Correlation between the Rheological Behaviours and Morphologies of PP/EPDM Blends in Various Dynamic Vulcanization Systems

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Received 29 September 2007; accepted 9 March 2008

ABSTRACT

Dynamic vulcanization is a well known technique which improves the mechanical properties such as compression set, tensile properties, fatigue, and chemical resistance of thermoplastic elastomers. In this study, three different curing systems (sulphur, peroxide, and phenolic resin) were applied on the polypropylene (PP)/ethylene propylene diene monomer (EPDM) blends. The weight ratio of the blends was PP/EPDM: 40/60. The samples were prepared in an internal mixer at rotor speed of 60 rpm and 190°C. Dynamic rheological parameters such as storage modulus (G’), loss modulus (G''), complex viscosity (η*), real and imaginary viscosities (η’ and η''), damping factor (tan δ), and linearity region were determined at 190°C. The non-linearity region of dynamic vulcanized samples was shorter than that of the thermoplastic elastomer without applying dynamic vulcanization. The Cole-Cole, Han, and van Gurp-Palmen plots for all samples were drawn to make correlation between rheologies and morphologies of the blends. It was found that the rheological behaviour of dynamically cured samples was different from uncured sample, because dynamic vulcanization could affect the morphology of the blends. All samples showed morphology of the EPDM rubber dispersed in the PP matrix (droplet-matrix) with different particle size.

INTRODUCTION

Dynamic vulcanization of rubber phase in the thermoplastic olefinic elastomer (TPO) was first introduced by Fisher [1] and developed by Coran et al. [2]. This process can improve some properties such as oil resistance, tensile properties, maximum service temperature, permanent set, etc. [3,4]. There are three main curing systems for dynamic vulcanization of ethylene propylene diene (EPDM) in PP/EPDM blends: sulphur, peroxide, and phenolic resin [5,6]. Each of these methods has its own advantages and disadvantages, for example; hygroscopicity and formation of black specks as demerits and higher service temperature and partial compatibilization as merits.
of resin curing system have been reported in other studies [6-9]. Several reports on the relationship between rheological and mechanical properties have been published while there are relatively few publications on the correlation between rheology and morphology properties of these blends [9-12]. Goharpey et al. have applied sulphur dynamic vulcanization on PP/EPDM blend and reported that there is a close relationship between rheology and morphology of thermoplastic elastomer vulcanizate (TPVs) particularly regarding the parameters that affect the formation of the network agglomerate structure between cured rubber particles [13,14]. Li et al. tried to characterize the rheological behaviour of droplet matrix and co-continuous morphology of poly (methyl methacrylate) and poly (styrene-co-maleic anhydride) systems. They found weighted relaxation time spectrum and significantly different Cole-Cole plots corresponding to dispersion and co-continuous morphology [15,16].

It is well known that dynamic vulcanization can change and stabilize the morphology of rubber phase in PP/EPDM blends. During dynamic vulcanization, rubber particle size decreases significantly and thus, the interfacial adhesion increases between two phases. In addition, the obtained morphology is stabilized because of weak coalescence tendency of rubber particles [6,14].

In this study, three different types of curing systems (sulphur, peroxide, and phenolic resin) were applied to PP/EPDM blends. Since there is a close relationship between the morphology and rheology of polymer blends, our aim was to find the morphological response of the blends with different curing systems and correlate them with rheological data. For this purpose, the dynamic rheological data were analyzed with respect to Cole-Cole, Han, and van Gurp-Palmen plots to obtain correlations between the rheology and morphology properties. In other words, we have tried to monitor the different morphologies due to various applied curing systems through rheological properties.

**EXPERIMENTAL**

**Materials**

EPDM was Vistalon 7500 from Exxon Mobile Co., Belgium (density=0.9 g/cm³, 55 wt% ethylene content) and PP was 570P (density=0.9 g/cm³, MFI=3 g/10 min) from SABIC Co., Saudi Arabia. Sulphur curing system additives (accelerator and activator) were purchased from Bayer Co., Germany. Peroxide was dicumyl peroxide (DCP) with Di-cup90 trade name from Hercules Co., Germany and divinyl benzene (DVB) as a co-agent in peroxide curing system were purchased from Fluka Co., Austria. Phenolic resin (SP1045) was prepared from Monsanto Co., France and stannous chloride (SnCl₂) in resin curing system was purchased from Loba Chemie Co., India.

**Sample Preparation**

The compositions of different curing systems are depicted in Table 1. The samples were prepared using an internal mixer (Haake SYS 90, USA) with

<table>
<thead>
<tr>
<th>Component</th>
<th>TPO</th>
<th>TPV-S</th>
<th>TPV-P</th>
<th>TPV-R</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>100*</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>PP</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>St Ac.</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MBTS</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TMTD</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DCP</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>DVB</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>SnCl₂.2H₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

(*) phr: per hundred of rubber; The letter after each TPV denotes the type of curing systems; (S:sulphur, P:peroxide, and R:resin).
Banbury blade rotor at 190°C and 60 rpm. PP was fed into the mixing chamber followed by addition of EPDM when PP was melted.

The mixing was continued for 5 min before the curing systems were fed. The total mixing time was 10 min and then, the samples were cooled to room temperature, the same condition was applied to prepare unvulcanized sample (TPO). Dynamic rheological properties were determined using a rheometric mechanical spectrometer (RMS) (Paar Physica USD200) in frequency mode with parallel plates. The frequency range was 0.01-1000 s⁻¹ and the temperature was 190°C.

Scanning electron microscopy (SEM) (Philips model XL30) was used to observe blend morphology. The samples were etched by cyclohexane at room temperature for 24 h.

Gel content of the samples was determined in accordance with ASTM D-2765, wherein about 0.8 g of ground sample was extracted through a 120-mesh stainless steel pouch in boiled cyclohexane for 24 h.

RESULTS AND DISCUSSION

Figure 1 shows the torque-time behaviour obtained from Haake internal mixer for three curing systems and TPO. In this figure, two peaks are observed up to fifth min of mixing time for all samples which are related to PP and EPDM loading torques, respectively. For TPV-S, the torque shows a peak after addition of curing ingredients which reaches a constant value higher than its value before dynamic vulcanization.

In TPV-R curve, after addition of phenolic resin, the torque falls abruptly due to resin melting and its internal lubricating effect in compound. The torque increases after reaction of phenolic resin and reaches a plateau higher than that of sulphur curing system. The torque-time behaviour of peroxide system (TPV-P) is similar to sulphur system except its ultimate lower plateau region. Chain scission of polypropylene in presence of peroxide is the main reason for this phenomenon as reported by other researchers [17,18].

Figure 2 illustrates the range of linearity region of samples which is obtained from strain sweep test at 190°C and 10 rad/s. As it can be seen, in comparison with PP, by addition of EPDM to PP the non-linearity region shifts to a lower critical strain. However, dynamic vulcanization of EPDM leads to non-linearity of three systems which are lower than that of TPO. Deviation from linearity is observed for peroxide curing system at the lowest strain. It seems that the main reason for this behaviour lies in the differences between stability and particle size of dispersed phase in various dynamic vulcanization systems. It is well-known that dynamic vulcanization leads to formation of more stable and finer dispersion morphology [9,12].

Figure 3 shows the storage modulus versus angular frequency for TPO and different cured samples at 190°C. The storage moduli of cured samples are higher than those of TPO in low frequency range. This
can be explained by the higher elasticity of cured samples due to dynamic vulcanization [12]. In other words, the cured dispersed elastomer can be assumed as filler in PP matrix which increases the storage modulus [13,19]. The highest storage modulus is related to sulphur curing system, because the efficiency of sulphur curing system is higher than those of other systems. The gel contents of sulphur, peroxide, and phenolic resin curing systems were 95.63%, 84.64%, and 92.7%, respectively.

Figure 4 illustrates the variation of complex viscosity with angular frequency for all samples at 190°C. It is obvious that complex viscosities of cured samples are higher than those of TPO at low frequencies because of dynamic vulcanization. As can be seen in Figure 4 the zero shear viscosity ($\eta_0$) of cured samples is higher than that of TPO. This can be explained by the decrease in free volume because of cross-linking of rubber phase in the blend. Thus, diminishing slippage between the polymer chains [4] leads to higher viscosity or resistance towards shear flow. The highest zero shear viscosity was related to sulphur curing system. It has been reported that due to mechanism and structure of the sulphur curing system, the probability of coalescence is higher than the other two curing systems which lead to the formation of larger size dispersed rubber domains [6].

On the other hand, because of more compatibility in resin cured samples, the size of rubber dispersed phase was finer and due to higher surface area the zero shear viscosity was higher than that of peroxide cured samples. At higher frequencies the viscosity of sulphur and resin curing systems reach the same values. The main reason for this behaviour maybe related to breakage of unstable sulphur linkage.

Complex viscosity of TPV-P intersects the TPO curve at around 2 s$^{-1}$ (Figure 4). At lower frequencies, the viscosity of blend is strongly affected by the elastic property of rubber. While, by increasing frequency, the rubber-like behaviour of blend disappears and peroxide degraded PP shows its effect on the viscosity which leads to decreased complex viscosity [10].

It can be expected, that with reducing the rubber phase and thus decreasing the elastic nature of the blends, the cross point shifts to lower frequencies. Another interesting point from Figure 4 is the slope of complex viscosity at low frequencies (terminal zone). As can be seen the slope of cured samples are higher than that of TPO which means higher sensitivity of TPVs to shear rate compared to TPO, since more pseudoplastic behaviour is obtained through dynamic vulcanization. The better extrudability of TPVs relative to TPO is the advantage of dynamic vulcanization [4,19].

**Cole-Cole Plot**

Cole-Cole plot is a well-known curve for investigation of rheological behaviours of two phase systems like polymer blends and filled polymer. This plot is
formed by drawing imaginary viscosity ($\eta''$) versus real viscosity ($\eta'$) [22]. Cole-Cole plot can interpret the mechanism of relaxation, mean or characteristic relaxation time ($\tau_c$) and zero shear viscosity ($\eta_0$) of polymer blend reported by other researchers [16,23-25]. Some of the rheological information, derived from Cole-Cole plot is shown schematically in Figure 5.

Cole-Cole plots of all samples are illustrated in Figure 6. It is clear that there is no circular arc for them; meaning that no miscibility exists for PP/EPDM blend even in resin curing system. In addition to non-circular form of Cole-Cole plot, $\tau_c$ cannot be determined with high accuracy. Comparison between Figures 5 and 6 shows that $\eta_0$ for dynamic vulcanized samples would be higher than that of sulphur curing system which has also been observed in Figure 4.

**Figure 5.** Schematic Cole-Cole plot and useful derived information at constant temperature.

**Figure 6.** Cole-Cole plots of samples at 190°C.

**Han Plot**

A log-log plot of storage modulus ($G'$) against loss modulus ($G''$) (Han plot) of different samples at a constant temperature (190°C) is shown in Figure 7. This plot is used for studying the sensitivity of the rheological behaviour of blends towards temperature and composition [26-28]. Since the Han plot for samples is not fitted into single curve it can be concluded that rheological behaviour is affected by both dynamic vulcanization and different curing systems [22,16]. However, it seems that the rheological behaviour of dynamic vulcanized samples is less dependent on the curing systems. At higher dynamic modulus (corresponding to higher frequencies) there is close proximity between the sulphur and resin cured samples curves. As described before, at high frequencies, the matrix plays important role in rheological behaviour which may be attributed to the degradation of polypropylene chains in the peroxide cured system, which is manifested into different behaviours.

**Figure 7.** Han plots of samples at 190°C.

**Figure 8.** van Gurp-Palmen plots of samples at 190°C.
van Gurp-Palmen Plot
The different rheological behaviours of samples are also observed in van Gurp-Palmen plot (Figure 8) that presents the phase angle (δ) versus complex modulus (G*). It is well established that compatibility and morphology of two phase systems can be studied by the related plot. It has been reported when the curve has a downward trend lower than its complex modulus, a droplet-matrix morphology is being formed [16,15]. From the characteristic shape of our samples it can be concluded that dispersion is common in all morphologies of the samples. This observation was confirmed by SEM micrographs discussed in the morphology section.

Morphology
Figure 9 shows the SEM micrographs of TPO and cured samples. It is observed that the dominant morphological feature of all samples is evident by EPDM dispersion in PP matrix. However the co-continuous morphology was observed in some parts of TPO samples. It is well-known that in dynamic vulcanization the viscosity of EPDM becomes higher than that of PP and thus it is PP which by its lower viscosity forms the continuous phase [4].

Therefore, the type of curing system and degree of cross-linking of rubber phase can be affected by the size of dispersed phase [12,14]. The finest particle size of dispersed phase was related to resin curing system because of compatibility effect of this curing system. The coarse dispersed morphology was obtained from sulphur system. Sulphur curing system in our study was semi-efficient (Table 1). Since, the semi-efficient system develops mono- and di-sulphide link-

![Figure 9. SEM Micrographs of: (a) TPO, (b) TPV-S, (c) TPV-P and (d) TPV-R.](image-url)
ages, the potential exchange of rubber particles becomes higher and the larger dispersed domain size or coalescence can be formed. The coalescence of rubber phase during sulphur dynamic vulcanization has been reported by Du et al. [6].

CONCLUSION

In this work, sulphur, phenolic resin, and peroxide curing systems were applied on PP/EPDM blends with 40/60 weight ratio in an internal mixer. The dynamic rheological behaviour of samples was determined and tried to correlate with the obtained morphologies. Some further deductions are as follows:

1. The non-linearity region of TPVs samples was shorter than that of TPO.
2. The storage modulus of TPVs samples was higher than that of TPO because of dynamic vulcanization.
3. The zero shear viscosity of TPV-S was the highest among all others due to its higher tendency for coalescence in comparison with other curing systems.
4. Due to compatibilization effect, the phenolic curing system showed the finest particle size morphology while degradation of PP in peroxide curing system showed different rheological behaviour.
5. Cole-Cole, Han, and van Gurp–Palmen plots showed some sensitivity of rheological behaviours towards curing systems which are related to different obtained morphologies.

REFERENCES