

# *In Situ* Dynamic Vulcanization Process in Preparation of Electrically Conductive PP/EPDM Thermoplastic Vulcanizate/Expanded Graphite Nanocomposites: Effects of State of Cure

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**ABSTRACT:** *In situ* melt dynamic vulcanization process has been employed to prepare electrically conductive polypropylene (PP)/ethylene-propylene–diene rubber (EPDM) (40/60 wt %) thermoplastic vulcanizates (TPVs) incorporated by expanded graphite (EG) as a conductive filler. Maleic anhydride grafted PP (PP-g-MAH) was used as compatibilizer and a sulfur curing system was designed and incorporated to vulcanize the EPDM phase during mixing process. Developed microstructures were characterized using scanning electron microscopy (SEM), melt rheomechanical spectroscopy (RMS), X-ray diffraction (XRD), and transmission electron microscopy (TEM) and were correlated with electrical conductivity behavior. For comparison, another class of TPV/EG nanocomposites was fabricated using a commercially available PP/EPDM-based TPV via both direct and masterbatch melt mixing process. Conductivity of the nanocomposites prepared by

*in situ* showed no significant change during dynamic vulcanization till the mixing torque reached to the stationary level where micro-morphology of the cured rubber droplets was fully developed, and conductivity abrupt was observed. *In situ* cured nanocomposites showed higher insulator to conductor transition threshold (3.15 vol % EG) than those based on commercially available TPV. All electrically conductive *in situ* prepared TPV nanocomposites exhibited reinforced melt elasticity with pseudosolid-like behavior within low frequency region in dynamic melt rheometry indicating formation of physical networks by both EG nanolayers and crosslinked EPDM droplets. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 32–40, 2012

**Key words:** electrical conductivity; nanocomposites; microstructure; expanded graphite; dynamic vulcanization; PP/EPDM; thermoplastic vulcanizate (TPV)

## INTRODUCTION

Polymer composites with electrical conductivity have attracted great attentions over the past few decades for numerous applications such as antistatic materials, pressure and gas sensors, electromagnetic shielding materials, etc.<sup>1–3</sup> Electrically conductive nanocomposites based on conductive nanofillers have shown distinct features including low conductivity threshold and hence light weight with better processability and mechanical properties.<sup>2–4</sup>

Natural graphite flake (NGF) is a layered material consisting of graphene layers formed by sp<sup>2</sup> hybridized carbons, resulting in delocalization of  $\pi$  bonds and high electrical conductivity of graphite layers ( $1.567 \times 10^3$  S cm<sup>-1</sup>). Single graphite sheets are stacked parallel to each other with gallery spacing of 0.335 nm.<sup>1–5</sup>

NGFs intercalated with acid [graphite intercalated compound (GIC)] can expand to 100 times of its initial volume, resulting in the separation of graphene nanosheets along the *c*-axis of graphene layers, which is called expanded graphite (EG).<sup>5</sup>

Thermoplastic vulcanizates (TPVs) with a matrix-dispersed type of morphology are blends of a crystalline polymer such as polypropylene (PP) as the matrix and a rubbery phase in the form of interconnected aggregates of crosslinked droplets which are mainly prepared via melt mixing process.<sup>6</sup> This class of polymeric materials offers wide range of interesting properties such as rubbery behavior at low temperatures and good processability like ordinary thermoplastics.<sup>7</sup> The expanded honey combed structure of EG with –OH and –COOH functional groups on the edges of nanolayers gives good miscibility with interfacially compatibilized polymer materials. Nevertheless, the dispersion and size distribution of EG in the polymer matrices govern the conductivity behavior and insulator to conductor transition threshold. These are controlled by the route of mixing, processing conditions, and degree of compatibilization.

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TABLE I  
The List of Used Acronyms

Acronym	Equivalent	Acronym	Equivalent
PP	Polypropylene	NGF	Natural graphite flake
EPDM	Ethylene-propylene-diene rubber	GIC	Graphite intercalated compound
SOC	State of cure	phr	Part per hundred part of rubber
TPV	Thermoplastic vulcanizate	D.C.	Direct current
EG	Expanded graphite	SBS	Styrene-butadiene-styrene
MAH	Maleic anhydride	PMMA	Polymethyl metacrylate
SEM	Scanning electron microscope	SWNT	Single wall carbon nanotube
RMS	Rheomechanical spectroscopy	CNT	Carbon nanotube
XRD	X-ray diffraction	PVC	Polyvinyl chloride
TEM	Transmission electron microscopy		

The main objective of the present work is to prepare dynamically vulcanized thermoplastic elastomer nanocomposites based on PP/ethylene-propylene-diene rubber (EPDM) and EG as electrically conductive filler via *in situ* vulcanization of EPDM phase in the presence of EG during melt mixing process, and investigating the effect of degree of vulcanization [state of cure (SOC)] of the rubbery and micro-morphology of the dispersed EPDM phase on the electrical conductivity behavior of the developed TPV nanocomposite. The conductivity threshold of the *in situ* prepared nanocomposites has been compared with another class of TPV/EG nanocomposites fabricated by melt mixing of a commercially available predynamically vulcanized PP/EPDM TPV with EG nanofiller in the presence of an interfacial compatibilizer. Relationship between melt rheological characteristics and insulator to conductor threshold ( $\sigma_c$ ) has been investigated for both groups of TPV/EG nanocomposites. Considering the difference in their microstructure, dependency of electrical conductivity on the EG volume fraction above the threshold has been checked with the existing percolation models.

## EXPERIMENTAL

The abbreviation list of different materials, test methods, and technical expressions, which are used in this article, is presented in Table I.

### Materials

Commercially available PP/EPDM-based TPV with the trade name of Santoprene 8211-35, Exxonmobil Chemical (US), in the form of white granules with the hardness of 38 Shore A, and specific gravity of  $0.93 \text{ g/cm}^3$  was used as prevulcanized TPV. Isotactic PP (iPP) with the trade name of Poliran PI0800 supplied by Bandar Imam Petrochemical Co. (Iran) having MFI value of  $8.00 \text{ g/10 min}$  ( $230^\circ\text{C}/2.16 \text{ kg}$ ), and EPDM with the trade name of Keltan 2340A supplied by DSM (Netherlands) having mooney viscos-

ity of ML (1 + 4,  $125^\circ\text{C}$ ) = 25 were used for preparing *in situ* dynamically vulcanized TPV samples. Maleic anhydride grafted PP (PP-g-MAH) supplied by Pluss Polymers (India), with the trade name of OPTIM P-424, having melt flow index of  $120 \text{ g/10 min}$  ( $190^\circ\text{C}/2.16 \text{ kg}$ ), graft ratio of 0.5–0.8 wt %, and density of  $0.91 \text{ g/cm}^3$  was used as a compatibilizer. GIC was supplied from Beijing Invention Biology Engineering and New Material Co. (China), with the commercial name of EX 9550-200N.

### Preparation of EG

Worm-like EG composed of nanolayers with the thickness of 100–400 nm was prepared by rapid heating of GIC at  $1200^\circ\text{C}$  for 20 s in a furnace.

### Preparation of nanocomposite samples

A brabender internal mixer operating at  $180^\circ\text{C}$  and rotor speed of 120 rpm with the filling factor of 75% was used for melt mixing process. The as-prepared compounds were ground into powder and then formed into sheets with the dimensions of  $100 \times 100 \times 1 \text{ mm}^3$  using a hydraulic hot press at  $180^\circ\text{C}$ . The prepared composite samples are coded as described in Table II. To find out the PP/EPDM ratio in Santoprene 8211-35 TPV matrix, boiled xylene extraction was performed, and the EPDM content was found to be about 35–38 wt %, which is comparable with the 40% of EPDM dynamically vulcanized TPV sample.

In the case of samples prepared by masterbatch melt mixing, EG and PP-g-MAH were first melt mixed at  $180^\circ\text{C}$  for 20 min, and then ground into powder. The required amount of dried masterbatch was then melt compounded with the predynamically vulcanized TPV (Santoprene 8211-35) granules to fabricate the TPV/EG nanocomposite. The volume fraction of EG in each sample is shown by a number after the code of the sample. For example, TPV-m3-1.25% describes the sample prepared by melt blending of predynamically vulcanized TPV with PP-g-MAH/EG (3/1 w/w) masterbatch and

TABLE II  
Coding of the Prepared TPV Samples

Sample code	Mixing method	$\frac{\text{PP-g-MAH}}{\text{EG}}$ (weight ratio)
TPV-Ref	Blend of predynamically vulcanized TPV and PP-g-MAH	–
TPV-m1	Melt blending of predynamically vulcanized TPV and PP-g-MAH/EG masterbatch	1
TPV-m3		3
TPV-d	Direct melt blending of predynamically vulcanized TPV, EG, PP-g-MAH	3
TPV-DV-Ref	Direct melt mixing of PP/EPDM/PP-g-MAH/curing system	–
TPV-DV	<i>In situ</i> dynamic vulcanization via direct melt mixing	3

composed of 1.25% volume fraction of EG. The EG volume fraction was calculated based on the 2.15 g/cm<sup>3</sup> density of solid graphite.<sup>8</sup> For the TPV/EG samples, which fabricated by direct melt blending, the pre-vulcanized TPV was fed onto the mixing chamber, and after 1 min the required amount of EG and compatibilizer were incorporated, and mixing was continued till the mixing torque reached to the stationary level with the total mixing time of 20 min.

*In situ* dynamically crosslinked samples were prepared by direct melt mixing of PP and EPDM in the presence of the curing ingredients (ZnO: 5 phr, stearic acid: 1.5 phr, TMTD: 1 phr, MBTS: 0.5 phr, and sulfur: 2 phr). EG and PP-g-MAH were fed into the mixer before the incorporation of the curing ingredients. Mixing process was continued till the mixing torque reached to a constant level. To evaluate the effect of SOC on the behavior and properties of *in situ* crosslinked TPV nanocomposites, samples were taken from the chamber of the ongoing mixer at various time intervals during vulcanization stage and cooled immediately. These samples have been coded such that the removal time is indicated.

### Characterization techniques

The volume conductivity ( $\sigma$ ) of the plate-like samples was measured at room temperature according to the IEC 9380 or ASTM D257 standard test method with a conductometer (Tettex Instruments, Switzerland) and a direct current (D.C.) generator (Chauvin Arnoux, France). Each measurement was carried out on three plates of each nanocomposite sample, and the average results are presented. Scanning electron microscopy (SEM; Seron, AIS-2100, Korea) was performed on cryofractured surface of samples to observe the dispersion of graphite nanolayers within the nanocomposite matrix. Nanoscale structures of various nanocomposites were also investigated by means of high-resolution transmission electron microscopy (TEM; EM 208, Philips Co.) operated at an accelerating voltage of 100 kV.

Melt rheological characterization was also performed on the samples using a parallel plate rheometer (Paar Physica USD 200, Austria) and disk shaped samples, with 2.5 cm in diameter and 1 mm

thickness. Linear viscoelastic region was first determined by strain sweep test in the range of 0.1–100% at 200°C, and then frequency sweep was carried out between 0.1 and 1000 s<sup>-1</sup>.

The structure of nanocomposites was further investigated by X-ray diffraction (XRD) using X-Pert Philips diffractometer (CuK $\alpha$  radiation,  $\lambda = 1.5406$  Å, generator voltage = 30 kV, and current = 30 mA). Samples were scanned at room temperature within the angle ( $2\theta$ ) range of 1–30° at scanning rate of 1°/min.

## RESULTS AND DISCUSSION

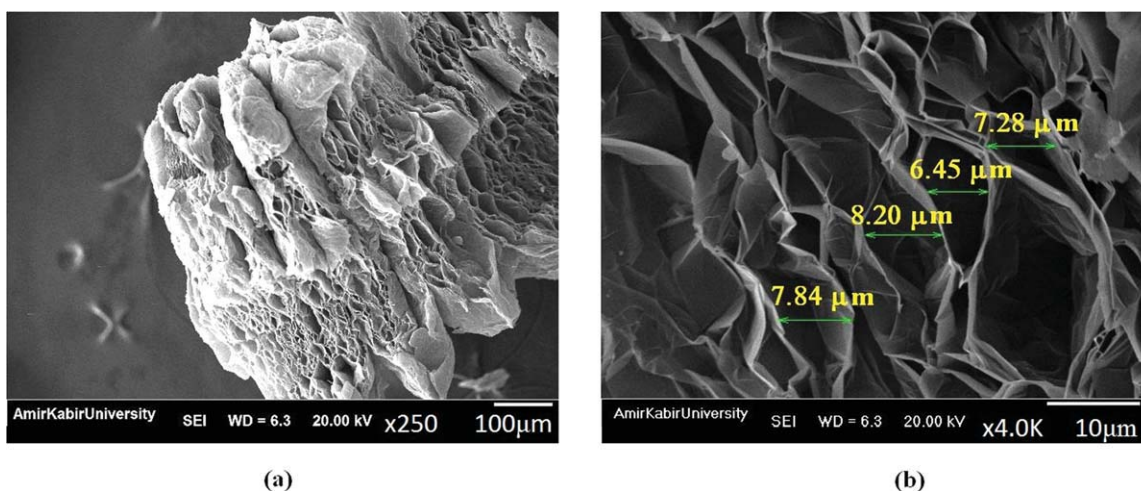
### Morphology studies

Figure 1 presents a typical SEM micrograph of EG in two different magnifications. The porous structure composed of nanolayers with the thickness of about 100 nm is clearly seen for the EG particle.

In Figure 2, SEM image of the nanocomposite prepared by direct melt mixing of pre-vulcanized TPV and EG with PP-g-MAH/EG ratio of 1 has been compared with the SEM micrograph of the counterpart sample prepared by *in situ* dynamic vulcanization method. Graphite nanolayers are more obvious in the microstructure of nanocomposite generated from predynamically vulcanized TPV, whereas in the case of the sample synthesized by *in situ* dynamic vulcanization, the nanolayers are seemed to be shelled by the dispersed EPDM phase.

The SEM micrographs of the nanocomposite samples generated by pre-vulcanized TPV via masterbatch melt mixing method are also illustrated in Figure 3. Better dispersion of the graphite nanolayers is clearly seen for the sample prepared by PP-g-MAH/EG ratio of 3, indicating enhanced intercalation between EG clusters and polymer phases. This is evidenced by the TEM micrographs illustrated in Figure 4 in which graphite nanolayers have appeared as dark lines, and light background is the TPV matrix. Comparing the two TEM images does also confirm better and uniform dispersion of the EG nanolayers in the TPV matrix of the sample generated from PP-g-MAH/EG ratio of 3.

Comparing SEM micrographs of the nanocomposites prepared by masterbatch and direct melt mixing of predynamically vulcanized TPV and EG



**Figure 1** SEM images of EG in two different magnifications,  $352 \times 150$  mm ( $96 \times 96$  DPI). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

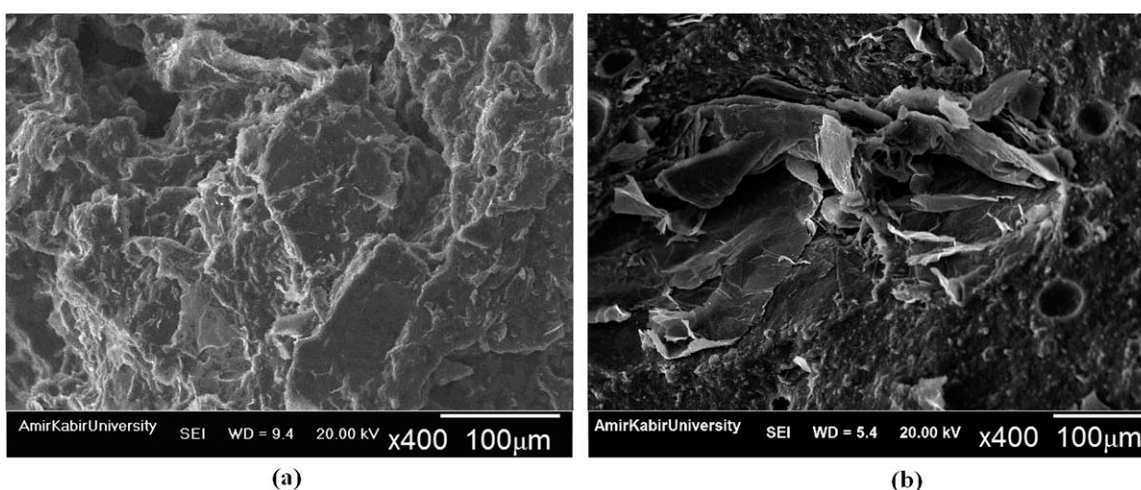
(Figs. 2 and 3) suggests more breakdown of the EG networks, and hence better dispersion of EG nanolayers in the structure of the sample fabricated by masterbatch method. This is attributed to the insufficient time for polymer/EG interaction, when EG is incorporated in the form of direct melt mixing process. This is confirmed by the decrease in the size of the graphite clusters from  $147 \mu\text{m}$  for the direct blended sample to  $16.2 \mu\text{m}$  and  $15.4 \mu\text{m}$  for the nanocomposites prepared by masterbatch mixing with PP-g-MAH/EG ratio of 1 and 3, respectively. The size measurements were carried out using image analysis software (ImageJ 1.42q), and size values are the average of three measurements.

Figure 5 illustrates the XRD patterns of the neat EG, unreinforced TPV (TPV-Ref), and TPV-m3-1.25% nanocomposite samples. It is clearly observed that the XRD characteristic peak of EG ( $2\theta = 26.35$ ) corre-

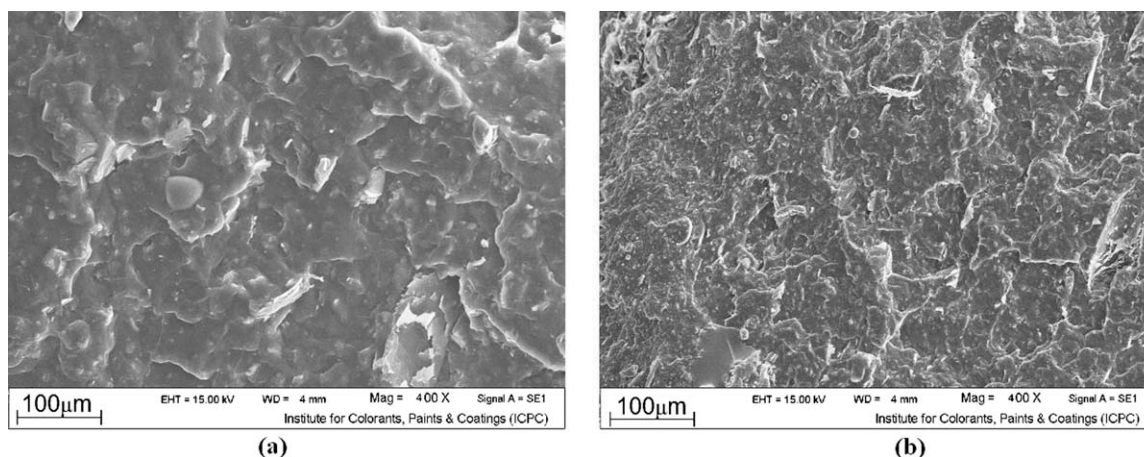
sponding to the gallery spacing of  $3.38 \text{ \AA}$  between the carbon nanolayers has also appeared in the XRD patterns of the EG-based composite without any significant change in its position. This implies that melt compounding of EG with polymer does not lead to the increase in the spacing between graphite nanosheets. Similar results have also been reported in our recently published work.<sup>8</sup> Therefore, without performing complimentary tests, XRD examination is not really able to give useful information about the microstructure of the nanocomposites based on EG compared with the other layered structure nanofillers such as nanoclay.<sup>8</sup>

#### Linear viscoelastic properties

Melt viscoelastic behavior is a useful tool to evaluate the microstructure of polymer nanocomposite



**Figure 2** SEM micrographs of nanocomposite samples prepared: (a) by *in situ* dynamic vulcanization method (TPV-DV-5%), removed at the final stage of vulcanization and (b) by direct mixing of predynamically vulcanized TPV with EG and PP-g-MAH (TPV-d-1.25%);  $343 \times 148$  mm ( $96 \times 96$  DPI).

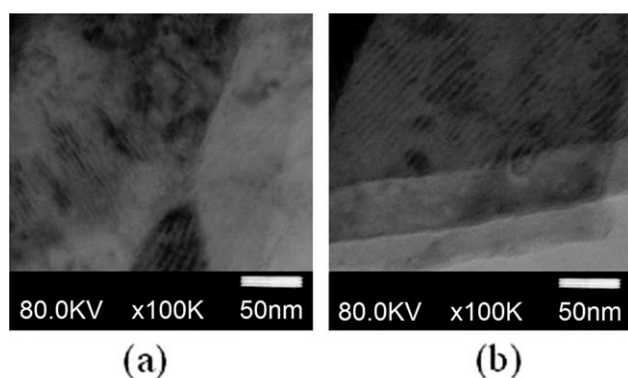


**Figure 3** SEM micrographs of nanocomposites based on prevulcanized TPV/EG prepared by masterbatch mixing method and composed of 1.25 vol % of EG: (a) PP-g-MAH/EG = 1 and (b) PP-g-MAH/EG = 3; 349 × 138 mm (96 × 96 DPI).

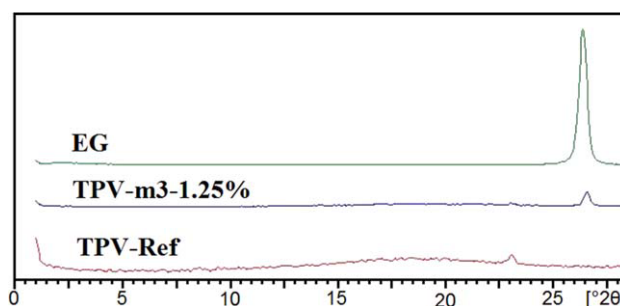
materials.<sup>9</sup> For this purpose, dynamic strain sweep is first needed to be performed on the nanocomposite sample to characterize the extent of strain dependency and linear viscoelastic region. As the melt viscosity ( $\eta$ ) and storage modulus ( $G'$ ) are sensitive to the possible changes in microstructure during dynamic melt rheometry, hence these two parameters have been followed in this study. Extent of dependency of storage modulus ( $G'$ ) on the strain amplitude ( $\gamma\%$ ) for the prepared nanocomposite TPVs, and TPV reference sample has been presented and compared in Figure 6. It is observed that all nanocomposite TPVs show nonlinear viscoelastic characteristic below the strain amplitude of 10% compared with the TPV-Ref, and unfilled *in situ* dynamically vulcanized TPV (TPV-DV-Ref) which exhibited nonlinearity above 30% and 20%, respectively. This implies the presence of mesoscopic networks formed by the EG nanolayers in the structure of the nanocomposites. Moreover, results show that the critical

strain value ( $\gamma_c$ ) at which nonlinear behavior starts varies with the preparation method. The TPV nanocomposite fabricated by masterbatch melt mixing process with PP-g-MAH/EG ratio of 3 not only exhibited higher  $G'$  values than the counterpart sample based on PP-g-MAH/EG ratio of 1 but also showed almost lower critical strain ( $\gamma_c$ ). These imply better separation of EG nanolayers, which leads to the formation of stronger physical networks, and hence, more strain dependency of  $G'$  for the sample generated by PP-g-MAH/EG ratio of 3.

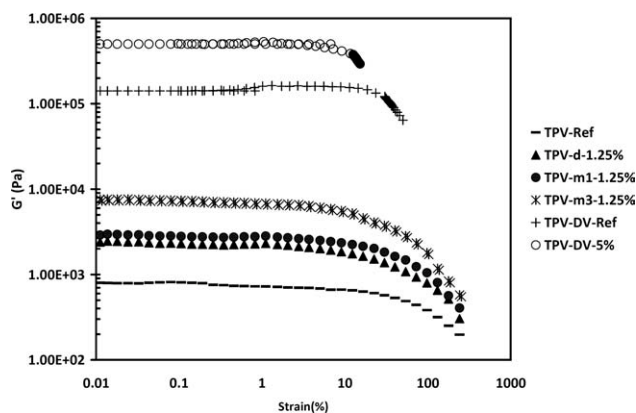
Melt dynamic frequency sweep test was performed on the samples within linear viscoelastic region ( $\gamma_c = 1\%$ ) to further investigate networks formation and microstructures of the prepared nanocomposites in detail. In this experiment, viscoelastic behavior, i.e., complex viscosity, storage modulus ( $G'$ ), in low frequency regime reveals information about the formation of networks by filler particles; whereas the rheological behavior at high frequency regime reflects the characteristics of the polymer



**Figure 4** TEM images of nanocomposites based on prevulcanized TPV/EG prepared by masterbatch mixing method and composed of 1.25 vol % of EG: (a) PP-g-MAH/EG = 1 and (b) PP-g-MAH/EG = 3; 295 × 156 mm (96 × 96 DPI).



**Figure 5** X-ray diffraction in the range of  $2\theta$  angles from  $1^\circ$  to  $30^\circ$ : for the neat EG, unfilled prevulcanized TPV, and nanocomposite prepared by masterbatch melt blending (PP-g-MAH/EG = 3); 203 × 105 mm (96 × 96 DPI). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

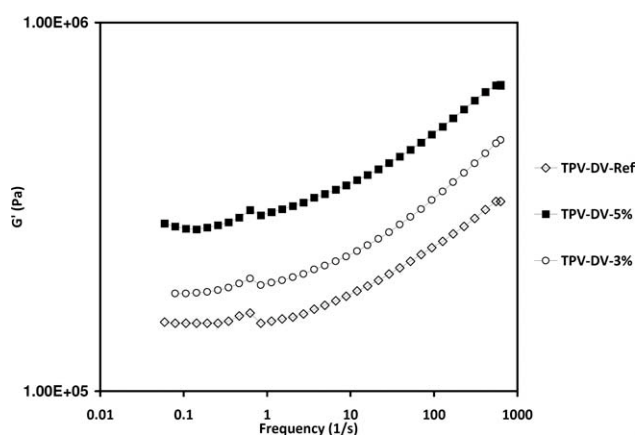


**Figure 6** Storage modulus as a function of strain amplitude at  $T = 200^{\circ}\text{C}$  and frequency of 1 rad/s;  $810 \times 523$  mm ( $96 \times 96$  DPI).

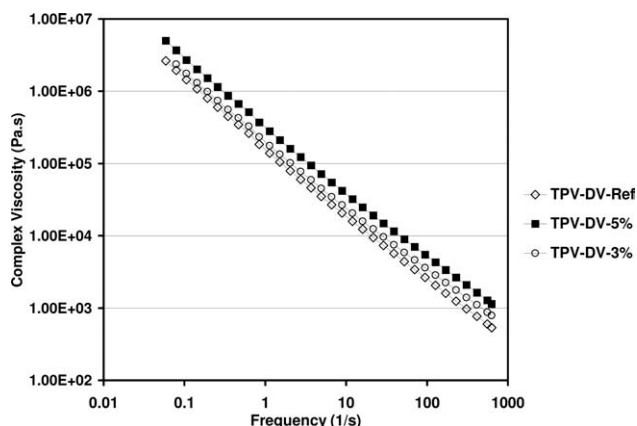
matrix and is rarely affected by the presence of the filler.<sup>10</sup>

Melt rheological behavior of *in situ* dynamically vulcanized TPV nanocomposites composed of 3 and 5 vol % of EG are presented in Figures 7 and 8. Storage modulus and complex viscosity of *in situ* dynamically vulcanized PP/EPDM/EG/PP-g-MAH nanocomposites showed to be higher at all frequencies than the unfilled *in situ* dynamically vulcanized PP/EPDM sample (TPV-DV-Ref). This is attributed to the existence of interconnected physical networks formed by the EG nanolayers throughout the PP matrix. This is consistent with the electrical conductivity behavior exhibited by the *in situ* vulcanized nanocomposite samples as insulator to conductive transition occurs above 3 vol % of EG, as will be shown in the following section.

It is clearly seen in Figure 8 that both of these two nanocomposites exhibit shear thinning characteristics similar to the *in situ* prepared reference TPV. This behavior is attributed to the presence of both meso-



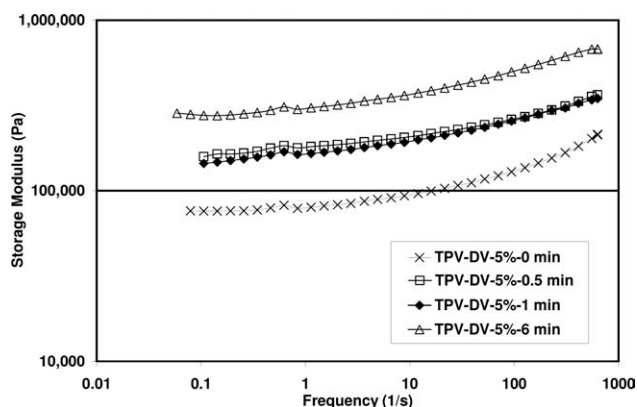
**Figure 7** Storage modulus as a function of frequency for *in situ* dynamically vulcanized PP/EPDM samples composed of 3 and 5 vol % of EG;  $803 \times 543$  mm ( $96 \times 96$  DPI).



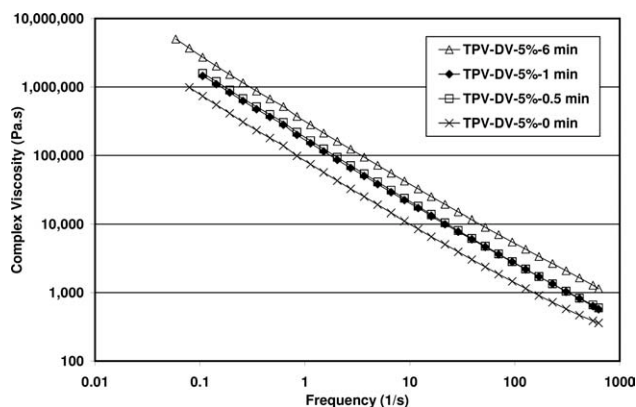
**Figure 8** Variation of melt dynamic complex viscosity versus frequency for *in situ* dynamically vulcanized PP/EPDM nanocomposites composed of 3 and 5 vol % of EG;  $808 \times 537$  mm ( $96 \times 96$  DPI).

scopic EG networks, and interconnected agglomerates formed by the dynamically vulcanized rubber droplets throughout the PP matrix of the EG reinforced TPVs.

Linear viscoelastic behavior of the *in situ* vulcanized TPV nanocomposites with different SOC has also been illustrated in Figures 9 and 10. It is clearly seen in Figure 9 that the sample removed before the onset of dynamic vulcanization (TPV-DV-5-0 min) exhibits the lowest melt storage modulus within the whole range of frequency. This is attributed to the lack of intensified interface between the PP matrix and uncrosslinked EPDM droplets with low stiffness. Dynamical vulcanization leads to the increase of melt elastic modulus as a result of the formation of crosslinked networks formed by the EPDM droplets. Increasing the SOC led to the increase in melt elasticity of the TPV nanocomposites as the interconnectivity between formed EPDM aggregates is enhanced by increasing the time of dynamic



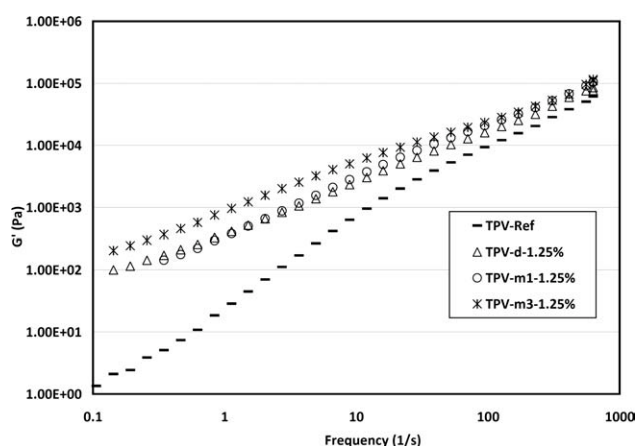
**Figure 9** Melt dynamic storage modulus versus frequency for *in situ* dynamically vulcanized TPV nanocomposites composed of 5 vol % EG removed at different time of dynamic vulcanization (SOC);  $812 \times 516$  mm ( $96 \times 96$  DPI).



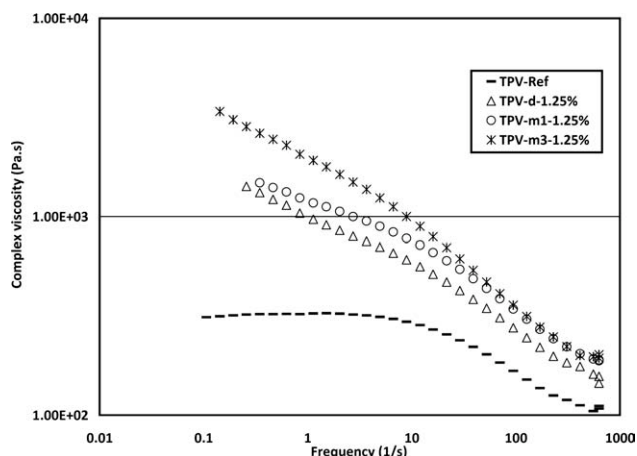
**Figure 10** Complex viscosity as a function of frequency for *in situ* dynamically vulcanized TPV samples composed of 5 vol % EG removed at different time of dynamic vulcanization (SOC); 812 × 518 mm (96 × 96 DPI).

vulcanization.<sup>11</sup> This is correlated with the electrical conductivity behavior exhibited by the samples with different SOC as is discussed in the next section.

Figure 11 represents the frequency dependency of TPV nanocomposites prepared via melt blending of prevulcanized TPV, PP-g-MAH, and EG. It is clearly seen that at high frequency region all nanocomposite samples prepared by this method exhibit similar behavior to that of the unreinforced TPV reference sample, indicating that at high frequency, melt elasticity is mainly originated by the dynamically cross-linked EPDM agglomerates dispersed throughout the PP matrix, and not affected by the EG particles. However, within low frequency regime, the TPV nanocomposite composed of 1.25 vol % of EG and PP-g-MAH to EG ratio of 3 showed higher  $G'$  value with more nonterminal behavior, which evidences the presence of higher physical networks formed by the EG nanolayers within the TPV matrix. This is con-



**Figure 11** Comparison between  $G'$ -frequency rheographs of unreinforced predynamically vulcanized TPV sample (TPV-Ref), and corresponding nanocomposites prepared by direct and masterbatch melt blending with EG; 818 × 569 mm (96 × 96 DPI).



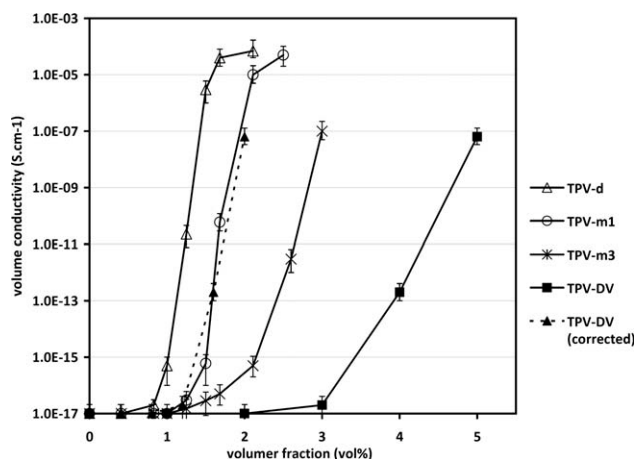
**Figure 12** Frequency dependency of melt dynamic viscosity of the unreinforced predynamically vulcanized TPV, and corresponding nanocomposites composed of 1.25 vol % EG; 815 × 585 mm (96 × 96 DPI).

sistent with higher melt complex viscosity and more shear sensitivity observed for this nanocomposite as illustrated in Figure 12. Higher melt dynamic viscosity at low frequency region for the masterbatch-based TPV nanocomposites implies the effectiveness of this method in enhancing polymer/filler interfacial interactions as well as dispersion state of the EG nanolayers. Comparing the dynamic storage modulus of the TPV-d-1.25% and TPV-m3-1.25% samples shows that in direct mixing process of EG with predynamically vulcanized TPV, distributive mixing of EG nanolayers is dominated to the dispersive mixing leading to less breakdown of the EG agglomerates and therefore weak dispersion of the EG nanolayers. This would result in a nonuniform response of the polymer segments towards the applied dynamic stress field, and hence higher viscous characteristics at low frequency region. More dispersive mixing in TPV-m3-1.25% has resulted in higher elastic response of the TPV nanocomposite sample.

## Electrical conductivity

Volume resistivity in  $\Omega$  cm, (the quotient of D.C. electric field strength and the steady state current density within a material) and conductivity percolation threshold are important properties in electrically conductive composites. EG is very attractive for its ability to increase the electrical conductivity of insulating polymers at very low concentrations.

Figure 13 illustrates the plot of electrical conductivity as a function of EG content for the TPV/EG nanocomposites prepared by direct and masterbatch melt mixing, and compared with those fabricated by *in situ* dynamic vulcanization. Both groups of nanocomposites display distinct percolation effects, namely conductivity enhances by several orders of magnitude above a critical EG volume fraction,



**Figure 13** Volume conductivity versus volume fraction of EG for the prepared TPV nanocomposites; 815 × 584 mm (96 × 96 DPI).

which is called percolation threshold. It is clearly seen that the nanocomposite sample generated by direct melt blending of predynamically vulcanized TPV with EG in the presence of PP-g-MAH shows lowest percolation threshold compared with those prepared by masterbatch melt mixing (TPV-m1 and TPV-m3). This leads to the conclusion that distributive mixing (direct method) is more beneficial in the formation of conductive paths, as lots of less broken graphite agglomerates link together via Vander Waals forces which simplify flow of electrical current throughout the nanocomposite matrix. This is consistent with the higher threshold exhibited by the sample generated from masterbatch melt mixing method with PP-g-MAH to EG ratio of 3 as a result of higher shear stresses imposed on the mix during melt blending which leads to the more breakdown of EG agglomerates and more separation of EG nanolayers. This is in agreement with higher melt viscosity and more melt elasticity exhibited by the TPV-m3 sample (Fig. 8). On the other hand, degree of fracture of the EG honeycomb structure in masterbatch mixing method has great influence on the lateral size of graphite nanolayers and their interconnectivity.

Comparing the conductivity of predynamically vulcanized TPV/EG nanocomposites with those prepared via *in situ* vulcanization shows a higher perco-

**TABLE III**  
Electrical Conductivity of *In Situ* Dynamically Vulcanized TPV/EG Nanocomposites Removed from the Mixer at Various State of Vulcanization (SOC)

Sample code	Electrical conductivity (S cm <sup>-1</sup> )
TPV-DV-5%-0 min	<1E-14
TPV-DV-5%-0.5 min	<1E-14
TPV-DV-5%-1 min	<1E-14
TPV-DV-5%-6 min	6.32E-8

**TABLE IV**  
Values of the Exponent Factor ‘n’ Reported by Various References

References	n-Value	References	n-Value
Duan <sup>15</sup>	0.85	Kymakis et al. <sup>20</sup>	2
Barrau et al. <sup>16</sup>	1.4–1.8	Barrau et al. <sup>21</sup>	2.28
Cruz-Estrada and Folkes <sup>17</sup>	1.355	Shekhar et al. <sup>22</sup>	1.96
Kovacs et al. <sup>18</sup>	2.7	Afanasov et al. <sup>23</sup>	1.9
Zheng et al. <sup>19</sup>	2.1	Lu et al. <sup>24</sup>	2.01

lation threshold for the *in situ* dynamically vulcanized samples. This is explained to be due to the partly encapsulation of EG nanolayers by the dispersed EPDM droplets before the onset of vulcanization, and hence increase in the level of required EG for insulator to conductor transition. Therefore, for the *in situ* dynamically vulcanized TPV samples based on PP/EPDM blend (60/40), a mathematical correction was done for the concentration of EG nanolayers in TPV samples. The correction was based on the fact that, if EG was divided equally between two phases, only 40% of graphite nanolayers would participate in making conductive percolative networks. The corrected curve is shown by dashed line in Figure 13. It is obvious that the real percolation threshold for both *in situ* dynamically vulcanized TPV/EG nanocomposite and masterbatch made samples (TPV-m1) is in the order of 1.68 vol % of EG.

The electrical conductivity of the *in situ* dynamically vulcanized nanocomposites with different SOC are presented and compared in Table III. It can be observed that the samples with low SOC or incomplete vulcanization show insulator behavior. This implies that the formation of conductive networks by the graphite nanolayers is retarded by the off cured viscous EPDM droplets. This is consistent with the linear viscoelastic behavior of the nanocomposites with various SOC as was discussed.

The electrical conductivity behavior of the prepared TPV nanocomposites was checked by the existing models. Various models have been proposed to predict and analyze the volume conductivity of electrically conductive composite materials. One of the most widely used is based on percolation theory.<sup>12,15–24</sup> According to this model, sudden increase in conductivity by increasing the concentration of the conducting filler evidences the presence of a percolation threshold. This has been described with a simple power law equation with the following form<sup>1,4,12,13</sup>:

$$\sigma_c = \sigma_m(\phi_f - \phi_{crit})^n$$

where  $\sigma_c$ , conductivity of the composite (S cm<sup>-1</sup>);  $\sigma_m$ , conductivity of the filler (S cm<sup>-1</sup>);  $\phi_f$ , volume



fraction of the filler  $\phi_{crit}$ , percolation threshold;  $n$ , exponent.

It has been reported that increasing the aspect ratio of the conducting filler would lead to the increase of value of exponent factor ( $n$ ). For one- and two-dimensional fillers,  $n$  value is often between 1.2 and 2.<sup>14</sup> This model has been used to characterize the conductivity behavior of polyaniline/graphite system,<sup>15</sup> polyepoxy/carbon nanotube (CNT) composites,<sup>16</sup> styrene-butadiene-styrene (SBS)/polyaniline composite,<sup>17</sup> epoxy/CNT composites,<sup>18</sup> polymethyl methacrylate (PMMA)/nanographite composite,<sup>19</sup> poly(3-octylthiophene)/single wall carbon nanotube (SWNT) composite,<sup>20</sup> polypyrrole-epoxy/CNT composite,<sup>21</sup> PVC/iron carbide nanoparticle composite,<sup>22</sup> coal tar pitch/EG composite,<sup>23</sup> and polyester resin/graphite nanosheets composite.<sup>24</sup> The reported values for the critical exponent ( $n$ ) for these polymer composites have been illustrated in Table IV. By fitting the experimental data to the equation derived from percolation theory, the value of the exponent factor for TPV-d and TPV-m1 samples were calculated to be 1.5 and 2.12, respectively. This evidences higher aspect ratio for the EG particles in masterbatch processed samples than direct mixed TPV samples, which implies better dispersion of graphite nanolayers for the samples generated from masterbatch mixing process, and therefore longer conductivity threshold. These results lead to the conclusion that conductivity is affected by the extent of interconnectivity of the graphite aggregates as well as dispersion state of graphite nanolayers. Therefore, better dispersion of the EG nanolayers may make samples with lower conductivity.

## CONCLUSIONS

Electrically conductive dynamically vulcanized thermoplastic elastomer nanocomposites based on PP/EPDM blend (40/60 w/w) and EG were successfully prepared via *in situ* melt dynamic vulcanization process as well as melt blending of a predynamically vulcanized TPV with EG. Effects of interfacially compatibilization and feeding route of the components on the dispersion state of the EG nanolayers throughout the TPV matrix, and hence on the electrical conductivity behavior were also investigated. The linear melt viscoelastic behavior as well as electrical conductivity of the TPV/EG nanocomposites, prepared by *in situ* dynamic vulcanization, showed to be affected by the SOC after the onset of vulcanization. Insulator to conductive transition was exhibited by nanocomposites obtained at high SOC,

where the rubber droplet aggregates are fully cross-linked and developed. Conductivity measurements showed lower percolation threshold for the nanocomposites generated by direct melt mixing of predynamically vulcanized TPV with EG and PP-g-MAH compared with those prepared via masterbatch mixing process. The *in situ* dynamically vulcanized samples generated from PP/EPDM/EG/PP-g-MAH exhibited longer conductivity percolation threshold than the nanocomposites based on predynamically vulcanized TPV.

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