Mechanical and Morphological Properties of White Rice Husk Ash Filled Polypropylene/Ethylene-Propylene-Diene Terpolymer Thermoplastic Elastomer Composites

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ABSTRACT: The performance of white rice husk ash (WRHA) as filler for polypropylene (PP)/ethylene–propylene–diene terpolymer (EPDM) thermoplastic elastomer (TPE) composites was investigated. The composites with different filler loadings were prepared in a Brabender plasticorder internal mixer. Both unvulcanized and dynamically vulcanized composites were prepared. Mixing and vulcanization processes of the composites were monitored through the typical Brabender torque–time curves. The mechanical properties and morphology of the composites were also studied. The Brabender torque curves revealed that the dynamic vulcanization process employed was successful and incorporation of filler has no adverse effect on the processibility of the composites. Incorporation of WRHA improves the tensile modulus and flexural modulus and lowers tensile strength, elongation at break, tear strength, and toughness of both types of composites. Dynamic vulcanization significantly enhances the mechanical and TPE properties of the composites. Dynamic mechanical analysis (DMA) study revealed the existence of two phases in both types of composites. It further shows that neither dynamic vulcanization nor filler agglomeration has played a prominent role in the compatibility of the composites. Thermogravimetric investigation shows that dynamic vulcanization or WRHA loading has not adversely affected the thermal stability of the composites. The scanning electron micrographs provide evidence for the tendency to form filler agglomerates with increasing filler loading, better filler dispersion of dynamically vulcanized composites over unvulcanized composites, and effective vulcanization of elastomer phase of the composites in the presence of filler. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 438–453, 2002

Key words: mechanical properties; morphology; thermoplastic elastomer composites; white rice husk ash; ethylene–propylene–diene terpolymer; polypropylene; dynamic vulcanization

INTRODUCTION

Thermoplastic elastomers (TPEs), particularly prepared through melt blending, have become a highly demanding class of materials replacing many conventional materials in various applications.[1–4] Apart from their dual characteristics of vulcanized rubber and thermoplastic properties, the possibility of adjusting their properties by different routes has caused TPEs to be a versatile class of materials. Incorporation of various additives is one such route. Among the different classes of additives, fillers are widely used addi-

tives in significant ratios in plastic and elastomer industry. A considerable amount of work was reported on this subject.[5–8] Incorporation of filler into a plastic or rubber matrix enhances some properties at the expense of some other properties. They may also affect the rheological properties (processibility), vulcanization properties, elastomeric properties, and so on. Incorporation of fillers into TPEs may have additional influences too. They could affect the compatibility of the components of the composite and its TPE properties, and so on. However, utilization of fillers in these types of blends has not gained much interest and is rarely reported. In the face of a growing number of polymer blends with different properties, it is important to study a new class of polymer blends (in the form of polymer composites) through incorporation of fillers into the blends as a means of further cutting down the material cost in competitive markets and achieving a different combination of properties. Magnesium hydroxide was used as filler in blends of polypropylene (PP) and different elastomers to achieve fire-retardant properties.[9] Another study carried out by Kuriakose and De[10] has shown that incorporation of carbon black and silica increases the storage and loss modulus of the natural rubber/PP TPEs. This study was based on single-filler loading and the influence of the filler loading on the performance of TPE properties was not addressed. Akhtar et al.,[11] who studied the use of silk fiber loading on fiber-reinforced TPEs of natural rubber and polyethylene, revealed that the tensile and tear properties were substantially enhanced, whereas ultimate elongation drastically decreased with increasing fiber loading. Consequently, TPE properties disappeared. Similar observations were reported by Gupta et al.,[12] who studied the glass fiber reinforced PP/ethylene–propylene–diene terpolymer (EPDM) blends. These limited investigations encourage the investigation of application of fillers into TPE composites.

In the present study, white rice husk ash (WRHA), a particulate-type filler which is derived from open burning of rice husk, was used as a filler for both unvulcanized and dynamically vulcanized PP/EPDM blends. Apart from high content of silica (Table I), utilization of WRHA offers some economical and environmental advantages too. Simplicity of the conversion process of waste rise husk to WRHA, abundance of the raw material in rice producing countries, and lack of established applications of rice husk or its derivatives

Table I   Chemical Composition of WRHA

Chemical Substance	Amount % (w/w)
CaO	0.1
MgO	0.4
Fe_2O_3	0.1
K_2O	1.6
Na_2O	0.1
Al_2O_3	trace
P_2O_5	trace
SiO_2	96.2
Lost on ignition	1.6

in large scale guarantee a low-cost silica-rich filler (WRHA). Conversion of the rice husk ash to an industrial raw material also contributes to solving the disposal problem of waste rice husk. It was also shown by other workers who used WRHA as a filler in elastomers and plastics that incorporation of filler could improve some mechanical properties of the composites.[13–14] PP/EPDM TPE was selected as the matrix of the composites in this study, as it is a widely used and demanded material in many applications because of its suitability for applications requiring outstanding aging and weathering characteristics, ozone and heat resistance, ease of fabrication, and low cost.[15] Therefore, this investigation determined the potential of WRHA as a large-scale filler in PP/EPDM composites. The work presented here focuses on the effect of dynamic vulcanization of the elastomer component of the plastic/elastomer composite (particularly in the presence of filler) and filler loading on the mechanical and morphological properties of the TPE composites. In addition, the influence of filler and dynamic vulcanization on the thermal stability of the composites are briefly discussed.

EXPERIMENTAL

Materials

The polypropylene used was a homopolymer (TITANPRO 6431) that was purchased from Titan PP Polymers (M) Sdn. Bhd., Johor, Malaysia with a melt flow index (MFI) value of 7.5 g/10 min at 230°C and a density of 0.9 g/cm³. The EPDM used was grade 950 from Mardec Precision (M) Sdn. Bhd., Penang, Malaysia with 4.5% of ethylidene-2-Norbonene (ENB) as a termonomer and 69% of ethylene content. Mooney viscosity (ML-4 at

Table II   Formulations Used in WRHA-Filled PP/EPDM Composites

Blend Code	PP (g)	EPDM (g)	WRHA (g)	Curative System[a]	% of EPDM by Weight
Unvulcanized Blend Systems					
UV0	50	50	0 (0)[b]	—	50
UV15	50	50	15 (13.04)	—	43.47
UV30	50	50	30 (23.08)	—	38.46
UV45	50	50	45 (31.03)	—	34.48
UV60	50	50	60 (37.50)	—	31.25
Dynamically Vulcanized Blend Systems					
DV0	50	50	0 (0)	X	50
DV15	50	50	15 (14.93)	X	43.47
DV30	50	50	30 (24.56)	X	38.46
DV45	50	50	45 (32.23)	X	34.48
DV60	50	50	60 (38.48)	X	31.25

[a] X; curative system contains zinc oxide 5.0%, stearic acid 1%, TMTD 0.2%, MBTS 0.1%, and sulphur 0.4% based on EPDM phase only.
[b] Parentheses indicate the calculated percentage by weight of total inorganic materials (including ZnO in the case of DV systems) of the composites.

100°C) and density of the elastomer were 24 ± 5 and 0.86 g/cm^3, respectively. WRHA with mean particle size of 5.4 μm; surface area of 1.4 m^2/g, and density of 2.2 g/cm^3 was obtained from Bernas Dominals Sdn. (M) Bhd., Kedah, Malaysia. The chemical composition of WRHA is shown in Table I.

Preparation of Blends

Table II shows the different formulations of WRHA in PP/EPDM composites used in this study. WRHA-filled 50/50 : PP/EPDM composites with different WRHA loadings were prepared in a Brabender plasticorder model PLE 331 coupled with a mixer/measuring head (W50H) at of 180°C and a rotor speed of 50 rpm. The melt mixing was conducted for 9 min. EPDM was first charged and preheated for 1 min prior to starting the melt mixing. The mixing sequence of the components was based on the author's previous report.[16] At the end of 10 min, the blend was taken out and sheeted through a laboratory scale two-roll mill at 2.0-mm nip setting. The corresponding dynamically vulcanized blends were also prepared in the same internal mixer under identical conditions except for an additional 1-min melt mixing.

The recipe used for dynamic vulcanization is also shown in Table II, which was suggested by Coran and Patel[17] for the dynamic vulcanization of unfilled PP/EPDM blends. However, to suit the filled systems, the mixing sequence of the curing ingredients was modified. Here, zinc oxide and stearic acid were mixed with WRHA and the mixture was charged to the chamber at the end of the second minute of shearing of EPDM. Another 2 min later (at the fifth minute), PP was added and was then followed by the additional mixture of TMTD and MBTS at the next minute. Mixing was allowed to continue for another 1.5 min and then sulfur was added. Mixing was continued for another 3.5 min until a maximum torque was achieved. Upon completion of the mixing cycle, the blend was taken out and passed through the two-roll mill. The sheet obtained was cut into small strips and charged back to the mixer and mixed for another 2 min at the same temperature and shear rate. The melted mass was then removed and sheeted again as before. Both unvulcanized (UV) and dynamically vulcanized (DV) blends were compression molded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 190°C for 6 min, followed by compressing for 4 min at the same temperature, and subsequent cooling under pressure for 4 min for the unvulcanized system. For dynamically vulcanized samples, the blends were compression
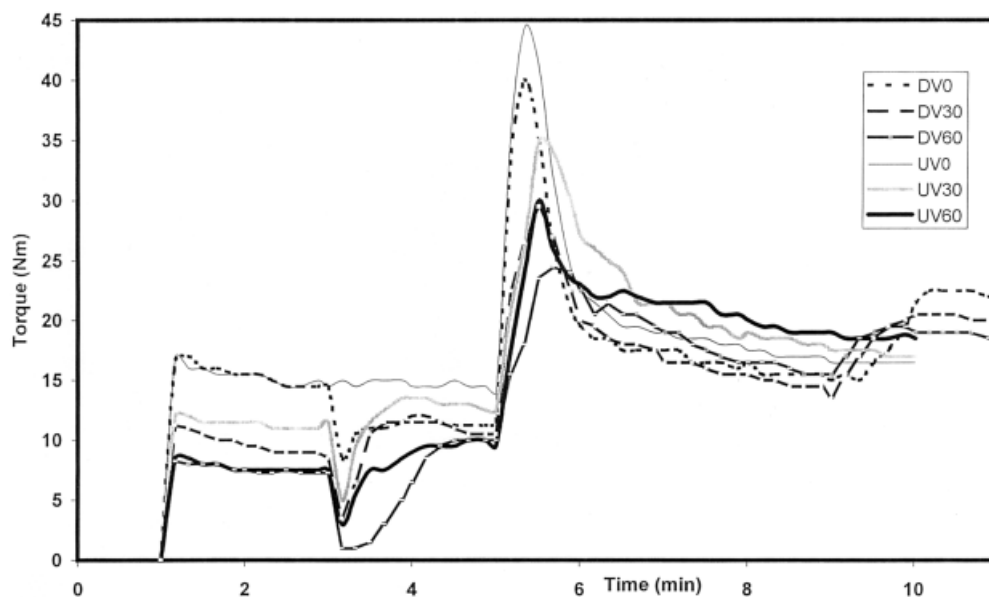
Figure 1 Mixing torque–time curves for WRHA-filled 50/50 : PP/EPDM composites with different filler loadings at 180°C and 50 rpm.

molded for 4 min after 4 min preheating at the same temperature. The molded sheet was immediately cooled under pressure for another 4 min.

Measurements

Tensile tests were carried out according to ASTM D638 on a Testometric tensometer M 500. Two-millimeter-thick dumbbell specimens were cut from the molded sheets with a Wallace die cutter. A crosshead speed of 50 mm/min was used and the tests were performed at $25 \pm 3°C$. Five specimens were used and the average was calculated in each case. Tear strength and flexural modulus were measured at same temperature using the same tensile machine according to ASTM D 624 and ASTM D 790-92, respectively. The morphologies of the tensile fracture surfaces were carried out by using a scanning electron microscope model Leica Cambridge S-360. The objective was to study the failure behavior of fracture surfaces. All the surfaces were examined after sputter coating with gold to avoid electrostatic charging and poor image resolution.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was carried out with a Perkin–Elmer 7 series thermal analysis system in the temperature/time-scan mode with a parallel plate. Temperature/time scanning was performed from -100 to $250°C$ at a heating rate of $5°C/min$ and frequency of 1 Hz.

Thermogravimetric Analysis

Thermogravimetric analysis of the composites was carried out with a Perkin–Elmer Pyris 6 TGA analyzer from 50 to $900°C$ at a nitrogen air flow of 50 mL/min and at a heating rate of $20°C$ min.

RESULTS AND DISCUSSION

Torque–Time Curves

The torque–time curves of UV and DV composites for 0, 30, and 60 php loading are shown in Figure 1. EPDM is charged into the mixer at the beginning and was allowed to preheat for 1 min. As rotors start at the end of the first minute, a sharp increase in torque is registered because of the resistance exerted by the EPDM elastomer against the rotors. The torque maxima around the first minute shows a decrease with filler loading due to subsequent decrease in the charge quantity of EPDM into the mixer (Table II). However, at the same filler loading, UV and DV blends exhibited more or less the same torque maxima as the same amount of EPDM charged in both cases. As mixing progresses, the torque shows an insignificant decrease, suggesting that EPDM was not

subjected to a mechanical degradation under the prevailing mixing conditions. Mechanical degradation of macromolecules causes a reduction in viscosity leading to a drop of the torque. A sharp decrease in the mixing torque was observed immediately after addition of filler (UV blends) or filler and additives (DV blends) at the third minute. This indicates the lubricant action of finer WRHA particles and additives. A similar drop in torque, immediately after the addition of additives such as fillers and curative ingredients, has been reported elsewhere.[16,18–19] Subsequent increases of the torque indicate the dispersion of WRHA in EPDM matrix. With dispersion of filler particles into the polymer matrix, the mobility of macromolecules of polymers was interrupted. Consequently, torque starts to rise. Upon completion of filler dispersion, the melt homogenizes at a torque value slightly higher to the pervious equilibrium torque value (1.5–3 min). However, UV0 blend shows a stable torque without such a drop in torque at the third minute, as additives (filler or curative ingredients) were not added for this system. This stable torque shows a slight decrease until the fifth minute, which may be due to a reduction in viscosity due to increase in stock temperature.

At the fifth minute, at which cold PP was charged into the mixer, a sharp peak is registered. This abrupt rise in torque represents the loading and fusion peak of PP. As fusion of PP is completed, torque starts to decrease gradually due to a decrease in viscosity to settle at a more or less stable value. A continued slight decrease in torque after initial stabilization at the end of fusion indicates a reduction of melt viscosity, as torque is an indirect indication of the viscosity.

Examination of torque values further reveals that final near-equilibrium torque values of UV composites show only a slight rise with increasing filler loading. This implies that melt viscosity of the composites at the processing temperature was not significantly affected by the incorporation of WRHA. However, at 60% filler loading, the composite achieved relatively higher equilibrium torque. With an increase in filler loading, filler particle agglomeration occurred as evidenced by the SEM studies (discussed later). This results in higher resistance (higher torque) to the flow of material that becomes significant as the filler loading reached 60%.

In DV blend systems, curing ingredients minus curative (sulfur) were added at the third and sixth minutes, while sulfur was added at 7.5 min of mixing. It can be seen that torque starts to increase and stabilize at higher values than corresponding UV composites after the addition of the curative. The raised equilibrium torque values of DV composites after the addition of curative agent was the first indication that curing was effected. It also indicates the higher energy requirement for the melt processing of DV composites than the UV counterparts.

Further, achievement of similar torque development and almost similar time taken to reach stable torque for both filled and unfilled DV composites indicate that incorporation of WRHA has no significant effect on the curing characteristics of the composites. The DV composites show a decrease in equilibrium torque as filler loading increases in contrast to the tendency shown by UV composites. This may be due to the reduced crosslink densities as elastomeric contents of the composites were decreased with the higher filler content. This observation suggests that crosslink density plays a greater role than filler loading on the processibility of these composites.

Mechanical Properties

Tensile Properties

The typical stress–strain curves of UV and DV PP/EPDM composites with different WRHA loadings are shown in Figure 2. The differences introduced by the incorporation of filler and dynamic vulcanization is evident from these curves. Shorter elongation and higher initial slope (higher tensile modulus) of the stress–strain curves of the UV composites with increasing filler loading suggest that incorporation of filler causes the materials to demonstrate more brittle behavior. All the UV composites show well-defined yield peak and finally fails by a necking-type rupture which reflects the plastic nature of the composites. In contrast, DV composites do not demonstrate such behavior even at the highest filler loading investigated. The DV composites exhibited no well-defined yield point; instead, the yield peak broadened while achieving higher elongations at break (%), indicating achievement of elastomeric nature. This implies that dynamic vulcanization conferred TPE properties to the composites. These stress–strain curves further suggest that vulcanized elastomeric properties can be achieved at curative concentrations as low as 0.4% phr (used in this study). This is further confirmed by the SEM studies, which will be discussed later. However, in WRHA-filled PP/EPDM composites,
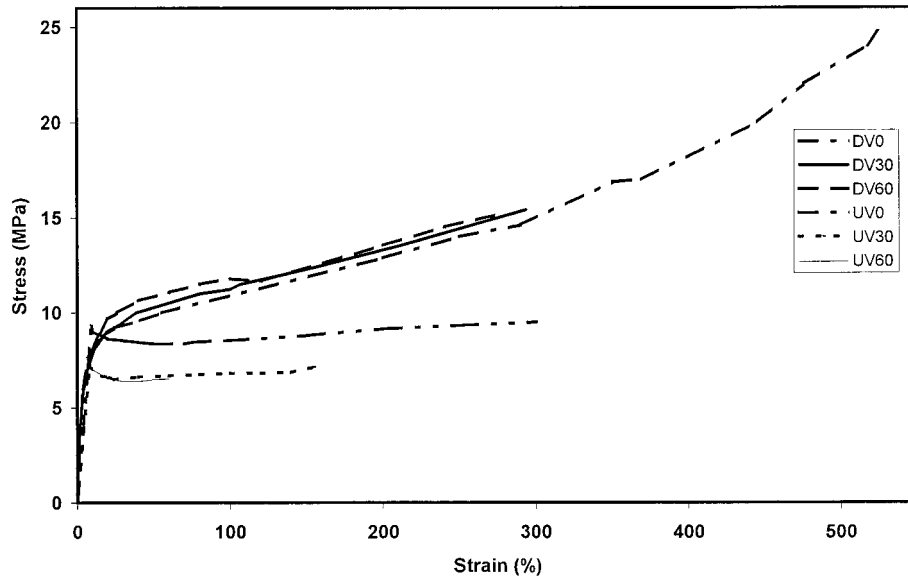
Figure 2 Stress–strain behavior of WRHA-filled 50/50 : PP/EPDM composites with different filler loadings at 180°C and 50 rpm.

yield stress is shown only for UV systems, whereas ultimate tensile strength and elongation at break (%) decreased and tensile modulus increased with WRHA loading for both UV and DV systems.

The tensile strength, elongation at break (%), and tensile modulus results are presented in Figures 3-5. It is clear from the results that the dynamic vulcanization process has significantly enhanced the tensile properties at all filler load-
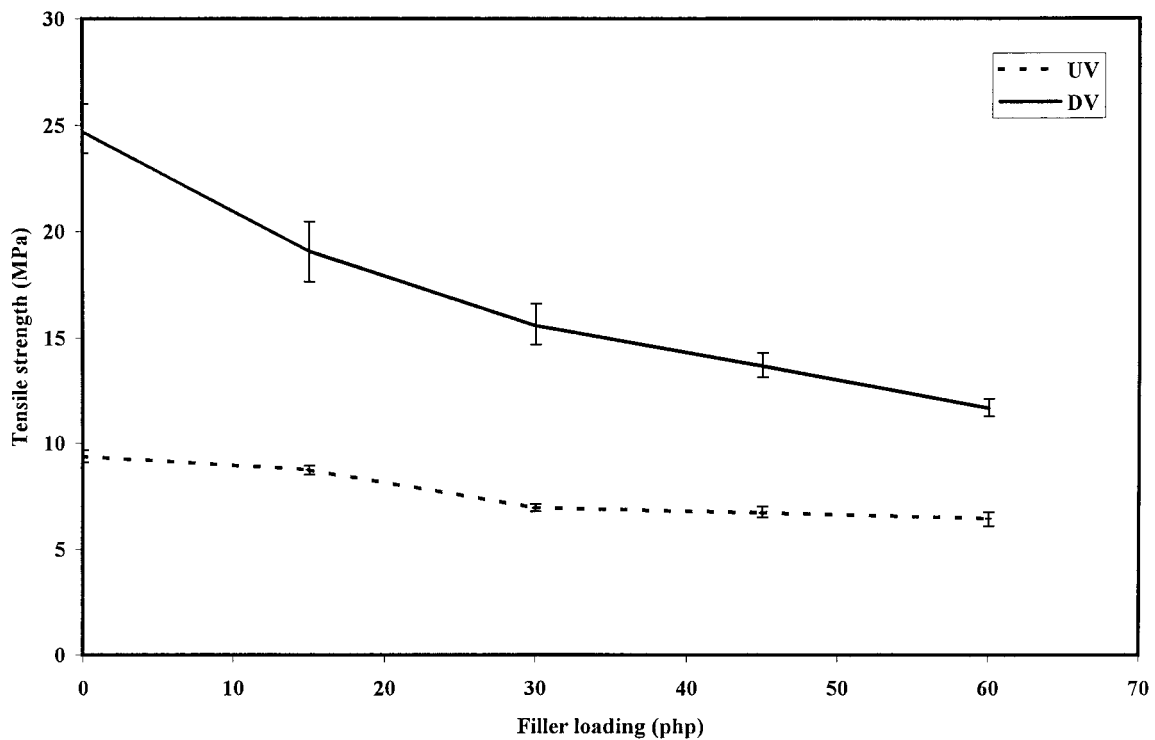
Figure 3 Effect of dynamic vulcanization and filler loading on tensile strength of WRHA-filled 50/50 : PP/EPDM composites.

Table III   Percentage Property Enhancement of WRHA Filled Dynamically Vulcanised PP/EPDM Blends as Compared with Unvulcanised Composites at Different Filler Loading[a]

Filler Loading	(%) of Property Enhancement					
	Tensile Strength	Elongation at Break	Tensile Modulus	Flexural Modulus	Tear Strength	Toughness
0	164	56	16	3	14	198
15	118	86	19	12	19	139
30	125	108	24	6	32	300
45	104	189	29	9	29	316
60	81	202	25	14	34	420

[a] % Property enhancement = {[Property (vulcanized) − property (unvulcanized)] × 100}/Property (unvulcanized).

ings. The enhanced tensile properties of vulcanized blends over the unvulcanized counterparts are well explained in the literature for unfilled plastic/elastomer blends.[20–22] Formation of crosslinks in the elastomer phase facilitating stress transfer is the clear factor contributing to such enhancements. As manifested by enhanced tensile properties, dynamic vulcanization could be effectively employed in the WRHA-filled composites too. The increased equilibrium torque of the DV systems over UV systems first indicated this possibility. The (%) of property enhancement, which is defined as the change in the property due to vulcanization over the same property of unvulcanized composites, are presented in Table III. Dynamic vulcanization has a more pronounced effect on tensile strength and elongation at break (%). (%) of property enhancement of elongation at break (%) with increasing filler loading (decreasing elastomer portion) implies that formation of crosslinks is not the only factor that governs this improvement. As evidenced by SEM studies, dynamic vulcanization has resulted in the interruption of filler agglomeration and enhances filler dispersion. Well-dispersed and finer filler particles contribute to enhanced mechanical properties. Therefore, interruption or breakdown of filler agglomeration during the dynamic vulcanization process plays an important role in achieving enhanced properties.

Figures 3, 4, and 5 further show a decrease in tensile strength and elongation at break (%) and an increase in tensile modulus with filler loading for both systems. Similar effects were observed by other researchers who studied incorporation of particulate fillers including WRHA into plastics.[23–25] However, incorporation of WRHA into elastomers has shown a different trend, where an

optimum WRHA loading was found for such properties as tensile strength, elongation at break (%), and tear strength.[26–27] The deterioration of tensile properties [tensile strength and elongation at break (%)] indicates the incapability of filler particles to support the transfer of stress from the polymer matrix to the filler. Poor adhesion of filler–matrix and agglomeration of filler particles as suggested by other workers[24–27] who worked on filled systems may equally be responsible for the deterioration of the properties of theses composites too.

As can be seen in the Figure 5, addition of WRHA increases the stiffness of both types of composites. Fillers are known to increase modulus provided the modulus of the filler is higher than that of the polymer matrix. Both Ahmad Fuad et al.[23] and Ismail et al.,[27] who worked on WRHA-filled polypropylene and epoxidized natural rubber, respectively, have reported that incorporation of WRHA increases the stiffness of PP and natural rubber composites. These results show that tensile modulus of the filled PP/EPDM composites follow the same trend with plastics and elastomers, although tensile strength and elongation at break (%) of filled PP/EPDM composites and filled natural rubber composite exhibit different trends to each other.

Flexural Modulus

Figure 6 illustrates the effect of filler loading on the flexural modulus, which is an indication of material stiffness for WRHA-filled PP/EPDM composites. Similar to the tensile modulus, the flexural modulus also increases with increasing filler loading. Various studies carried out on filled plastics including WRHA-filled PP have shown
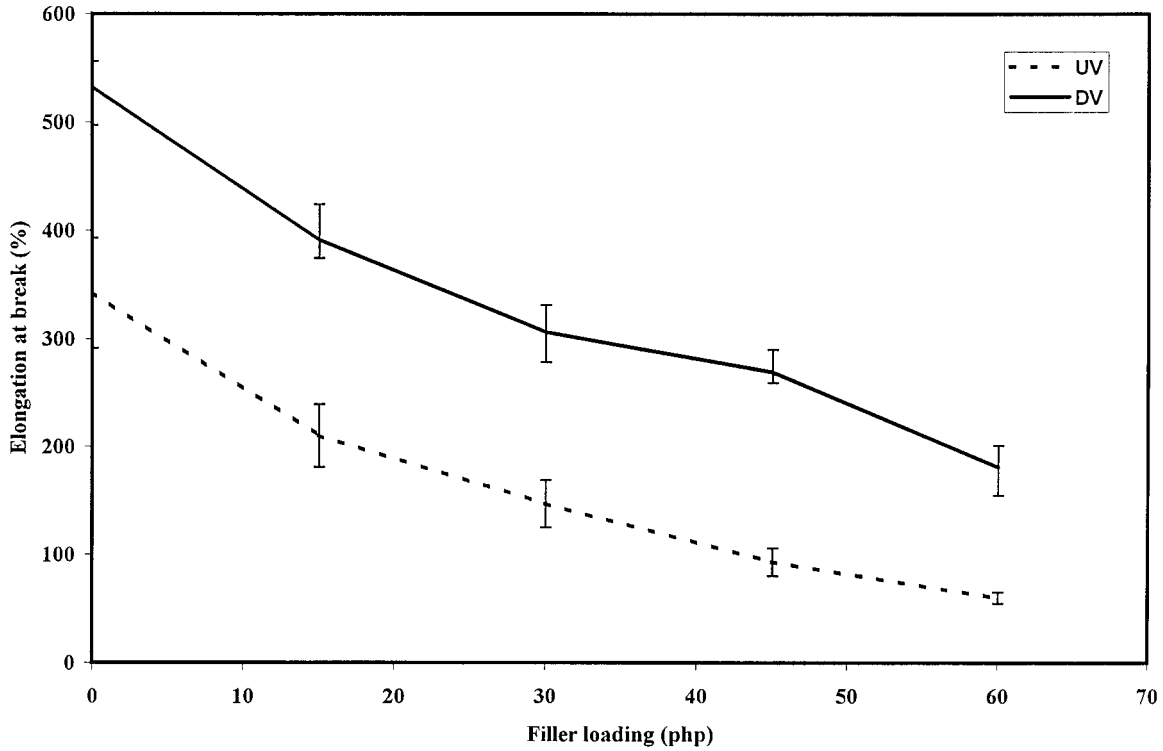
Figure 4   Effect of dynamic vulcanization and filler loading on elongation at break (%) of WRHA-filled 50/50 : PP/EPDM composites.
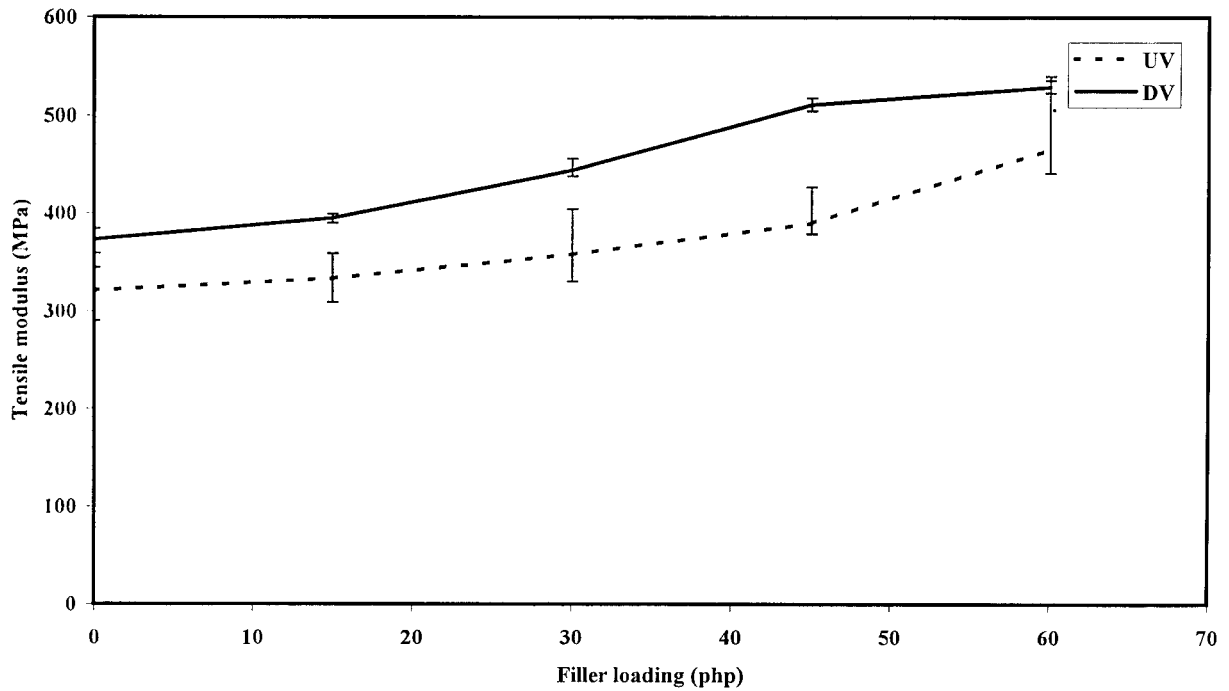

Figure 5   Effect of dynamic vulcanization and filler loading on tensile modulus of WRHA-filled 50/50 : PP/EPDM composites.
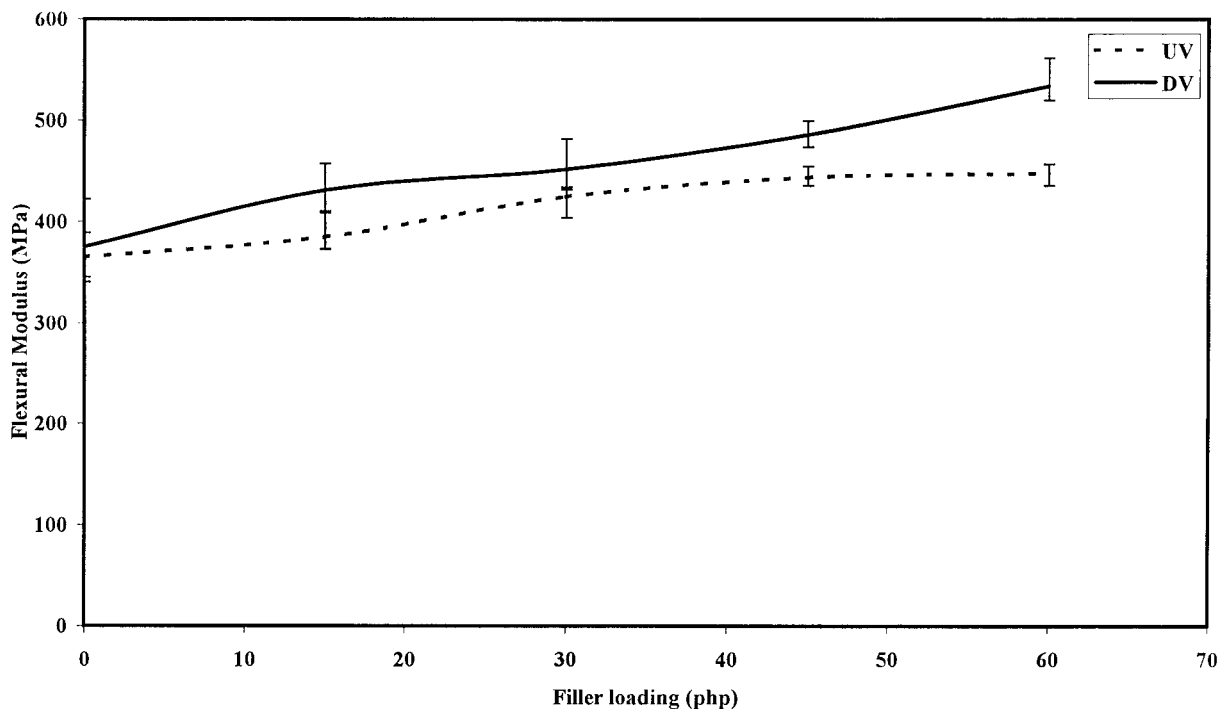
Figure 6 Effect of dynamic vulcanization and filler loading on flexural modulus of WRHA-filled 50/50 : PP/EPDM composites.

similar observations.[23] This signifies that the effect of WRHA loading on flexural modulus of the filled blends is similar to that of other filled plastic composites. In addition, it can be seen in Figure 6 that DV systems show higher flexural modulus than UV systems. Introduction of crosslinks makes the blend more difficult to deform. Consequently, flexural modulus increases. As explained earlier, reduction of the degree of filler agglomeration due to dynamic vulcanization increases the surface area of filler particles leading to more contact with the matrix. This also may be a possible reason for increased flexural modulus of vulcanized blends. However, it is worth noting that similar to the (%) of tensile modulus enhancement, the (%) flexural modulus enhancement is also lower than (%) of tensile strength and elongation at break (%) enhancements (Table III).

Tear Strength

As shown in Figure 7, tear strength decreases with increasing WRHA loading. This could be due to the same factors causing the deterioration of tensile strength. As the filler particles form agglomerates, the particles cannot be properly wetted by macromolecules and hence adhesion between the filler and matrix become poor. Thus, the energy required to propagate a crack become less, resulting in lower tear strength. However, due to the formation of crosslink network structure, DV blend systems exhibited higher tear strength.

Toughness

Toughness is defined as the ability of a material to absorb applied energy without a failure. Direct blending of plastic with rubber was widely used to improve toughness, albeit it reduces stiffness.[23–28] The incorporation of fillers may increase or decrease the toughness of a material depending on the nature of the filler and the degree of adhesion to the matrix while increasing stiffness. The effect of dynamic vulcanization and filler loading on the toughness, which is determined as the area under the stress–strain curve of the material, is shown in Figure 8. After the introduction of crosslinking, toughness increased in all composites irrespective of filler loading. This significant (%) of property enhancement presented in Table III and Figure 8 shows how vulcanization can effectively be used to improve the toughness of the filled blends even with non-rein-
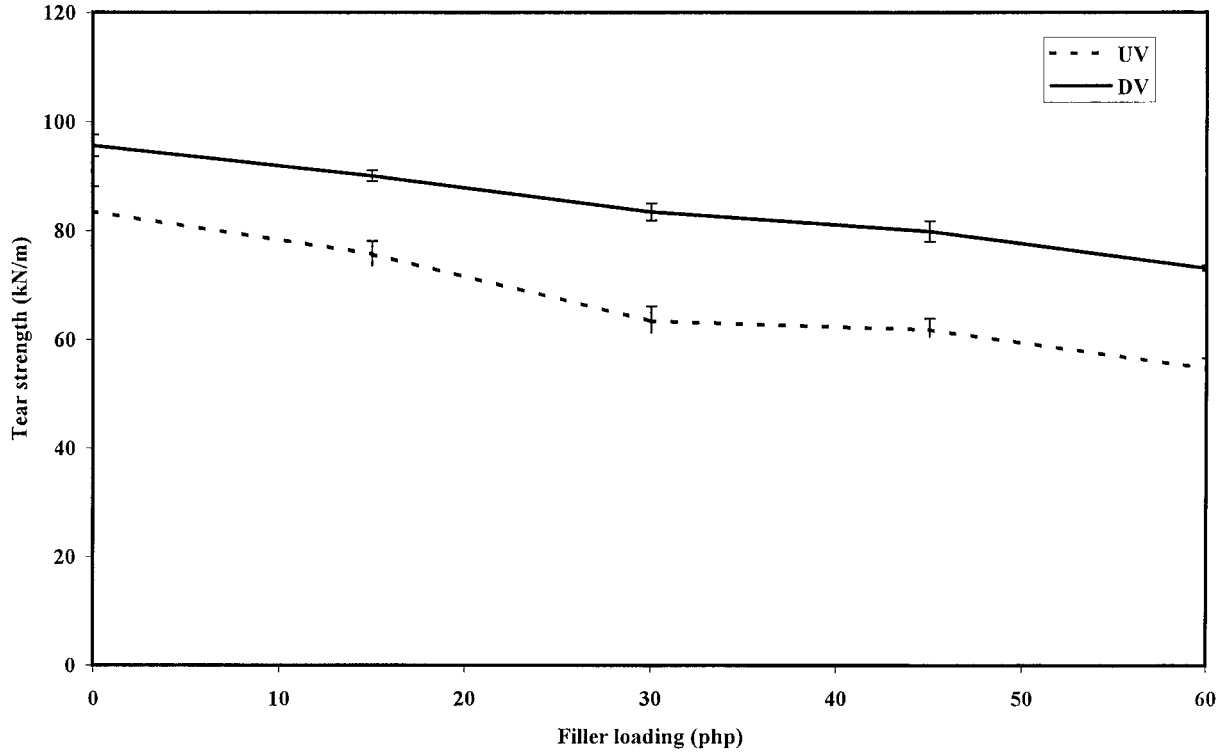
Figure 7 Effect of dynamic vulcanization and filler loading on tear strength of WRHA-filled 50/50 : PP/EPDM composites.

forcing fillers. There are two factors that could have contributed to the above enhancement. First, crosslinked EPDM particles can absorb the stress through deformation of the elastomer particles better than unvulcanized rubber particles. In addition, smaller size and well-dispersed filler
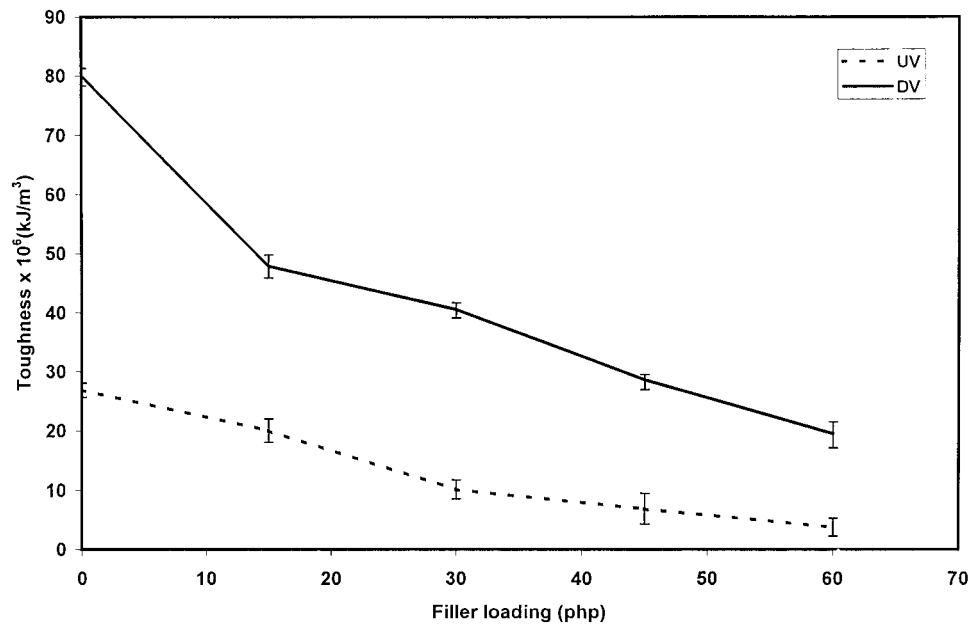

Figure 8 Effect of dynamic vulcanization and filler loading on toughness of WRHA-filled 50/50 : PP/EPDM composites.
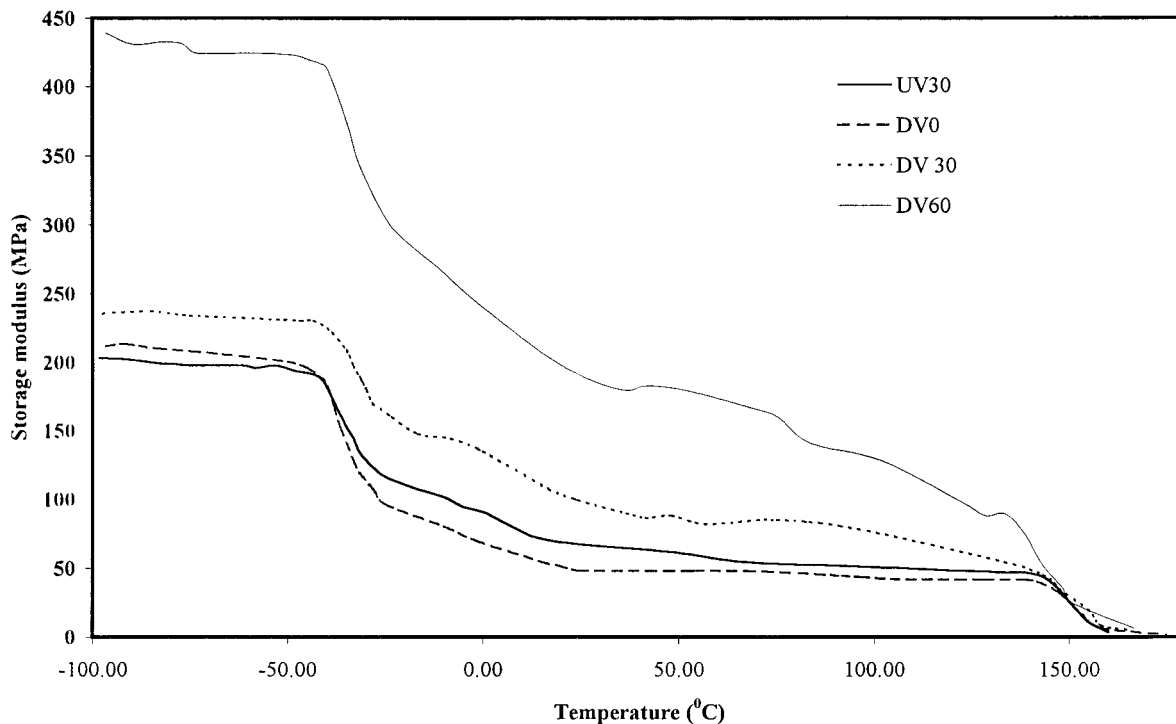
Figure 9   The variation of storage modulus of WRHA-filled 50/50 : PP/EPDM composites.

particles may also contribute to the enhancement of toughness due to increased surface area, which facilitates transfer of stress from the matrix to the filler. Increasing concentration of filler, however, reduces the toughness of the material in both UV and DV composites. Poor adhesion of the filler and matrix becomes dominant and weakens the stress transfer from the polymer matrix to the filler and deteriorates the impact strength at higher filler loading.

Dynamic Mechanical Analysis

The effects of dynamic vulcanization and filler loading on the dynamic mechanical properties were studied in the -100 to $200°C$ temperature range. The storage modulus, loss modulus, and tan δ curves are shown in Figures 9-11. As shown in Figure 9, dynamic vulcanization increases the storage modulus (in comparison to UV30 and DV 30 curves). Incorporation of filler has also increased the storage modulus of the DV composites (in comparison to DV0, DV30, and DV60 curves). These observations support the tensile modulus and flexural modulus results discussed earlier, while providing additional evidence for successful dynamic vulcanization of filled blends. Although the storage modulus of the composites decreases

with an increase in temperature, it demonstrates that filled blends exhibited higher modulus than unfilled blends over the whole temperature range studied. It is believed that WRHA has the ability to absorb heat and retard the softening of the polymers, as fillers are known to enhance dimensional stability. The sharp drop of the storage modulus around $-33°C$ represents the glass transition temperature (T_g) of the elastomer phase. The second inflection point at around $15°C$ corresponds to the glass transition temperature of PP. These two transitions can clearly be seen in the loss modulus curve peaks (Fig. 10). The presence of these two peaks indicates that PP and EPDM exist as two separate phases. A similar observation was reported by other workers,[23] who studied DMA properties of unfilled PP/EPDM blends. The existence of these two peaks at the same location in loss modulus curve without a significant shift in temperature inferred that neither dynamic vulcanization nor incorporation of filler positively or negatively influenced the compatibility of the two polymer components. It is also clear from Figure 10 that both incorporation of filler and dynamic vulcanization results in an increase in loss modulus.
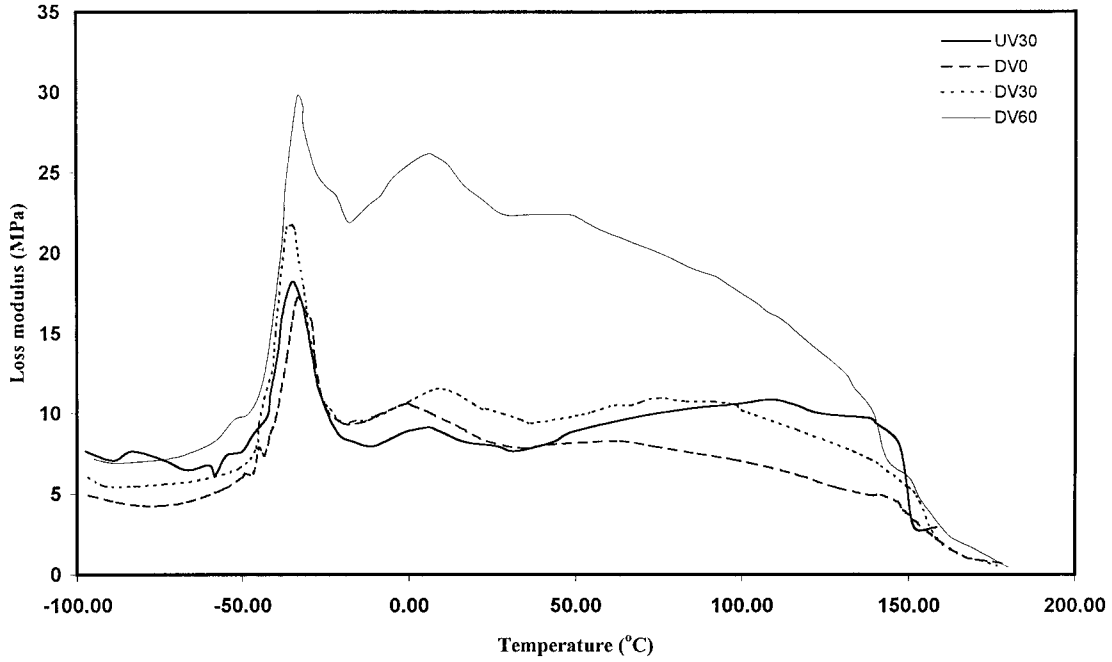
Figure 10 The variation of loss modulus of WRHA-filled 50/50 : PP/EPDM composites.

The two tan δ peaks at the temperatures that correspond approximately to the temperature at which the two peaks are observed for loss modu-

lus can be seen in the tan δ curves (Fig. 11). As discussed earlier, these two peaks reflect the T_g of EPDM and PP, suggesting that two polymer com-
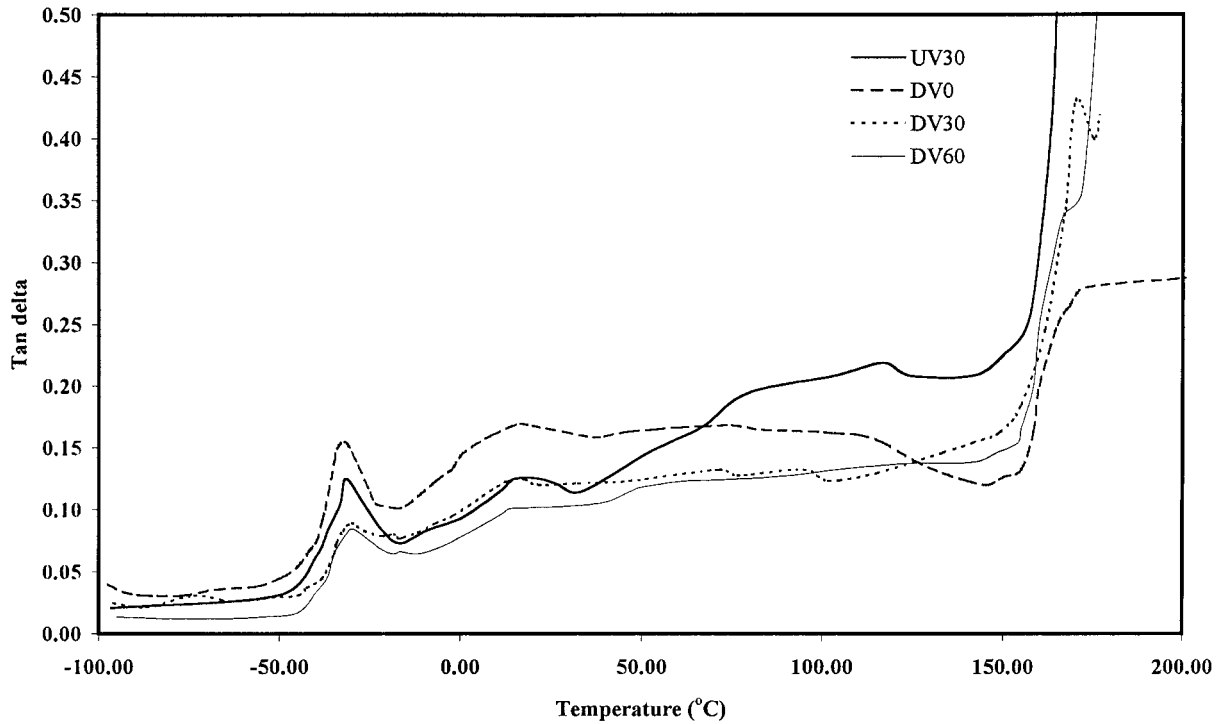

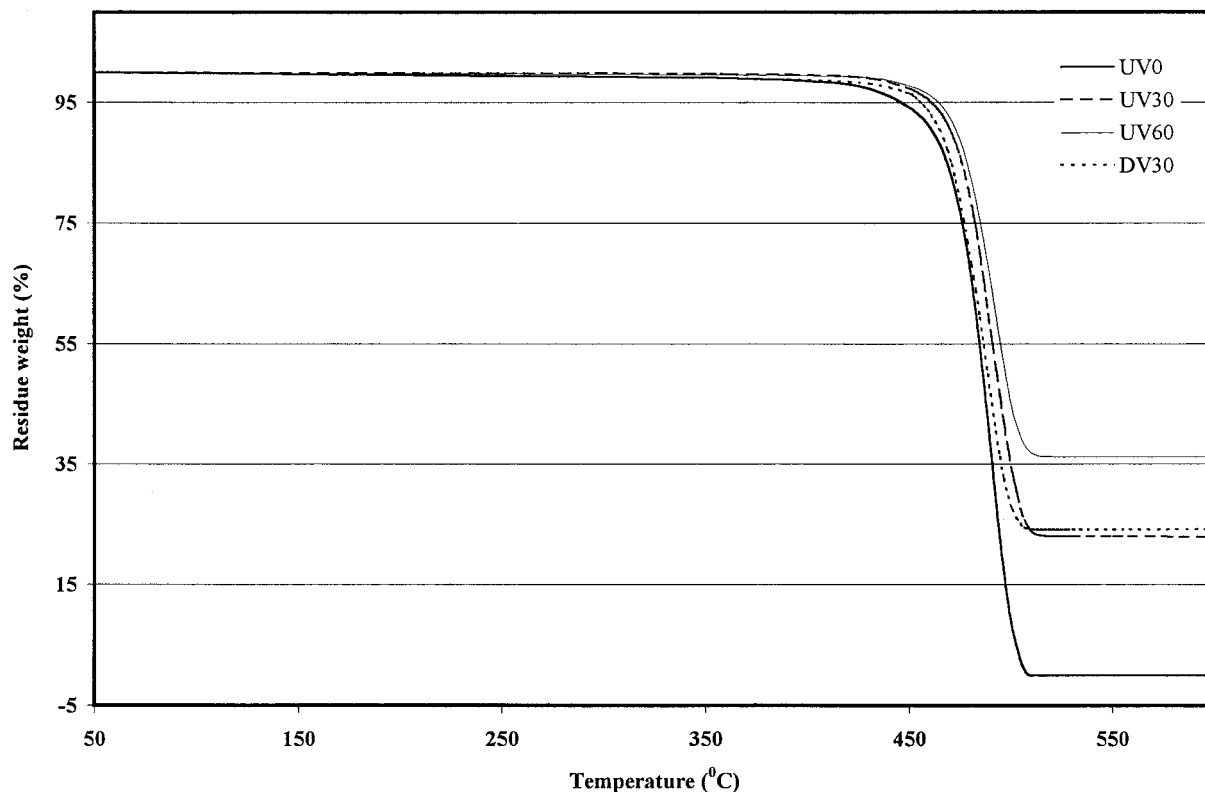**Figure 11** The variation of tan δ of WRHA-filled 50/50 : PP/EPDM composites.

Figure 12 Thermogravimetric results of WRHA-filled 50/50 : PP/EPDM composites.

ponents retain their identities in the composites. Dynamic vulcanization results in the reduction of tan δ_{max} as an introduction of crosslinking decreases viscous flow. Filler loading also affects the tan δ_{max} in a similar manner. In Figure 9, it is shown that storage modulus increases with the filler loading. Therefore, such reduction in tan δ_{max} indicates that the filler has a pronounced effect on storage modulus albeit a similar effect on loss modulus affecting T_g. A comparison of tan δ peaks (corresponding to the EPDM) of UV30 and DV30 composites, DV 30 system, shows a decrease in tan δ_{max} and is relatively broader. It is known that crosslinking decreases the damping and broadens the peak width. This observation indicates that crosslinking of the elastomer phase has occurred. The smaller tan δ peak of filled compared to the unfilled systems implies that incorporation of filler has changed the damping properties of the filled composites.

TGA Studies

Figure 12 shows the thermal degradation pattern of UV composites at 0, 30, and 60 WRHA loading and DV composites at 30 WRHA loading. It is evident from the graph that irrespective to the crosslinking density or filler loading all the blends are thermally stable until around 400°C. The highly stable residue obtained in each case is the silica and other metal oxides present in WRHA. The slightly higher residue content of the DV composites over its UV counterpart is probably due to the extra amount of inorganic curing agents used such as zinc oxide. The percentages of these total inorganic materials (silica, other metal oxide, and ZnO) are close to the expected residue values based on inorganic content. For example, for UV60, calculated inorganic content is 37.5 wt % (Table II), whereas the value 36.8 wt % (Fig. 12) is indicated on the TGA curve. This observation highlights an important property of WRHA as filler (i.e., small amount of metal oxides present in the WRHA has not caused the degradation of the material). Instead, it can be seen that WRHA has offered slight thermal stability as indicated by the slight shift of the thermal curve toward the right at around decomposition range. It is believed that WRHA can absorb heat faster than polymer matrix, protecting the polymer matrix. In contrast, dynamic vulcanization seems to slightly favor the
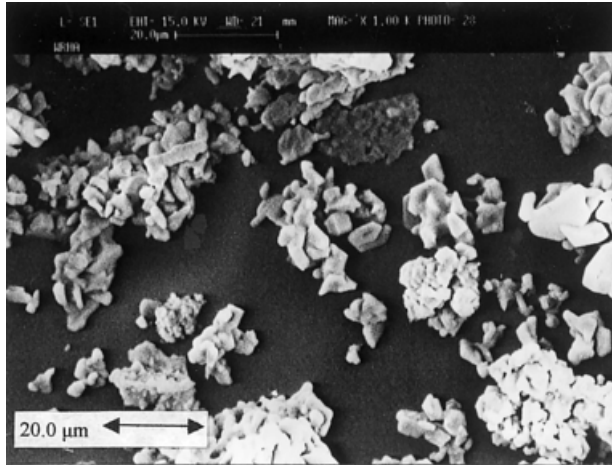
Figure 13 SEM micrograph of white rice husk ash (magnification, ×1000).

Figure 15 SEM micrograph of the tensile fracture surface of unvulcanized 50/50 : PP/EPDM at 30 (php) filler loading (magnification, ×1000).

degradation of the filled matrix. Although this is not so significant, the fact that PP/EPDM composites (filled and unfilled) have no tendency to absorb moisture is indicated as no weight loss is registered around 100°C.

SEM Studies

Figure 13 shows the irregular shapes and the tendency toward aggregate formation of WRHA particles. Therefore, as filler loading increases, formation of agglomerates is inevitably detrimental to mechanical properties. Figures 14-16 are the SEM micrographs of the tensile fracture surfaces of unvulcanized composites at 0, 30 and 60
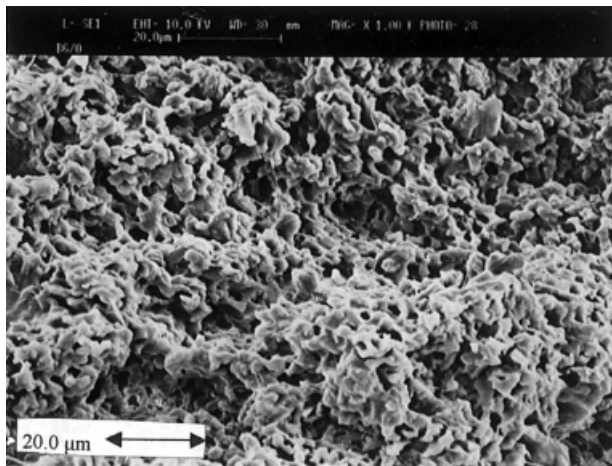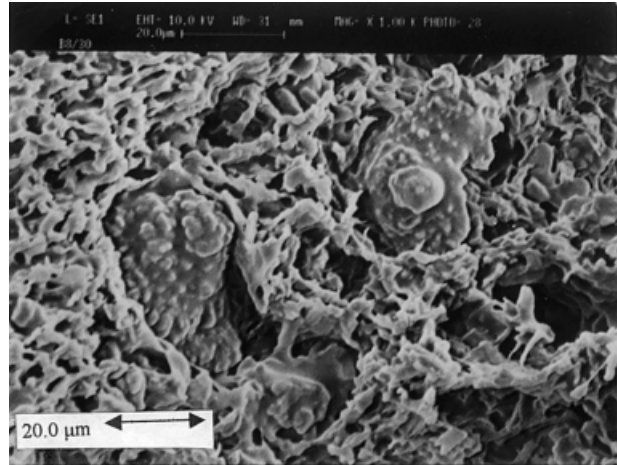
(php) filler loadings, respectively. Irrespective of the filler loading, all three micrographs show more or less brittle-type failure mode. This implies that these matrices exhibit plastic behavior in support of observations based on stress–strain curves with clear yield points. As shown in Figure 14, PP/EPDM blends appear homogenous, thus indicating that blending was essentially effective. Figures 15 and 16 revealed poor adhesion of the filler to matrix as evident from the voids between the matrix and filler particles. These voids act as stress concentration points and contribute to the decrement of mechanical properties. Furthermore, a comparison of Figures 15 and 16 reveals
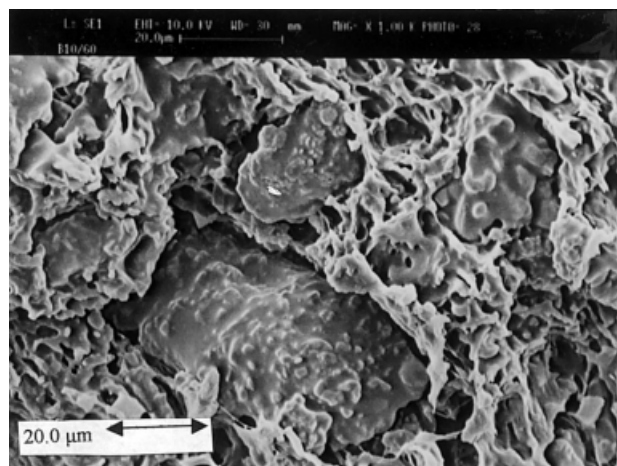

Figure 14 SEM micrograph of the tensile fracture surface of unvulcanized 50/50 : PP/EPDM at zero (php) filler loading (magnification, ×1000).

Figure 16 SEM micrograph of the tensile fracture surface of unvulcanized 50/50 : PP/EPDM at 60 (php) filler loading (magnification, ×1000).
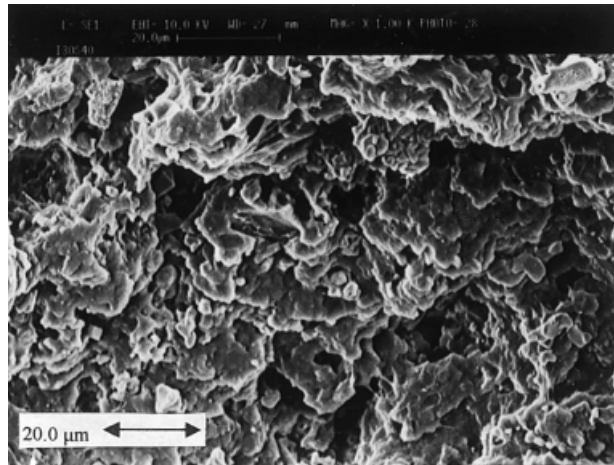
Figure 17 SEM micrograph of the tensile fracture surface of vulcanized 50/50 : PP/EPDM at zero (php) filler loading (magnification, ×1000).

that as filler loading increases, the size of the agglomerates also increases. As the amount of filler loading increases, the tendency for filler–filler interaction increases, resulting in bigger filler agglomerates. This results in a higher level of dewetting of filler particles by the matrix. Consequently, composites with higher filler loading exhibit poorer mechanical properties such as tensile strength and tear strength. This is further evidence in support of the trends in mechanical properties discussed earlier.

Figures 17-19 are the SEM micrographs of the tensile fracture surfaces of dynamically vulcanized PP/EPDM composites with filler loadings of
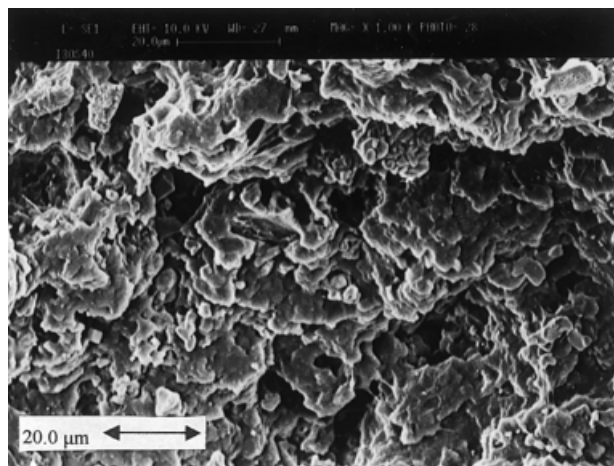

Figure 18 SEM micrograph of the tensile fracture surface of vulcanized 50/50 : PP/EPDM at 30 (php) filler loading (magnification, ×1000).
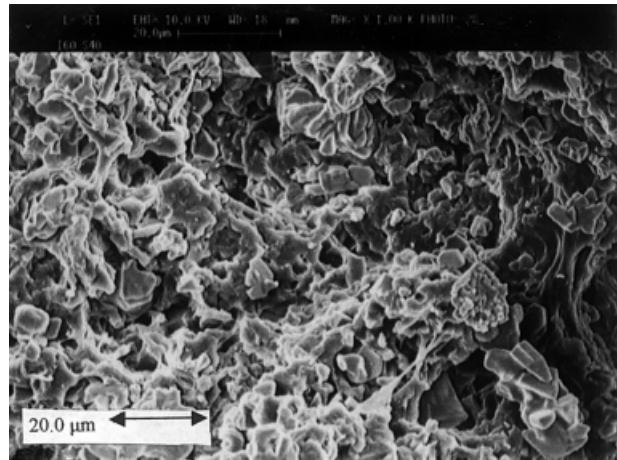

Figure 19 SEM micrograph of the tensile fracture surface of vulcanized 50/50 : PP/EPDM at 60 (php) filler loading (magnification, ×1000).

0, 30, and 60 php, respectively. These fracture surfaces exhibited completely different characteristics. In contrast to the near brittle-type failure shown by the UV composites, these fracture surfaces indicate rough surfaces with matrix tearing. This nature of failure reveals that the blends achieved vulcanized elastomeric properties due to the formation of crosslinks. Therefore, SEM micrographs of DV composites provide further evidence for effective vulcanization of the elastomeric component and thus justifies the significant improvements in mechanical properties. Similar to the SEM micrographs of UV systems, as the filler content increases, the size of filler agglomerates increases, as evident in Figures 17 and 18, albeit the filler agglomerates are much smaller in size. This observation revealed that dynamic vulcanization has greatly interrupted the filler agglomeration and improved filler dispersion. Simultaneously, the voids in the filled vulcanized systems are much less obvious. Both of these factors contribute to the enhancement of mechanical properties in addition to the property enhancement due to crosslink formation. As for UV composites, the level of filler agglomeration could account for the deterioration of the mechanical properties of the DV composites with increasing filler loading, apart from the decreasing crosslink density (due to decreasing elastomer content).

CONCLUSION

From the study, it was found that WRHA-filled PP/EPDM composites could also be dynamically

vulcanized successfully, similar to unfilled composites, to achieve thermoplastic elastomer materials with substantially improved mechanical properties. Dynamic vulcanization of filled blends exhibited significantly higher elongations at break, indicating TPE characteristics. Interruption of filler agglomeration and improvement of filler dispersion were found to be the possible reason of such improvements apart from the formation of crosslinks in the rubber phase. Incorporation of WRHA resulted in improvement of some properties at the expenses of some other properties. Morphology studies of the composites indicate that the filler agglomeration becomes pronounced as the filler loading reaches a higher level, particularly in UV blends. Dynamic vulcanization has changed the fracture surface behavior from brittle behavior to ductile type as evidenced from the morphology studies. Dynamic mechanical analysis indicates the existence of two phases of the composites, although no phase separation can be seen in the micrographs of the composites because selective staining was not done. It also shows that WRHA filler does not play a major role in the T_g's of the blend components. TGA studies indicated no adverse effect of WRHA on the thermal stability of the blends. Overall, the study shows that filled blends can also be made to achieve TPE characteristics of higher toughness with improved stiffness through dynamic vulcanization of filled plastic rubber blends.

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