Rheological Behaviour of PP/EPDM Blend: The Effect of Compatibilization

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ABSTRACT

Due to different polarity and structure between the thermoplastic and elastomeric phases, most thermoplastic elastomers are incompatible. Poor interfacial adhesion and high interfacial tension between rubber and thermoplastic phases are main reasons for incompatibility of these systems. The blends of polypropylene (PP)/ethylene propylene diene monomer (EPDM) containing 20% EPDM may be compatibilized with maleic anhydride grafted PP (PP-g-MAH) and maleic anhydride grafted EPDM (EPDM-g-MAH) ranging from 0 to 6 phr. The dynamic rheological behaviour of the blends in presence of compatibilizer and applying dynamic vulcanization were studied using parallel plate rheometric mechanical spectrometer (RMS) at 190°C. The Cole-Cole and van Gurp-Palmen plots for all samples were plotted to make correlation between rheology and the obtained morphology of the blends. It was found that the complex viscosity ($\eta'$) of the dynamic vulcanized blends levelled up with increase of compatibilizer concentration while for un-vulcanized blends it was levelled off for the same ratio of PP/EPDM. Storage modulus of compatibilized samples showed two relaxations shoulder at high concentration of compatibilizer which at low frequencies is attributed to interfacial relaxation and at high frequencies is related to EPDM droplets. There was no considerable difference among intersection frequencies ($\omega_c$) for un-vulcanized samples which means compatibilizer is more effective in combination with dynamic vulcanization. Morphological study showed that the size of dispersed phase decreased with combination of dynamic vulcanization and compatibilization.

INTRODUCTION

Due to good mechanical properties, low density and low cost, polypropylene (PP) is one of the most versatile commodity polymers. The main disadvantage of this polymer is its low temperature impact resistance. To improve impact resistance, blending of ethylene propylene diene monomer (EPDM) with PP (in both academic studies and industrial products) is a well known technique [1-4]. However, this type of thermoplastic elastomer olefinic (TPO) has an unstable morphology because of coalescence of dispersed rubber particles and low compatibility between rubber phase and thermo-
plastic matrix.

To stabilize the morphology of the blend, the rubber phase is vulcanized in-situ during the melt blending while to improve compatibility and achieve finer dispersion of rubber particle, using appropriate compatibilizer and block or graft copolymer have been reported [5,6]. Dynamic vulcanization of rubber phase in the thermoplastic elastomer (TPV) was first introduced by Fisher [7] and developed by Coran et al. [8]. This process can improve properties such as oil resistance, tensile properties, maximum service temperature, permanent set and etc. [9,10].

Because of the incompatibility of most TPOs systems due to poor interfacial adhesion and high interfacial tension of the two phases of rubber and thermoplastic components [11,12] the system suffers of poor mechanical properties. The incompatibility between PP and EPDM may also be attributed to differences in crystallinity of two polymers [13].

Limited works so far have been published on the use of compatibilizer for PP/EPDM and their effect on the dynamic rheological behaviour. Kristine et al. have used 1% hexa(allylamino)cyclophosphonitrile (HAP) and peroxide during reactive extrusion for PP/EPDM [14]. They have observed an increase in low-temperature impact strength and an enhanced dispersion of EPDM in the PP matrix in the presence of peroxide and HAP as new multifunctional coupling agent. Kim et al. [15] have used poly(ethylene-co-methacrylic acid) (EMA) as ionomer and have applied dynamic vulcanization to control miscibility of the PP/EPDM blends. Their results have demonstrated that the dynamic vulcanized PP/EPDM blend containing 15 wt% of Zn-neutralized ionomer and 1.0 phr dicumyl peroxide (DCP) leads to thermoplastic interpenetrating polymer networks (IPN) structure and leads to enhancement of the blend miscibility. Naskar and his co-worker selected three potential compatibilizers for PP/EPDM blend: PP-g-EPDM, styrene-ethylenebutylene-styrene (S-EB-S) and trans-polyoctenamer (TOR) [16].

They found that only the first one showed some compatibilizing action in straight un-vulcanized blends, as evidenced by a slight increase in tensile strength of the blend and a somewhat smaller EPDM particle size within the PP matrix. In addition, dynamic mechanical analysis in particular $T_g$s of the PP and EPDM component showed some signs of compatibilization [16].

The main objective of this work is to contribute to this topic by studying the effects of compatibilizers on the dynamic rheological behaviour with and without dynamic vulcanization in PP/EPDM blend containing 20% of EPDM. Maleated EPDM (EPDM-g-MAH) and maleated PP (PP-g-MAH) were used in various concentrations as compatibilizer in the same ratio. To find the relationship between different morphological studies and rheological data obtained, various parameters were evaluated and scanning electron microscopy (SEM) observations were examined. In addition, the dynamic rheological data were analyzed with Cole-Cole and van Gurp-Palmen plots to find a correlation between rheology and the obtained morphology.

**EXPERIMENTAL**

**Materials**

Ethylene propylene diene monomer (EPDM, Vistalon7500, density = 0.9 g/cm³, 55% ethylene content) used in this study was a commercial grade of Exxon Mobil Co. (Belgium), polypropylene (PP, 570P, density = 0.9 g/cm³, MFI = 3 g/10min) was provided by Sabic Co (KSA). Additives (accelerator and activator) for sulphur curing system were provided by Bayer Co. (Germany). Maleated EPDM (OPTIM TP-613/P with MAH content = 0.5-1%, MFI = 13.2 g/10min) was supplied by Pluss Polymer Pvt. Ltd. (China) and maleated PP (MFI = 64 g/10min, MAH content = 0.1%, trade name Priex 20070) was purchased from Solvey (Belgium) and it was used as compatibilizer.

**Sample Preparation and Measurement**

The composition and abbreviation of blends are presented in Table 1. The samples were prepared by an internal mixer (Haake SYS 90, USA) with banbury blade rotor at 190°C and 60 rpm. PP and PP-g-MAH dry mixed and then fed into the mixing chamber, after PP melted, and a dry mixed EPDM and EPDM-g-MAH was added. In addition PP-g-MAH and EPDM-g-MAH were separately compounded to investigate
the effect of single compatibilizer in rheological behaviour of the blends. The mixing time for TPO-C samples was 10 min. For TPV-CS samples, sulphur curing system was added into mixer at the 5th min of mixing time. Uncured and uncompatibilized samples were prepared in the same procedure. The rheological behaviour and melt viscoelastic properties of the samples were studied using a rheometric mechanical spectrometer (RMS, Paar Physica USD200) with a parallel plate on samples with 25 mm diameter and around 2 mm thickness at the angular frequency range of 0.01-1000 s\(^{-1}\) and 190°C. Strain sweep test was carried out at 190°C and 10 rad/s. To study the morphology, cryogenically surface fractured of samples were etched and investigated using scanning electron microscopy (SEM) (Philips model XL30). Etching accomplished by cyclohexane at room temperature for 24 h.

### RESULTS AND DISCUSSION

#### Dynamic Rheological Analysis

Figure 1 shows the effect of compatibilizer on linear viscoelasticity of samples which are obtained from strain sweep test at 190°C and at a frequency of 10 rad.s\(^{-1}\) for the PP/EPDM: uncured (TPO), uncured compatibilized (TPO-C, TPO-CP, TPO-CE), dynamically vulcanized (TPV) and compatibilized dynamically vulcanized (TPV-CS, TPV-CSP, TPV-CSE) samples. As it can be seen from Figure 1b the critical strain of TPO samples does not change with compatibilizer significantly while for TPV samples it shifts to lower strains (Figure 1a). In addition, the linear zone of samples containing one compatibilizer (TPO-CP, TPO-CE) was similar to other samples. The critical strain for TPV-CSE and TPV-CSP were higher than those of compatibilized vulcanized samples. It seems
that the main reason for this behaviour is due to different morphologies derived from compatibilized TPO and TPV samples. In other words, with the addition of compatibilizer, the linear viscoelastic region of compatibilized blends is lower than that of the uncompatibilized blend. This implies that some interactions exist between polymer chains and compatibilizer at interfacial region. The similar results have been reported by other researchers [17,18].

The variation of complex viscosity ($\eta^*$) with frequency ($\omega$) for different compatibilized TPO and TPV samples is illustrated in Figure 2 at 190°C. At lower frequencies, the complex viscosity increases with increase of compatibilizer content for TPV samples (Figure 2a). In compatibilized TPV samples, compatibilizer chains are located in the interface of two phases and form a strong interaction which leads to decreased interfacial tension and increased interfacial adhesion. As a result of compatibilization, the interface thickness increases which leads to effective stress transfer between the EPDM dispersed particles and PP matrix phases. This stronger interfacial phase contributes to reduction in interlayer slippage and therefore an increase in viscosity [19,20]. In other words, it is believed that the compatibilizer chains restrict the mobility of the matrix chains and form a brush-like structure between matrix and disperse chains. The existence of this structure causes better dispersion and stabilization of the blend morphology [21]. This phenomenon is shown schematically in Figure 3 for compatibilized PP/EPDM blend.

As can be seen in Figure 2a, the viscosity of samples containing one compatibilizer is lower than other samples, which means the efficiency of compatibilization is not significantly high.

At higher frequencies a different behaviour was observed. It is well established that at lower frequencies the viscosity of blends is strongly affected by elastic nature of rubber (which is under the influence
of compatibilizer agent) while at higher frequency, rubber like behaviour of blend disappears and PP plays its main role for variation of viscosity (Figure 2b) [22].

For TPO-C samples the viscosity was lower than virgin TPO. This may be attributed to inadequate concentration of compatibilizer in the compound which could not be able to form a sufficient interaction between two phases.

To reconfirm the formation of strong interfacial adhesion the tensile properties of sample containing 3 phr of compatibilizer were determined (Table 2). The results showed the highest tensile strength was related to compatibilized samples with dynamic vulcanization.

The frequency dependencies of storage modulus for compatibilized and uncompatibilized samples are demonstrated in Figure 4 at 190°C. As can be seen in Figure 4a, for TPV samples at higher concentration of compatibilizer there is two clear relaxation shoulders in the curves. The relaxation shoulder at low frequencies is attributed to interfacial relaxation and at high frequencies it is related to EPDM droplets.

It should be considered that, the first shoulder is affected by type and the molecular structure of compatibilizer and the second shoulder is affected by droplet size [17]. In terminal zone ($\omega \to 0$) with increase of compatibilizer content, the storage modulus increases which is an indication of increased elasticity and interfacial adhesion. However this trend was not observed for un-vulcanized samples (Figure 4b). This can be explained as follows: since the droplet dimension in TPO samples is higher than that of TPV samples (due to coalescence) and there is a weak interfacial adhesion between two phases, the elasticity of compatibilized TPO samples is lower than virgin TPO. In other words, it seems the compatibilizer acts as a lubricant in the interface of these compounds and presumably interlayer slippage occurs. Although, two relaxation peaks were observed for TPV-CSE and TPV-CSP, due to lack of compatibilization, $G'$ was decreased.

A different rheological behaviour for samples was observed in van Gurp-Palmen plot (Figure 5) which

### Table 2. Tensile strength of TPO, TPO-C3, TPV-S, and TPV-CS3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength(MPa)</th>
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<tbody>
<tr>
<td>TPO</td>
<td>18.76</td>
</tr>
<tr>
<td>TPO-C3</td>
<td>19.75</td>
</tr>
<tr>
<td>TPV-S</td>
<td>18.77</td>
</tr>
<tr>
<td>TPV-CS3</td>
<td>27.05</td>
</tr>
</tbody>
</table>
Figure 5. van Gurp-Palmen plot of samples at 190°C for (a) TPV and (b) TPO samples.

Figure 6. Cole-Cole plots of samples at 190°C for (a) TPV and (b) TPO samples.

present the phase angle ($\delta$) versus complex modulus ($|G'|$). It is well established that compatibility and morphology of two-phase systems can be studied by this plot. It has been reported that, when the curve has the valley at its lower complex modulus, a droplet matrix morphology is formed [23,24]. From the characteristic shape of our samples it can be concluded that the dominant morphology for all samples is of droplet-matrix type. Another interesting result from van Gurp-Palmen plot is that with increase in compatibilizer content (Figure 5a) the phase angle of TPV samples decreases and shifts to value less than 45° while for TPO samples (Figure 5b) it does not change considerably. This behavior implies that the elasticity of TPV increases after compatibilization.

Cole-Cole plot is a well known curve for investigation of rheology of two-phase systems like polymer blends and filled polymer which forms by a plot of imaginary viscosity ($\eta''$) versus real viscosity ($\eta'$). Cole-Cole plot can interpret mechanism of relaxation, mean or characteristic relaxation ($\tau_c$) and zero shear viscosity ($\eta_0$) of polymer blend. Zero shear viscosity is calculated by fitting the Cole-Cole representation and extrapolation to the x-axis ($\eta'$ at $\eta''=0$), whereas the mean relaxation time is given by the inverse frequency where the maximum occurs [23,25,26]. The Cole-Cole plot for TPO and TPV samples are shown in Figure 6. From Figure 6a, one can find with increasing compatibilizer concentration in TPV samples, the relaxation process occurs at longer time. It seems, the presence of compatibilizer in compound causes the formation of finer droplet-matrix morphology. These droplets retard the relaxation of the systems and increase the relaxation time. On the other hand, no similar trend manifests for TPO samples. In the absence of dynamic vulcanization the compatibilizer does not show adequate efficiency, therefore coarse droplet-matrix morphology will be formed and
two relaxation mechanisms corresponding to two phases are observed because of non-homogeneity. The tail in Figure 6b confirms the existence of two relaxation mechanisms [27,28].

Dynamic intersection frequency ($\omega_c$) which is related to crossing of $G'$ and $G''$ curves is another rheological criterion [29-31]. This frequency indicates the separation of viscosity and elasticity. At this point:

$$G_c(\omega_c) = G'(\omega_c) = G''(\omega_c)$$

(1)

the value of $\omega_c$ depends on homogeneity of the systems. The lower value of the $\omega_c$ indicates finer dispersion of system which shows the structure of the blend is more homogeneous. As shown in Figure 7 there is no considerable difference among intersection frequencies for un-vulcanized samples. However, with increase of compatibilizer concentration, $\omega_c$ is decreased for vulcanized samples (Figure 8). It can be concluded that compatibilizer is more effective in combination with dynamic vulcanization. Although at
lower frequencies for most polymers \( G' \) is higher than \( G'' \) it should be noted that, by combination of dynamic vulcanization and compatibilization the elasticity of the system increases considerably. In addition the shifting of the \( G'-G'' \) cross-point towards lower frequencies, means relaxation times are increased [23,32,33]. Another interesting point in Figure 8 is that there is no intersection for samples containing compatibilizer above 1 phr. For these samples \( G' \) is always higher than \( G'' \) which indicates greater elasticity because of better compatibility. This trend can be confirmed by considering van Gurp-Palmen plots (Figure 5). In van Gurp-Palmen plots of mentioned samples the curves were less than 45° phase angle base line which implies:

\[
\delta < 45° \rightarrow \tan\delta = \frac{G''}{G'} < 1 \rightarrow G'' < G'
\]  

(2)

Figure 8. Storage \((G'(\bullet))\) and loss modulus \((G'(\bigcirc))\) versus angular frequency \((\omega)\) at 190°C for TPV samples.
Morphology
The morphology of the blends is elucidated using SEM. Figure 9 shows the SEM micrographs of TPO, TPV-S, TPO-C3, and TPV-CS3 samples. As seen for TPO samples because of etching, EPDM appears as dark hole while for TPV samples due to dynamic vulcanization the EPDM droplets could not be extracted by the solvent and looks as white droplets. The compatibilization action is evident from the changes associated with compatibilizer incorporation. From Figure 9, one can find droplet-matrix morphology for all samples with EPDM particles being dispersed in PP matrix. By comparing the micrographs, it seems in the absence of compatibilizer and dynamic vulcanization, interface adhesion is very poor (Figure 9a). In dynamic vulcanization, however, the coalescence tendency is suppressed in blend (Figure 9b) while by combination of dynamic vulcanization and compatibilization the coalescence is highly suppressed. This implies that, finer dispersion of EPDM particles in PP matrix is due to increasing interfacial adhesion and decreasing interfacial tension.

CONCLUSION
In this study, the effects of compatibilization on the rheological behaviour of PP/EPDM blend with and without sulphur dynamic vulcanization was studied. It was found that the fine dispersion of EPDM droplet can be obtained with combination of dynamic vulcanization and compatibilization. Some results are listed below:
- Complex viscosity of dynamic vulcanized blends levelled up with increase of compatibilizer concentration while for un-vulcanized blends it was levelled off.
at the same ratio of PP/EPDM.
- Cole-Cole plots showed that there are different relaxation processes in samples due to different morphology. The EPDM droplet retarded the relaxation of the system and increased the relaxation time. The coarse droplet-matrix morphology showed two relaxation mechanisms.
- Van Gurp-Palmen plots showed the compatibilizer increased the elasticity of the blend and the morphology of samples is droplet-matrix.
- Storage modulus showed two relaxations shoulder at high concentration of compatibilizer which at low frequencies is attributed to interfacial relaxation and at high frequencies it is related to EPDM droplets.
- The compatibilization effects of PP-g-MAH and EPDM-g-MAH individually were lower than that of their combined blend.

REFERENCES

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