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The Effects of Chemical Modifiers on the Thermal Properties of Calcium Carbonate Filled Polypropylene/Ethylene Propylene Diene Terpolymer Composites

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ABSTRACT

A chemical modifier (acrylic acid) was used to improve the thermal properties of polypropylene/ethylene propylene diene terpolymer/calcium carbonate (PP/EPDM/$CaCO_3$) composites. Treated and untreated PP/EPDM composites were filled by $CaCO_3$ at 0, 20 and 40% wt. The composites were prepared using Z-blade mixer machine at 180°C and 50 rpm of rotor speed. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) methods were used to analyze the thermal properties of the composites. Thermogravimetric analysis indicated that the total weight loss of PP/EPDM/$CaCO_3$ composites decreased with the increasing filler loading for the treated and untreated composites. Meanwhile, the presence of acrylic acid was found to have increased the thermal stability and crystallinity of PP/EPDM/$CaCO_3$.

Keywords: Calcium carbonate, polypropylene, ethylene propylene diene terpolymer, chemical modifiers, composites

INTRODUCTION

Nowadays, the application of polymer composites has increased tremendously because it is a relatively easy way to obtain new materials with balanced properties. The name polyolefinic thermoplastic elastomer (TPE) has been coined to refer to a specific family of thermoplastic alloys that offers the main advantages of two types of polymeric materials, namely elastomeric behaviour at room temperature and thermoplastic behaviour at processing temperatures. This dual behaviour is obtained because the morphology consists of small rubber particles dispersed in a continuous thermoplastic matrix.

Since the past decade, the use of inorganic filler to improve the physical properties of polymer composites has become widespread, particularly in the production of high-performance materials. Adding inorganic filler can enhance their stiffness but it also results in a decrease of toughness. In order to overcome the drawback resulted by only adding elastomer or filler, a lot of work has been done on polymer/elastomer/filler ternary system, where both elastomer and filler were used to enhance the toughness and stiffness simultaneously (Zhang *et al.*, 2000; Jancar and Dibenedetto, 1995).

Acrylic acid is classified as a surface modifier in polymer composite industry. One of the methods used for rubber surfaces is surface modification using acrylic acid. Okrasa *et al*. (2001) reported that a larger modification of the molecular relaxation processes was observed in

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the hydroxypropyl cellulose: poly (acrylic acid), (HPC:poly(AA)) composites, where stronger intermolecular interactions were also present.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are commonly used to investigate the thermal properties of polymer. Thermal analysis of polymers is very important in determining their utility under various environmental conditions, high temperature application, decomposition mechanism, etc. Thermogravimetric analysis furnishes data on weight loss as a function of temperature and provides a means to estimate kinetic parameters or thermal decomposition reaction. It is also possible to establish a pyrolysis mechanism, a rapid comparison of thermal stabilities and a decomposition temperatures of different polymers. In addition, Differential Scanning Calorimetry (DSC) is thermoanalytical technique used to investigate the difference in the amount of heat required to increase the temperature of a sample while reference is measured as a function of temperature (Alonso *et al*., 1997; Dudic *et al*., 2001; Salmah *et al*., 2005).

In the previous study based on tensile properties, water absorption and morphology analysis, the present of acrylic acid on polypropylene/ ethylene propylene diene terpolymer/ calcium carbonate (PP/EPDM/$CaCO_3$) composites showed an improvement compared to untreated composites. Meanwhile, the incorporation of chemical modifiers, acrylic acid (AA) increased the tensile strength and modulus of elasticity but decreased the elongation at break. A better water resistance was shown in the treated composites with acrylic acid compared to untreated composites. The presence of acrylic acid has improved the filler-matrix distribution, adhesion and compatibility between $CaCO_3$ and PP/EPDM matrix, and it has consequently improved the properties of the composites that can be seen through the morphology analysis (Siti Rohana *et al*., 2008).

In this analysis, acrylic acid was used as a chemical modifier in order to increase the thermal properties of polypropylene/ethylene propylene diene terpolymer/ calcium carbonate (PP/EPDM/$CaCO_3$) composites.

EXPERIMENTAL DESIGN

Materials

Polypropylene used was grade S12232 G112 from Polypropylene Malaysia Sdn. Bhd. Meanwhile, ethylene propylene diene terpolymer (EPDM) grade Vistalon 2504N was obtained from Exxonmobile Chemical while calcium carbonate ($CaCO_3$) was supplied by Ipoh Ceramic Sdn. Bhd. in Perak, Malaysia. With an average particle size of 8.3µm, $CaCO_3$ was dried in a vacuum oven at 100°C for 4 hours to remove its moisture. Acrylic acid anhydrous coupling agent grade 01730 was supplied by Fluka. Table 1 shows the formulation for both the untreated and treated PP/EPDM/$CaCO_3$ composites used in this study.

Filler Treatment

Calcium carbonate was modified using 3% acrylic acid in ethanol and stirred for 1 hour. The calcium carbonate was filtered out, washed with distilled water and dried in oven at 80°C for 24 hours.

Mixing Procedure

The mixing of composites was prepared in Z-blade mixer machine for 15 minutes at the temperature of 180°C and rotor speed of 50 rpm. Firstly, polypropylene was discharged to the chamber and allowed to melt. The polypropylene was completely melted in 7 minutes. Then, $CaCO_3$ was added, and this was followed by EPDM at tenth minute. Mixing was continued for 5 more minutes, and was completed in 15 minutes. For the treated composites, the sequences were similar to that of the untreated composites.

The formulation of PP/EPDM/$CaCO_3$ composites with acrylic acid was similar to the preparation of the untreated PP/EPDM/$CaCO_3$ composites with different filler loadings. After 7 minutes, $CaCO_3$ treated with acrylic acid was added into the mixing chamber. *Fig. 1* shows the chemical reaction of $CaCO_3$ with acrylic acid.

Then, the composites were taken out from the mixing machine and sheeted with roll mill to obtain composites with 2.0 mm thickness. The samples were press-moulded in a compression moulding machine model GT 7014A to perform 1.0 mm sheet of composites. The hot–press procedures involve pre-heating at 180°C for 6 minutes, followed by compressing for 4 minutes at the same temperature and subsequent cooling under pressure for 4 minutes. The samples were cut from the moulded sheets by using Wallace die cutter model S/6/1/4 to obtain the dumbbell specimens (ASTM D-638).

Measurement of the Thermal Properties

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermo analytical technique. It is used to study the behaviour of heated polymer, as well as to determine the thermal transitions that take place in polymer when it is heated. In addition, DSC measures the difference in the amount of heat required to increase the temperature of a sample, while a reference is measured as a function of temperature.

The melting characteristics and crystallization behaviour of the composite samples were carried out using Perkin Elmer DSC Q10 V8.2 Build 268 analyser equipments. Samples of about 10 - 25 mg were heated from 20 to 220°C in nitrogen air flow of 50 ml/min and the heating rate of 20°C/min. The crystallinity percentage of composites (X_{com}) was determined using equation (1):

$$X_{com}\ (\%\ crystalinity) = \Delta H_f / \Delta H^0_f\, x\ 100\% \quad (1)$$

Where ΔH_f and ΔH^0_f are enthalpy of the system's fusion and enthalpy of fusion of perfectly (100%) crystalline PP, respectively. As for ΔH^0_f (PP), a value of 209 J/g was used for 100% crystalline PP. X_{com}, which is calculated using this equation. However, it gives only the overall crystallinity of the composites based on the total weight of composites including non-crystalline fractions. Also, it is not the true crystallinity of the PP phase. The value of crystallinity for PP phase of the fraction (X_{pp}) was normalized using equation (2):

$$X_{pp} = (X_{com}) / Wf_{pp} \quad (2)$$

Where Wf_{pp} is the weight fraction of PP in the composites.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical method where the change of mass of a sample as a function of the temperature and time is measured. The thermogravimetric analysis of composites was carried out using the Perkin Elmer analyzer equipments. The samples with the weight between 15 to 25 mg were scanned from 50 to 600°C using a nitrogen air flow of 50 ml/min and a heating rate of 20°C/min. The sample size was kept almost the same for all the sample tests.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry (DSC)

Fig. 2 shows the differential scanning calorimetry (DSC) curve of the untreated and treated PP/EPDM/$CaCO_3$ composites with AA at 40 php $CaCO_3$. The highest melting temperature occurred at 40 php calcium carbonate loading of the treated composites with AA. It could be seen from Table 2 that the value of $\Delta H^0_{f(\mathrm{com})}$ and X_{com} decreased with the increase in the calcium carbonate loading. This might be due to the decreasing PP concentration at a higher $CaCO_3$ loading. At a similar filler loading, composites with AA exhibited a higher value of $\Delta H^0_{f(\mathrm{com}),}$ X_{com} and X_{pp} than the composites without AA. The increase in crystallization of esterification with acrylic acid of PP/EPDM/$CaCO_3$ composites might be due to the enhancement of calcium carbonate as a nucleation agent.

Thermogravimetric Analysis

The comparison of thermogravimetric analysis curves of the untreated and treated PP/EPDM/$CaCO_3$ composites with AA composites at 0, 20 and 40 php $CaCO_3$ is shown in *Fig. 3*. For all the composites, the weight loss in a nitrogen atmosphere is very similar, proceeding principally in a single step which leads to significant weight losses above 350ºC with the maximum rate at 480 - 500ºC. The subsequent weight loss above 600ºC was due to the degradation of the calcium carbonate filler. It could be seen from Table 3 that degradation temperature corresponding to the major total weight loss decreased with esterification of the composite. From this table, it could clearly be observed that the treated composites with AA at higher loading of calcium carbonate have more resistance against degradation and a better thermal stability compared to the untreated composites. Consequently, this indicates that the presence of acrylic acid has increased the thermal stability in PP/EPDM/$CaCO_3$ composites.

Acrylic acid polymers are known to show a significant decomposition at 360ºC (McNeill and Sadeghi, 1990). Higher thermal stability of the polymers is due to an interaction between calcium ions and carboxylate ions. McNeill and Sadeghi (1990), McNeill (1997), and Kramer *et al*. (2007) observed that polymers formed by the reaction of calcium carbonate of acrylic acid are stable up to the temperature of 440ºC

TABLE 1
The formulation of PP/EPDM/$CaCO_3$ composites with and without AA at different loadings

Materials	PP/EPDM/$CaCO_3$ (without AA)	PP/EPDM/$CaCO_3$ (with AA)
Polypropylene (PP) (wt%)	70	70
Ethylene propylene diene terpolymer (EPDM) (wt%)	30	30
Calcium carbonate ($CaCO_3$) (wt%)	0, 10, 20, 30, 40	0, 10, 20, 30, 40
Acrylic acid (AA) (wt%)	-	3

TABLE 2
Parameters of DSC of the untreated and treated PP/EPDM/$CaCO_3$ composites with AA at different filler loadings

Composites	Melting temperature *Tm* (°C)	$\Delta H^0_{f(com)}$ (J/g)	X_{com} (% crystalinity)	X_{pp} (%)
PP/EPDM/$CaCO_3$: 70/30/0 (Untreated)	163.33	55.50	26.56	37.94
PP/EPDM/$CaCO_3$: 70/30/20 (Untreated)	163.86	46.49	22.24	38.15
PP/EPDM/$CaCO_3$: 70/30/40 (Untreated)	162.87	43.41	20.73	41.54
PP/EPDM/$CaCO_3$: 70/30/20 (Treated with AA)	163.91	70.63	33.79	57.97
PP/EPDM/$CaCO_3$: 70/30/40 (Treated with AA)	164.30	82.33	39.39	78.78

TABLE 3
Percentage of weight loss for the untreated and treated PP/EPDM/$CaCO_3$ composites with AA at different filler loadings and temperatures

Temperature (°C)	Weight loss (%)				
	Untreated			Treated with AA	
	70/30/0	70/30/20	70/30/40	70/30/20	70/30/40
100	0.00	0.21	0.07	0.01	0.02
200	0.05	0.03	0.03	0.03	0.01
300	0.73	0.47	1.14	0.12	0.06
400	11.91	8.92	12.14	1.12	0.78
500	86.96	73.15	57.68	77.28	68.05
600	0.23	0.05	0.12	2.59	1.65
Total	99.88	82.83	71.18	81.15	70.57

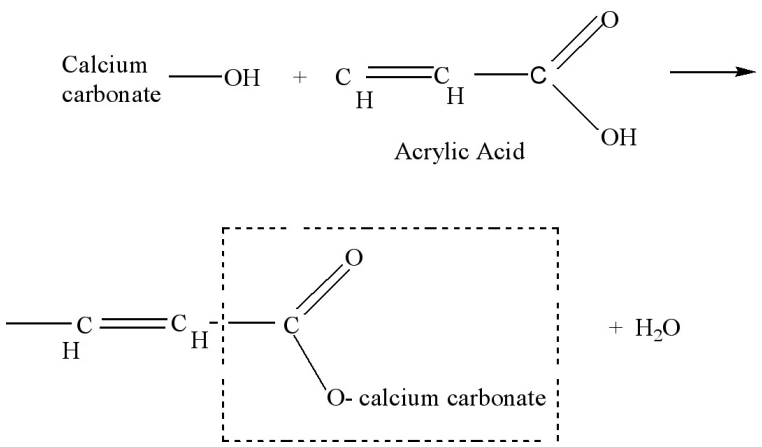

Fig. 1: Chemical reaction of calcium carbonate with AA

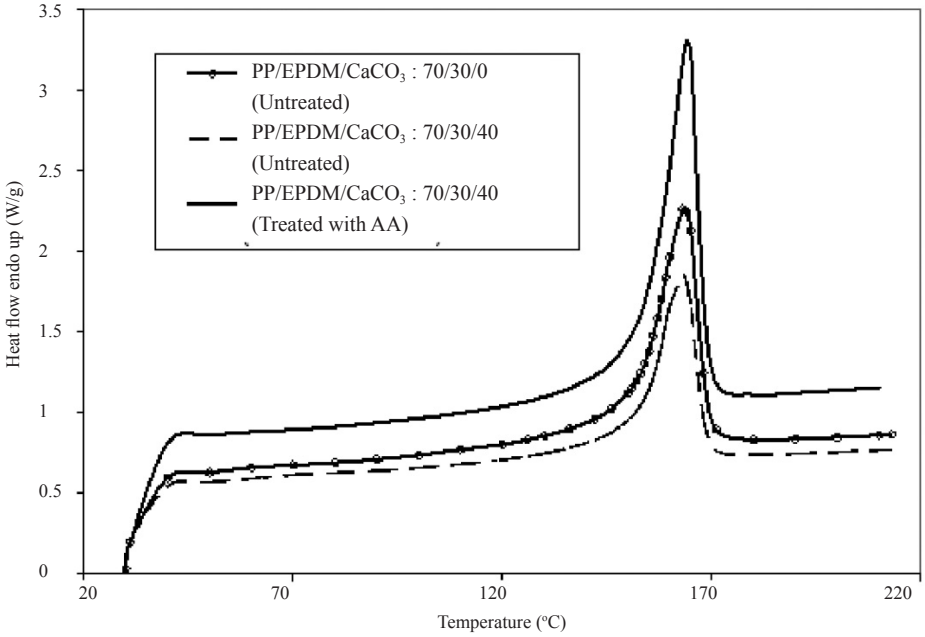

Fig. 2: Comparison of differential scanning calorimetry (DSC) curves of the untreated and treated PP/EPDM/$CaCO_3$ composites with AA at 40 php $CaCO_3$

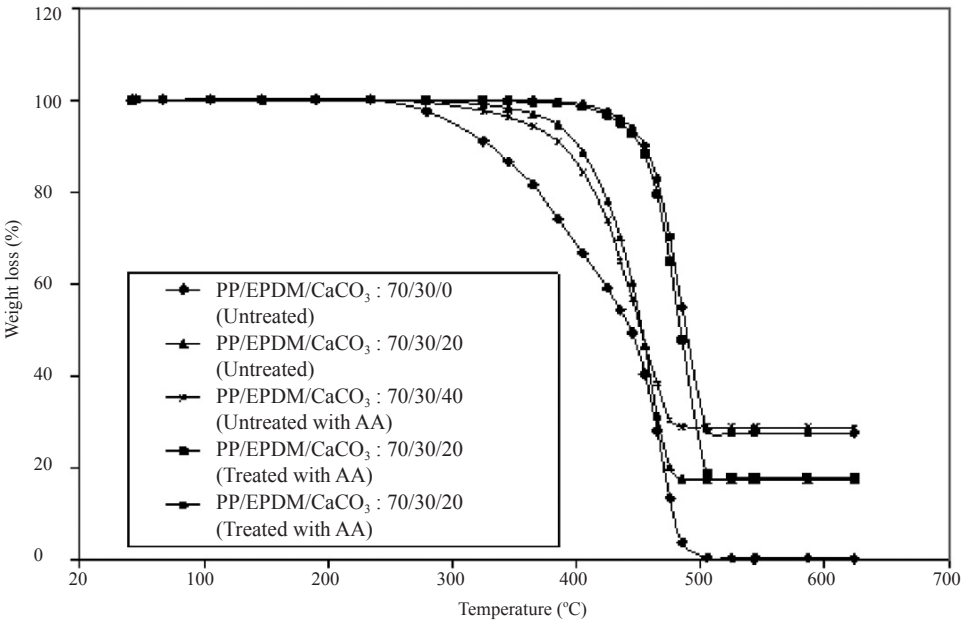

Fig. 3: Comparison of thermogravimetric analysis curves of the untreated and treated PP/EPDM/$CaCO_3$ composites with AA at different loadings

CONCLUSIONS

The thermogravimetric analysis indicates the improved thermal stability of the treated acrylic acid composites. The crystallinity of PP/EPDM/$CaCO_3$ composites increased with the presence of AA as chemical modifiers. The improvement of thermal properties could be achieved by the presence of AA due to the interaction between calcium ions and carboxylate ions.

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