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Thermal properties, thermo-oxidation and UV-thermo-humidity complex stability of polyethylene/modified fly ash/ultraflow composites

Nguyen Thuy Chinh, Nguyen Thi Thu Trang, Tran Thi Mai, Nguyen Vu Giang, Tran Huu Trung, Mai Duc Huynh, Thai Hoang[*]

Institute for Tropical Technology, Vietnam Academy of Science and Technology

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Abstract

This study concerns the effect of ultraflow (UTF) content on the thermal property; thermo-oxidation and photo thermal-humidity stability of composites based on high density polyethylene (HDPE) and modified fly ash (MFA). The different scanning calorimeter analysis (DSC) results show that the relative crystallinity of HDPE/MFA and HDPE/MFA/UTF composites is lower than that of HDPE. The thermal properties of HDPE/MFA/UTF composites were studied by using thermogravimetric analysis (TGA) characteristic. Thermal stability of HDPE/MFA/UTF composites is higher than HDPE and HDPE/MFA composite. The tensile properties (tensile strength, elongation at break and Young's modulus) of the composites after thermal aging test had a tendency to reduce with increasing the UTF contents. The retention of tensile strength and Young's modulus of HDPE/MFA/UTF composites is larger than that of HDPE/MFA composite while the elongation at break of HDPE/MFA/UTF composites is less than that of HDPE/MFA composite. The results of accelerated weathering test showed that the tensile strength, elongation at break and Young's modulus of HDPE/MFA/UTF composites after 168 hour accelerated weathering test were increased much higher than those of HDPE/MFA composites.

Keywords. Ultraflow, thermal property, thermal oxidation, accelerated weathering test, HDPE composite.

1. INTRODUCTION

Annually, the thermal power plants have discharged large amounts of fly ash (FA), which caused environmental pollution, occupied huge land area and affected adversely on human health [1]. Because of many advantages such as low cost, thermal stability, small size, FA has been a useful additive in concrete and cement [2, 3]. It is also considered as potential filler for polymers and composites [4-8]. The obtained results showed that FA improved thermal, electric properties and flammable resistance of polymers [5, 7-8]. Surface modification of FA by organic substances increases interactions, adhesion and dispersion between modified FA and polymer matrix [3, 7, 9-14], leading to enhancement in properties of polymer/modified FA composites.

Up to now, the use of ultraflow (UTF) such as stearate zinc salt for composites based on polyethylene and modified FA has not been much considered. In previous paper, the tensile, electrical properties and morphology of high density polyethylene/modified fly ash composites using ultraflow were investigated [15]. The obtained result showed that that relative melt viscosity of HDPE/stearic acid modified FA (MFA) composites was decreased with adding UTF as a processing aid agent and lubricant. The MFA particles were dispersed more regularly in HDPE matrix due to the presence of UTF as a compatibilizer between MFA and HDPE [15]. In this paper, we continue to present the effect of UTF content on thermal property, thermo-oxidation and UV-thermo-humidity complex stability of HDPE/MFA composites.

2. EXPERIMENTAL

2.1. Materials

High density polyethylene (HDPE) was produced by Honam Co. (Korea) with the density of 0.96 g/cm^3. Fly ash silo (FA) was provided by Pha Lai Power Plant (Vietnam). The average particle size of selected FA is about 5 µm, total weight of SiO_2, Al_2O_3 and Fe_2O_3 is more than 86 % and moisture content is less than 0.3 %. FA was modified by stearic acids in solid state as process in [12]. Stearate zinc salt with commercial name of ultraflow (UTF) was fabricated in Korea.

2.2. Preparation of composite materials

The content of MFA was fixed in 10 wt.% while UTF weight portion is changed from 1 to 7 wt.% in comparison with HDPE weight in the composites. The composites obtaining is carried out by melt mixing method in a Haake Rheomixer (Germany) at 180 ^{o}C and rotor speed of 50 rpm for 6 min. After that, the composites were molded by hydraulic press machine (Toyoseky, Japan) at 180 ^{o}C for 3 min with pressing pressure of 12-15 MPa. Then the samples were cooled and stored at least 24 hours before determining properties and morphology. This process of composite preparation was conducted at Institute for Tropical Technology, VAST.

2.3. Characterizations

2.3.1. Differential Scanning Calorimeter (DSC)

DSC diagrams were recorded by NETZSCH DSC 204F1 under nitrogen gas from room temperature to 250 ^{o}C and at a heating rate of 10°C/min. The relative crystallinity (χc) of the samples was calculated using the following equation [16, 17]:

$$Xc = \Delta H_f \times 100/\Delta H^*_f$$

where ΔH^*_f is the fusion enthalpy of the perfectly polyethylene crystal (298 J/g) and ΔH_f is the enthalpy of fusion of the samples.

2.3.2. Thermogravimetric Analysis (TGA)

Thermal stability of samples was determined through a Thermogravimetric Analyzer DTG-60H (TGA/DTA) (Shimadzu, Japan) in nitrogen conditions. All samples were heated from room temperature to 600 ^{o}C at a heating rate of 10 ^{o}C/minute.

2.3.3. Thermo - oxidation testing

The composite specimens were thermally aged in the convection air-circulating oven at 70 ^{o}C during 168 hours. The decrease in the mechanical properties (tensile strength, elongation at break and Young modulus) of HDPE/MFA/UTF composites was used to determine their thermal oxidative stability.

2.3.4. UV-thermo-humidity complex testing

UV-thermo-humidity complex testing of HDPE/MFA/UTF composites was carried out in UV CON 327 accelerated weathering test chamber (Atlas, United State) according to ASTM D 4587-4595 with alternating cycles of UV light and moisture at controlled, elevated temperatures. Each cycle of testing includes 8 hours of UV irradiation at 60 ^{o}C, and then 4 hours of condensing humidity at 45 ^{o}C. After 14 cycles of testing, the samples were removed and characterized to assess the photothermal - humidity stability of HDPE/MFA composites.

3. RESULTS AND DISSCUSION

3.1. Thermal properties

In our previous research [15], it shows that the most suitable content of UTF in HDPE/MFA/UTF composites is 3 wt.%. Thus, the sample prepared with 3 wt.% of UTF was chosen for investigation on thermal properties and thermal stability. Figure 1 and table 1 show DSC diagrams and characteristics of HDPE, HDPE/MFA and HDPE/MFA/3 wt.% UTF composites. The onset and endset temperature of the composites do not shift much in comparison with HDPE. However, the intensity of peak corresponding to melting of HDPE in the composites is lower than that of HDPE. The relative crystallinity of HDPE is decreased by adding MFA and UTF due to the inhibited the connection of HDPE chains caused by strong interactions between MFA, UTF and HDPE such as the hydrogen bonds and dipole – dipole interactions between C=O, C−O−C groups of stearic acid grafted onto FA surface and C=O, C−O−C groups of UTF [16].

Table 1: DSC characteristics of HDPE, HDPE/MFA and HDPE/MFA/3 wt.% UTF composites

Samples	T_m (^{o}C)	ΔH_m (J/g)	χ_c (%)
HDPE	142.6	219.9	73.79
HDPE/MFA composite	139.2	191.5	64.26
HDPE/MFA/3 wt.% UTF composite	138.8	192.1	64.46

3.2. Thermal stability

TGA diagrams of HDPE, HDPE/MFA and HDPE/MFA/3 wt.% UTF composites were presented in Fig. 2. Observably, the TG curve slopes of all samples were similar to each other. All investigated samples have the loss of weight negligible from room temperature to 400^{o}C. The samples started decomposition quickly at temperature higher than 400^{o}C and the percentage of weight loss at this step was about 90 %. At 500^{o}C,

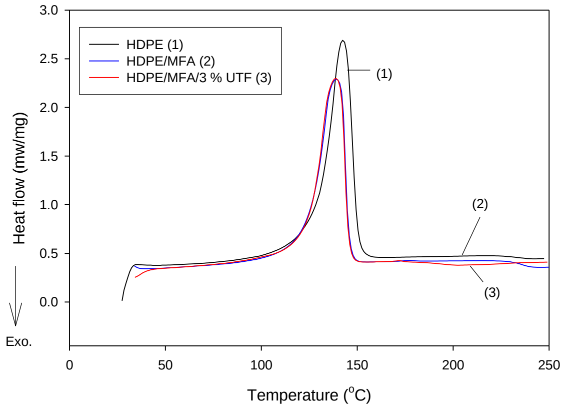

Figure 1: DSC diagrams of HDPE, HDPE/MFA and HDPE/MFA/3 wt.% UTF composites

HDPE was completely decomposed while the weight of HDPE/MFA and HDPE/MFA/3 wt.% UTF composites was remained about 3.89 % and 8.94 %, respectively. Besides, the melting temperature (T_m) and maximum degradation temperature (T_{max}) of HDPE/MFA/3 wt.% UTF composite is also higher than those of HDPE and HDPE/MFA composite (see table 3). This confirms that the HDPE/MFA/3 wt.% UTF composite has better thermal stability more than HDPE and HDPE/MFA composite and it may due to the improvement in dispersibility of MFA in HDPE matrix in the presence of UTF as above mentioned. However, the temperature at 2 % weight loss of HDPE/MFA/3 wt.% UTF composite is lower than that of HDPE and HDPE/MFA composite can due to the degradation of stearate group in UTF (table 2).

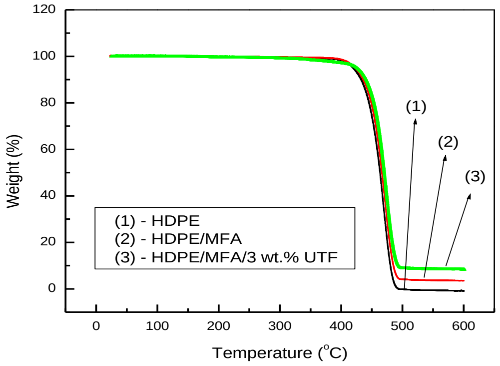

Figure 2: TGA diagrams of HDPE, HDPE/MFA and HDPE/MFA/3 wt.% UTF composites

Table 2: Thermal characteristics of HDPE, HDPE/MFA and HDPE/MFA/3 wt.% UTF composites

Samples	T_m (°C)	$T_{2\%}$ (°C)	T_{max} (°C)	Weight percentage (%) at		
				400 °C	500 °C	600 °C
HDPE	138.63	402.20	473.11	98.13	0	0
HDPE/MFA composite	140.56	406.74	474.72	98.37	3.89	3.27
HDPE/MFA/3 wt.% UTF composite	141.02	362.34	474.82	97.14	8.94	8.37

T_m: melting temperature; $T_{2\%}$: temperature loss of 2 % weight, T_{max}: maximum degradation temperature.

3.3. Thermo-oxidation stability

Table 3 presents the tensile strength, elongation at break and Young’s modulus of HDPE/FA/UTF composites before and after aging test and % retention of them. Interestingly, the tensile strength and Young modulus of HDPE/MFA/UTF composites have tends to reduce with increasing the UTF contents but higher than that of HDPE/MFA composite. For example, the HDPE/MFA/UTF composites have retention of tensile strength about 88.57 % up to 90.88 % while the retention of tensile strength of HDPE/MFA composite is 87.29 %. Similarly, the retention of Young’s modulus of HDPE/MFA and HDPE/MFA/3 wt.% UTF was 70.04 and 86.12 %, respectively. This can be explained by the dispersion more regularly of MFA in the HDPE matrix in the presence of UTF thanks to formation of hydrogen bonds and dipole – dipole interactions between C=O, C−O−C groups of stearic acid grafted onto FA surface and C=O, C−O−C groups of stearate in UTF and the moiety of stearate in UTF is easy to mix with ethylene unit chain in HDPE macromolecules. The good dispersion of MFA in HDPE/MFA/UTF composites plays a role as effective barriers which limit the permeation of oxygen into the composites as well as reduction of thermo-oxidation degradation, scission reaction of HDPE macromolecules [17, 18]. It is indicated that the thermo-oxidative stability of HDPE/MFA/UTF composites was improved in the presence of UTF.

Among tensile properties, elongation at break of the composites seemed to be more sensitive to thermo-oxidative testing with higher reduction as compared to tensile strength and Young's modulus. This decrease in the elongation at break of the composites is due to reduction in segmental mobility of the polymer chains and increase in the cross linked density that hindered the extension of chains resulting in lower elongations [19].

Table 3: Tensile properties of HDPE/MFA/UTF composites before and after thermal aging test

UTF content (wt.%)	Tensile strength			Elongation at break			Young's modulus		
	Before (MPa)	After (MPa)	Retention percentage (%)	Before (%)	After (%)	Retention percentage (%)	Before (MPa)	After (MPa)	Retention percentage (%)
0	29.26	25.54	87.29	854.00	564.21	66.07	917.22	642.40	70.04
1	31.81	28.91	90.88	509.31	286.62	56.27	1032.31	797.84	77.29
3	31.02	27.53	88.75	578.00	298.54	51.65	920.66	792.88	86.12
5	28.65	25.95	90.58	528.04	206.67	39.14	1107.66	827.41	74.70
7	27.81	24.63	88.57	192.23	57.93	30.14	826.36	700.19	84.73

3.4. UV-thermo-humidity complex stability

The effect of UTF content on tensile properties of HDPE/MFA/UTF composites after accelerated weathering test is demonstrated in table 4. Although the tensile properties of HDPE/MFA/UTF composites after accelerated weathering test have a tendency of decrease in comparison with that before accelerated weathering test, the retention of tensile properties of HDPE/MFA/UTF is increase in the presence of UTF content. For instance, the tensile strength of HDPE/MFA/UTF composites after accelerated weathering test has grown up from 23.48 MPa to 24.86 MPa at 1 and 3 wt.% of UTF and then dropped to 24.64 MPa and 23.29 MPa at 5 and 7 wt.% of UTF, respectively. Similarly, Young's modulus and elongation at break of HDPE/MFA/UTF composites have increased as rising content of UTF up to 3 wt.% and higher than that of HDPE/MFA composite. The first, the reduction in tensile properties of the composites can be explained by the effect of UV irradiation, humidity and temperature leading to the formation of carbonyl, carboxyl, hydroperoxide groups and free reactive radicals in polymer chains, causing the occurrence of chain scission, thus deteriorating the mechanical properties of the composites [17-20]. The degradation mechanism of PE in the composites samples could be proposed as mentioned in Ref. 17-18. Moreover, the cracking of polymer chain will pave the way for oxygen penetration and defect creation inside the material structure, continuously degrade PE in the composites and reduce the tensile properties of the composite samples.

The secondary, the increase in tensile properties of HDPE/MFA/UTF in the presence of UTF after accelerated weathering test in comparison with HDPE/MFA composite can be attributed by UTF - as a compatibilizer - was contributed to improve the dispersibility, adhering and mixing MFA and polymer matrix due to interactions above mentioned. This leads to the transformation in properties of polymer matrix and additives, resulting in improvement the rigidity of network polymer-additive that contributes to significant enhancement of tensile [10, 21].

Table 4: Tensile properties of HDPE/MFA/UTF composites before and after accelerated weathering test and their retention

UTF content (wt.%)	Tensile strength			Elongation at break			Young's modulus		
	Before (MPa)	After (MPa)	Retention percentage (%)	Before (%)	After (%)	Retention percentage (%)	Before (MPa)	After (MPa)	Retention percentage (%)
0	29.26	19.85	67.84	854.00	249.97	29.27	917.22	336.16	36.65
1	31.81	23.48	73.81	509.31	190.23	37.35	1032.31	404.77	39.21
3	31.02	24.86	80.14	578.00	211.72	36.63	920.66	576.43	62.61
5	28.65	24.64	86.00	528.04	220.19	41.70	1107.66	475.19	42.90
7	27.81	23.29	83.75	192.23	53.13	27.64	826.36	570.85	69.08

4. CONCLUSION

In conclusion, the HDPE/MFA/UTF composites have thermal oxidative, thermal and UV-thermal – humidity complex stability higher than HDPE/MFA composite and HDPE. Adding MFA and UTF into HDPE leads to the reduction in relative crystallinity of HDPE. The polymer chains of HDPE and the HDPE/MFA, HDPE/MFA/UTF composites were degradated by irradiation, humidity and temperature to form carbonyl, carboxyl, hydroperoxide groups and free reactive radicals. The most suitable content of UTF is 3 wt.% to archive good thermal and UV-thermal - humidity complex stability.

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Corresponding author: **Thai Hoang**
Institute for Tropical Technology
Vietnam Academy of Science and Technology
18, Hoang Quoc Viet road, Cau Giay district, Hanoi, Viet Nam
E-mail: hoangth@itt.vast.vn.