Mechanical Behaviour of the Polypropylene-Devulcanized Natural Rubber Compound upon Natural Weathering

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Abstract. This study aims to investigate the mechanical behaviour of the polypropylene/devulcanized natural rubber (PP-DeVulcNR) compound upon natural weathering. The DeVulcNR was used to improve the mechanical properties of the PP-DeVulcNR compound at the range of 0 – 20 phr. These samples were subjected to natural weathering test at a duration range of 0 – 6 months to further study the weatherability of the compound. It was found that with the addition of 5 phr DeVulcNR in PP has the highest weatherability as it has obtained the optimum value of the tensile strength after 6 months outdoor exposure. Besides that, there is more fibrils formation on the fractured surface due to better dispersion of DeVulcNR particles in PP matrix. The Young’s Modulus and elongation at break of the PP-DeVulcNR compounds reduced after 6 months outdoor exposure due to the embrittlement of the materials. The presence of the hydroxyl (O-H) and carbonyl (C=O) stretching vibration indicated that the photo-oxidation occurs in the compound during outdoor exposure.

1. Introduction
Most of the polymers are prone to degradation caused by the natural environment in which involved with ultraviolet and atmospheric oxygen and lead to chain scission in polymer chains. It may be accelerated by the elevated temperatures from the sun [1]. Photo-oxidation degradation occurs when the oxygen present by the activation of the polymer macromolecule with the absorption of photon from light in the polymer [2]. Polypropylene (PP) is well used in many applications due to its unique properties, such as high melting temperature, high chemical resistance and heat resistance. The superior properties of PP are mainly contributed by its high crystallinity structure and stability of the methyl group. However, the major drawback of the PP is poor in impact strength which gives limitation to several other applications [3]. Furthermore, PP has low resistibility towards degradation in the atmospheric environment. For instance, it is enough to initiate the degradation within the range of the sunlight wavelength at the earth’s surface which is over 290 nm and caused discoloration, chalking and embrittlement of PP [4]. In order to decrease the effect of environmental degradation and
expand the lifespan of PP polymer, devulcanized natural rubber (DeVulcNR) has been introduced to combine with the PP polymer to obtain better material. Hence, this paper focused on the mechanical behaviour of the polypropylene/devulcanized natural rubber (PP-DeVulcNR) compound upon natural weathering.

2. Experimental Procedure

2.1 Materials
Polypropylene (PP) with the grade of TITANPRO 6331 produced by Titan Chemicals Corporations Sdn Bhd, Malaysia was used in this study. The density and MFI of the PP were 0.9 g/cm³ and 14 g/10 min respectively. Devulcanized natural rubber (DeVulcNR) was purchased from SRI Elastomers Sdn Bhd, Malaysia.

2.2 Sample Preparation
The various content of devulcanized natural rubber mix with 100 phr of PP was extruded by using twin screw extruder at 190 °C. The extruded compound cooled by chilled water. Then, the extruded compound was pelletized using pelletizer before compression molded at 170 °C into sheet form using 25 tons hot molding press. The compound was cooled to room air temperature for 20 min.

2.3 Natural Weathering Test
The natural weathering test was conducted according to ASTM D1435. The samples were placed on the rack by adjusted to face the equator at an angle of 45°. The rack was located in an open area where it was free from overshadowed by other objects and exposed to all environmental effects such as rain, sunlight, wind and etc. The samples were collected after 2, 4 and 6 months to determine the degree of degradation by UV source. at the surface of the samples was removed with a clean towel and left in air for 24 hours at room temperature before proceeding for further testing. The sample surface was cleaned by using a clean towel to remove water droplets due to condensation and leaved in air at room temperature for 24 hours before further testing.

2.4 Tensile Test
The tensile test was conducted by using Instron Universal Testing Machine 5582 series IX tensile tester. The 3 mm thick sheets were cut into dumbbell shapes accordance to the ASTM D638 (Type IV) standard. The tensile strength, elongation at break and Young’s Modulus of the samples were obtained as the average of five specimens.

2.5 Scanning Electron Microscope (SEM) Analysis
The surface morphologies of the fractured surface for all the samples were scanned using Hitachi Scanning Electron Microscope model BS 340 TESLA. The fractured surfaces of the samples were cut into 3 mm height and placed on the copper stub with a fractured surface facing up. The samples were coated with a thin layer of gold before proceeding to SEM scanning. The SEM micrographs were recorded at a magnification of 1000x.

2.6 Fourier Transform Infrared Spectroscopy (FTIR)
The interaction of chemical functional group of the specimens was analyzed by using Perkin Elmer Spectrum EX1. The infrared spectra were recorded with 32 scans for each measurement over the wavelength range of 500 – 4000 cm⁻¹.

3. Results and Discussion
With reference to Figure 1(a), the tensile strength of the pristine PP was decreased drastically with around 45% of reduction after 6 months outdoor exposure. The photo-degradation process occurs which the high-energy of UV radiation from sunlight attacks the macromolecule and generates free radicals at the tertiary C-atom of the PP chain [5]. This effect leads to chain scissoring process which
molecular weight of the PP reduced. Thus, it reduced the tensile strength of the pristine PP. It is noteworthy that the addition of 5 phr DeVulcNR into PP matrix could give higher tensile strength than pristine PP after outdoor exposure. The existing of the carbon black particles in DeVulcNR acts as UV absorber and antioxidant by absorbing all the incident lights and inhibits photo-oxidation via its chemical properties [6]. Therefore, it increased the ability of PP matrix to resist the straining stress. However, further addition of DeVulcNR up to 20 phr into PP matrix could gradually reduce the tensile strength of the compounds after outdoor exposure. This is due to the DeVulcNR particles tend to agglomerate together at higher concentration and weaken the interaction between DeVulcNR and PP. Thus, this effect has deteriorated by the photo-degradation process and lower resistance against the straining stress.

With reference to Figure 1(b), the Young’s Modulus of the pristine PP reduced from 422.38 MPa to 337.53 MPa after 6 months outdoor exposure. The photo-degradation process causes the molecular chain scission causing the breakdown of tie chain molecules and entanglements in the amorphous region [7]. Thus, it has weakened the rigidity of pristine PP and induced it to change from ductile to the brittle material. Moreover, it can be noticed that the addition of DeVulcNR into PP could slightly increase the Young’s Modulus of the compounds when exposed to outdoor for 2 months. This might be caused by the photo-oxidation which increasing in crosslinking due to the high rate of radical termination in the bulk of the polymer where O₂ from photo-oxidation cannot gain access [8]. Thus, it resulted in increasing the rigidity of the PP-DeVulcNR compound. In contrast, the Young’s Modulus of the PP-DeVulcNR compounds gradually reduced with longer exposure period up to 6 months. This might be due to the predominance of the chain scission occurs during photo-degradation process has decreased the rate of radical termination in the bulk of the polymer. Therefore, the rigidity of the PP-DeVulcNR compounds reduced as the chain scission leads to embrittlement of the materials.

With reference to Figure 1(c), the elongation at break of the pristine PP and PP-DeVulcNR compounds reduced after exposed to outdoor for 6 months. The photo-degradation process caused the surface crack and defect as a result of disruption of crystalline order which in turn the crack become breakage concentrators [5]. Therefore, it reduced the elongation ability of the PP matrix and accelerated the breakage of the PP matrix by straining stress applied. On the other hand, it is noteworthy that the addition of DeVulcNR up to 15 phr into PP exhibits a higher value of elongation at break compared to pristine PP. The incorporation of DeVulcNR into PP matrix reduces resilience and toughness of the compounds due to its rubber-like properties [9]. Thus, it increased the elongation ability of the PP-DeVulcNR compound under tensile stress. As per contra, 20 phr DeVulcNR added in PP after 6 months outdoor exposure exhibits the lowest elongation at break (2.39%). The excessive of the DeVulcNR particles in PP matrix caused the uneven distribution of DeVulcNR particles in the compound. Hence, it limits the flow and mobility of the PP matrix when straining stress applied.
Figure 1: (a) Tensile strength (b) Young’s Modulus (c) elongation at break for different DeVulcNR composition of PP-DeVulcNR compound subject to natural weathering.

Figure 2 represents SEM micrographs of the fractured surface for different DeVulcNR composition of PP-DeVulcNR compound after 6 months outdoor exposure. According to the Figure 2(a), it can be seen that the fractured surface of pristine PP exposed under sunlight for 6 months has severely deteriorated with large and long surface cracks formed. This might be due to the chemi-crystallization which release of entangled segments and tie chain molecules in the amorphous region that unable to crystallize during the original solidification process caused by molecular chain scission. Thus, these freed segments then rearrange into a crystalline phase to provide them with enough mobility resulted in a contraction of the surface layer by crack formation [7]. With reference to Figure 2(b), it can be seen that with the addition of 5 phr DeVulcNR in the PP could improve the fractured surface with more fibrils formation as a better dispersion of DeVulcNR particles in PP. Moreover, the presence of carbon black particles in DeVulcNR caused the compound more resistant toward weathering as it acts as UV absorber and antioxidant by absorbing all the incident lights and inhibits photo-oxidation with its phenolic and quinoid groups [10]. However, the fractured surface of the PP-DeVulcNR compound become more flake-like appearance with further increasing of DeVulcNR up to 15 phr as depicted in Figure 2(c) and Figure 2(d). The photo-oxidation process has deteriorated the
interaction between DeVulcNR and PP as the predominance of chain scission occurs. According to Figure 2(e), it can be noticed that 20 phr DeVulcNR added in PP has a long crack surface formed after 6 months exposure. At the high concentration of DeVulcNR, it tends to agglomerate together and weakens the interaction between DeVulcNR and PP. Furthermore, photo-degradation process deteriorated the PP matrix and allowed a higher rate of oxygen penetration into the interior of the compound. As a result, long crack surface formed and weaken the structure of the compound.

Figure 2: SEM micrographs of fractured surface for different DeVulcNR composition of PP-DeVulcNR compound after 6 months outdoor exposure under magnification of 1000x.

Figure 3 shows the FTIR absorption spectra of the PP-DeVulcNR compound with different composition of DeVulcNR upon natural weathering made in the range of 4000 - 650 cm⁻¹. The appearance of the absorption peak at 3300 cm⁻¹ and 1710 cm⁻¹corresponding to hydroxyl (O-H) and carbonyl (C=O) stretching vibration respectively represented that the photo-degradation occurs after 6 months outdoor exposure. It can be seen that the intensity of absorption peak around 2915 cm⁻¹ assigned to asymmetric C-H stretching vibration reduced significantly after 6 months outdoor exposure due to the oxidation occurs by photo-degradation lead to the formation of hydroxyl and carbonyl group. Furthermore, higher DeVulcNR composition could increase the intensity of the peak at 1640 cm⁻¹ representing C=C stretching due to more C-C bonding formed by DeVulcNR particles with PP matrix. Other than that, the peak around 1454 cm⁻¹ and 1372 cm⁻¹ corresponding to CH₂ bending vibration and CH₃ bending vibration, respectively [11]. Moreover, 3 small peaks visible at 1160, 980 and 836 cm⁻¹ were due to –CH₃ symmetric deformation vibration, –CH₃ rocking vibration
and –CH2 rocking vibration of PP [12]. The wavenumber of asymmetric C-H stretching vibration for the addition of DeVulcNR composition up to 15 phr in PP gradually increased with longer exposure time. This result indicated that good distribution and dispersion of DeVulcNR in the PP matrix has improved the stiffness of the matrix. Furthermore, carbon black particles in DeVulvNR absorb all the incident lights and inhibit photo-oxidation via its chemical properties. Therefore, photo-oxidation required higher energy to enable the vibrational effect of the asymmetric C-H stretching. However, the wavenumber for 20 phr DeVulcNR added in PP reduced upon natural weathering. This might be due to the DeVulcNR particles tend to agglomerate together at high concentration and weaken the interaction between DeVulcNR and PP. Thus, O2 from photo-oxidation can easily gain access to PP matrix and weaken the C-H group bonding.
Figure 3: FTIR absorption spectra of PP-DeVulcNR compound with different composition of DeVulcNR before and after natural weathering.

4. Conclusions
The mechanical behaviour of the different DeVulcNR compositions added in PP upon natural weathering was investigated. It was found that 5 phr of DeVulcNR added in PP compound obtained the highest tensile strength after 6 months outdoor exposure. There is more fibrils formation on the fractured surface as better dispersion between DeVulcNR and PP at low DeVulcNR composition. The Young’s Modulus and elongation at break of the PP-DeVulcNR compounds reduced after 6 months outdoor exposure due to the predominance of the chain scission occurs during photo-oxidation process has decreased the rate of radical termination in the bulk of the polymer. The presence of the hydroxyl (O-H) and carbonyl (C=O) stretching vibration indicated that the photo-oxidation occurs in the compound during outdoor exposure.

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