

Effect of Benzyl Urea on Thermal Properties of Recycled High Density Polyethylene/Ethylene Vinyl Acetate/Eggshell Powder Composites

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Abstract – Recycled high density polyethylene/ethylene (vinyl acetate)/eggshell powder (rHDPE/EVA/ESP) composites were prepared using an internal mixer and benzyl urea as a compatibilizer. The thermal stability of the components was studied by thermogravimetric and differential scanning analysis. The compatibilized rHDPE/EVA/ESP composites had better thermal stability in terms of decomposition than uncompatibilized composites. The results also indicated that the percentage of crystallinity of the compatibilized composites was lower than composites without the compatibilizer. **Copyright © 2014 Penerbit Akademia Baru - All rights reserved.**

Keywords: Composites, Eggshell, Recycled high density polyethylene, Ethylene vinyl acetate

1.0 INTRODUCTION

Polyolefin blends have been studied to improve the properties and processability of the homopolymers involved [1-3]. High density polyethylene (HDPE) is a semicrystalline polyolefin, which is one of the mostly used thermoplastic materials as commodity plastics due to its low price and easy processability. However, because of its low toughness, weather resistance, and environmental stress cracking resistance, its application in many technologically important areas are limited [4]. This can be overcome by blending HDPE with EVA, leading to the production of a new material with so many attractive characteristics. The crystallization behavior affects the properties of polymer blends. Therefore, the thermal stability of polymer blends plays an important role in polymer processing. The degree of crystallinity and thermal degradation are among the most important parameters in characterizing semicrystalline polymers. The aim of this study was to investigate the effect of benzyl urea as a compatibilizer on the thermal stability of the rHDPE/EVA/ESP composites using thermogravimetric and differential scanning analysis.

2.0 METHODOLOGY

2.1 Materials

rHDPE with a melt flow index of 0.7 g/10 min (190°C) and a density of 939.9 kg/m³ was used. EVA contains 6.5 wt% VA, with melt index of 2.5 g/10 min (80 °C; 2.16 kg) and a density of 0.93 g/cm³ was supplied from A.R. Alatan Sdn. Bhd., Kedah Darul Aman, Malaysia. The eggshell was obtained from a local poultry industry in Negeri Sembilan, Malaysia.

2.2 Sample preparation

For the ESP preparation, the eggshell was washed, dried, and ground to powder using kitchen blender. ESP with average filler sizes of 63 μm was dried in a vacuum oven at 80 °C until the constant weight was obtained as reported by Suhadah *et al* [5]. For composites preparation, the compounding of the blends was carried out by melt blending in Brabender internal mixer. The rHDPE was first mixed in the internal mixer at 190 °C and 50 rpm for 4 min, and then the pre-weighed amount of EVA, BU, DCP, and ESP were added to the mixer for the next 6 min. Each of the molten samples was compressed and molded into sheets of 2 mm thickness using a hydraulic press at 190 °C for 2 min and cooled under pressure for 4 min. Table 1 shows the formulation used in this study.

Table 1: Formulations of rHDPE/EVA/ESP and rHDPE/EVA/ESP_{BU} composites

Composite code	rHDPE[phr]	EVA[phr]	ESP[phr]	BU[phr]	DCP[phr]
rHDPE/EVA	50	50	-	-	-
rHDPE/EVA/ESP5	50	50	5	-	-
rHDPE/EVA/ESP10	50	50	10	-	-
rHDPE/EVA/ESP15	50	50	15	-	-
rHDPE/EVA/ESP20	50	50	20	-	-
rHDPE/EVA/ESP25	50	50	25	-	-
rHDPE/EVA/ESP5 _{BU}	50	50	5	6	1
rHDPE/EVA/ESP10 _{BU}	50	50	10	6	1
rHDPE/EVA/ESP15 _{BU}	50	50	15	6	1
rHDPE/EVA/ESP20 _{BU}	50	50	20	6	1
rHDPE/EVA/ESP25 _{BU}	50	50	25	6	1

2.3 Characterization and measurements

Thermal stability of the composites was investigated by thermogravimetric analysis (TGA) by using a Perkin Elmer TGA instrument [Model: Pyris Diamond TG/DTA] from ambient temperature to 700°C at a programmed heating rate of 10 °C/min in nitrogen. A sample weight of approximately 10 mg was taken for all the measurements. The weight loss against temperature was recorded. The melting and crystallization behavior of rHDPE/EVA/ESP composites were evaluated using Perkin Elmer DSC thermal system USA. Samples were scanned at a heating and cooling rate of 10 °C/min in nitrogen atmosphere. Samples weighing about 5 mg were used for the DSC. The percentage crystallinity (X_c) of the rHDPE phase has been determined by Eq. 1, where ΔH_m is the heat of melting of the semi-crystalline rHDPE composites, and ΔH_m^0 is the heat of melting for 100 % crystalline rHDPE, which is 293 J/g [6].

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (1)$$

3.0 RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis

Figures 1(a) and 1(b) demonstrate the thermogravimetric curves of rHDPE/EVA/ESP and rHDPE/EVA/ESP_{BU} composites at different filler loading. As shown in Figure 1, all samples display a two-step thermal degradation process. The first stage occurring between 250 and 300 °C is related to the deacylation of the EVA phase through radical and ionic β -elimination mechanisms [7]. In addition, the second step (400–450 °C) involves the degradation of the HDPE phase accompanied with the decomposition of the polyacetylene-ethylene chains formed in the first stage [7].

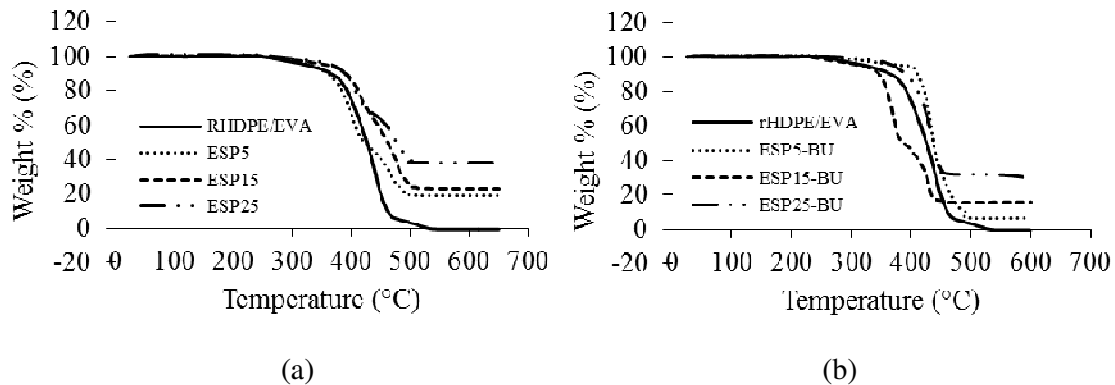


Figure 1: TGA curves of (a) rHDPE/EVA/ESP and (b) rHDPE/EVA/ESP-BU composites with different filler loading.

Table 2 shows the temperature of 50 % weight loss ($T_{50\%wt}$), final decomposition temperature, and residual mass for both series of the composites. Table 2 shows that the temperature at 50% weight loss, the final decomposition temperature, and the residual mass

of the rHDPE/EVA/ESP and rHDPE/EVA/ESP_{BU} composites increased with an increase in the filler loading. These results show that higher filler loading gives the rHDPE/EVA/ESP composites more thermal stability than the lower filler loading. Meanwhile, the temperature of 50% weight loss and final decomposition temperature for rHDPE/EVA/ESP_{BU} are higher than rHDPE/EVA/ESP composites. This indicates that the present of BU increased the thermal stability of the composites due to better interfacial adhesion between ESP and rHDPE/EVA matrix.

3.2 Differential Scanning Calorimetry

DSC thermograms of rHDPE/EVA/ESP composites and rHDPE/EVA/ESP_{BU} composites are shown in Figure 2. The values of melting temperature (T_m) and % crystallinity for rHDPE/EVA/ESP and rHDPE/EVA/ESP_{BU} composites are summarized in Table 2. The DSC curves in Figure 2 show endothermic melting peaks around 126-127 °C. Although there was very little change in the melting peak temperatures of the composites, it be seen that the melting endothermic temperature seem to decrease with the increase of filler content for both sets of the composites.

Table 2: Data for $T_{-50 \text{ wt.}}$, final decomposition temperature, and residual mass of rHDPE/EVA/ESP and rHDPE/EVA/ESP_{BU} composites at different ESP loading.

Blend composition	$T_{-50 \text{ wt.}}$ (°C)	Final decomposition temperature (°C)	Residual mass (%)
rHDPE/EVA	425.82	531.33	0.002
rHDPE/EVA/ESP-5	426.66	693.05	1.628
rHDPE/EVA/ESP-15	460.56	693.28	3.800
rHDPE/EVA/ESP-25	470.76	694.28	4.645
rHDPE/EVA/ESP-5 _{BU}	436.92	700.00	6.238
rHDPE/EVA/ESP-15 _{BU}	462.28	700.00	15.460
rHDPE/EVA/ESP-25 _{BU}	472.31	700.00	23.820

The increasing amount of filler in the composites decreased the melting enthalpies. This expected, since the melting enthalpies are related to the amount of polymer in the sample, hence the melting peak sizes and related enthalpies should decrease correspondingly [8]. However, the presence of the filler may influence the crystallization behaviour of the composites. The results show that the percentage of crystallinity for both composites decreased as the filler loading increased.

This may be due to the immobilized rHDPE/EVA matrix by the addition of ESP, which results in a reduced crystallization of the composites [9]. On the other hand, rHDPE/EVA/ESP_{BU} composites displayed slightly higher melting temperatures but lower crystallinity than rHDPE/EVA/ESP composites at the same filler loading. Li *et al.* [10] reported that the compatibilizer improved wood flour/polypropylene interactions, which restricted the mobility of PP chains and hindered the crystallization process.

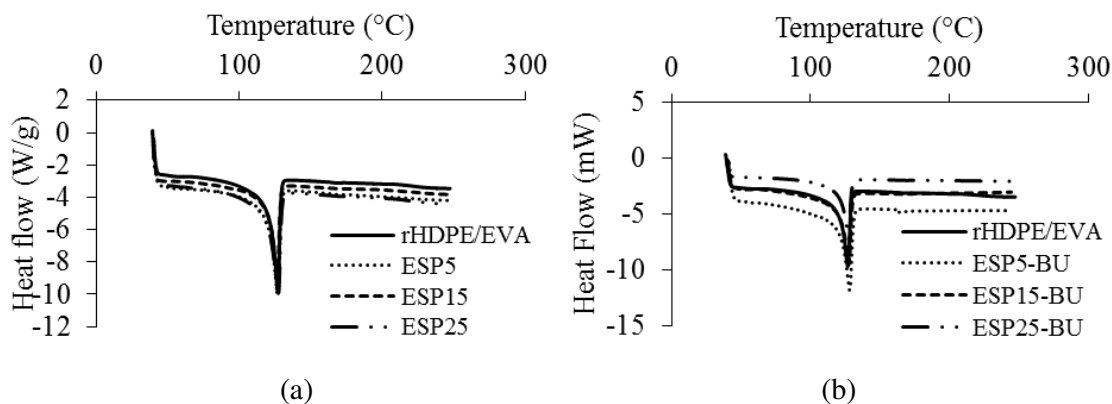


Figure 2: DSC curves of (a) rHDPE/EVA/ESP and (b) rHDPE/EVA/ESP_{BU} composites with different filler loading.

Table 3: Thermal DSC parameters for rHDPE/EVA/ESP and rHDPE/EVA/ESP_{BU} composites at different ESP loading.

Blend composition	T_m (°C)	Percentage of crystallinity (%)
rHDPE/EVA	126.91	40.85
rHDPE/EVA/ESP-5	127.14	35.25
rHDPE/EVA/ESP-15	126.66	32.28
rHDPE/EVA/ESP-25	127.22	31.28
rHDPE/EVA/ESP-5 _{BU}	128.02	35.24
rHDPE/EVA/ESP-15 _{BU}	127.64	32.23
rHDPE/EVA/ESP-25 _{BU}	127.28	27.11

4.0 CONCLUSION

The addition of BU as a compatibilizer in the rHDPE/EVA/ESP composites was evaluated. The thermal degradation of the composites increased the addition of filler. The compatibilizer BU enhanced the thermal stability of the composites due to better interfacial adhesion between the components of the composites. Meanwhile, the presence of the filler reduced the crystallization of the composites due to immobilized rHDPE/EVA matrix by filler. On the other hand, the BU compatibilizer improved the interactions of the component, and therefore the percentage of crystallization of compatibilized composites lower than the composites without the BU compatibilizer.

REFERENCES

- [1] D. Imren, A. Boztug, E. Yılmaz, H.B. Zengin, Viscometric investigation of compatibilization of the poly(vinyl chloride)/poly(ethylene-co-vinyl acetate) blends by terpolymer of maleic anhydride–styrene–vinyl acetate, *Journal of Molecular Structure* 891 (2008) 329-332.
- [2] C. Li, Q. Kong, J. Zhao, D. Zhao, Q. Fan, Y. Xi, Crystallization of partially miscible linear low-density polyethylene/poly(ethylene-co-vinylacetate) blends, *Materials Letters* 58 (2004) 3613-3617.
- [3] B. Na, Q. Zhang, Q. Fu, G. Zhang, K. Shen, Super polyolefin blends achieved via dynamic packing injection molding: The morphology and mechanical properties of HDPE/EVA blends, *Polymer* 43 (2002) 7367-7376.
- [4] Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotis, Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties, *Progress in Polymer Science* 35 (2010) 357-401.
- [5] S. Shuhadah, A.G. Supri, H. Kamaruddin, Thermal analysis, water absorption and morphology properties of egg-shell powder filled low density polyethylene composites, in: *Proceeding MUCET 2008*, (2008).
- [6] L. Minkovaa, Y. Penevaa, E. Tasheva, S. Filippib, M. Pracellac, P. Magagninib, Thermal properties and microhardness of HDPE/clay nanocomposites compatibilized by different functionalized polyethylenes, *Polymer Testing* 28 (2009) 528-533.
- [7] S. Akhlaghi, A. Sharif, M. Kalae, A. Elahi, M. Pirzadeh, S. Mazinani, et al., Effect of stabilizer on the mechanical, morphological and thermal properties of compatibilized high density polyethylene/ethylene vinyl acetate copolymer/organoclay nanocomposites, *Materials & Design* 33 (2012) 273-283.
- [8] D.G. Dikobe, A.S. Luyt, Morphology and properties of polypropylene/ethylene vinyl acetate copolymer/wood powder blend composites, *eXPRESS Polymer Letters* 3 (2009) 190-199.
- [9] N. Gamze Karsli, A. Aytac, M. Akbulut, V. Deniz, O. Güven, Effects of irradiated polypropylene compatibilizer on the properties of short carbon fiber reinforced polypropylene composites, *Radiation Physics and Chemistry* 84 (2013) 74-78.
- [10] L. Li, Q. Wang, C. Guo, The influence of wood flour and compatibilizer (m-TMI-g-PP) on crystallization and melting behavior of polypropylene, *Journal of Thermal Analysis and Calorimetry* 107 (2012) 717-723.