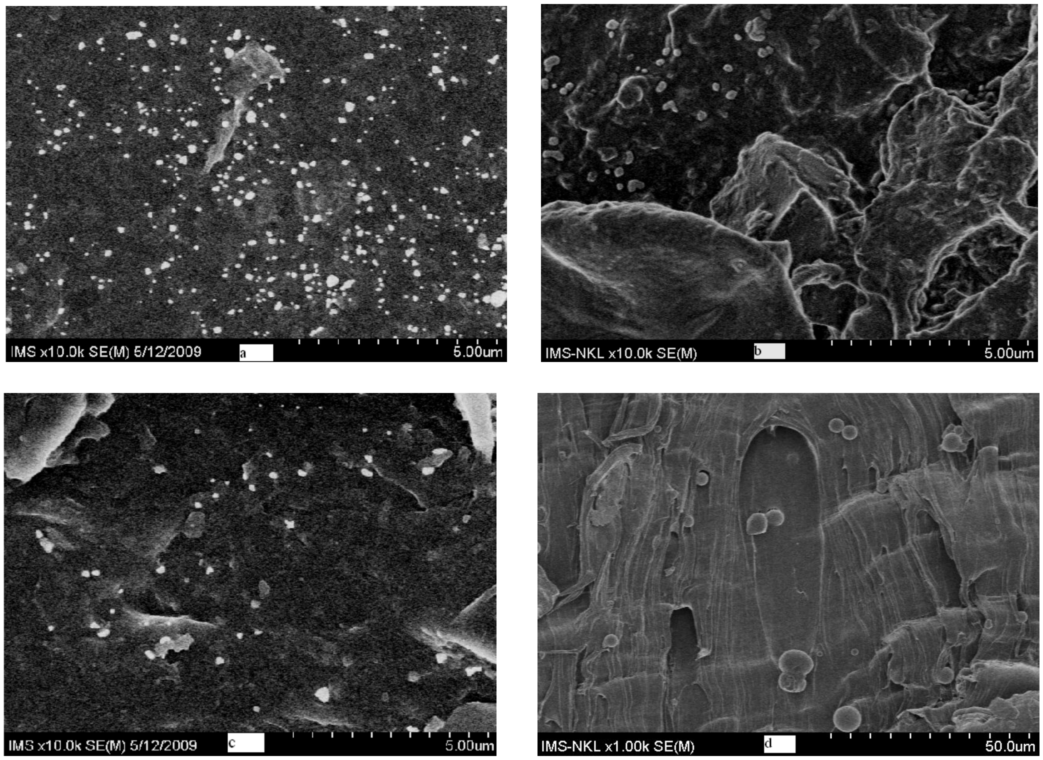

Fig. 4: FESEM photomicrographs of surface of PE/OFA (a), PE/MFA-OFA (b), PE/MFA(c) and cross surface of PE/MFA-OFA (d)

3.4. Thermal properties

The influence of the FA in PE matrix was illustrated by the thermal analysis (TGA, DTA) as showed in Figs. 5, 6 and table 4. Table 4 shows the onset temperatures (T_o) of PE/FA composites (from 238^{o}C to 243^{o}C) are higher than that of neat PE (237^{o}C). The TGA curve of PE is on the left of those of PE/FA composites (Fig. 5). It means that degradation rate of PE is higher than these of PE/FA composites. PE leaves no residue at temperature higher than 500^{o}C, while PE/FA composites leave the same amount of residue corresponding to the inorganic part of FA added. FA shields the polymer from the action of oxygen, dramatically increasing the thermal stability in oxidative conditions. The TGA curve of PE/MFA-OFA composite is on the right in Fig. 5. It shows that the thermal stability of PE can be improved significantly by using MFA with small content (15% MFA/OFA). However, when using MFA with large content (15% MFA), the thermal stability of PE decreases due to organo-silane in MFA is decomposed at high temperature.

DTA curves of PE/FA composites are showned in Fig. 6. The endothermic effect observed on the Fig. 6 is because of melting of polymer (120-150^{o}C). The composites have a first step of weight loss between 240°C and 320°C corresponding the exothermic effect in Fig. 6 due to thermal degradation of PE and elimination of organic substances on side of FA particles and impurity residued in FA (such as organic substances containing N, S, ect.). The second stage of weight loss of composites corresponding the exothermic effect in Fig. 6 about 420 - 450°C is thermo-oxidation of PE while neat PE is oxidized at temperature lower than 400°C. The results in Figs. 5, 6 and table 4 indicate that by using OFA, MFA and MFA-OFA mixture, thermal stability of PE can be improved, and among them, MFA-OFA mixture showed the better characteristic than OFA, MFA.

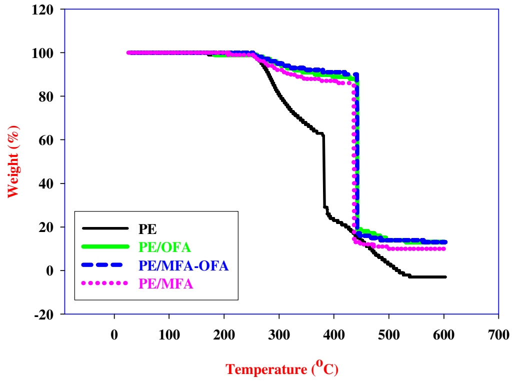

Fig. 5: TGA curves of PE, PE/OFA, PE/MFA-OFA and PE/MFA composites

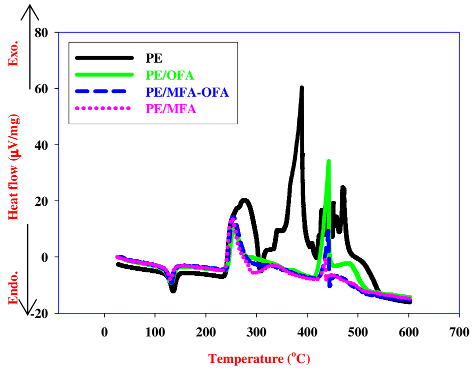

Fig. 6: DTA curves of PE, PE/OFA, PE/MFA-OFA and PE/MFA composites

Table 4: TG characteristics of PE and PE/FA composites

Sample	T_o, °C	Weight loss (%) at				
		350	400	450	500	550
PE	237	32.9	76.7	85.8	96.9	0.0
PE/OFA	243	8.9	10.6	78.8	85.9	86.6
PE/MFA -OFA	241	7.7	9.0	83.7	86.0	86.4
PE/MFA	238	11.7	13.4	86.2	89.6	89.9

T_o: onset decomposition temperature.

4. CONCLUSION

4.1 The smaller the torque of the composites (or viscosity of the composites) of PE/FA at high mixing temperature, high rotor speed and long mixing time, the easier producing composites will be.

4.2 The suitable conditions to produce PE/FA composites in the melt state are mixing temperature 180°C, mixing speed 50 rpm and mixing time 5 minutes.

4.3 The dispersion, adhesion and interaction of MFA with PE matrix are better than those of OFA.

4.4 The thermal stability of PE can be improved by using MFA/OFA mixture.

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