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PROPERTIES OF THERMOPLASTIC ELASTOMER BASED ON PP/EPDM/ENR25 AND PP/EPDM/NR BLENDS

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Abstract. The effects of partially substitutions of ethylene-propylene diene terpolymer (EPDM) with natural rubber (NR) and epoxidized natural rubber (ENR25) on the processability, tensile properties, oil resistance and morphologycal studies of PP/EPDM/NR and PP/EPDM/ENR25 blends were investigated. The blends were prepared in a laboratory internal mixer at 180°C and a rotor speed of 50 rpm followed by compression molding. The results indicated that PP/EPDM/ENR25 blend was slightly easier to process than PP/EPDM/NR blends and the torque values increased as the NR and ENR25 contents increased. Tensile strength and elongation at break decreased as NR and ENR25 content in the blends increased. PP/EPDM/NR blends showed higher tensile strength and elongation at break than PP/EPDM/ENR25 blends in all blends composition. However PP/EPDM/ENR25 blends exhibited better oil resistance than PP/EPDM/NR blends. From the morphological studies PP/EPDM/NR exhibit more homogeneous phases than PP/EPDM/ENR25 blends.

Key Words: Thermoplastic elastomer; polypropylene; ethylene-propylene diene terpolymer; epoxidized natural rubber; blend.

Abstrak. Kesan penggantian separa etilen propilen dien terpolimer (EPDM) dengan getah asli (NR) dan getah asli terepoksi (ENR25) terhadap sifat pemprosesan, regangan, rintangan minyak dan sifat-sifat morfologi bagi adunan PP/EPDM/NR dan PP/EPDM/ENR25 telah dikaji. Adunan tersebut telah disediakan dengan menggunakan pencampur dalaman pada suhu 100°C dan kelajuan rotor 50 rpm diikuti dengan pengacuanan mampatan. Didapati bahawa adunan PP/EPDM/ENR25 adalah agak mudah untuk diproses berbanding dengan adunan PP/EPDM/NR. Nilai tork adunan juga meningkat dengan penambahan NR dan ENR25. Kekuatan regangan dan pemanjangan pada takat putus menurun dengan penambahan NR dan ENR25 dalam adunan. Adunan PP/EPDM/NR menunjukkan kekuatan regangan dan pemanjangan pada takat putus yang lebih tinggi berbanding dengan PP/EPDM/ENR25 pada komposisi adunan yang sama. Walau bagaimanapun adunan PP/EPDM/ENR25 menunjukkan rintangan minyak yang lebih tinggi berbanding dengan adunan PP/EPDM/NR. Daripada kajian morfologi didapati adunan PP/EPDM/NR mempamerkan fasa yang lebih homogen berbanding adunan PP/EPDM/ENR25.

Kata kunci: Elastomer termoplastik; poli propilena; etilen propilen dien terpolimer, getah asli terepoksida, adunan.

1.0 INTRODUCTION

The reasons for the development of blends especially thermoplastic elastomers are [1]:

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(i) to improve the mechanical properties such as toughness
(ii) to produce useful materials with wide range of applications
(iii) to improve the polymer processability, and
(iv) to meet the market force (recycling process).

If a material can be generated at a lower cost with properties meeting the specifications, the manufacturer must exploit it to remain competitive. Blending of PP/EPDM are the most common combination for impact strength improvement of PP [2]. This blend has been used as material in the manufacture of car bumpers, fender extensions and rubber strips. Many recent works reported the structure property relationship of impact modified PP through its melt blending with EPDM [3-10]. However, EPDM is a synthetic rubber and generally must be imported. This means that the cost is expensive. Therefore this research was carried out to investigate the possibility of replacement or partial replacement of EPDM by NR or ENR.

Ethylene-propylene diene terpolymer (EPDM) is obtained by polymerizing ethylene and propylene with small amount of a non-conjugated diene (3 to 9%) [11]. Due to the unsaturated positions in the terpolymers, which lie outside the main chain, the good ageing characteristics, the ozone and cold resistance and the excellent electrical resistance of a saturated olefin remain. EPDM has a broad resistance to chemicals but not to oil and other hydrocarbons [12]. Meanwhile, an isotactic polypropylene is a stiff material, highly crystalline with high melting point. Typical uses of polypropylene include sterilizable hospital items, dishes, appliance parts, dishwasher components, containers, automotive ducts, trim, etc.

Natural rubber has been studied and reported on extensively because of its superior performance in tire application. Its behavior is governed by the composite properties of the vulcanizate and the base rubber. Meanwhile, epoxidized natural rubber (ENR) is a chemical modification of natural rubber. It developed some years ago and entered commercial production in 1989. The production involves natural rubber field latex, which under controlled conditions is converted to an epoxidized form by the *in situ* generation of peroxy formic acid. The epoxidation increased the polarity, which brought about an improved resistance towards hydrocarbon oil [13].

The objective of this work is to study the effect of partial replacement of EPDM with NR and ENR25 on the processability, tensile properties and oil resistance of PP/EPDM/NR and PP/EPDM/ENR25 blends.

2.0 MATERIALS

Polypropylene homopolymer used in this study was injection molding grade (TITANPRO 6331 grade) with a MFI value of 14 g/10 min at 230°C. Ethylene-propylene diene terpolymer (EPDM), grade "950", Natural Rubber (NR) and Epoxidized Natural Rubber (ENR 25).

3.0 EXPERIMENTAL PROCEDURE

Thermoplastic elastomer blends were prepared by melt mixing in an internal mixer, HAAKE Polydrive with Rheomix R600/610 at 180°C and 50 rpm of rotor speed using the following mixing cycle:

0 minute – add polypropylene
2 minutes – add rubber (EPDM/ENR25 or EPDM/NR) and antioxidant
6 minutes – Dumping

The formulations used in the preparation are shown in Table 1.

Table 1 Formulations of PP/EPDM/ENR25 and PP/EPDM/NR blends

Blend No.	PP (%wt)	EPDM (%wt)	ENR25 (%wt)	NR (%wt)
1	50	50	-	-
2	50	40	10	-
3	50	30	20	-
4	50	20	30	-
5	50	10	40	-
6	50	-	50	-
7	50	40	-	10
8	50	30	-	20
9	50	20	-	30
10	50	10	-	40
11	50	-	-	50

At the end of 6 minutes, the blends were taken and the samples were sheeted on a roll mill while it was still hot, and allowed cooling to form 2 mm thick slab. The sheets were compressed using compression molding. The conditions of compression molding samples of 2 mm thick were as follows:

Temperature – 180°C
Preheating time – 4 minutes
Compression time – 4 minutes
Cooling time – 4 minutes

Tensile tests were carried out according to ASTM D412 on Testometric tensometer M 500. 2 mm thick dumbbell specimens were cut from the moulded sheets with a Wallace die cutter. A cross head speed of 50 mm/min was used and the tests were performed at 25°C.

Determination of the swelling percentage of blends was carried out according to ASTM D471. Samples of dimension $30 \times 5 \times 2$ mm were weighed using an electrical balance and this was considered to be the original weight (W_1). The test pieces were immersed in oil (IRM 903) at room temperature for 72 hr. The samples were then removed from oil, wi ped with tissue paper to remove excess oil from the surface and weight (W_2). The swelling percentage of the blends was then calculated as follow:

$$\text{Swelling percentage} = \frac{W_2 - W_1}{W_1} \times 100\%$$

Studies on the morphology of tensile fracture surfaces of PP/EPDM/NR and PP/EPDM/ENR25 blends were carried out using a scanning electron microscope (SEM), model Leica Cambridge S-360. The fractured ends of the specimens were mounted on aluminum stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

4.0 RESULTS AND DISCUSSION

Typical torque curves for PP/EPDM/NR and PP/EPDM/ENR25 blends are shown in Figure 1. The initial peaks (P) and (R) observed were due to polypropylene and rubber loading respectively. PP was charged into the mixing chamber for 2 minutes. The torque increases due to the resistance exerted on the rotors by the unmelted PP. As the PP melted and subjected to mechanical shearing, the temperature inside the chamber increased resulting in a reduction of torque value (at 2 minutes). With the addition of rubber the torque increases sharply. This can be explained by the increase in viscosity as more rubber are added to the PP, thus contributing to the raised mixing torques. As the mixing becomes homogeneous, the torque decreases. Upon completion of the mixing the torque remains almost constant (at 6 minutes). As the NR and ENR25 content increase the torque values are seen to increase. In comparison between PP/EPDM/ENR25 and PP/EPDM/NR blends, it shows that the torque values of blend containing NR are slightly higher than the blends containing ENR25.

Figure 2 shows the stabilization torque values after 6 minutes of mixing. Stable torque is determined from the plateau region that characterises the viscous nature of the melt blending. This figure shows that the PP/EPDM/ENR25 system has slightly lower torque value than PP/EPDM/NR.

The effect of partial replacement of EPDM by NR or ENR25 on tensile strength and elongation at break are presented in Figures 3 and 4 respectively. The addition of NR or ENR25 in the blend decreases the tensile strength (Figure 3). Moreover the tensile strength of the blend decreased with increasing proportion of either NR or ENR25. This indicates that the addition of NR or ENR25 has reduced the compatibility of PP/EPDM blend. In comparison between PP/EPDM/NR and PP/EPDM/ENR25 blends, it showed that the strength of PP/EPDM/NR blend was higher than PP/EPDM/ENR25 blend. This might be due to the polarity of the components [14]. All components in PP/EPDM/NR blends are nonpolar, whereas ENR25 is a polar component. Due to the same polarity of PP/EDPM/NR, the compatibility of the blend are better than PP/

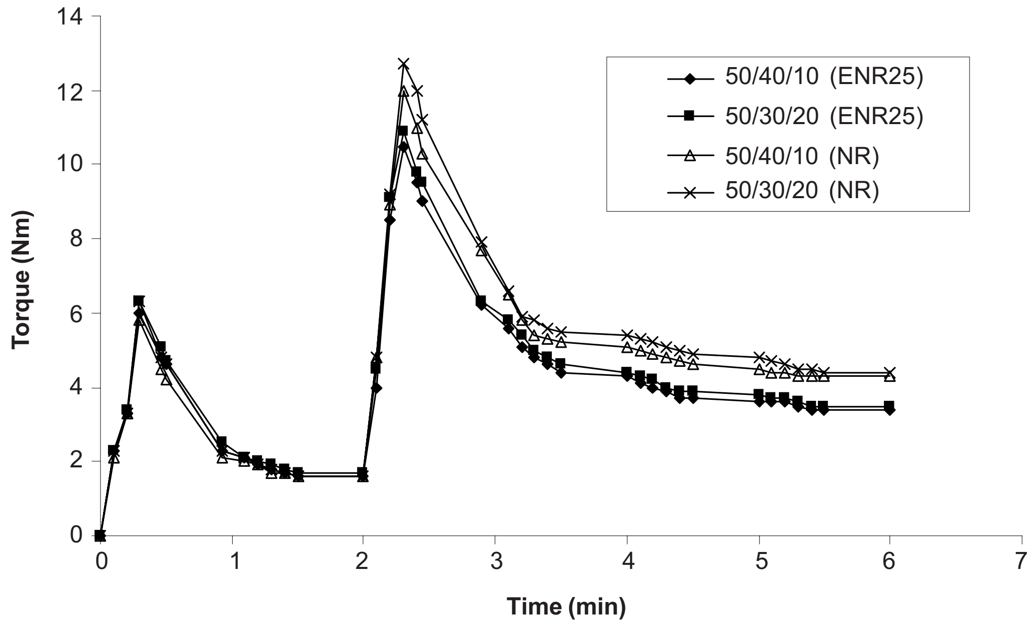

Figure 1 Torque- time curve obtained during blending of PP/EPDM/NR and PP/EPDM/ENR25

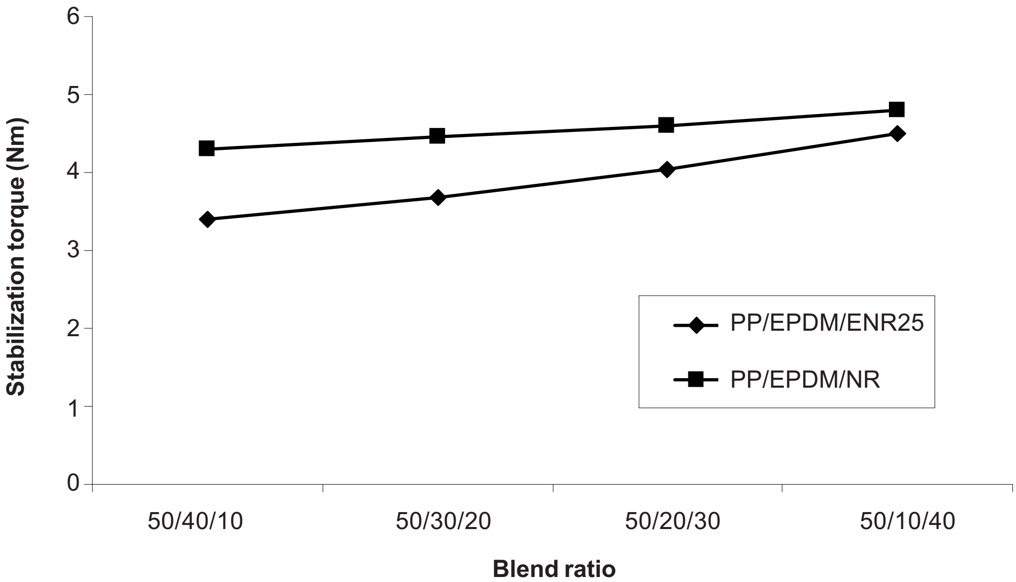

Figure 2 The Effect of blend composition on stable torque of PP/EPDM/NR and PP/EPDM/ENR25 blends

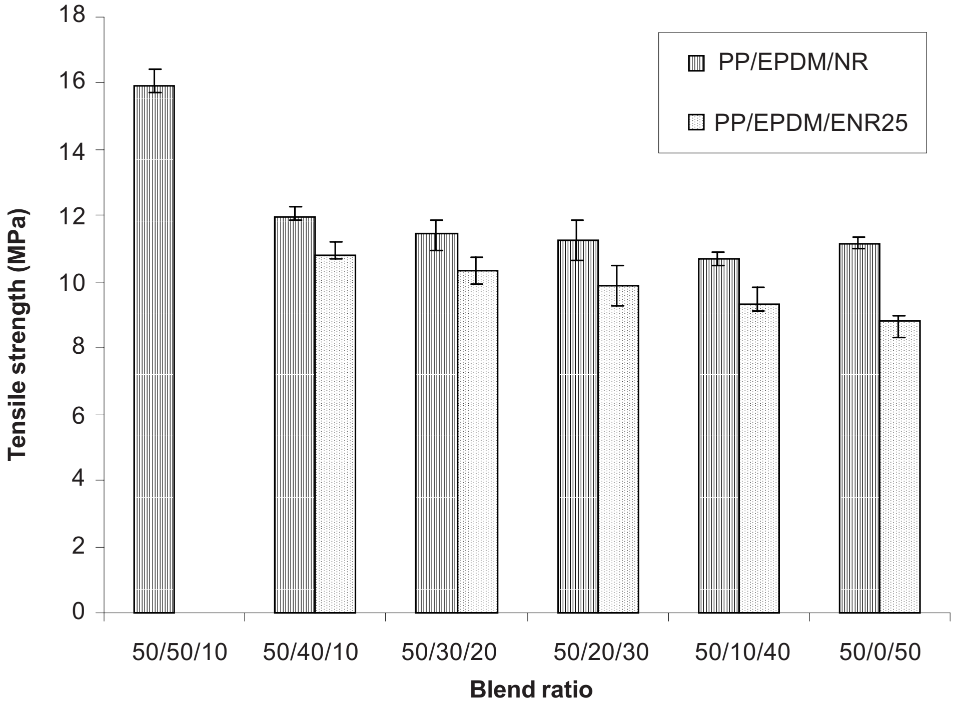

Figure 3 The effect of blend composition on tensile strength of PP/EPDM/NR and PP/EPDM/ENR25 blends

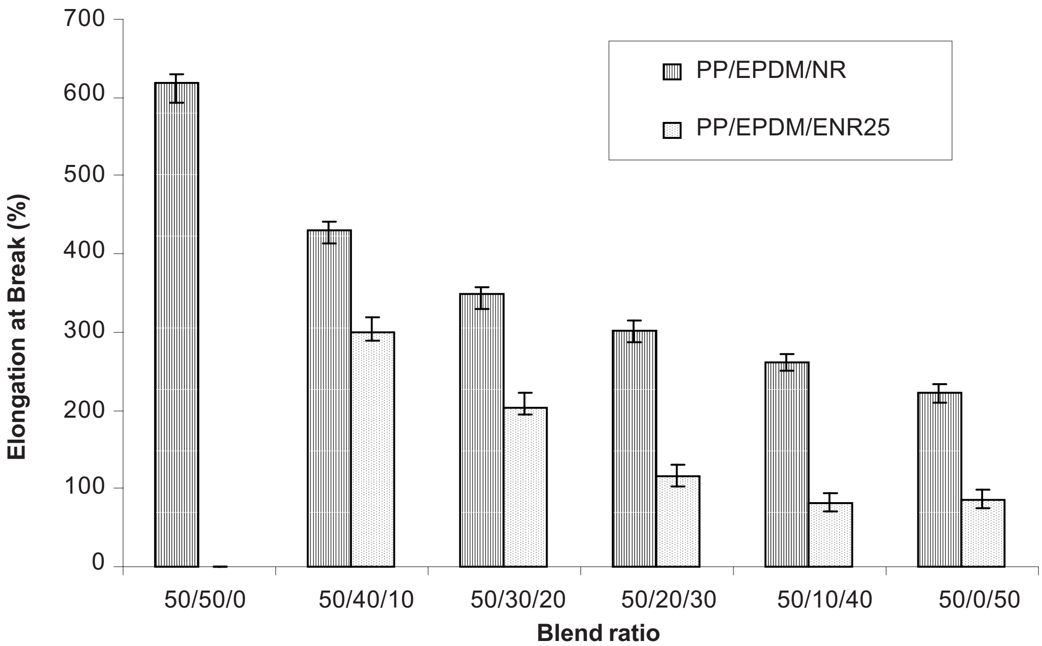

Figure 4 The effect of blend composition on elongation at break of PP/EPDM/NR and PP/EPDM/ENR25 blends

EPDM/ENR25. Consequently, the strength of PP/EPDM/NR blend is higher than PP/EPDM/ENR25.

A similar trend has been found for elongation at break (Figure 4). Replacement of EPDM with NR or ENR25 reduce the elongation at break of the blend. However, for PP/EPDM/NR and PP/EPDM/ENR25 blends, the sharp reduction occurred for PP/EPDM/ENR25 blend. Again, this observation might be due to the polarity of ENR25 which reduced the compatibility of PP/EPDM/ENR25 blend.

Figure 5 shows the effect of blend composition of PP/EPDM/NR and PP/EPDM/ENR25 blends on oil resistance. Rubber will swell most in a liquid of similar polarity to itself. EPDM and NR (low polarity) will swell most in oil (low polarity). ENR25, on the other hand will swell less. The epoxidation introduces polarity into ENR25 and the oil resistance is expected to increase with increased in polarity. Therefore, the swelling degree of PP/EPDM/ENR25 blend is much lower than PP/EPDM/NR blend. It can also be seen that the oil resistance of the blend decreases as the NR content increases. However, PP/EPDM/ENR25 blend shows more stable oil resistance than PP/EPDM/NR blend.

Figure 6 shows the SEM micrographs of the tensile fracture surfaces of PP/EPDM/NR and PP/EPDM/ENR25 blends at room temperature. Figure 6a shows quite regular shapes and homogeneous blend. It reveals that PP/EPDM blend yields good interfacial

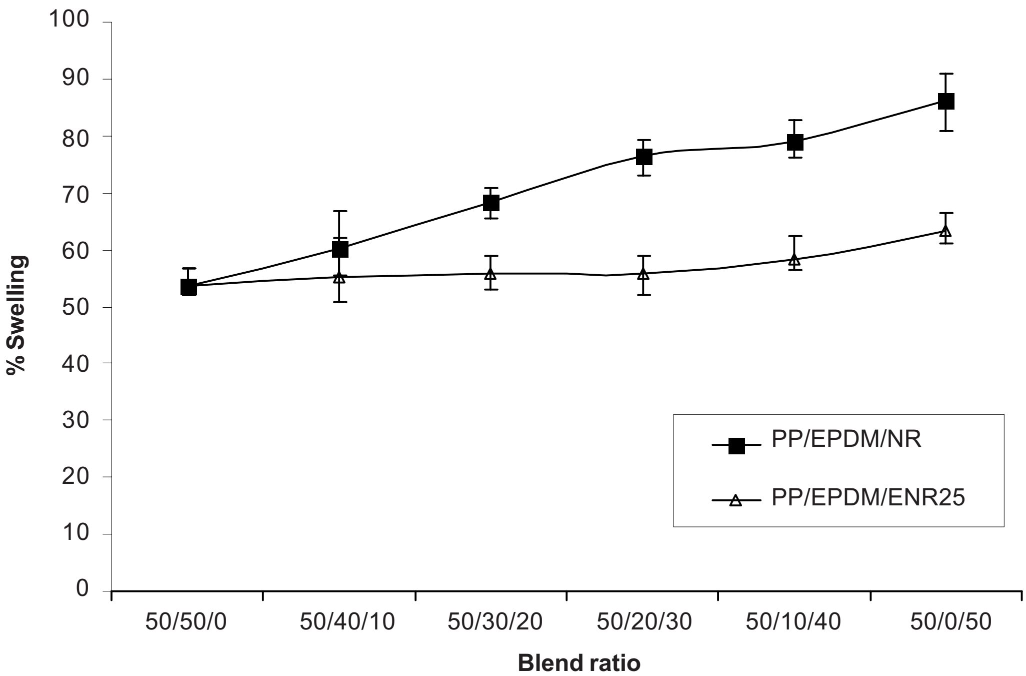

Figure 5 Percent swelling of PP/EPDM/NR and PP/EPDM/ENR25 blends

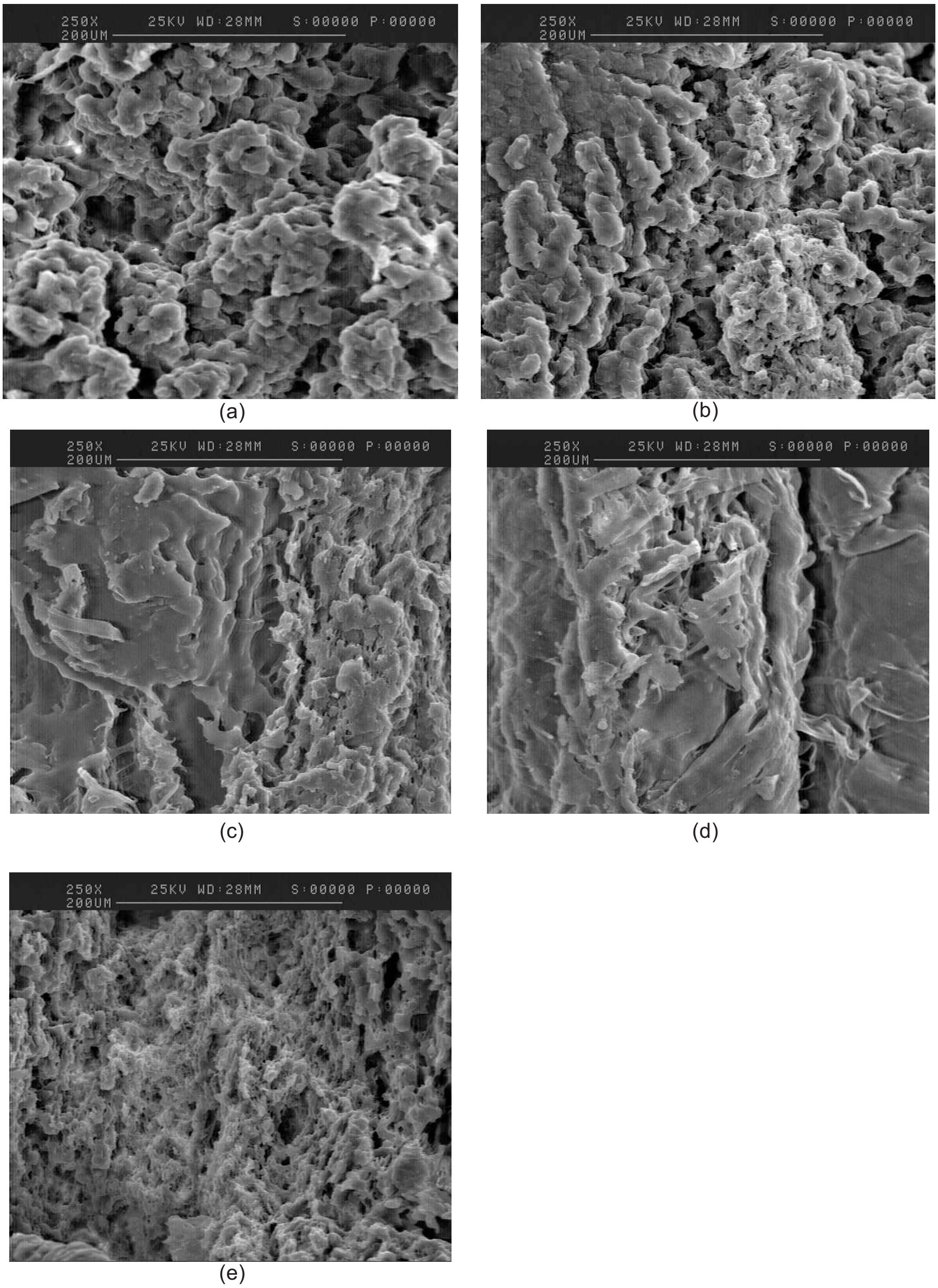

Figure 6 SEM micrograph of fracture surfaces of (a) 50/50 PP/EPDM, (b) 50/30/20 PP/EPDM/NR, (c) 50/30/20 PP/EPDM/ENR25, (d) 50/50 PP/ENR25 & (e) 50/50 PP/NR

adhesion. The fracture surface of the blend shows a plastic deformation even at 50/50 concentration. This was also observed by Wang and Chang [15]. In comparison with Figure 6b PP/EPDM/NR blend (50/30/20), where the fracture surface exhibits less homogeneous blend, PP/EPDM blend (50/50) shows more homogeneous fracture surface. As discussed before PP/EPDM blend (50/50) exhibits higher tensile strength than PP/EPDM/NR blend (50/30/20).

Figure 6c shows the micrograph of PP/EPDM/ENR25 blend (50/30/20). A highly inhomogeneous blend can be seen in this figure. This indicates that the incorporation of ENR25 to the PP/EPDM blend reduces the compatibility of the blend and consequently reduces the mechanical properties of the blend. The inhomogeneous distribution of blend can also be seen in PP/ENR25 blend (50/50) (Figure 6d). In comparison between Figures 6d and 6e, it is clear that PP/NR blend (50/50) exhibits rough failure surface, which indicates better tensile properties than PP/ENR25 blend (50/50).

5.0 CONCLUSION

Torque value of the blends has been increased by the incorporation of NR and ENR25. Partial replacement of EPDM by NR or ENR25 has resulted in reduction of mechanical properties such as tensile strength and elongation at break. However, PP/EPDM/NR blend show better tensile strength and elongation at break than PP/EPDM/ENR25. Oil resistance of the blend has decreased as the NR content in PP/EPDM/NR blend increased, whereas PP/EPDM/ENR25 blend have shown constant oil resistance for all blend compositions. At a similar blend composition, PP/EPDM/NR blend exhibit more homogeneous phases than PP/EPDM/ENR25 blend. In future studies, the incorporation of coupling agents or compatibilisers are suggested to improve the properties of the ternary blend.

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REFERENCES

[1] Ibrahim, A. and M. Dahlan. 1998. "Thermoplastic Natural Rubber Blends". *Prog. Polym. Sci.* 23: 665.
[2] Dennis, J. S., F. S. Sheridan and G. K. Emmanuel. 1990. "EPDM-Polypropylene Blends". In De, S. K. and A. K. Bhowmick. (Eds), *Thermoplastic Elastomers from Rubber-Plastic Blends*. Chichester. Ellis Horwood: 130.
[3] Wang, M. D. and M. Cakmak. 2001. "Influence of Processing History and Composition on the Basic Structure and Biaxial Deformation Behavior in Dinamically Vulcanized PP/EPDM Blends". *Rub. Chem. Tech.* 74: 745.
[4] Danesi, S. and R. S. Porter. 1978. "Blends of Isotactic Polypropylene and Ethylene-Propylene Rubbers: Rheology, Morphology and Mechanics". *Polymer.* 19: 448.

[5] Jing Ho, W. and R. Salovey. 1981. "Processing of Polyolefin". *Polym. Eng. Sci.* 21: 839.
[6] Kocsis, J. K. and V. N. Kuleznev.1982. "Dynamic Mechanical and Impact Properties of Polypropylene/ EPDM Blends". *Polymer*. 23: 699.
[7] Antony, P., S. Bandyopadhay and S. K. De. 1999. "Thermoplastic Elastomers Based on Ionomeric Polyblend of Zinc Salts of Maleated Polypropylene and Maleated EPDM Rubber". *Polym. Eng. Sci*. 39: 963.
[8] Zaharescu, T., M. Chipara and M. Postolache. 1999. "Radiation Processing of Polyolefin Blends II. Mechanical Properties of EPDM-PP Blends". *Polymer Degradation and Stability*. 66: 5.
[9] Jiang, W., S. C. Tjong and R. K. Y. Li. 2000. "Brittle-Tough Transition in PP/EPDM Blends: Effects of Interparticle Distance and Tensile Deformation Speed". *Polymer*. 41: 3479.
[10] Da Silva, A. L. N. and F. M. B. Coutinho. 1996. "Some Properties of Polymer Blends Based on EPDM/PP". *Polymer Testing*. 15: 45.
[11] Ciesielski, A. 1999. *An Introduction to Rubber Technology.* London. Rapra Technology Ltd.
[12] Gary, V. S. 1989. Ethylene-Propylene Elastomer. In Mark, H. F., N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwits. Eds. *Encyclopedia of Polymer Science and Engineering*. 6. Canada. John Wiley.
[13] Baker, L. A., I. R. Gelling and R. Newell. 1984. "Epoxidized Natural Rubber". *Rub. Chem. Tech*. 58: 67.
[14] Chanda, M. and S. K. Roy. 1993. *Plastics Technology Handbook.* Marcel Dekker: New York.
[15] Wang, C. and C. I. Chang. 1999. "Fracture Energies and Tensile Strength of an EPDM/PP Thermoplastic Elastomer". *J. Appl. Polym. Sci.* 75: 1033.