

## The Effects of Natural Weathering Test on Styrene Butadiene Rubber/Recycled Acrylonitrile Butadiene Rubber (SBR/NBRr) Blends with Trans-Polyoctylene Rubber (TOR) as a Compatibilizer

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**Abstract:** The styrene butadiene rubber/recycled acrylonitrile butadiene rubber (SBR/NBRr) blends with and without trans-polyoctylene rubber (TOR) as a compatibilizer were prepared. Effects on tensile properties and morphological of SBR/NBRr blends with and without TOR on 6 months period of natural weathering test were investigated. The result indicated that, after 6 exposure, the incorporation of TOR in SBR/NBRr blends have better tensile strength (TS), elongation at break ( $E_b$ ), tensile modulus (M100) and retentions compared with blends without TOR. The scanning microscopy (SEM) on the exposed surface of SBR/NBRr/TOR revealed a least cracks compared with blends without TOR indicated that TOR contributed to a better dispersion of NBRr particles in SBR matrix; located at interfacial area between SBR and NBRr which can act as protective layer to the blends thus minimize the degradation process with SBR/NBRr blends.

**Key words:** SBR/NBRr blends; TOR; tensile properties retention; SEM

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### INTRODUCTION

Natural weathering of polymer refers to the exposure of polymers to natural outdoor conditions where direct or indirect sunlight, heat, oxygen, moisture and other factors contribute to the degradation of materials properties. Micro organisms, ozone, airborne chemical pollutants such as sulphur oxides and nitrogen oxides and salt are some of the factors that are of significance. Polymer degradation involves the change of one or more physical properties, resulting in loss of the suitability of the material for the intended application (Tulin Sahin, 2007). When referring to weathering exposure there are a type of degradation that should be considered such as ultraviolet light degradation which is the rubber affected by UV light and photodegradation and also the ozone degradation. Although ozone is present in the atmosphere at concentrations normally in the range of 0–7 parts per hundred million (pphm), it can severely attack on non resistant rubbers. The interaction of rubber with ozone is best noted when the rubber is stressed or stretched in use. A series of cracks develop, over time, which are perpendicular to the applied stress. Further exposure of these cracked surfaces to ozone cause the crack to become wider and deeper until the rubber fails (Findik, F., 2004; Sulekhaa, P.B., 2002).

Styrene rubber (SBR) is a general purpose synthetic rubber having high filler loading capacity; good flex resistance, crack-initiation resistance and abrasion resistant, which make it useful for several engineering and industrial application. Nevertheless, like other unsaturated rubbers, its highly vulnerable to degradation due to presence of double bonds in the main chain (Radhakrishan, C.K., 2006). Acrylonitrile-butadiene rubber (NBR) is a synthetic rubber of copolymerized acrylonitrile and butadiene and the most important characteristics is fuel resistant and low gas permeability, and its depends on the content of acrylonitrile. It is the most widely used rubber in industry as a sealant and especially for lip seals of ball-bearings due to its moderate cost, excellent resistance to oils, fuels and greases, processability and very good resistance to swelling by aliphatic hydrocarbons (DeGrange, J.M., 2005; Tariq Yasin, 2003). Eventhough, both of SBR and NBR have susceptible to degradation such as ozone resistance because of their double bonds, the blends of these rubbers is a good for oil-resistant application.

Trans-polyoctylene rubber (TOR) has been introduced as a compatibilizer for incompatible rubber blends containing polar rubbers, such as acrylonitrile butadiene-rubber (NBR) and non-polar rubber styrene butadiene rubber (SBR), and as a processing aids for an extremely stiff rubber compound, such as highly filled rubber compounds for skim-coating of steel wires for tyres (Nah, C., 2002). Trans-polyoctylene rubber (TOR) is a low-molecular-weight polymer, made from cyclo-octene by metathesis polymerization, it is a high-performance

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polymer that presents a dual character: during processing, it has the function of a plasticizer, and after vulcanization, it behaves as a rubber and has been known as a compatibilizer for incompatible blends. Tor can provide good processability in the temperature range of rubber processing (100°C-150°C) as well as good collapse resistance below the melting temperature, 54°C, due to recrystallization (Ismail, H., 2007). It also has linear and cyclic macromolecules which are un-branched and contain one double bond for every eight carbon atom with prevalently trans isometric double bonds (Commereuc, S., J. Lacoste, 1997).

In Malaysia, the output of nitrile rubber gloves was found abundantly. Most of this material originates from medical, industrial as well as research activities. After a certain period of time these polymeric materials are not serviceable and mostly discarded. To solve this environmental issue, a recycled NBR gloves (waste) obtained from industrial floor were used in effort to create a value added instead of being scrapped. Recently, the authors (Noriman, N.Z., 2008; Noriman, N.Z., 2009) reported the comparison properties of virgin and recycled NBR (NBRr) of SBR/NBRr blends. However, less attention has been given on the details of compatibilization of TOR in polar-nonpolar rubber such as SBR/NBR blends particularly involved with waste rubber. To the best of our knowledge, the tensile properties (retention) and morphology of SBR/NBRr/TOR after 6 months exposed to natural weathering were examined.

## 2. Experimental:

### 2.1 Materials and Preparation of Blends:

The materials used in this study were styrene butadiene rubber (SBR), recycled acrylonitrile-butadiene rubber (NBRr) – a recycled product from waste gloves with a range of sizes 117-334 µm, trans-polyoctylene rubber (TOR), carbon black N330, N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), zinc oxide, stearic acid, sulphur and processing oil. Their characteristics are shown in Table 1.

**Table 1:** Characteristics of materials.

| Materials   | Description   | Source   |
|---|---|--|
| Styrene butadiene rubber (SBR)  | 1502  | Bayer (M) Ltd  |
| Recycled acrylonitrile-butadiene rubber (NBRr)  | Size : 117 - 334 µm,  | Juara One Resources Sdn Bhd, Bukit Mertajam, Penang, Malaysia. |
| trans-polyoctylene rubber (TOR)   | Vestamer 8012<br>ML <sub>1+4</sub> at 100°C<10<br>MW = 100000<br>T <sub>m</sub> = 51°C, T <sub>g</sub> = -65°C<br>Crystallinity at 23°C = 27% | Huls, Germany  |
| Carbon black  | N330  | Malayan Carbon (M) Ltd   |
| N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), zinc oxide, stearic acid, sulphur and processing oil |   | Anchor Chemical Co (M) Ltd                                     |

The SBR/NBRr blends with and without TOR were formulated with blends ratio of 95/5, 85/15, 75/25, 65/35 and 50/50 as given in Table 2. The rubber was pre-blended and the mixing procedure was carried out according to ASTM D 3184-89 (2001) using a two-roll mill at room temperature. Cure characteristics were studied using a Monsanto Moving Die Rheometer (MDR 2000) according to ASTM D 2084-01 (2001). About 4 g samples of the respective compounds were used and test at vulcanization temperature (160 °C). The rubber compounds then were compression molded at 160 °C using a hot press according to respective cure times, t<sub>90</sub>.

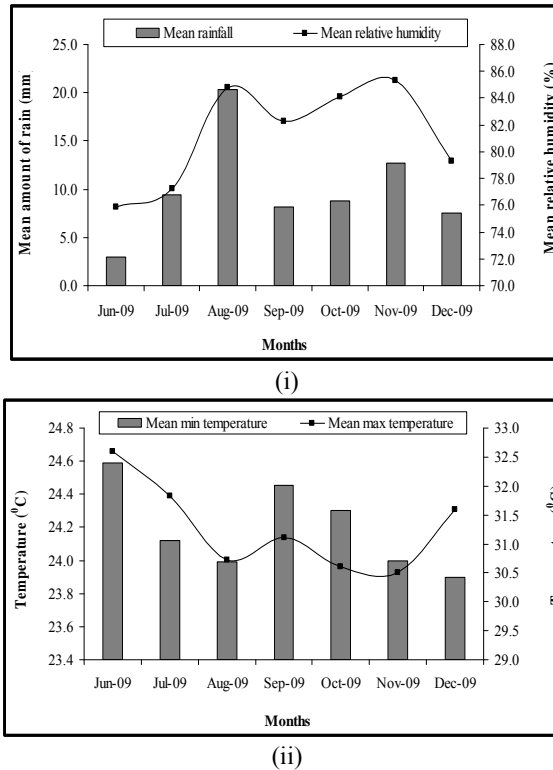
**Table 2:** Formulation for SBR/NBRr blends with and without TOR.

| Ingredients (phr)                              | Blend |     |     |     |     |
|--|-------|-----|-----|-----|-----|
|  | R05   | R15 | R25 | R35 | R50 |
| SBR  | 95    | 85  | 75  | 65  | 50  |
| NBRr   | 5     | 15  | 25  | 35  | 50  |
| trans-polyoctylene rubber (TOR)                | 0&5   | 0&5 | 0&5 | 0&5 | 0&5 |
| Zinc oxide                                     | 5     | 5   | 5   | 5   | 5   |
| Stearic acid                                   | 2     | 2   | 2   | 2   | 2   |
| Sulfur   | 2     | 2   | 2   | 2   | 2   |
| N-cyclohexyl-2-benzothiazole sulfenamide (CBS) | 1     | 1   | 1   | 1   | 1   |
| Processing oil                                 | 5     | 5   | 5   | 5   | 5   |
| Carbon black (N330)                            | 50    | 50  | 50  | 50  | 50  |

### 2.2 Weathering Exposure:

The natural weathering test was performed at School of Materials and Mineral Resources Engineering Universiti Sains Malaysia, Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia for a period of 6 months; from Jun 2009 to Dec 2009. **Figure 1(i,ii)** show the weather condition such as average rainfall, minimum and maximum temperature and relative humidity which obtained from the Butterworth Meteorological Station, Penang, Malaysia (Butterworth Meteorological Station, Penang, 2008). The natural weathering test was done

accordingly to ISO 877.2. The exposed specimens were plates of dumbbell-shaped samples. The specimens were arranged on the expose rack at angle of 45° which located at an open area without being exceeded by other objects. The specimens were collected after 3 months and 6 months exposed to environmental effects to determine the degree of degradation. The specimens were dirt-free using towel and left in air for 24h at room temperature before proceeding to the required test.



**Fig. 1:** Weather parameters throughout 4th weathering test (Jun 2009 until Dec 2009) (i) mean rainfall and relative humidity (ii) mean minimum and maximum temperature

**2.3 Measurement of Tensile Properties:**

Tensile tests were determined using an Instron 3366 according to ISO 37. The exposed specimens were pulled out at constant cross-head speed of 500 mm/min and at a temperature of 25 ± 3 °C. The readings of tensile strength, elongation at break (E<sub>b</sub>) and tensile modulus, M100 (stress at 100% elongation) were recorded. The retention in each properties were evaluated according to eq.1.

$$\text{Retention (\%)} = \frac{\text{Value after weathering}}{\text{Value before weathering}} \times 100 \quad (1)$$

**2.4 Scanning Electron Microscopy (SEM):**

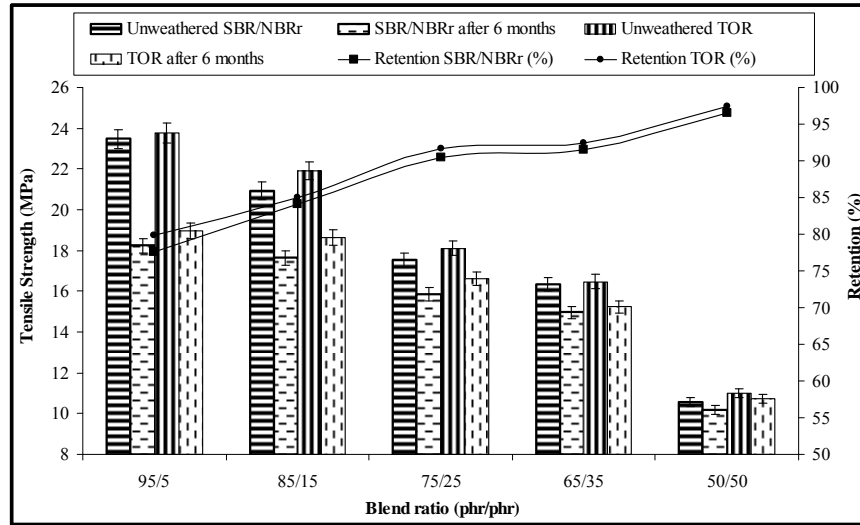
Scanning Electron Microscopy (VPFESEM), model Zeiss SUPRA 35VP was used to analyse the surface aspects of the unexposed and exposed areas of the specimens. The surfaces of the samples were mounted on aluminium stubs and sputter coated with a thin layer of gold about 2 nm thickness prior to avoid electrostatics charging and poor resolution during examination

**RESULTS AND DISCUSSION**

**3.1 Tensile Retention:**

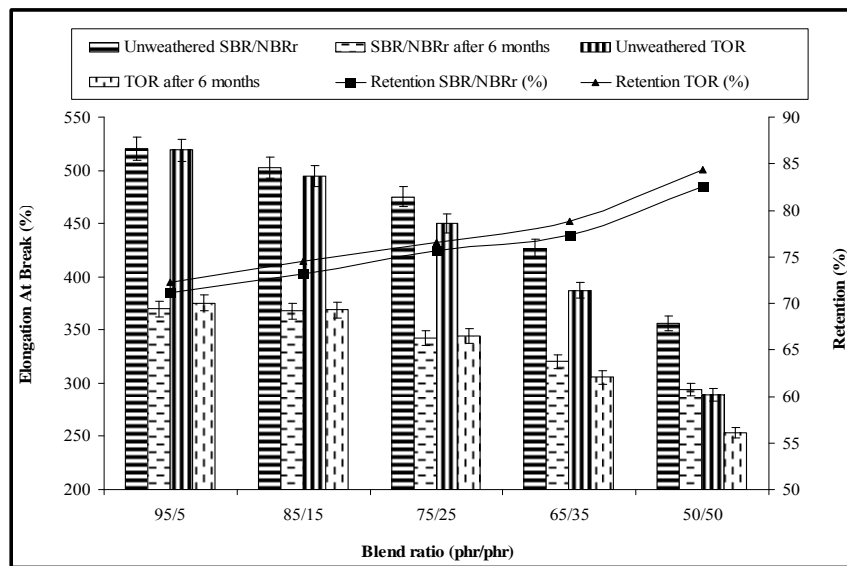
Figure 2 show the tensile strength and retention of SBR/NBRr blends and SBR/NBRr/TOR blends after 6 months of natural weathering. The results indicated that tensile strength of SBR/NBRr/TOR blends have a better tensile strength than SBR/NBRr blends after exposure periods. This can be explained due to a better stress transfer between phases in the system with TOR as illustrates in morphology observation later. The improvement in weathering resistance (tensile retention) for the TOR containing blend is attributed to the better

dispersion of the NBRr particles in the SBR matrix, which is aided by TOR. That is, more finely dispersed NBRr particles prohibit the growth of ozone cracks initiated in the SBR matrix before the crack grows over the critical length. Chang et al., 1999 suggested that fine dispersion of EPDM particles in the NR matrix, which is achieved by the addition of TOR, leads to a significant increase in ozone resistance of the NR/EPDM blend (Chang, Y.W., 1999). In addition, TOR has showed more stable polymer against ozone attack in comparison with other rubbers such as BR and CR (Ivan, G., M. Giurginca, 1998).



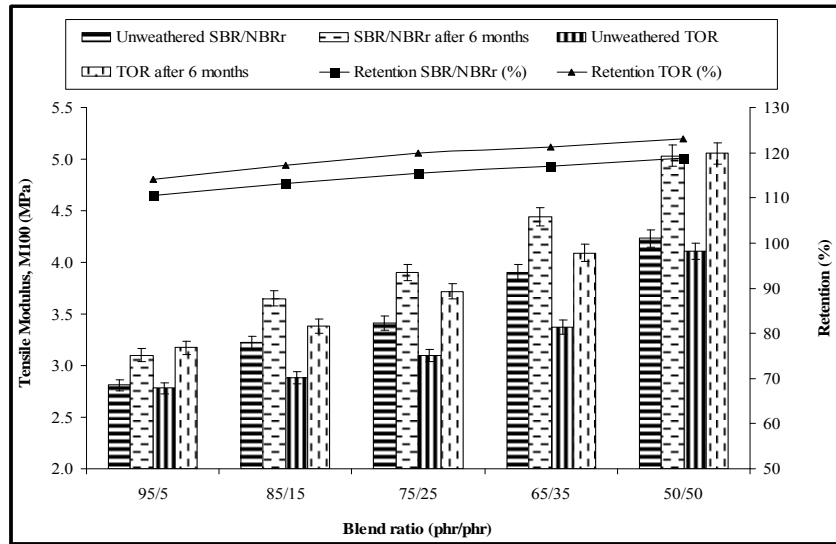
**Fig. 2:** The tensile strength and its retention of SBR/NBRr blends and SBR/NBRr/TOR blends after 6 months of natural weathering.

**Figure 3** depict the effects on  $E_b$  and retention of SBR/NBRr blends and SBR/NBRr/TOR blends after 6 months after exposure. It can be seen that, the  $E_b$  value and retention of SBR/NBRr/TOR were higher than SBR/NBRr blends after 6 natural weathering. A better  $E_b$  retention of SBR/NBRr/TOR blends after 6 exposure can be explained due to presence of TOR at interfacial area between SBR and NBRr which can act as protective layer to the blends thus minimize the degradation process.



**Fig. 3:** The  $E_b$  and its retention of SBR/NBRr blends and SBR/NBRr/TOR blends after 6 months of natural weathering.

**Figure 4** show the effects of the M100 and retention of SBR/NBRr blends and SBR/NBRr/TOR blends after 6 months of natural weathering. Results indicated that, the M100 and retention value of both blends increased correspondingly after exposure at 6 months weathering. This probably due to radical recombination during exposure to some cross-linking reactions (Naddeo, C., 2004). Furthermore, when more NBRr particles added with SBR matrix together with TOR, it is believed that blend becomes more rigid which associated with the increment in crosslinked density value. Therefore, combination the effect of high crystallinity of TOR (Nah, C., 2002) and the presence of various additives, cross-linked precursors and unreacted curative in the NBRr has responsible for a better M100 retention.

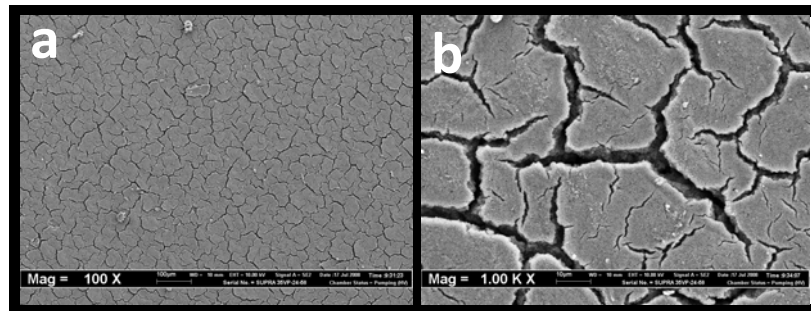


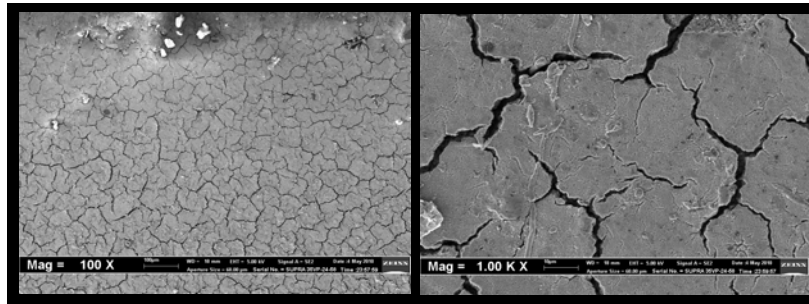
**Fig. 4:** The M100 and its retention of SBR/NBRr blends and SBR/NBRr/TOR blends after 6 months of natural weathering.

### 3.2 Morphology:

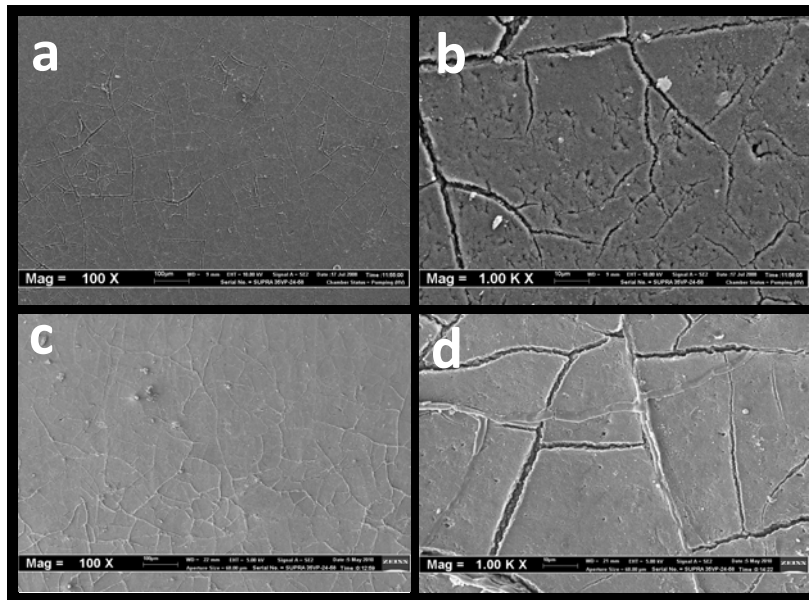
**Figure 5** show the SEM micrograph of exposed surfaces of (a) and (b) SBR/NBRr blends without TOR, (c) and (d) SBR/NBRr blends with TOR at 95/5 blend ratio after 6 months natural weathering, at magnification 300X and 1.00X. It can be seen that the exposed surface of SBR/NBRr/TOR demonstrates least cracks propagate compared with SBR/NBRr blends indicating minimal degradation occurred. At 95/5 blend ratio (low NBRr particles) after 6 months exposure, it is believed that TOR had located at the interface between phases (NBRr and SBR matrix) and helps to decrease in phase coalescence processes. In addition, due to the degradation of TOR layer as a result of TOR ability to encapsulate a higher viscosity polymer during the mixing process (Lohmar, J., 1986).

**Figure 6** illustrate the morphology of the exposed surface of (a) and (b) SBR/NBRr blends without TOR, (c) and (d) SBR/NBRr blends with TOR at 50/50 blend ratio after 6 months natural weathering, at magnification 300X and 1.00X. From the observation, it can be seen that SBR/NBRr/TOR blends shows shorter and minimum cracks than SBR/NBRr blends particularly after 6 month exposure, which confirms that crack growths were stopped more effectively by finely dispersed NBRr particles in SBR matrix. It is believed that with the fine dispersion of NBRr particles in the SBR matrix, which is achieved by the addition of TOR, leads to a significant increase in weathering resistance of SBR/NBRr/TOR blends.





**Fig. 5:** SEM micrograph of (a) and (b) SBR/NBRr blends without TOR, (c) and (d) SBR/NBRr blends with TOR at 95/5 blend ratio after 6 months natural weathering, at magnification 300X and 1.00X



**Fig. 6:** SEM micrograph of (a) and (b) SBR/NBRr blends without TOR, (c) and (d) SBR/NBRr blends with TOR at 50/50 blend ratio after 6 months natural weathering, at magnification 300X and 1.00X

**4. Conclusion:**

The improvement in weathering resistance (tensile strength, elongation at break and tensile modulus) for the TOR containing SBR/NBRr blend is attributed to the better dispersion of the NBRr particles in the SBR matrix, which is aided by TOR. It believed that TOR contributed to a better dispersion of NBRr particles in SBR matrix; located at interfacial area between SBR and NBRr which can act as protective layer to the blends thus minimize the degradation process with SBR/NBRr blends.

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