

## **Effects of Dynamic Vulcanization on Thermal Properties of Calcium Carbonate Filled Polypropylene/Ethylene Propylene Diene Terpolymer Composites**

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### **ABSTRACT**

In this study, dynamic vulcanization process was used to improve the thermal properties of calcium carbonate filled composites. The composites were prepared using a Z-blade mixer at 180°C and rotor speed 50rpm. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) techniques were used to analyze the thermal properties of the composites. The vulcanized and unvulcanized PP/EPDM composites were filled by CaCO<sub>3</sub> at 0, 10, 20, 30, and 40 %wt. Meanwhile, thermogravimetric analysis indicates that the total weight loss of PP/EPDM/CaCO<sub>3</sub> composites decreased with increasing filler loading. Dynamic vulcanized composites have higher thermal stability, while the crystallinity of PP/EPDM/CaCO<sub>3</sub> composites were increased as compared to unvulcanized composites. Therefore, the thermal properties were improved by the presence of dynamic vulcanization process.

**Keywords:** Calcium carbonate, polypropylene, dynamic vulcanization, ethylene propylene diene terpolymer, composites

### **INTRODUCTION**

To date, thermoplastic elastomer compositions based on polypropylene (PP)/ ethylene polypropylene diene terpolymer (EPDM) composites have increased tremendously in application. These composites are used for a wide range of products including automotive parts such as rub strips, sight shields, bumper covers, side claddings, etc. PP/EPDM composites have excellent weatheability, low density and impose relatively low cost to make them a common component in a number of exterior and interior automotive applications (De and Bhowmick, 1990).

Mineral filler, such as calcium carbonate (CaCO<sub>3</sub>), is used in the PP/EPDM composites to reduce cost and improve the properties of the composites. Besides, this type of filler has a primary function as a mechanical property improver; for instance it can slightly increase modulus of elasticity (Zuiderduin *et al.*, 2003; Lazzeri *et al.*, 2005). In addition, it is also available in different grades, such as dry processed, wet or water ground, and can easily be surface treated (Osman *et al.*, 2004) which is usually micron-sized (easier to disperse) with a broad size distribution and irregular shapes (Ismail *et al.*, 2004).

Vulcanization or cross-linking is the process in which polymer is mainly converted from a plastic state to an elastic state or a hard rubber state. The process is brought about by linking macromolecules at their reactive sites (Ismail *et al.*, 2004). Dynamic vulcanization (DV) is a process of cross-linking the elastomer during its melt mixing with molten plastic. It can improve properties such as mechanical properties (Mehrabzadeh and Delfan, 2000), as well as resistance

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to heat and resistance to attack by fluid (Ismail *et al.*, 2001). It is quite obvious that the cross-link density of the dispersed rubber phase plays a key role in achieving higher strength (Mousa *et al.*, 1997; Jain *et al.*, 2000; Katbab *et al.*, 2000). DV also offers several improvements such as reduced set, improved ultimate properties, fatigue resistance, and resistance to hot oils.

Based on the tensile properties, water absorption and morphology analysis in the previous study, the present of dynamic vulcanization on polypropylene/ethylene propylene diene terpolymer/calcium carbonate (PP/EPDM/CaCO<sub>3</sub>) composites showed an improvement compared to unvulcanized composites such as the higher tensile strength, elongation at break, and modulus of elasticity of dynamic vulcanized composites than unvulcanized composites. Better filler dispersion and crosslink formation in PP/EPDM matrix resulted in increases of mechanical properties in the dynamic vulcanized (DV) composites. A study on water absorption indicates that the use of dynamic vulcanization reduced the amount of water absorbed by the composites. Therefore, water absorption of DV composites indicates a lower value compared to unvulcanized (UV) composites. The calcium carbonate embedded in the PP/EPDM matrix and less pores of filler pull-out were observed from the SEM analysis (Siti Rohana *et al.*, 2008).

Thermogravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to characterize a wide variety of materials. TGA provides complimentary and supplementary characterization information to the most commonly used thermal technique, i.e. DSC. A thermoanalytical technique, in which the difference in the amount of heat required to increase the temperature of a sample and reference, is measured as a function of temperature called Differential scanning calorimetry (DSC).

In this analysis, dynamic vulcanization was used to increase the thermal properties of calcium carbonate (CaCO<sub>3</sub>) filled polypropylene/ethylene propylene diene terpolymer (PP/EPDM) composites.

## EXPERIMENTAL DESIGN

### *Materials*

Polypropylene used was of grade S12232 G112 from Polypropylene Malaysia Sdn. Bhd. Meanwhile, ethylene propylene diene terpolymer (EPDM) of grade Vistalon 2504N was obtained from Exxonmobile Chemical and Calcium carbonate (CaCO<sub>3</sub>) supplied by Ipoh Ceramic Sdn. Bhd., Perak, Malaysia. CaCO<sub>3</sub> with an average particle size of 8.3µm was dried in a vacuum oven at 100°C for 4 hours to remove moisture. The types of curative include stearic acid from Acid Chem. International Sdn. Bhd., zinc oxide from Metroxide Malaysia Sdn. Bhd., N-cyclohexyl-2-benzothiazol-2-sulphenamide (CBS) from Meyors Chemical Inc. Limited, Tetramethyltiuram disulfide (TMTD) from DEUTSCHland CimbH, Germany and sulphur from Taiko Marketing Sdn. Bhd., Selangor. Table 1 shows the formulation of unvulcanized and dynamic vulcanized PP/EPDM/CaCO<sub>3</sub> composites used in this study.

### *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. For the unvulcanized composites, polypropylene was initially discharged to the chamber and it started the melt. Polypropylene completely melted after 7 minutes. Then, CaCO<sub>3</sub> was added followed by EPDM at the tenth minutes. Mixing was continued for 5 more minutes. This mixing was completed at 15 minutes.

TABLE 1  
The formulation of unvulcanized (UV) and dynamic vulcanized (DV) PP/EPDM/CaCO<sub>3</sub> composites

Materials	UV	DV
Polypropylene, PP (wt%)	70	70
Ethylene propylene diene terpolymer, EPDM (wt%)	30	30
Calcium carbonate, CaCO <sub>3</sub> (wt%)	0, 10, 20, 30, 40	0, 10, 20, 30, 40
Zink oxide (wt%)	-	5
Stearic acid (wt%)	-	2
N-cyclohexyl-2-benzothiazol-2-sulphenamide (CBS) (wt%)	-	2
Tetramethyltiuram disulfide (TMTD) (wt%)	-	2.5
Sulphur (wt%)	-	1

\*based on wt% of EPDM

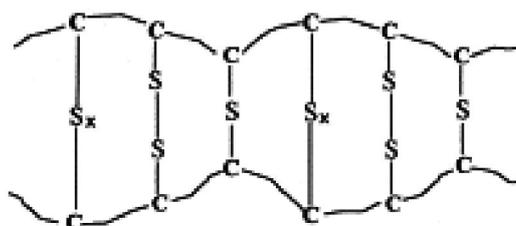


Fig. 1: Schematic representation of the crosslink formed during the dynamic vulcanization using sulphur

However, for dynamic vulcanized composites, the whole mixing process was conducted in 17 minutes. First, PP was charged into the chamber and allowed to melt, while CaCO<sub>3</sub> was charged into the chamber at 7 minutes. Meanwhile, EPDM was charged into the chamber at 10 minutes and mixing was allowed for 5 more minutes. At 15<sup>th</sup> minute, zinc oxide, stearic acid, CBS, TMTD, and sulphur were added into the chamber and mixing was continued for another 2 minutes.

Finally, the composites were then taken out and sheeted through a laboratory scale, in two roll mills at 2.0 mm nip setting. The samples were compress-moulded in a compression moulding machine (model GT 7014A) to perform 1.0 mm sheet of composites. Hot-press procedures involved a preheating 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 using Wallace die cutter model S/6/1/4 in order to obtain the dumbbell specimens (ASTM D-638).

### Measurement of Thermal Properties

#### Differential Scanning Calorimetry (DSC)

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

The melting characteristics and crystallization behaviour of the samples composites were carried out using Perkin Elmer DSC Q10 V8.2 Build 268 analyser equipment. The samples in 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 the relationship in equation (1) below:

$$X_{com} (\% \text{ crystallinity}) = \Delta H_f / \Delta H_f^0 \times 100\% \quad (1)$$

where  $\Delta H_f$  and  $\Delta H_f^0$  are enthalpy of fusion of the system and enthalpy of fusion of perfectly (100%) crystalline PP, respectively. As for  $\Delta H_f^0$  (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. Moreover, 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)

The thermogravimetric analysis (TGA) is an analytic method with that the change of mass of a sample, as a function of the temperature and time, is measured. The thermogravimetric analysis of the composites was carried out using the Perkin Elmer analyzer equipments. The sample weights 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 nearly the same for all the sample tests.

## RESULTS AND DISCUSSION

#### Differential Scanning Calorimetry (DSC)

The DSC curves of dynamic vulcanized of PP/EPDM/CaCO<sub>3</sub> composites at 0, 20 and 40 wt% are given in Fig. 2. Table 2 indicates the values of  $T_m$ ,  $\Delta H_{f(com)}^0$ ,  $X_{com}$  and  $X_{pp}$  for the unvulcanized and dynamic vulcanized of PP/EPDM/CaCO<sub>3</sub> composites. It can be seen from Table 2 that the values of  $\Delta H_{f(com)}^0$  and  $X_{com}$  for all the composites decreased with the increase in calcium carbonate loading. Dynamic vulcanized composites exhibit a higher value of enthalpy during crystallization process as compared to the unvulcanized composites. The increasing crystallinity of the DV composites was due to the increasing crosslink between calcium carbonate and matrix that increased the nucleation activity of calcium carbonate.

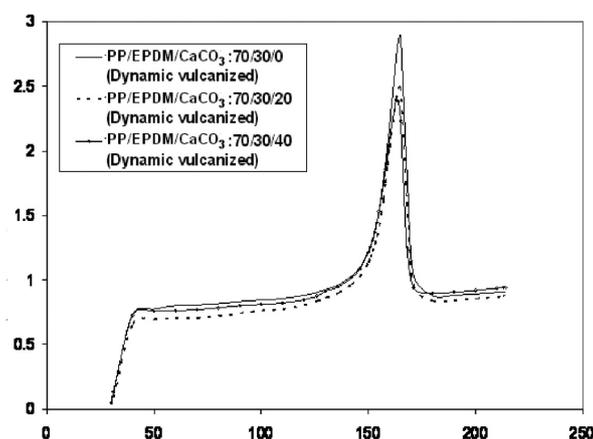


Fig. 2: A comparison of the differential scanning calorimetry (DSC) curve of the unvulcanized and dynamic vulcanized PP/EPDM/CaCO<sub>3</sub> composites at 40 php CaCO<sub>3</sub>

TABLE 2  
Parameter DSC for the unvulcanized and dynamic vulcanized PP/EPDM/CaCO<sub>3</sub> composites with different filler loadings

Composites	Melting temperature T <sub>m</sub> (°C)	$\Delta H_{f(\text{com})}^0$ (J/g)	X <sub>com</sub> (% crystallinity)	X <sub>pp</sub> (%)
PP/EPDM/CaCO <sub>3</sub> : 70/30/0 (Unvulcanized)	163.33	55.50	26.56	37.94
PP/EPDM/CaCO <sub>3</sub> : 70/30/20 (Unvulcanized)	163.86	46.49	22.24	38.15
PP/EPDM/CaCO <sub>3</sub> : 70/30/40 (Unvulcanized)	162.87	43.41	20.73	41.54
PP/EPDM/CaCO <sub>3</sub> : 70/30/0 (Dynamic vulcanized)	164.78	76.84	36.76	52.52
PP/EPDM/CaCO <sub>3</sub> : 70/30/20 (Dynamic vulcanized)	164.64	68.20	32.63	55.97
PP/EPDM/CaCO <sub>3</sub> : 70/30/40 (Dynamic vulcanized)	163.41	61.30	29.33	58.66

The heat of fusion values is dependent on the crystallinity of the material. In the case of compatible blends, the decrease in the melting temperature is related to the extent of interaction between the components. Choudhary *et al.* (1991), George *et al.* (2000), and Xiao *et al.* (2002) reported a similar result in the DSC curves of dynamic vulcanized composites. Ha *et al.* (1986) reported that cross-linking of EPDM in the molten PP restricted the crystallinity of PP.

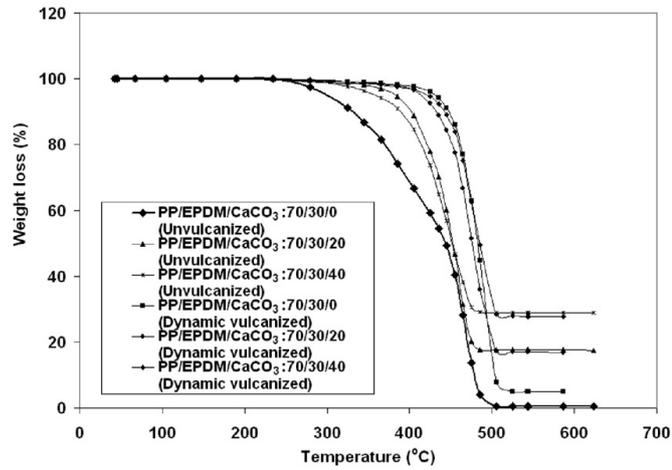


Fig. 3: A comparison of the thermogravimetric analysis curves of the unvulcanized and dynamic vulcanized PP/EPDM/CaCO<sub>3</sub> composites at 20 and 40 php CaCO<sub>3</sub>

*Thermogravimetric Analysis*

The thermogravimetric analysis (TGA) curve of unvulcanized and dynamic vulcanized of PP/EPDM/CaCO<sub>3</sub> composites at 0, 20, and 40 php of calcium carbonate loading are shown in Fig. 3 and summarized in Table 3. It can be seen from Table 3 that the total weight loss of the dynamic vulcanized composites is lower than the unvulcanized composites. The better thermal stability of dynamic vulcanized composites might be due to the presence of inorganic curing agents such as zinc oxide, stearic acid and accelerator, etc. Generally, the vulcanization of rubbers improves the degradation temperature because more energy is required to break the bonds formed during vulcanization. All of the PP/EPDM/CaCO<sub>3</sub> composites were vulcanized using the sulphur system.

TABLE 3  
Percentage of weight loss for the unvulcanized and dynamic vulcanized PP/EPDM/CaCO<sub>3</sub> composites at different filler loadings and temperatures

Temperature (°C)	Weight loss (%)					
	Unvulcanized			Dynamic vulcanized		
	70/30/0	70/30/20	70/30/40	70/30/0	70/30/20	70/30/40
50-100	0.00	0.21	0.07	0.05	0.10	0.02
100-200	0.05	0.03	0.03	0.16	0.07	0.01
200-300	0.73	0.47	1.14	0.61	0.78	0.68
300-400	11.91	8.92	12.14	1.41	2.11	2.12
400-500	86.96	73.15	57.68	87.24	77.50	64.20
500-623	0.23	0.05	0.12	5.68	1.45	3.22
Total	99.88	82.83	71.18	95.15	82.01	70.25

## CONCLUSIONS

The Differential Scanning Calorimetry analysis indicated that the increasing crystallinity of DV composites was due to the increasing crosslink between calcium carbonate and matrix that subsequently improved the nucleation activity of calcium carbonate. In the thermogravimetric analysis, the total weight loss of the dynamic vulcanized composites was lower than the unvulcanized composites. The better thermal stability of the dynamic vulcanized composites might be due to the presence of inorganic curing agents such as zinc oxide, stearic acid and accelerator, etc. The improvement is dependent on the formation of more crosslinks between rubber chains.

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