

Dynamic Rheological Behavior of Thermoplastic Elastomers from PA6,66 /EPDM Blends: Effect of Blend Ratio, Compatibilization and Dynamic Vulcanization

Cibi Komalan

S. N. M. College, Maliankara, Kerala, India

Abstract: *In this work rheological behavior of PA6,66/EPDM blends have been investigated. Viscoelastic properties such as complex viscosity(η^*), Storage modulus and loss modulus of uncompatibilized, compatibilized and dynamically vulcanized blends on the rheological behavior is discussed in detail. The effect of compatibilisation on the interfacial tension between the polymers is also discussed. Attempts were done to correlate the phase morphology with rheological data.*

Keywords: Rheology, Complex viscosity, Storage modulus, loss modulus

I. INTRODUCTION

Rheological studies are useful for understanding the effect of various parameters on flow behaviour of materials for optimising the processing conditions. For the fabrication of articles of good finish and dimensional stability, knowledge about the processability of the material under high frequency is required. Dynamic rheological measurements offers several advantageous over the conventional steady shear rheometry because of its unique ability to assess and provide important dependence of rheological properties of the materials without disturbing the conformation of the material.

The rheological properties of the components in immiscible polymer blends affect the processing, morphology and property relationships[1]. A large number of studies have been reported on the melt flow behavior of thermoplastic elastomers [2]–[10]. Utraki and Kamal[11] have reviewed the rheological behavior of many polymer blends. Increase in the viscosity upon the incorporation of rubber in a plastic phase has been reported in various systems[12][13]. Melt rheology and morphology of nylon6/ethylene propylene rubber (EPR) blends was studied as a function of composition, and compatibilizer loading by Oommen et al.[14]. The structure-rheology relationship of polyvinylidene fluoride/hydrogenated nitrile rubber blends with special reference to the effect of mixing time was studied by Anil K.Bowmick et al. [15], Recently many researchers reported about the rheological investigations of different polymer blends [16][17][18][19][20].

Effect of graphite micro structure on the melt rheology on interfacially compatibilized PP-EPDM vulcanizate was studied by AA Katbab et al.[21]. Several researchers have studied the effect of dynamic vulcanization on the rheological behavior of rubber/plastic blends[22] [3][23]. N Ghahramani et al.[17] extensively studied the rheology of Thermoplastic vulcanizates (TPVs) especially PP/EPDM rubber system. According to them TPVs exhibit complex rheological fingerprints similar to those of soft elastic solids due to the presence of crosslinked rubber particles. They made an attempt to draw correlation between the rheology with morphology. Kumar et al.[24]studied the effect of various vulcanizing agents on the rheological behavior of nylon/NBR blends.

In this paper the effect of blend ratio, compatibilization and dynamic vulcanization on rheology of PA6,66 (Nylon 6,66) and Ethylene Propylene diene EPDM blends are narrated in detail.

II. EXPERIMENTAL

2.1 Materials

PA6, 66 (Nylon6,66) supplied by SRF Ltd. Madras, India. EPDM with E/P ratio 58/37.5 wt % and DCPD content 4.5wt % was obtained from DSM (Netherlands). The EPM-g-MA was supplied by Exxon Chemical Company. All the rubber grade chemicals such as Zinc oxide, stearic acid, Tetramethyl thiuram disulphide, mercaptobenzothiazole, triallyl cyanurate, Sulphur and dicumyl peroxide were purchased from the local market.



2.2 Preparation of the blends

Uncompatibilized blends were prepared by adding EPDM to the melted PA6,66 in a Haake rheomix. It is designated as N0 for neat EPDM, N30 for 30/70 PA6, 66/EPDM, N50 for 50/50 PA6, 66/EPDM, N70 for 70/30 PA6, 66/EPDM and N100 for neat PA6, 66. The compatibilized blends were prepared by the addition of different weight percentage of EPM-g-MA into the melted PA6, 66/EPDM blend system for N70 system. They are designated as N701, N702.5, N705, N7010 according to the different weight percentage of the compatibilizer added. Dynamically vulcanized blends were prepared by the addition of curatives along with the additives to the melted PA6,66/EPDM. The PA6,66 /EPDM Thermo plastic vulcanizates compositions employed for this study are N70S,N70D,N70S+D and N70S+D+Comp.

III. RESULTS AND DISCUSSIONS

3.1 Uncompatibilised Blends

In the Figure.1 the frequency dependence of the complex viscosity (η^*) of uncompatibilised blends at 190°C is depicted. Due to the pseudoplastic behaviour of the polymer and their blends the complex viscosity of the pure components and their blends decreases with increase in frequency. This is because on application of high shear rate, randomly oriented and entangled polymer chains gets disentangled and oriented in the direction of shear[25]. So the shear rate increases with increase in frequency. EPDM has got a higher viscosity than PA6,66 in all range of frequencies. The complex viscosities of all the blend ratios are found to be intermediate between the neat polymers. By the addition of EPDM viscosity increases. Such an increase in viscosity on incorporation of rubber phase has been reported by Varughese et al.[12]. The increase in viscosity is due to the entanglement of long chains of EPDM with themselves and also with the PA6,66 chains. These entanglements inhibit the flow of the melt at low shear rates and consequently, the viscosity becomes higher. PA6,66/EPDM blends showed lower viscosities than pure EPDM at high shear rates due to the higher disentangling effect of EPDM chains due to repulsion. Moreover in polymer blends, the viscosity depends on the compatibility between the individual polymers. From the Figure 1 it is seen that the complex viscosity of the PA6, 66/EPDM blends shows a negative deviation and this indicates the incompatibility of the blends.

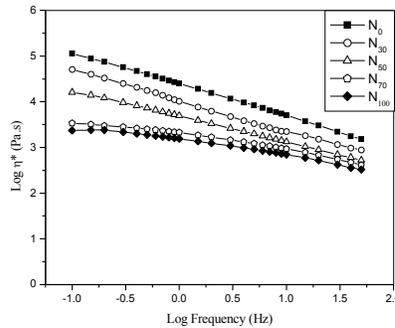


Figure 1 Effect of blend ratio on the complex viscosity of uncompatibilized

PA6,66/EPDM blends

The viscosity ratio of PA6,66 and EPDM is very much sensitive to the frequency fluctuations due to their highly incompatible nature. This is evidenced from the Table 1, which shows the viscosity ratio of the polymers at selected frequencies.

Table 1 Viscosity ratio of EPDM and PA6, 66 at various frequencies

Table with 4 columns: Frequency(Hz), Complex viscosity (η*)Pa.s (subdivided into EPDM and PA), and Viscosity ratio (ηEPDM/ηPA). Rows show data for frequencies 0.1, 0.5, 1, 5, 10, and 15 Hz.

20	3030	1280	2.4
30	2200	1080	2.1
50	1520	800	1.9

As the frequency increases the viscosity ratio decreases. It should also be noted that the viscosity difference between the polymers has significant impact on the phase morphology of the blends. The SEM micrographs of the etched samples of the blends are given in the Figure 2.

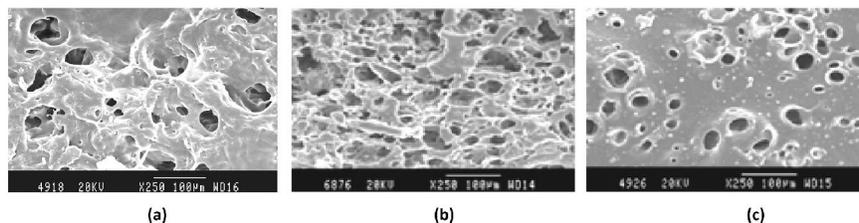


Figure 2: Scanning electron micrograph of PA6,66/EPDM blends (a) N₃₀, (b) N₅₀ (c) N₇₀

The large difference in viscosity with respect to frequency will reflect on the phase morphology stability of the blends and thereby the ultimate properties. If the minor component has lower viscosity compared to the major one, it will be uniformly dispersed in the major continuous phase owing to the diffusion restrictions imposed by the matrix.

According to Wu [26] the dispersed particles become larger when the viscosities of the two phases are closely matched. Since there is a large difference between the viscosities of the two polymers as seen in Table 1 one can expect a considerable difference between the phase morphologies of PA6,66 rich and EPDM rich blends and in the case of 50:50 blends. Phase morphology of PA6,66/EPDM uncompatibilized blends will be coarse, non-uniform and unstable as the polymers in molten state are very sensitive to frequency change. All these facts are found to be true in PA6,66/EPDM uncompatibilized system and thus it is believed that there is a perfect correlation between the morphology and rheology of uncompatibilized PA6,66/EPDM blends.

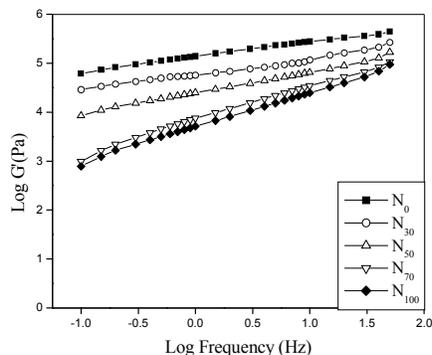


Figure 3 Effect of blend ratio on the storage modulus of uncompatibilized PA6,66/EPDM blends

The storage modulus (G') and loss modulus (G'') of various PA6,66/EPDM blends with different compositions at 190°C as a function of frequency is shown in the Figure 3 and 4. The storage and loss modulus shows similar variations with the composition of the blends. Both storage and loss modulus are higher for EPDM compared to PA6,66. As seen from the graph, storage and loss modulus increase with frequency due to the fact that the polymer chains get less relaxation time with increase in frequency. Here also the storage modulus and loss modulus values of all the blends are found to be intermediate between the neat polymers. As we know, G' can reflect the elasticity of the samples, it is evident that elasticity of the blends increased with the incorporation of EPDM. At higher frequencies storage modulus and loss modulus of PA6,66 increased substantially compared to the lower frequency.

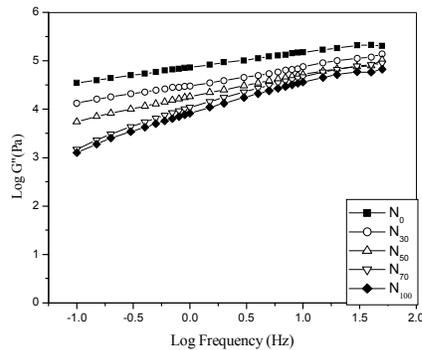


Figure 4: Effect of blend ratio on the loss modulus of uncompatibilized

PA6,66 /EPDM blends

PA6,66 melt shows η^* , G' and G'' values lower than that of EPDM rubber. It was reported that all the dynamic viscoelastic property values would increase with molecular weight increase, at a given frequency [27]. This indicates that PA6,66 may have lower molecular weight than that of EPDM rubber.

3.2 Compatibilized Blends

The effect of compatibilizer on the rheological properties of 70/30 blend of PA6,66 and EPDM is shown in the Figures 5,8 and 9. As depicted in the Figure 5 we found that complex viscosity of the blends increased as the amount of compatibilizer loading increases up to critical micelle concentration (CMC) in the whole frequency range. The increase in complex viscosity can be taken as an evidence for the compatibilizing action of EPM-g-MA. The viscosity increase is due to the chemical reaction taking place between anhydride group in EPM-g-MA and amine group in PA6,66. As the result of the chemical reaction, the molecular weight increases and it is the major reason for the viscosity increase of blends. In fact, the compatibilizer decreases the interfacial tension, and increases the interaction between PA6,66 and EPDM.

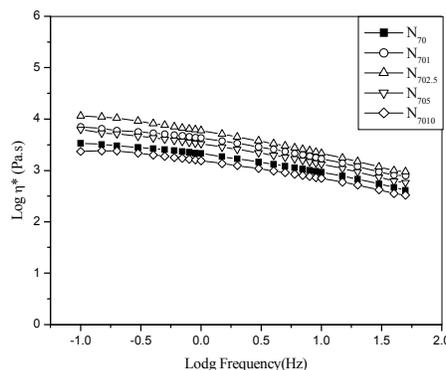


Figure 5 Effect of compatibilization on complex viscosity of N_{70} PA6,66/EPDM blends containing different levels of compatibilizer

The graft copolymer formed during the chemical reaction locates at the blend interface and holds the two phases together. The localization of the compatibilizer at the interface makes the interface more broad, less mobile and stable. Similar observations were reported by Wang et al. [28] for PA6/EPDM-g-MA, Hong et al.[29] for PA6/PP systems and Martin et al.[30]. In the case of uncompatibilized blends, there will be high extent of interlayer slippage between the phases due to the presence of sharp interface and poor interfacial attraction. Upon the addition of the compatibilizer, there will be less slippage at the interface. However, beyond CMC, at high concentration of the compatibilizer, the complex viscosity is even lower than that of the uncompatibilized blends. The decrease in the viscosity may be due to the cumulative effect of the micelle formation and the lower viscosity of the EPM-g-MA. These observations are in perfect correlation with the phase morphology of the blends given in figure 6.

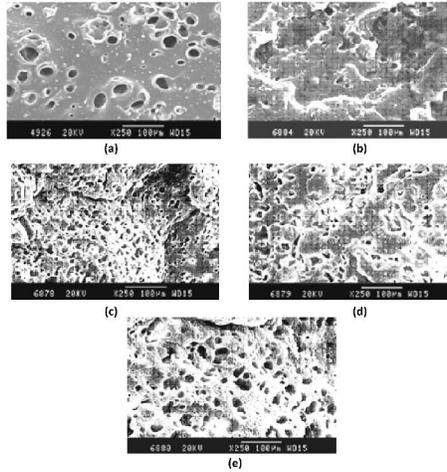


Figure 6: Scanning electron Micrographs of 70/30 blend containing different levels of EPM-g-MA (a) 0% (b) 1% (c) 2.5% (d) 5% (e) 10%

Figure 7 & 8 shows the effect of compatibilization on the storage and loss modulus of the 70/30 PA6,66 and EPDM blends. It is clear from the Figure 7 that storage modulus of compatibilized blends shows a linear increase. The increase in storage modulus is an indication of the pronounced elastic properties of the blends due to enhanced interfacial adhesion in the presence of compatibilizer. It should be noted that beyond critical micelle concentration (CMC), the storage modulus decreases. As shown in the Figure 8, the tendency of the loss modulus is similar to that of the storage modulus.

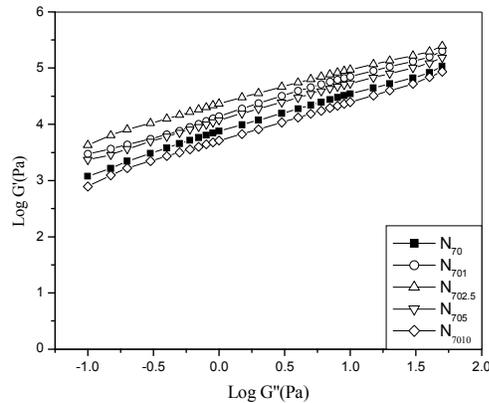


Figure 7 Effect of compatibilization on the storage modulus of N₇₀ PA6,66 /EPDM blends containing different levels of compatibilizer

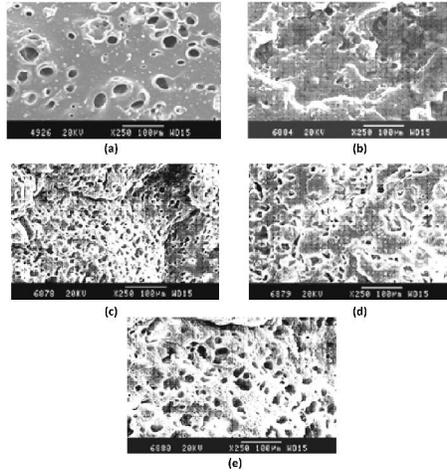


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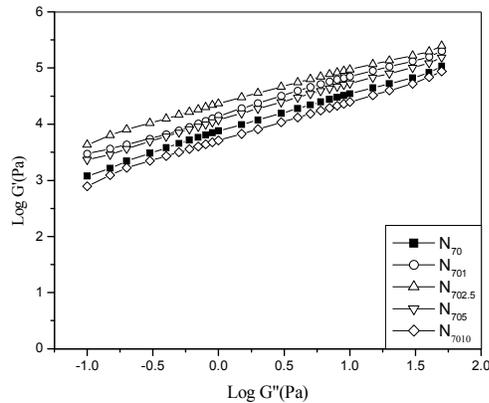


Figure 7 Effect of compatibilization on the storage modulus of N₇₀ PA6,66 /EPDM blends containing different levels of compatibilizer

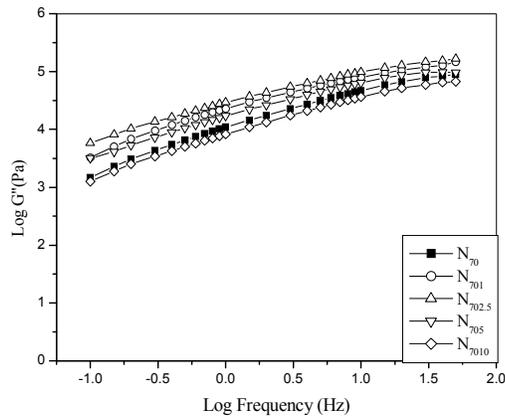


Figure 8 Effect of compatibilization on the loss modulus of N70 PA6,66 /EPDM blends containing different levels of compatibilizer

3.3 Dynamically Vulcanised blends

It was shown that fully cured thermoplastic vulcanizates exhibit highly pseudoplastic behaviour. Han and White [3] studied the rheological behaviour by various measurement techniques and find out that the dynamically vulcanized blends show behaviour, which is characteristic of materials with a rest state structure.

Figure 9,10 and 11 illustrates the results of complex viscosity η^* , storage modulus G' and loss modulus G'' behaviour of dynamically vulcanized samples of PA6,66/EPDM system. Different crosslinking system under investigation are sulphur, peroxide, a mixture of sulphur + peroxide and a mixture of sulphur + peroxide + compatibilizer. All the curves indicate pseudo plastic behaviour as the viscosity decreases with increasing frequency. During vulcanization three dimensional crosslinks are formed. This leads to increase in viscosity compared to the unvulcanized blends due to the decrease in the mobility of the polymer chains. Among the four vulcanized systems used, it is found that viscosity is highest for sulphur cured system followed by mixed + compatibilizers system, mixed system and DCP cured system. In the case of peroxide viscosity decreases due to the chance for the degradation of Pa6,66 at higher temperature. In the mixed system the degradation of PA6,66 over shadows the effect of crosslinking. In the mixed system with compatibilizer, in addition to the crosslinks some chemical bonds are also present. This also helps to enhance the viscosity of the system.

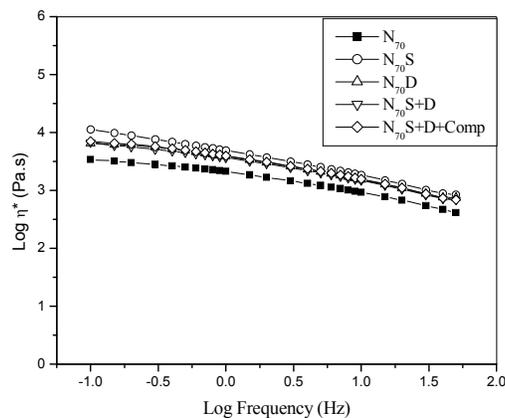


Figure 9: Effect of dynamic vulcanization on complex viscosity of N70 PA6,66/EPDM blends containing different types of crosslinking system

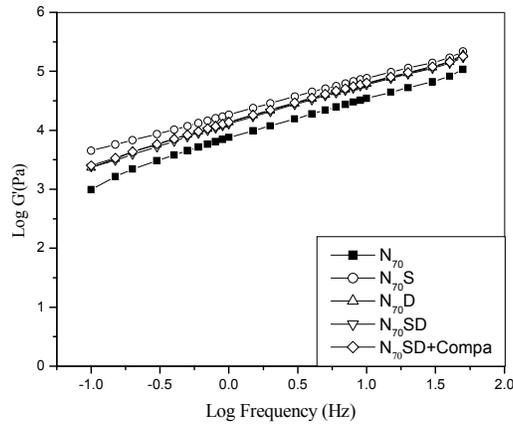


Figure10 Effect of dynamic vulcanization on storage modulus of N_{70} PA6,66/EPDM blends containing different types of crosslinking systems

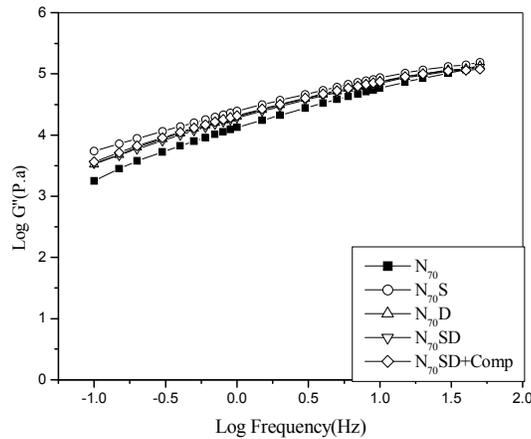


Figure 11 Effect of dynamic vulcanization on loss modulus of N_{70} PA6,66/EPDM blends containing different types of crosslinking systems

Figure 10 and Figure11 shows the storage modulus (G') and loss modulus (G'') of vulcanized PA6,66/EPDM blends. By comparing these results, one can clearly notice that the melt viscoelastic properties of the thermoplastic vulcanizates samples are considerably different from those shown by the simple blend samples. It is clear from the above figures that the storage modulus and loss modulus of vulcanized blends are higher than that of the binary blends. The increase in the values shows the same trend as in the case of complex viscosities. During dynamic vulcanization the crosslinked rubber face becomes finely and uniformly distributed in the plastic matrix and attains a stable morphology. The morphology of crosslinked samples was shown in the Figure 12.

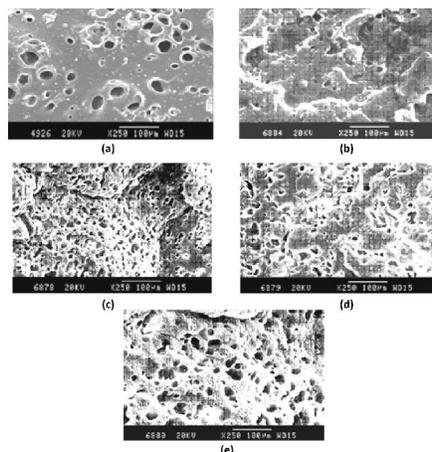


Figure 12 Scanning electron micrographs of dynamically vulcanized PA6,66/EPDM with different curative systems

(a)N₇₀ (b) N₇₀S₁ (c)N₇₀DCP₁ (d)N₇₀ Mixed (e) N₇₀ Mixed +2.5% compatibilizer

The PA6,66/EPDM blend vulcanized with sulphur system has got the lowest domain size while the blend vulcanized with peroxide has got the highest. The blend vulcanized with mixed system and mixed with compatibilizer has got a domain size in between those of sulphur and peroxide cured system.

IV. CONCLUSION

Dynamic rheology of PA6,66/EPDM blends was analyzed with special reference to blend ratio, compatibilization and dynamic vulcanization. It was found that complex viscosity of EPDM is maximum and that of PA6,66 is minimum. The complex viscosities of uncompatibilised blends were found to be intermediate between the neat polymers. All the blends showed a decrease in viscosity with increase of frequency, indicated the pseudoplastic behavior. The viscosity ratio between the polymers was very sensitive to frequency, which gives an indirect idea about the unstable morphology. The elastic properties such as storage and loss modulus are maximum for EPDM. The elastic properties showed similar variations with the composition of the blends. A good correlation was found between the rheology and morphology. Effect of compatibilization on the rheological properties revealed that complex viscosity increased with increase in compatibilizer concentration up to critical micelle concentration (CMC). Beyond CMC, a reduction in complex viscosity is observed. The micelle formation is believed to be responsible for the decrease in viscosity at higher compatibilizer loading. This increased viscosity for the compatibilized blends has been attributed to the increased interaction between the PA6,66 and EPDM as a result of decrease interfacial tension and coalescence due to the introduction of the compatibilizer. It was found that, the rheology and phase morphology of the compatibilized blends were intimately related. Dynamically vulcanized blends also registered an increase in viscosity with crosslinking. Among the dynamic crosslinked blends, the sulphur crosslinked blends showed the highest viscosity compared to other curative systems.

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