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Mechanical Properties of Polypropylene/Epoxydized Natural Rubber Blend via Mixing Ratio Analysis

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ABSTRACT: This research is to investigate the effect of mixing ratio on the properties of polypropylene (PP) when incorporated with epoxidized natural rubber (EPNR). The EPNR blend was prepared by melt compounding using an internal mixer and vulcanized through vulcanization. Mechanical testing such as tension and hardness test and impact test was performed to determine the properties of EPNR blend. It was clearly observed that EPNR percentage in EPVNR blend increases the hardness and flexibility of the samples. As compared to pure PP, 40% EPVNR blend showed improvement of elongation at break with impact strength up to 64% and 36% respectively. It showed the tensile strength and hardness decreases as the amount of PP increases. It was concluded by properties imparted by elastomer chains to cross-linked EPNR. The obtained properties showed good correlation with fracture surfaces observed in microscopic analysis performed by Field Emission Scanning Electron Microscope (FE-SEM) at magnification of 500X and 5000X.

Keywords: Polypropylene, Epoxydized Natural Rubber, Blend, Mechanical properties

I. INTRODUCTION

Thermoplastic elastomers (TPEs) belong to a class of material that combines physical properties of thermoplastic and elastomers. They exhibit properties typical of rubber materials but can be processed like thermoplastics. Blending of polymers is a common technology, frequently applied in order to develop a product with superior mechanical properties from inexpensive polymer materials (Zarin 2006). It is aimed to obtain materials, which also as possible combine the advantages, but not their disadvantages. Furthermore, TPEs give better material utilization than thermosetting materials because waste and rejects can be recycled and re-used (Jimal et al. 2001).

Thermoplastic elastomers based on natural rubber and thermoplastic blends are classified as “thermoplastic natural rubber” (TPNR) blends. There are two types of TPNRs: (1) prepared by blending NR with thermoplastic such as polyolefin to get co-continuous phase morphology and it is technologically classified as “thermoplastic polyolefin (TPO)”, (2) is known as “thermoplastic vulcanizates (TPV)” which prepared by blending NR with polyolefin and the rubber phase is vulcanized during the mixing process at high temperature, the process is known as “dynamic vulcanization (DV)” (Nakada et al. 2006).

Polypropylene (PP) is an additional polymer with a large molecular weight distribution (Mayer and Klumper 2005). There are three types of PP such as atactic (a-PP), isotactic (i-PP) and syndiotactic (s-PP) (Seybold, 1995, 1999). It has wide range of applications due to its unique properties such as high melting temperature, low density, high chemical resistance, and resistance to heat. On the other hand, PP exhibits poor impact strength which gives limitation to several applications (da Costa et al. 2010, Hugel et al. 1997, Stach1998).

Epoxydized natural rubber (ENR) is a material of great interest, exhibiting a double functionality for cross-linking (double bond and apolyene site) while retaining most of the properties of natural rubber (Fale et al. 2010). The application of natural rubber can be performed using peroxide, generated from reaction of formic acid and hydrogen peroxide (Lin 1998). The properties of ENR are gradually changed with increasing degree of epoxidation (Miyata et al. 2010; Lim 1998). Processes of apolyene groups in rubber chains imparted great properties to natural rubber such as oil resistance, low gas permeability, good wear grip and high damping characteristics (Mohamed et al. 2006, 2010; Thirumannam et al. 2007).

The main objective of blending elastomeric phase (ENR) into PP is to improve its flexibility and behavior at low temperatures (Lopes Madiedo et al. 2001). In polymer blends with a crystallizable component, the final properties are determined by (1) mode and site of dispersion of rubbery domains in the crystalline matrix, (2) the texture, dimensions and size distribution of spherulites of the matrix, (3) the lamellae of spherulites, i.e., lamellar and interlamellar thickness, (4) physical structure of interlamellar boundary region and amorphous inter
lamellar regions; and (5) the adhesion between the subraye
domain and the crystalline matrix (George et al., 2000). 
In a study by Kooliy et al. (referred to in George et al.,
2000), the crystallinity of the blends decreased with the increase in
NR content, and the interfacial distance, d values increased on the addition of NR indicating the migration of NR phase into the interlamellar space of EVA. Blends of polyepehylene with nitrile rubber possess the excellent
processing characteristics and mechanical properties of
polyethylene with the oil resistance and flexibility of NR.

Studies conducted on PP/EPR or EBR/PP blend were
focusing more on studying the effect of dynamic vulcanisation (Nakazawa et al., 2006, 2008; Teichmann et al., 2007) or induction (Senna et al., 2008) to the properties of the blend. There is no significant effect on studying the effect of PP, EBR ratio to its physical or mechanical properties. In this paper, we have investigated the effect of mixing ratio between thermoplastic and rubber material to mechanical properties of polyethylene/nitrile rubber blends. The properties were supported by morphology analysis on the fracture surfaces.

II. EXPERIMENTAL

A. Material

PP used in this research is Polypropylene homopoly-
euryn TITANPRO 650 (biscuit type) with a specified melt flow index of 3.5 g/10 min. It was supplied by Titan PP Polymers (M) Sdn. Bhd. EBR was supplied by the Malaysian Rubber Board under the brand name of EBR 20 with 20% cis-1,4 polymer. The average Mooney viscosity measured at ML (1+4) 100°C was 25.5, and the average specific gravity at approximately 25°C was 0.9366. Sulfur was used as vulcanizing agent whereas zinc oxide and stearic acid were used as activators in the sulfur curing system. The sulfur, zinc oxide, and stearic acid were purchased from Sin Rokh Ltd.

B. Mixing and preparation of sample

The formulation of PP/EBR blends is given in Table 1. 
The dynamic vulcanisation was carried out using a Haake Rheomix OS internal mixer. Mixing chamber was 60 cm³ and the batch size was 20 ± 5 g. The mixer was operated at a constant rotor speed between 60 rpm-80 rpm at temperature range of 170°C - 200°C. The mixing for each batch took place for 10 minutes. Firstly, PP and EBR was added into the mixing chamber and mixed for 8 minutes; then, sulfur was added and mixing continued for another 2 minutes to complete the dynamic vulcanization.

The produced PP/EBR was immediately removed from the
chamber and left at room temperature for 24 hours. Then,
samples were pressed using CT2014-A hot press from Gebr. about 3 minutes at pressure of 1800 kPa. Subsequently, the samples were cooled down under presser to room temperature for 3 minutes. Samples were cut into desired sizes according to ASTM standards of various mechanical testing. It was then kept at room temperature for 24 hours before further testing.

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume (g)</th>
<th>45°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>120</td>
<td>45.00</td>
<td>45.00</td>
</tr>
<tr>
<td>EBR</td>
<td>80</td>
<td>30.00</td>
<td>30.00</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>2.0</td>
<td>2.20</td>
<td>2.50</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.5</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.0</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>50%</td>
<td>50%</td>
</tr>
</tbody>
</table>

C. Mechanical properties

Tensile test was carried out according to ASTM D638.
It is the most common plastic strength specifications and
covers the tensile properties of fabricated and moulded
plastics. This test method using standard "dumbbell" or "dogbone" shaped specimens at room temperature. Dumbbell specimens of PP/EBR blend were cut from moulded sheets using a Gebr. rubber machine. The tensile test was performed using Autograph AG-JC Universal Testing
Machine from Shimadzu Scientific Instruments at a cross
head speed of 2.0 mm/minute at room temperature, 25°C.

Hardness of the samples was tested using a Shore Type
D hardness tester according to ASTM D2240. The standard
hardness tester for ASTM D2240 is 64 ± 2.7 ± 3.2 mm (2% x 5% x 1/8 inch). The most common specimen thickness is 3.2 mm (0.125 inch), but the preferred thickness is 6.4 mm (0.25 inch) because its not as likely to bend or crack.

Samples prepared according to ASTM D 256 were
tested for impact strength for Izod pendulum impact
machine using an impact tester. Unnotched specimen
was held as a vertical cantilever beam and impacted by a
pendulum.

III. RESULTS & DISCUSSIONS

Mechanical Properties

Figures 1 and 2 show the comparison of tensile strength
and Young's modulus between pure PP and PP/EBR blends. It can be seen that the tensile strength and Young's modulus decreases with increasing rubber content in the blends. These reductions were due to the increased in blend rigidity with increasing EBR content. At lower rubber content (below 30%), the elongation at break was increased. At the rubber content increased further,

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particle-particle interaction of the rubber phases hance occlusion and accounts for the observed decrease in tensile strength and Young’s modulus of PP/ENR blends. In PP/ENR blends, the molecular entanglements in the rubber phase prevent rapid flow and disturbed the ability of the PP to move (Kedzierska et al., 2012) and to be reassigned crystallized in response to the applied stress.

As illustrated in Figure 1, PF/ENR 40/60 had the highest value of elongation to break (EBR) if compared to pure PF and 70/30 PP/ENR. It depicts the better elasticity, toughness and flexibility of the material. The pure PF shows the lowest value of EBR whereas 70/30 PP/ENR shows moderate value in between pure PF and 40/60 PF/ENR. The EBR value increases with increasing ratio of ENR in thermoplastic (Serma et al., 2008). It is directly represents the improvement on the ability of the material to absorb energy as rubber content increases since crosslinking in rubber phase (ENR-50) will impart the elastic behavior to the blend (Serma et al., 2006). Besides, the 50 wt% addition of ENR into PP increased the inter phase distance (d value) which indicates that rubber particles are present in the inter-spherulitic structure of PP (George et al., 2000). As the concentration of ENR increased to 50 wt% and above the d value decreased resulted from occlusion of rubber particles in inter-spherulitic regions due to the large size of ENR at higher concentrations.

According to George et al. (2000), rubber particles are present in inter- and intra-spherulitic regions of the crystalline phase plastic (Figure 3). Hence the observed increase in crystallinity is due to the fact that the formation of crystallites in the blend was affected by the presence of rubber particles. This results in the lower tensile strength of the PP/ENR blend if compared to virgin PP. Furthermore, the presence of crosslinking in thermoplastic matrix limits the flow and mobility which contribute to the rigidity of the polypropylene phase of the 70/30 PP/ENR blend increase the stiffness of the blend (Serma et al., 2006). In contrast, the crosslinking in rubber matrix of 40/60 PP/ENR blend impact elastic behaviors and lowers the Young’s modulus of FP due to rubber-like properties introduced by the ENR (Serma et al., 2008).
Figure 5 shows the hardness versus rubber content in PP/ENR blend. The pure PP (0 wt% of ENR) shows the highest hardness in the range of 73 to 76 Shore D compared to 40/60 PP/ENR and 70/30 PP/ENR. Hardness indirectly represents the stiffness or rigidity of the material which means the ability of the material to be scratched or indented by other material. The stiffness decreases as the rubber content increases in the sample. It was clearly observed in 40/60 PP/ENR sample. The samples show the lowest hardness in the range of 40 to 44 Shore D which indicate reduction of about 44% compared to pure PP. This is highly contributed by elastic properties of rubber phase in the blend. It shows good agreement with the EB values obtained in tensile test (Figure 4).

Figure 6 shows the impact strength of PP/ENR blends in comparison with pure PP. The 40/60 PP/ENR blends shows the highest impact strength in the range of 2.1 to 2.7 J/m compared to pure PP and 70/30 PP/ENR. Higher impact strength represents a higher resistance of the material to fracture under impact loading. This is related to toughness of the material whereby it measures the ability of the material to withstand both plastic and elastic deformations. It improves the amount of energy that required by the material to break the bond before fracture. It was in agreement with what is observed in tensile test whereby EB values increase as the ENR content increases. In this case, ENR is tougher than PP and makes it a good candidate to increase the flexibility of thermoplastic material. However, the impact strength of 70/30 PP/ENR deviated from this conclusion as it shows the lowest impact strength in the range of 0.9 to 1.1 J/m if compared to virgin PP or 40/60 PP/ENR. Localized and catastrophic deformation in impact test lowers the ability of rubber particles in interphasic structure of PP to absorb energy, efficiency. These rubber acts as frozen bodies and initiate brittle failure of the blend. It concludes that energy dissipation in a brittle test cannot be correlated with the level of toughness at impact strain (Chen and Evans 2008, Mohamad et al. 2011).

Table 2 summarizes the tensile properties, hardness and impact strength of PP/ENR blends. Tensile strength and EB decrease as the ENR loading increases. On the other hand, Young’s modulus also decreases with increasing of ENR in the blends. In terms of hardness, increase of rubber decreases the hardness of PP/ENR blends. While, increase of ENR higher than 50 wt% increased the impact strength of PP/ENR.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PP</th>
<th>70/30 PP/ENR</th>
<th>40/60 PP/ENR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>20.31</td>
<td>7.70</td>
<td>4.25</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>0.09</td>
<td>0.27</td>
<td>0.385</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>9.09</td>
<td>12.37</td>
<td>15.00</td>
</tr>
<tr>
<td>Hardness (Shore D)</td>
<td>74.30</td>
<td>60.92</td>
<td>42.39</td>
</tr>
<tr>
<td>Impact Strength (J/m)</td>
<td>1.03</td>
<td>0.83</td>
<td>2.15</td>
</tr>
</tbody>
</table>

5. Morphological Analysis

Figure 7, and 8 shows the tensile fracture surfaces of PP, 70/30 PP/ENR and 40/60 PP/ENR blends. The dark phase represent the ENR and the bright phases correspond to the PP. Most of the fracture surfaces show spherical shaped dimples from pulled-out of PP domains or ENR domains except for the fractograph of unfilled PP as it can be seen in Figure 7(a) and Figure 8(a). The fractograph of the unfilled PP shows characteristics of ductile fracture under uniaxial tensile loads with the obvious pattern of micro yielding on the surface. In Figure 7(b) and 8(b), fracture surfaces of 70/30 PP/ENR blend reveals that the ENR were dispersed as domains in a continuous PP phase. This is the stage where ENR is present in the interphasic structure of PP (Figure 3). In Figure 7(c), the ENR phase started to enlarge its size and formed bigger ENR domains in PP matrix. The structure was slightly in between proposed structure of 50/50 PP/ENR and 70/30 PP/ENR in Figure 3. In addition, there were smaller PP domains (PP particles) situated in ENR phases as depicted in 8(c). It clearly has shown the condition where coacervation of ENR
IV. CONCLUSIONS

As a conclusion, it was found that the thermoplastic vulcanizates of PP/ENR at high rubber content shows improvement in its toughness and flexibility. The elongation at break values increases as the rubber content increased in the blend. On the other hand, the addition of rubber content increases impact strength of more than 50 wt. % into the thermoplastic matrix. It was clearly proven when 40/60 PP/ENR blend showed increment of impact strength to 2.55 J/m as compared to 1.65 J/m in pure PP. However, the addition of rubber content lowers the tensile strength, Young's modulus and hardness of the blend due to the reduction in PP. These properties are highly contributed by the rigidity of PP chains and ability of it to be strain-crystallized. In contrast, the presence of crosslinking in rubber matrix of 60/40 PP/ENR imparted elastic behaviours and decreased the Young's modulus of PP due to rubber-like properties introduced by the ENR.

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