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Abstract
The effects of \textit{trans}-polyoctenylene rubber (TOR) addition on the tensile properties of vulcanized polypropylene/ethylene-propylene diene terpolymer/natural rubber (PP/EPDM/NR) blends were investigated. Blends were prepared in several blend ratios in Haake Polydrive with temperature and rotor speed of 180°C and 50 rpm respectively. Results indicated that the tensile strength and the stress at 100% elongation (M100) of vulcanized blends containing TOR are higher than without TOR leading to the formation of extended crosslinking. Scanning electron microscopy (SEM) micrographs from the surface extraction of the blends containing TOR support that the compatibilization have occurred during dynamic vulcanization.

Keywords: polypropylene, natural rubber, TOR.

Introduction
\textit{trans}-polyoctenylene rubber (TOR) is a low molecular weight polymer with broad molecular weight distribution. It is derived from metathesis polymer of cyclooctene with prevalently transisomeric double bonds and consists of linear as well as cyclic macromolecules [1,2]. It contains one double bond per eight carbon atoms with 80% of the double bonds arranged in a \textit{trans} configuration [3]. TOR also shows very low melt viscosity (approximately 120 ml/gr) above its melting point temperature [1,2]. Therefore, TOR has been recommended for use especially to improve processability of rubber compounds in uncured state [1-6]. Obviously, a structure-induced interaction takes place between the long chain molecules of the blend partner and larger rings of TOR. In the deformation of the non-crosslinked blend by external forces, e.g. in the internal mixer, the interaction occurred in the form of loose entanglements and sometimes showed no improvement in the mechanical properties.

TOR can also be vulcanized by sulfur, peroxide and other crosslink agents. The particular technical importance of TOR is the co-vulcanization possibilities with other rubbers. These might account for the thermal
stability of the blends, for the hindrance of the orientation of the rubber chain molecules in the internal mixer, for the improved elastic and dynamic properties of the vulcanizates and for swelling behavior in the liquids [1].

It has been reported by Chang, et al. [7], the use of TOR was effective in reducing the scale of phase morphology for vulcanized NR/EPDM blend. The homogeneity of highly incompatible NR/EPDM blend was greatly improved by TOR. A high degree of unsaturation in cyclic structure provides good cure compatibility in blends with other unsaturated elastomers. TOR accomplishes this by interacting in the network structure by co-vulcanized with rubber particles during crosslinking reaction [1]. This interaction increases the interfacial adhesion between the phases.

Meanwhile, PP/EPDM blends are one of the most studied of thermoplastic elastomers. However, synthetically produced EPDM rubber is more expensive than natural rubber (NR). Therefore, possibility of replacement of EPDM by NR has been investigated. We have reported in our previous work [8] that partially replacement of EPDM by NR in PP/EPDM/NR ternary blend decreases the properties of the blends due to the reduction in the compatibility of PP/EPDM. Therefore, dynamic vulcanization has been introduced to improve the properties of PP/EPDM/NR blends [9-11]. In this study TOR, a low molecular weight polymer was used and is expected to act as compatibilizing agent for vulcanized PP/EPDM/NR ternary blend. Here, the processability, tensile properties, morphology, oil resistances and gel content of vulcanized PP/EPDM/NR blends containing TOR along with the accompanying analysis in the thermal properties are reported and compared to the vulcanized blend without TOR addition.

**Experimental**

**Material**

Polypropylene homopolymer used in this study was an injection-molding grade, supplied by Titan PP Polymers (M) Sdn Bhd, Johor, Malaysia (TITANPRO 6331 grade) with a melt flow index (MFI) value of 14 gr/10 min at 230 °C and 2.16 kg. Ethylene-propylene diene terpolymer (EPDM - EPT 3072E), with Mooney Viscosity M1 (1+4) at 100 °C of 74 was purchased from Luxchem Trading Sdn. Bhd. Natural rubber (SMR L - HSL), with Mooney viscosity M1 (1+4) at 100 °C of 73 was obtained from Hokson Rubber Trading Sdn. Bhd, Seremban. Curatives and crosslink agent (sulfur) were purchased from Bayer Sdn. Bhd. trans-polyoctenylene rubber (TOR) used was supplied by Hüls, Germany with a trade name of Vestenamer® 8012 which contains 76% trans and 24% cis. Figure 1 shows the chemical structure of trans-polyoctenylene (TOR).

**Preparation and Processing**

Studies were conducted on PP/EPDM/NR blends consist of two systems viz. dynamic vulcanization and the combination of dynamic vulcanization and TOR where each system covering different blend compositions viz. 50/50/0, 50/40/20, 50/30/20, 50/20/30, 50/10/40 and 50/0/50. Blends were prepared by melt mixing in an internal mixer, Haake Polydrive with Rheomix R600/610 at temperature and rotor speed of 180°C and 50 rpm respectively. Table 1 shows the mixing sequence of components in preparation of the blends.

![FIGURE 1: Chemical Structure of trans-polyoctenylene (TOR) [6]](image-url)
Polypropylene (PP) was first loaded into the internal mixer and pre-mixing for two minutes. The rubbers (EPDM and NR) were added after two minutes. For dynamically vulcanized blend the curatives i.e. 5 phr of zinc oxide (ZnO); 1.5 phr of stearic acid; 1 phr of N-cyclohexyl-2-benzothiazol sulfenamide (CBS) and 0.4 phr of antioxidant were added after 5 minutes of mixing and followed by cross-link agent i.e. 2 phr of sulfur at 7th minutes, the mixing time was set for 10 minutes. For dynamic vulcanization containing TOR, the mixing process was completed after 11 minutes, where TOR was added after five minutes of mixing and followed by the addition of curatives and sulfur at 6th and 8th minutes respectively. At the end of the mixing process, the torque values were recorded. The samples were then sheeted by passing through 2 roll-mills and allowed to cool at room temperature.

Specimens for testing were compression molded using electrically heated hydraulic press machine. The machine was pre-heated at 180°C for six minutes and followed by another four minutes of compression under the same temperature. The specimen was allowed to cool under pressure for another four minutes. The same procedure was adopted for all blend systems.

### Tensile Properties

Tensile tests were carried out according to ASTM D412 on Instron machine. 2 mm thick dumbbell specimens were cut from the moulded sheets with a Wallace die cutter. The specimen was tested using a constant rate (50 mm/min) at room temperature of 25°C. The results were quoted based on the average value of five specimens tested for each blend system.

### Morphology Studies

Morphological evaluations of PP/EPDM/NR surfaces were done using a scanning electron microscope (SEM), model Stereoscan 200 Cambridge. The vulcanized samples were etched with nitric acid for two days, washed with water, and then dried. All the samples were mounted on aluminum stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination. The examinations were done within 24 hours of preparation.

### Results and Discussion

#### Tensile Properties

Figure 2 shows the effect of TOR addition on tensile strength of vulcanized PP/EPDM/NR blends. It can be seen that the vulcanized blends containing TOR show higher tensile strength than the vulcanized...
blend without TOR. This is due to a better stress transfer between phases in vulcanized blend containing TOR. This implies that the incorporation of TOR in dynamic vulcanization has improved the crosslink formation in rubber phase and compatibilization.

It should be mentioned that at this moment the chemistry of interfacial bonding by TOR addition is not clear.

However, it is suggested that the interfacial bonding between rubbers may be formed, due to the vulcanizability of TOR in the presence of sulfur. It is expected that during the vulcanization process, TOR which located at the interface may be co-vulcanized with component rubbers, and lead to the formation of interfacial bonding. It is also observed that the interfacial bonding, which is created in the presence of TOR during the vulcanization process, may produce finer phase morphology in the rubber blends. This observation is based on the property that proves the improvement of the interfacial strength between PP, EPDM and NR layers in the presence of TOR.

The comparison of stress at 100% elongation (tensile modulus, $M_{100}$) between vulcanized blend with TOR and vulcanized blend alone is presented in Figure 3.

![FIGURE 2: The Effect of TOR Addition on the Tensile Strength of Vulcanized PP/EPDM/NR Blends](image)

![FIGURE 3: The Effect of TOR Addition on the Tensile Modulus ($M_{100}$) of Vulcanized PP/EPDM/NR Blends](image)
The increase of $M_{100}$ vulcanized blend containing TOR is again due to the formation of crosslink by sulfur and compatibilization as a result of co-vulcanization of TOR. However, the tensile modulus ($M_{100}$) of vulcanized 50/10/40 and 50/0/50 blends containing TOR is not reported as it rupture before 100% elongation is achieved. Here, the vulcanized blends could not withstand the deformability of the macromolecules. In addition, according to Rajan et al.,\[12\] the increased in $M_{100}$ are evidence for strain-induced crystallization from a higher molecular weight due to the formation of crosslink. This phenomenon is can be related to the increase of crystallinity and hence provide stiffness.

The effect of TOR addition on the elongation of break of vulcanized blends is shown in Figure 4. It shows that the elongation at break of vulcanized blend containing TOR is lower than that of without TOR for all blends compositions. This indicates that the incorporation of TOR in vulcanized blend decreased the deformability of blend, which is due to the high degree of crosslink formation in rubber phase.

**Morphology Study**

The surfaces morphology of the vulcanized PP/EPDM/NR blends with and without TOR addition after extraction in the solvent is shown in Figure 5 (a-f). Dynamic vulcanization increases molecular weight, and higher molecular weight of vulcanized blend containing TOR was more effective in reducing and stabilizing the domain size of the dispersed phase (Figs. 5b and d) than the vulcanized blend without TOR (Figs. 5a and c). SEM technique, however, could not distinguish between different particles of NR or EPDM which embedded in the PP matrix.

It could be seen that the presence of TOR in vulcanized blend resulted in a decrease in the size and the amount of the voids present in the samples (Figs. 5b and d). Moreover, the rubber particles seem to adhere strongly to the PP matrix; therefore, the particles are hardly to be extracted by the solvent. The solvent is not successful in dissolving the finely dispersed rubber phase caused by the co-vulcanization reaction which has taken place by the addition of TOR. As mentioned before, co-vulcanized TOR had located at the interface between phases leading to a decrease in phase coalescence processes.

This promotes to the formation of interfacial bonding which contributed to the finer phase morphology in the blend.

Consequently, an improvement in morphological stability was obtained by lowering the interfacial tension between the phases. Draxler [1] also reported that the incorporation of TOR containing cyclic macromolecules without free chain ends into the rubber network might change the
network-structure, which then improves the vulcanized properties.


This result justified the improvements of tensile properties of the blend as mentioned before. It can be attributed to two effects: firstly, the TOR co-vulcanized with rubbers which are located at the interface between the phases and enhance the stress transfer which resulting in improvement of the tensile properties, particularly tensile strength and $M_{100}$. Secondly, upon addition of TOR, the number and size of the drops dispersed decreased leading to improve the tensile properties.

**Conclusions**

The presence of TOR in the vulcanized PP/EPDM/NR blend which is located at the interface was co-vulcanized with rubber
components and leads to the formation of interfacial bonding which increased the tensile properties. The SEM micrographs also exhibit the ability of TOR in reducing and stabilizing the domain size of the vulcanized rubber particles.

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References