MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF NANO-ZnO FILLED PP/EPDM BLENDS

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The effect of different blend ratios and nano-ZnO addition on mechanical and thermal properties of thermoplastic elastomer based on polypropylene (PP) and Ethylene Propylene Diene Monomer (EPDM), was studied. Phase morphology observation of the blends was carried out using SEM. The addition of EPDM into PP significantly decreased the tensile strength and tensile modulus of the composite samples. As expected, the elongation at break increased with addition of EPDM due to EPDM flexibility. Tensile strength and tensile modulus were slightly increased with incorporation of 2 vol.% of nano-ZnO into the blends; however, the elongation at break decreased due to the increase in brittleness. Through TGA, EPDM based composite was observed to have better thermal stability compared to PP based and the blends. Morphological studies on the cryogenic-fractured surface of the samples revealed the immiscibility of the blends through the presence of EPDM cavitations.

Keywords: Mechanical, Thermal, Morphology, Nanocomposite

INTRODUCTION

Nowadays, thermoplastic elastomers (TPEs) are among the rapidly growing materials in the polymer industry and have extremely high potential growth in the future. Owing to unique combination of elastic property of elastomer with the ease of processability inherently belonging to thermoplastic polymers, many commercial TPEs have been developed for various applications such as footwear, cable insulation, medical industries, packaging, piping etc [1, 2]. PP and EPDM blend is a special class of TPEs which has been widely reported by many researchers [1-5]. PP, as a thermoplastic resin has a number of advantages such as low cost, good processability and good mechanical properties at room temperature. However, due to relatively high glass transition temperature, PP shows brittle behavior at low temperatures. In order to improve the impact strength at low temperatures, PP has been usually blended with elastomers, and EPDM is one of the extensively used elastomers in the blend.

PP/EPDM blends are used primarily in the automotive industries to the manufacturing of profiles, hoses, and car bumpers, as well as in other segments as tooth brushes, handle tools, and covering wire [6]. In addition, due to low dielectric constant and high electric resistance of PP/EPDM TPEs, they are desirable for electrical applications [2]. The flexibility of EPDM over a wide temperature range and its resistant to moisture and weather makes it a good way of developing PP/EPDM blend as TPE candidate for high voltage insulators [7].

In the present work, ZnO nanofiller was added into PP/EPDM which was blended at various ratios. The effect of different blend ratios and nanofiller addition on the mechanical and thermal properties of PP/EPDM nanocomposites was studied. The results were supported by morphological observation using scanning electron microscopy (SEM).

MATERIALS AND METHODS

Material

Commercial grade of homopolymer PP (Titanpro 6431) with melt index of 7 g/10min and density of 0.9 g/cm^3 was supplied by Titan Polymer (M) Sdn. Bhd. EPDM grade Buna 3950 (Mooney viscosity: 24 ± 5 MU, ML (1+4) 125°C, density: 0.86) containing 69 wt % ethylene and 11.5 ethylidene norbornene was supplied by Bayer (M) Sdn. Bhd. Dicumyl peroxide (DCP) was also supplied by Bayer (M) Sdn. Bhd. Zinc oxide (ZnO) with the average particle size of 35 nm from Sigma Aldrich was used as filler in this study. The surface of the nanofiller was not functionalized and used as purchased.

Sample Preparation

The compounding process of PP/EPDM/ZnO was carried out in a Haake internal mixer with the total mixing time of 10 minutes according to the formulations given in Table 1. PP was first discharged into the mixer to allow it melted for 3 minutes which was then followed by the addition of EPDM. After 5 minutes, ZnO was added and mixed for 3 minutes. Then, DCP was added into the blend and mixed for another 2 minutes. Finally, the samples were

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compression molded at 180 °C in an electrically heated hot press. It is noted that for pure EPDM and EPDM/ZnO, the optimum cure time (t_{90}) was initially determined before the compression moulding. This was done at 170 °C by using Monsanto Rheometer, model MDR 2000. The t_{90} for both samples were 9.90 and 9.82 minutes, respectively. The compression molding temperature used for these EPDM based samples was 170 °C.

Tensile Test

Tensile testing according to ASTM D638 was conducted by using an INSTRON testing machine. 5 dumbbell samples from each formulation were prepared by using Wallace die cutter with the gauge length of 50 mm. The dumbbell samples were stretched at a speed of 50 mm/min.

Thermogravimetric Analysis (TGA)

TGA and derivative TGA of the blends were obtained from Perkin-Elmer Pyris 6 TGA analyzer. Samples of 10 mg were prepared for the test. The samples were heated from 30–600 °C at 20° C/min in a nitrogen atmosphere.

Differential Scanning Calorimeter (DSC)

DSC measurements were performed using Perkin-Elmer DSC-6. Samples of about 5–10mg crimp-sealed in aluminum pans were first heated at 50 °C/min from room temperature to 200 °C under nitrogen atmosphere and held for 5 min to eliminate previous thermal history. The sample was then cooled from 200 °C to 50 °C at a heating rate of 20 °C/min. Subsequently, the sample was heated again from 50 °C to 200 °C at 20 °C/min. The percentage of crystallinity was calculated from the ratio of the heat of fusion on the blend to that of the 100% crystalline PP (ΔH_{PP} = 138 J/g) [8].

Scanning Electron Microscope (SEM)

The morphological analysis of 100PP/2ZnO, 75PP25EPDM/2ZnO, 50PP50EPDM/2ZnO and 100EPDM/2ZnO was carried out using SEM (model ZEISS SUPRA 35 VP). The samples were first cryogenically fractured using liquid nitrogen. For 75PP25EPDM/2ZnO and 50PP50EPDM/2ZnO samples, after fractured they were etched by using toluene at 23°C for 1 hour in an ultrasonic cleaner in order to remove EPDM phase from the fractured surface. After that, the samples were coated with gold palladium layer using Sputter Coater Polaron SC and ready to be analyzed.

Table 1. Formulations used in the preparation of PP/EPDM/ZnO.

Formulation	PP (wt. %)	EPDM (wt. %)	ZnO (vol. %)	DCP (phr)
100PP	100	-	-	-
85PP15EPDM	85	15	-	2
75PP25EPDM	70	25	-	2
50PP50EPDM	50	50	-	2
100EPDM	-	100	-	2
100PP/2ZnO	100	-	2	-
85PP15EPDM/2ZnO	85	15	2	2
75PP25EPDM/2ZnO	75	25	2	2
50PP50EPDM/2ZnO	50	50	2	2
100EPDM/2ZnO	-	100	2	2

RESULTS AND DISCUSSION

Tensile Properties

Tensile properties of PP/EPDM blends filled with ZnO nanofiller were evaluated. Fig. 1(a) and (b) shows tensile strength, tensile modulus and elongation at break of the samples as a function of the blend ratio of PP and EPDM. The strength of PP specimens was observed to be approximately 30 times greater than the virgin EPDM. With the increase of EPDM content in the composite samples, tensile strength decreased accordingly. Furthermore, the strength of the composite samples increased slightly with the addition of ZnO. The same trend was observed in the tensile modulus with and without presence of ZnO nanofillers in PP/EPDM blends. The observed decrease in the strength and modulus with the increase of EPDM proportion was well expected as the soft EPDM phase had decreased the crystallinity of PP phase (refer to Table 2). Based on the previous work [9], the spherulite growth of isotactic PP in blends with rubber was hindered by the presence of the rubber phase. Meanwhile, the increase in the strength and modulus of the filled samples was due to the presence of ZnO that acted as reinforcing filler in the blend [10]. As expected, the elongation at break showed the opposite behavior with the tensile strength and tensile modulus as it increased with EPDM content. This can be explained by the rubbery nature and flexibility of EPDM. After the addition of ZnO, the elongation also decreased as the fillers increased the brittleness of the composite samples.

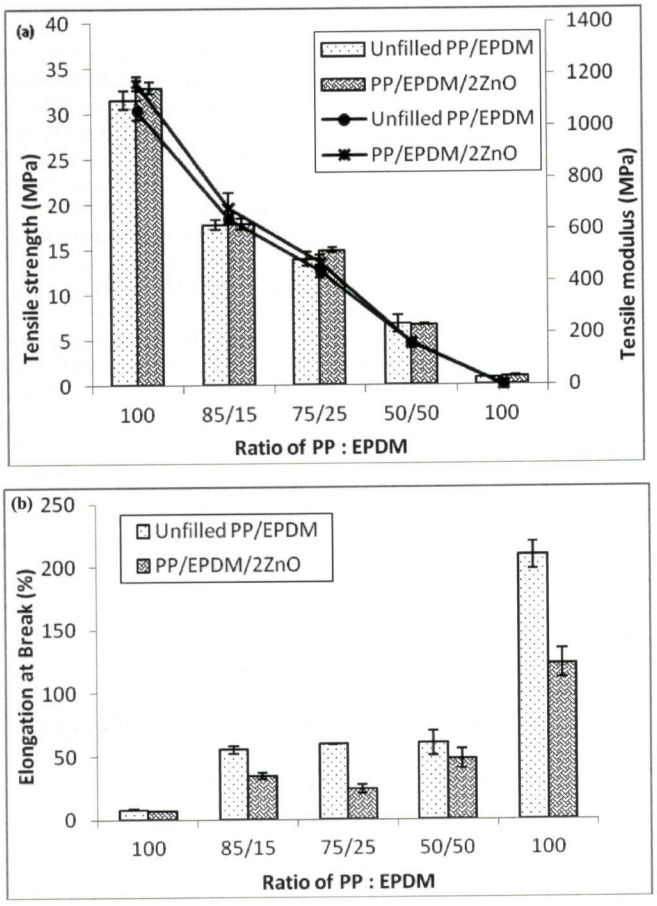

Fig. 1. (a) Tensile strength and tensile modulus; (b) elongation at break of PP/EPDM/ZnO nanocomposites.

Thermal Properties

The effect of different blend ratio of PP and EPDM on thermal behaviour of PP/EPDM/ZnO nanocomposites is revealed through TGA spectra and DTG curves as shown in Fig. 2. It was observed that the stage of degradation for all samples occurred at 400-500 °C. Each stage of degradation on the TG curves is reflected in one maximum peak on the DTG curves. The temperature of maximum peak (T_{max}) in each stage of degradation corresponds to the degradation temperature of the maximum rate as listed in Table 2. The blends were noticed to start early degradation compared to both PP and EPDM based polymer especially for the blend with high PP content. This is probably due to the presence of DCP which had lead to degradation of PP [11]. The purpose of adding DCP was to introduce crosslinking between PP and EPDM; however, this crosslinking was relatively low at high percentage of PP [12]. According to Huang et al., [11] at high temperature, the degradation of PP caused by DCP occurs when the cured EPDM is dispersed in PP matrix. Furthermore, with the increase in EPDM content, the degradation temperature was slightly increased. This can be explained by the crosslinking reaction which was prominent at high EPDM content, bringing out thermal stability to some extent by introducing crosslinks at the interface of PP and EPDM [13]. The higher thermal stability experienced by EPDM based compared to PP and the blends was the result of chemical crosslinking by DCP which restricted the mobility of polymer chain.

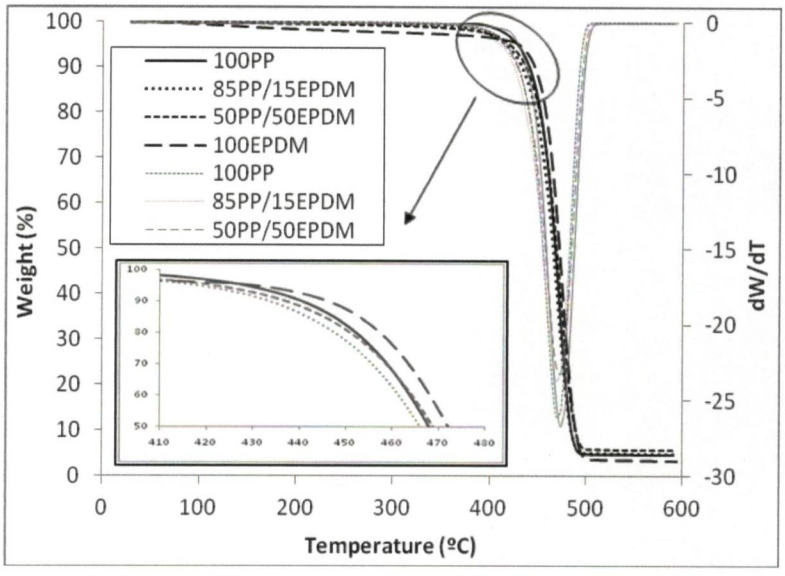

Fig. 2. TGA and DTG curves of PP/EPDM blends.

Table 2. Degradation temperature, weight residue and crystallinity of PP/EPDM blends.

Sample	Degradation temperature, $T_{5\%}$ (°C)	Maximum degradation temperature, T_{max} (°C)	Weight of residue (%)	Crystallinity (%)
100PP	424	472	4.588	77.3
85PP15EPDM	416	470	4.842	43.9
50PP50EPDM	419	473	5.741	26.7
100EPDM	428	475	3.288	-

Morphology

The morphology of the fracture surface of the composite samples is shown in Fig. 3. Fig. 3(a) represents the micrograph of PP/ZnO which is characterized by the dispersed ZnO nanofillers in PP matrix phase. The presence of nanofillers was associated with the slight improvement in the tensile strength and tensile modulus as in Fig. 1(a). The addition of EPDM into PP matrix resulted in two-phase morphology which indicated that the blend was immiscible. This is in accordance with Tang et al., [14] in their study on the effect of dynamic photocrosslinking on PP/EPDM blends where they stated that PP and EPDM are immiscible in the blends through the presence of two-phase morphology. The EPDM was observed to present as dispersed particles in the continuous PP matrix. The formation of cavities which is observed in Fig. 3(b) was associated to the extraction of EPDM particles from PP during etching with toluene. With the increase of EPDM content up to 50% as shown in Fig. 3(c), the inversion of dispersed phase to continuous phase of EPDM was observed which was characterized by the large cavities formed throughout the blend. Fig. 3(d) shows the continuous phase of EPDM characterized by a smooth, rubbery failure (which is a smooth failure in the case of rubber samples without the formation of cracking). The nanofillers were observed to have good dispersion in PP based (Fig. 3a) and in the blends (Fig. 3b and c), but not in EPDM based (Fig. 3d) where the distribution was found to be very poor and the agglomeration of particles was observed everywhere (refer to circled area).

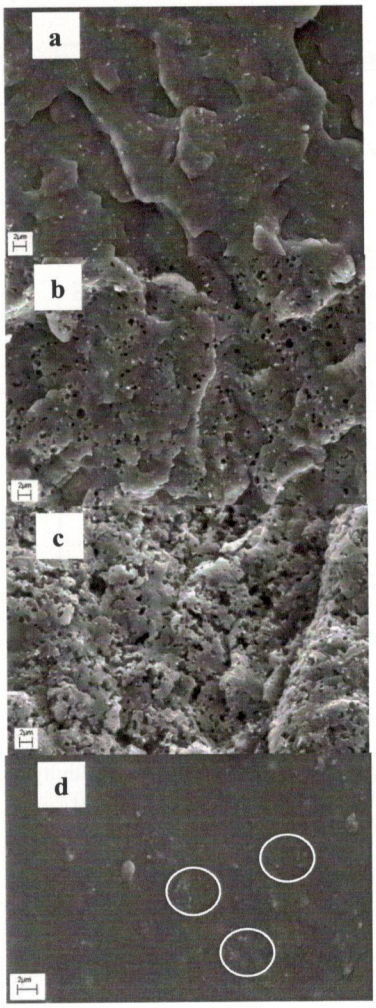

Fig. 3. SEM micrographs of (a) 100PP/2ZnO; (b) 85PP15EPDM/2ZnO; (c) 50PP50EPDM/2ZnO; (d) 100EPDM/2ZnO

CONCLUSIONS

Increase of EPDM content in the PP/EPDM blends reduced the tensile strength and tensile modulus of the blends due to the decrease in crystallinity. However, their elongation at break increased as the presence of rubber gave flexibility to the samples. The addition of nanofiller slightly improved the tensile properties of the nanocomposites. The blends started to degrade at lower temperature than those of pure PP and EPDM due to the presence of DCP that affect their thermal stability. PP and EPDM blend is immiscible which is defined through the presence of two-phase morphology in the volume. The as-received nanoparticles were poorly dispersed in pure EPDM where particle agglomerates were clearly observed.

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