STUDY ON SOME PROPERTIES AND MORPHOLOGY OF COMPOSITES BASED ON POLYETHYLENE GRAFTED ACRYLIC ACID/ETHYLENE-VINYL ACETATE COPOLYMER/CALCIUM CARBONATE

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ABSTRACT

Composites based on polyethylene grafted acrylic acid (PE-g-AAc)/ethylene-co-vinylacetate copolymer (EVA)/calcium carbonate (CaCO_3) were prepared by melt mixing. Relative melt viscosity, morphology, mechanical properties and thermostability of the composites were studied. The experimental results show that the presence of (CaCO_3) activated by stearic acid (10 - 20 wt.%) changes lightly stable torque of polymer blend of PE-g-AAc/EVA. Use of modified PE improves compatibility of PE and EVA as well as makes the components disperse into each other better than in blends using unmodified PE. Tensile strength and elongation at break of both polymer blends decrease with presence of CaCO_3 . However, tensile strength of the composites of PE-g-AAc/EVA/ CaCO_3 is higher than that of composites of PE/EVA/ CaCO_3 . Beside that, the composites of PE-g-AAc/EVA/ CaCO_3 have thermostability higher than the composites of PE/EVA/ CaCO_3 .

Keywords: Polyethylene, ethylene-co-vinylacetate copolymer, calcium carbonate, polymer blend, composite, mechanical properties, morphology, thermostability.

1. INTRODUCTION

In recent years, study on composites formed by mixing polymers with additives or/and fillers is attracting many scientists due to their promising application in the living and technique fields. Many polymers are mixed with fine particles of the above substances to improve some properties of polymer matrix such as tensile strength, abrasion resistance, heat resistance, *etc.* Polymer blend based on polyethylene (PE) and ethylene-co-vinylacetate copolymer (EVA) has many good properties because it can combine advantages of both PE and EVA. Particularly, EVA has an ability of mixing with a large amount of fillers such as CaCO_3 , $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, clays to enhance some properties of polymer blend [1 - 5]. Because of difference of chemical structure between PE and EVA, PE is difficult to compatibilize with EVA. Modification of PE by grafting acrylic acid (AAc) onto PE can improve compatibility of PE with EVA.

This paper presents the results related to some properties and morphology of the composites formed by mixing polymer blend (unmodified- and modified PE/EVA) with CaCO_3 activated by stearic acid in melt state. The experimental results show that relative melt viscosity of the

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polymer blend of PE/EVA is changed lightly with the presence of CaCO_3 . The tensile strength and elongation at break of the composite decrease with increasing content of CaCO_3 . However, these properties of the composites of PE-g-AAc/EVA/ CaCO_3 are higher than those of the composites of PE/EVA/ CaCO_3 (in the same content of components). Grafting AAc onto PE enhances phase interaction, adhesion of PE with EVA and makes CaCO_3 disperse more regularly into PE and EVA.

2. EXPERIMENT

2.1 Chemicals and materials

- Linear low density polyethylene (LLDPE) is supplied by Daelim Corporation (Korea) in grain form, density of 0.91 g/cm^3 , melt index of 2.63 - 2.66 g/10 minutes (190°C , weight load of 2.16 kg), melt temperature of $120 - 125^\circ\text{C}$.
- Copolymer ethylene - vinyl acetate (EVA) is Korean commercial product in grain form with vinyl acetate content of 18%, melt temperature about $95 - 99^\circ\text{C}$, density of 0.93 g/cm^3 , melt index of 3.5 g/10 minutes (190°C , weight load of 2.16 kg).
- Acrylic acid (AAc) is Korean commercial chemical with density of 1.05 g/ml , boiling temperature about $140 - 142^\circ\text{C}$.
- Dicumyl peroxide (DCP) supplied by Junsei Corporation (Japan).
- KOH, xylene and toluene are Chinese industrial chemicals; 1,2 - dicloethane is Japanese commercial product.
- CaCO_3 treated by 2% stearic acid was supplied by Hoang Lien Son Porcelain Company (Vietnam), in white powder form.

2.2 Preparation of the composites of unmodified- and modified PE/EVA/ CaCO_3

- Preparation of PE-g-AAc was carried out in a reactive extruder with L/D of 24. Content of AAc grafted onto PE determined by the method of titration with KOH/ethanol 0.1N is 0.67 wt.% [6].
- The composites of unmodified- and modified PE/EVA/ CaCO_3 were prepared in the internal mixer Haake (German) connected to PolyLab 3.1 software to conduct the mixing process. The above components were mixed at 160°C , mixing speed of 40 rpm during 5 minutes. The composition ratio of PE/EVA and PE-g-AAc/EVA was 30/70 (wt./wt.) in all samples investigated.

2.3 The experimental methods

- *Relative melt viscosity* of the composites was expressed on the torque – mixing time diagrams of the mixture recorded by PolyLab 3.1 software connected to Haake device.
- *Morphology of the composites* was observed on the scanning electron micrographs (SEM) taken by SEM - JEOL 5300 Instrument (Japan) with magnification of 1000 times.
- *Mechanical properties of the composites* were determined according to ASTM-D 638 – 84 with Universal ZWICK Instrument (Germany).

- *Thermostability of the composites* was evaluated based on thermogravimetric analysis (TGA). The process of TGA was carried out with TA Instrument (Shimadzu DT 30A TGA) at a scanning rate of 10°C/min. in natural air.

3. RESULTS AND DISCUSSION

3.1 Relative melt viscosity of the composites of PE-g-AAc/EVA/CaCO₃

Relative melt viscosity of the composites is expressed by torque during mixing the components in the melt state. Diagram in figure 1 exhibits the dependence of torque on mixing time of polymer blend of PE-g-AAc/EVA (30/70) and the composites of PE-g-AAc/EVA/CaCO₃ (30/70/10) and PE-g-AAc/EVA/CaCO₃ (30/70/20). It is clear that the presence of CaCO₃ (10 and 20 wt.%) does not make changes in the shape of the curves of torque – mixing time of polymer blend of PE-g-AAc/EVA. The shape of the curves is similar to that of polymer blend of PE/EVA (30/70) with and without CaCO₃ (10 and 20 wt.%).

Fig. 1: Diagram of torque - mixing time of PE-g-AAc/EVA (30/70), PE-g-AAc/EVA/CaCO₃ (30/70/10) and PE-g-AAc/EVA/CaCO₃ (30/70/20).

Under the condition of high temperature and the rotate movement of the rotors, the polymers such as PE-g-AAc and EVA are melted and mixed with each other and CaCO₃. The torque of mixtures reaches almost constant value is called the stable torque. It is an important processing parameter. Table 1 shows that the stable torque of polyme blend of PE-g-AAc/EVA increases in presence of CaCO₃. This is due to limitation of movement of polymer chains of PE, EVA by solid particles of CaCO₃ in melt state. However, EVA has melt temperature and relative melt viscosity lower than PE-g-AAc, so the use of large amount of EVA (70 wt.%) makes the mixtures melt easier and the components intermix each other advantageously. Therefore, the

stable torque of composites only increase lightly with rising content of CaCO_3 . Preparation of the composites is carried out effectively at the investigated contents of CaCO_3 .

Table 1: Stable torque of the composites of PE-g-AAc/EVA (30/70) with different content of CaCO_3 .

Content of CaCO_3 (wt.%)	0	5	10	15	20
Stable torque (Nm)	6.9	7.1	7.3	7.5	7.8

3.2 Morphology of the composites of unmodified- and modified PE /EVA/ CaCO_3

In the Figs. 2a and 2b, the scanning electron micrographs (SEM) for polymer blend of PE/EVA and PE-g-AAc/EVA (in the same composition ratio of 30/70) indicate that grafting AAc onto PE improves dispersion of PE into EVA, PE dispreses into EVA more regularly with smaller size.

Fig. 2: Scanning electron micrograph (SEM) of PE/EVA (30/70) (a), PE-g-AAc/EVA (30/70) (b), PE/EVA/ CaCO_3 (30/70/20)(c) and PE-g-AAc/EVA/ CaCO_3 (30/70/20) (d).

The SEM of the composites of PE/EVA/CaCO₃ (30/70/20) (Fig. 2c) shows that CaCO₃ disperses into polymer blend of PE/EVA irregularly with large size (5 - 22 μm) and surrounding CaCO₃ particles, there are holes with diameter about 8 - 14 μm in the polymer blend. That indicates the bad adhesion of the particles of CaCO₃ with the polymer blend of PE/EVA. The SEM of the composites of PE-g-AAc/EVA/CaCO₃ (in the same composition ratio) demonstrates that the adhesion of the particles of CaCO₃ and polymer blend of PE-g-AAc/EVA is improved (Fig. 2d). The particles of CaCO₃ disperse into polymer blend of PE-g-AAc/EVA more regularly and with smaller size (about 3 - 10 μm). Surrounding these particles and in the polymer blend, the number and the size of holes decrease clearly. This may confirm that grafting AAc onto PE not only enhances the compatibility of PE with EVA but also improves adhesion of the particles of CaCO₃ and the polymer blend.

3.3 Mechanical properties of the composites of unmodified- and modified PE/EVA/CaCO₃

Mechanical property of unmodified- and modified PE/EVA/CaCO₃ composites in table 2 indicates that the presence of CaCO₃ considerably decrease in tensile strength and elongation at break of polymer blend of PE/EVA. This can be explained as follows: CaCO₃ exists in inorganic mineral particles with large size (figure 2a). It prevents the compatibility of PE and EVA. On the other hand, the presence of particles of CaCO₃ also rises the large holes because of the bad adhesion between these particles and polymer blend as mentioned above. In this case, the composites with some defects are easy to form [4,5,7]. Thus, tensile strength and elongation at break of the composites of PE/EVA/CaCO₃ are decreased.

Table 2: Tensile strength (σ) and elongation at break (ε) of the composites of unmodified- and modified PE/EVA/CaCO₃.

Content of CaCO ₃ (wt.%)	PE/EVA		PE-g-AAc/EVA	
	σ (MPa)	ε (%)	σ (MPa)	ε (%)
0	15.18	775	17.08	668
10	13.84	575	15.26	650
15	13.41	575	15.28	650
20	12.19	542	15.55	647

Comparing with the composites of PE/EVA/CaCO₃, the composites of PE-g-AAc/EVA/CaCO₃ exhibit the tensile strength with higher values at the same contents of CaCO₃. Elongation at break of the composites of PE/EVA/CaCO₃ is lower than that of the composites of PE-g-AAc/EVA/CaCO₃ at the contents of CaCO₃. All above obtained results permit to confirm that grafting AAc onto PE is an important reason for improvement of tensile property of polymer blend of PE/EVA reinforced by CaCO₃.

3.4 Thermostability of the composites of unmodified- and modified PE/EVA/CaCO₃

Figure 3 presents TG diagrams of the composites of PE/EVA/CaCO₃ (30/70/20) and PE-g-AAc/EVA/CaCO₃ (30/70/20). The slope of the TG curve of the composite using PE-g-AAc is lower than that of the composite using unmodified PE. The initial decomposition temperature and weight loss at 300 and 350°C of the composites of unmodified- and modified PE/EVA/CaCO₃ are performed in table 3.

Fig. 3: TG diagrams of the composites of PE/EVA/CaCO₃ (30/70/20) and PE-g-AAc/EVA/CaCO₃ (30/70/20).

Table 3: TG data of the composites of unmodified- and modified PE/EVA/CaCO₃.

Sample	Initial decomposition temperature (°C)	Weight loss (%) at	
		300°C	350°C
PE/EVA (30/70)	230.0	11.23	35.06
PE/EVA/CaCO ₃ (30/70/20)	230.7	10.96	33.79
PE-g-AAc/EVA (30/70)	231.5	9.14	20.35
PE-g-AAc/EVA/ CaCO ₃ (30/70/20)	232.4	3.30	19.09

The TG data in table 3 expresses that grafting AAc onto PE enhances thermostability not only for polymer blend of PE/EVA but also for the composites of PE/EVA/CaCO₃. The addition of CaCO₃ into polymer blends also makes the materials become more thermostable. The composite of PE-g-AAc/EVA/CaCO₃ (30/70/20) has thermostability higher than the composite of PE/EVA/CaCO₃ (30/70/20). The initial decomposition temperature of the composite using PE-g-AAc is higher than that of the composite using unmodified PE. The weight loss at the same temperature of the composite of PE-g-AAc/EVA/CaCO₃ is clearly lower than that of the composite of PE/EVA/CaCO₃. This can be explained by interfacial adhesion of the particles of

CaCO₃ and polymer blend of PE-g-AAc/EVA is better than that of the particles of CaCO₃ and polymer blend of PE/EVA. Therefore, the structure of the composite of PE-g-AAc/EVA/CaCO₃ becomes closer and more regularly. This structure is able to prevent permeation of oxygen, so reduces the thermal oxidation degradation of the composite.

4. CONCLUSION

- a. The presence of CaCO₃ (10 and 20 wt.%) changes lightly stable torque of polymer blend of PE-g-AAc/EVA.
- b. Interfacial adhesion and dispersion of the particles of CaCO₃ into polymer blend of PE-g-AAc/EVA are better than those of particles of CaCO₃ into polymer blend of PE/EVA.
- c. Tensile strength of the composites of PE-g-AAc/EVA/CaCO₃ is higher than that of the composites of PE/EVA/CaCO₃.
- d. The composite of PE-g-AAc/EVA/CaCO₃ has thermostability higher than the composite of PE/EVA/CaCO₃.

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