

## Effect of Thermal Cycles on Physical and Tensile Properties of Newly Modified NR/EPDM Blend

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### ARTICLE INFO

### ABSTRACT

#### Article history:

Received 31 August 2018

Received in revised form 12 November 2018

Accepted 5 December 2018

Available online 12 December 2018

Natural rubber/ethylene propylene diene monomer (NR/EPDM) blend is a well-known engineering material used in automotive as well as manufacturing components. It combines the superior physical and mechanical properties with excellent resistance to weathering except for heterogeneous dispersion of EPDM domains in NR which could be deleterious to mechanical properties especially under thermal effect. This study focuses on the effect of thermal cycles on tensile properties of newly modified NR/EPDM blend. The blends were prepared via melt blending using a Haake internal mixer at a temperature of 110 °C, rotor speed of 40 rpm and mixed for 7 minutes and subsequently cured using a hot press machine at 150 °C. The blends were then exposed to two different temperatures of 60°C and 120 °C and cooled down to room temperature alternately for 10 minutes and repeated for 0, 5, 35, 70, and 150 times. The tensile behavior of NR/EPDM blends illustrates consistent value at 60 °C thermal cycles and changed drastically down to ~70% at 120°C. It experienced molecular degradation due to absorption of thermal energy during the thermal cycles hence decreasing the crystallinity via transformation from rubbery to glassy behavior as supported by scanning electron microscopy and X-ray diffraction analyses.

#### Keywords:

Natural rubber, Ethylene propylene diene monomer, Blend, Thermal cycles

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## 1. Introduction

Elastomer are macromolecular materials which can instantly return to their approximate shape from which they have been substantially distorted by a weak stress [1]. Natural rubber (NR) is a highly non-saturated and natural biosynthesis polymer with excellent properties such as superior elasticity, high resilience, low level of strain sensitivity, fatigue resistance, and great processing characteristics [2]. However, NR is prone to degradation by environmental factors such as radiation, humidity, moisture, light and ozone due to highly unsaturated and chemically reactive of NR structure. In contrast, EPDM has a saturated and stable backbone structure with the only

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unsaturated bonds at the side groups [3]. The saturated polymer backbone structure gives the exceptional resistance of ozone, heat, as well as weather to EPDM [4]. It has outstanding electrical resistivity and resistance to polar solvent including of water, phosphate esters, acids, alkaline, and varies type of ketones and alcohols due to the non-polar elastomers characteristics [5].

Nowadays, an alternative simple route in developing new engineering material with improved properties is through blending. Polymer blends can be classified based on the polymeric materials used in their component such as thermoplastic, thermoset or rubber polymers. They can be categorized into elastomer-elastomer blends, elastomer-thermoplastics blends and thermoplastic-thermoplastic blends. Rubber blend is a mixture of two or more rubbers/ elastomers to create a new material with different physical properties [6]. It is economical compared to synthesizing an overall new rubber compound which is always associated with complex technical uncertainties [7]. It is prepared with specific objectives in mind, such as to enhance the physical, chemical and mechanical performance as well as the processing characteristics [7-8].

NR/EPDM investigated in present study is a type of elastomer-elastomer blends which constitute components of natural rubber and ethylene propylene diene. They are of considerable practical importance, since about 75 % by volume of all rubbers used are in the form of blends. Elastomers which are more or less incompatible are commonly blended together to improve the properties as well as the process-ability of material [7]. There are significant numbers of studies conducted to enhance the properties of NR/EPDM for their versatility in automotive and manufacturing engineering [7, 9-12]. Numerous researches have been conducted on tensile properties, swelling behaviour [9], cure characteristics [10] and physical properties [11] of NR/EPDM blends due to their issues on lack in miscibility [12]. Unfortunately, there are scarce research conducted to understand the effect of thermal cycles on mechanical properties of NR/EPDM blend.

There is numerous rubber based components in the automotive and manufacturing industry such as tire, engine mounts, profiles, hoses and seals, gasket, cable insulation and jacketing as well as conveyor belting. In service, most rubber components experienced tensile loading and exposed to accumulated heat from mechanical friction and surroundings hence its degradation. Service temperature may accidentally exceed the nominal parameters and cause the materials to experience multi-stress degradation. Thus, a modification of heat transfer efficiency of a rubber material via structural alteration is crucial [13]. The good heat adsorption and faster heat dissipation may enhance the performance and prolong the life span of the component.

This study is aimed to determine the physical and tensile properties of NR/EPDM rubber blends under the influence of thermal cycles. The properties were compared at two different temperatures; 60 and 120°C.

## 2. Methodology

Natural rubber (SMR 20) grade and ethylene propylene diene monomer (EPDM Buna® EPT 9650) used in this study were supplied by Rubber Research Institute of Malaysia (RRIM). The compounding process was performed per ASTM D 3192 using a Haake internal mixer. About 50 grams at one time was mixed with fill factor of 0.7. Both NR and EPDM were first masticated at 30 °C for 10 minutes using two-roll mill prior to rubber blend preparation. The formulations recipe for NR/EPDM blends were summarized in Table 1. Firstly, NR, EPDM and ENR-50 were masticated for 1 min before all ingredients except sulphur and accelerators were added. Then, sulphur and accelerators were added and mixed for 1 min before the mixture was dumped and left to cooled down to ambient temperature.

The blend from previous step was carefully filled into mold cavity. NR/EPDM blends then were compressed using GT7014-A hot press from Gotech. The samples were prepared under compression of 1800 kg/cm<sup>2</sup>. From this stock, sheets for both NR/EPDM blend was vulcanized approximately 2 mm thick with a semi-efficient vulcanization system with a hot press at 150 °C at the respective cure times,  $t_{90}$  which was derived from a rheometer test in accordance with ASTM D 2084. After the fabrication process, the samples were cut into 64 mm x 10 mm dog bone sample size (Figure 1). Then the samples were heated for 0, 5, 35, 70, and 150 times alternately for 10 minutes at 60 and 120 °C before tested for tensile properties according to ASTM D1822 using Universal Testing Machine (Toyoseiki Strograph). The testing was performed at ambient temperature and at a cross-head speed of 500 mm/min. For every set of experiments required minimum seven testing samples were required to make sure a high confidence level.

After that, the fractured surface morphologies of selected samples were investigated using a scanning electron microscopy, model EVO-50 from Zeiss. The samples were placed onto aluminum stubs and sputter coated with thin layer of gold, about 20 nm thickness. All samples were examined with secondary electron imaging mode.

**Table 1**  
NR/EPDM Formulation Recipe

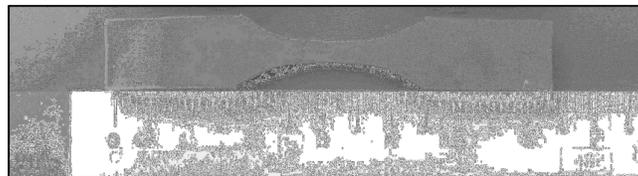
Ingredients	70NR/ 30 EPDM/10 ENR (phr)*
NR (SMR 20)	70
EPDM	30
ENR-50	10
Zinc oxide	5.0
Stearic acid	2.0
Sulphur	1.5
MBTS <sup>a</sup>	1.0
TMTD <sup>b</sup>	0.3
6PPD <sup>c</sup>	2.0

\* Part per hundred rubber

<sup>a</sup> 2,20-dithiobis (benzothiazole)

<sup>b</sup> Tetramethylthiuram disulphide

<sup>c</sup> N-(1,3-Dimethylbutyl)-N'-phenyl-p  
phenylenediamine



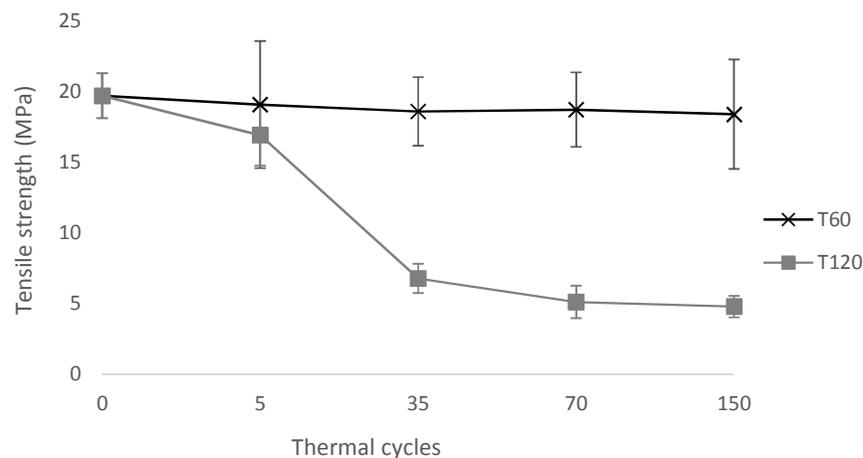
**Fig. 1.** Dog bone sample size

Meanwhile, XRD analysis was performed to validate the rubber transformation from rubbery to glassy state via level of crystallinity. The crystal structure of samples was characterized using PANalytical X'Pert PRO diffractometer and the data was analyzed using X'pert PRO software. The x-ray source used was CuK $\alpha$  radiation with  $\lambda = 1.5418$  nm and all samples were characterized under conditions of  $2\theta$  scanning range (5 to 40°), 1 sec of dwell time, and step size of 2° in  $2\theta$  min.

### 3. Results and Discussion

#### 3.1 Tensile Properties Under Thermal Cycles

Tensile test was conducted to evaluate the effect of thermal cycles on NR/EPDM blends at different temperature. Figure 2 shows the critical degradation experienced by the blend at temperature of 120 °C in compared with temperature at 60 °C and control sample; without thermal cycle at room temperature. The tensile strength for both samples show a different trend as the number of thermal cycles increases. The graph was observed to be consistent for the blend exposed to thermal cycles at 60 °C. On the other hand, a drastic drop of an average of 36% was observed for the blend exposed to the thermal cycles at 120 °C with the highest loss percentage recorded at 35 thermal cycles with a decrease of approximately 70%. This was due to the chains breakage of NR/EPDM molecules at elevated temperature which transformed the material to glassy state. The blend became brittle as indicated by its fractured morphologies under the tensile loading. This phenomenon is also explained by the XRD results (Figure 7).

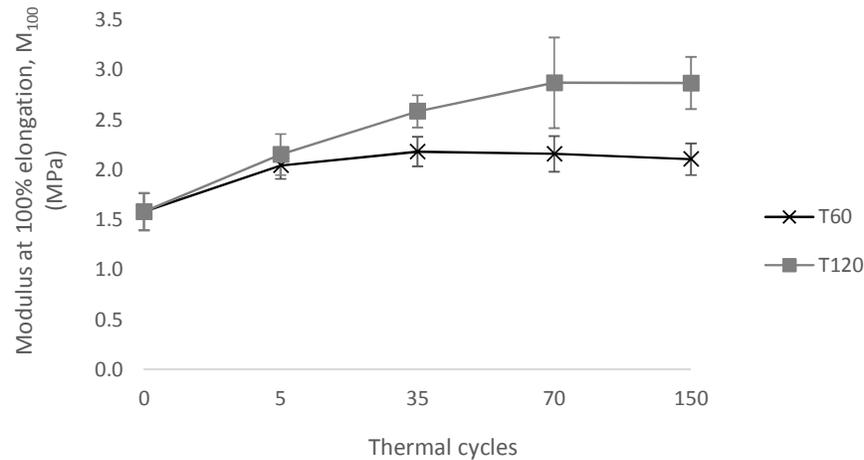


**Fig. 2.** Effect of thermal cycles at 60°C and 120°C on the tensile strength of NR/EPDM blend

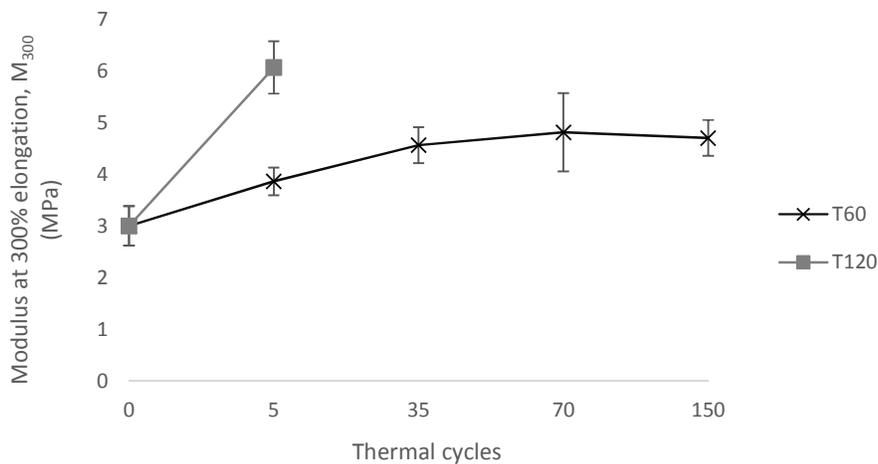
#### 3.2 Modulus At 100% ( $M_{100}$ ) and 300% ( $M_{300}$ ) Elongation

Figure 3 and 4 show the tensile modulus of NR/EPDM blend at 100% and 300% elongation. The  $M_{100}$  and  $M_{300}$  constantly increases with the increase of thermal cycles except of trivial changes for sample exposed to 60°C. It is well accepted that modulus of a material is directly correlated to its stiffness. So, this trend indicates that the stiffness of rubber blend raises with the increase of thermal cycles. Increasing stiffness could be associated to the chain embrittlement of the rubber due to oxidation. For NR/EPDM blends exposed to thermal cycles at 60°C, the value does not change much due to smaller temperature difference between the exposed temperature with glass transition temperature of the blend. In addition, the blends undergone properties recompense by softening mechanism of the rubber chains during heating. In contrast, blends exposed to higher temperature at 120°C experience accelerated embrittlement mechanism. The chain's weakening diminishes the structural integrity of the blend [14] whilst endured chain scission at only limited softening effects. The effect was

further prevailed when blends exposed to 120°C failed at around 300% elongation once the thermal cycles exceeded 5 cycles.



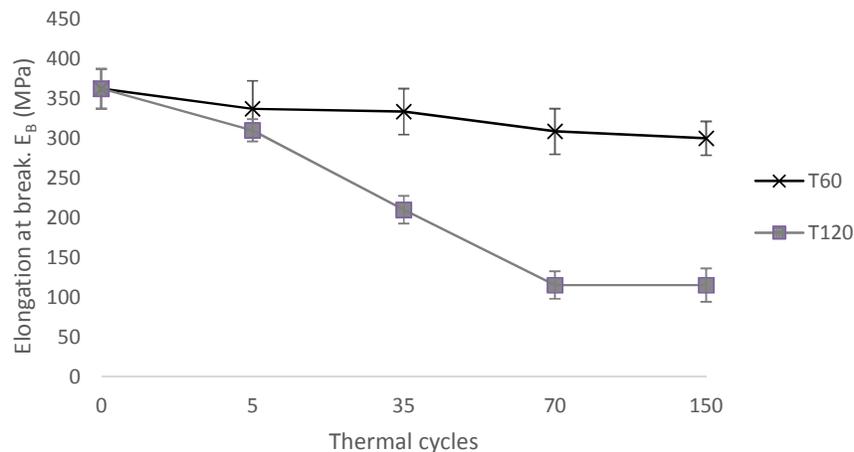
**Fig. 3.** Effect of thermal cycles at 60°C and 120°C on the modulus at 100% elongation of NR/EPDM blend



**Fig. 4.** Effect of thermal cycles at 60°C and 120°C on the modulus at 300% elongation of NR/EPDM blend

### 3.3 Elongation at Break ( $E_B$ )

The Figure 5 shows that the  $E_B$  decreases gradually for blends exposed to 120°C but, the changes are almost stationary with the raise of the number of thermal cycle for the one exposed to 60°C. This observation is in good agreement with the decrease in tensile strength at 120°C. The  $E_B$  for blends at 120°C was drastically reduced as the thermal cycles exceeded 5 cycles if compared to trivial decrement experienced for blends at 60°C. This in an indicator that 5 thermal cycles is the threshold point for the NR/EPDM blends to maintain structural integrity due to thermal cycles effect at 120°C. This is explained by the morphological observation in Figure 6(c). It is concluded that higher temprature thermal cycles accelerate the chain breakage mechanism hence increase the tendency for brittle failure to a ductile NR/EPDM matrix.



**Fig. 5.** Effect of thermal cycles at 60°C and 120°C on the elongation at break ( $E_b$ ) of NR/EPDM blend

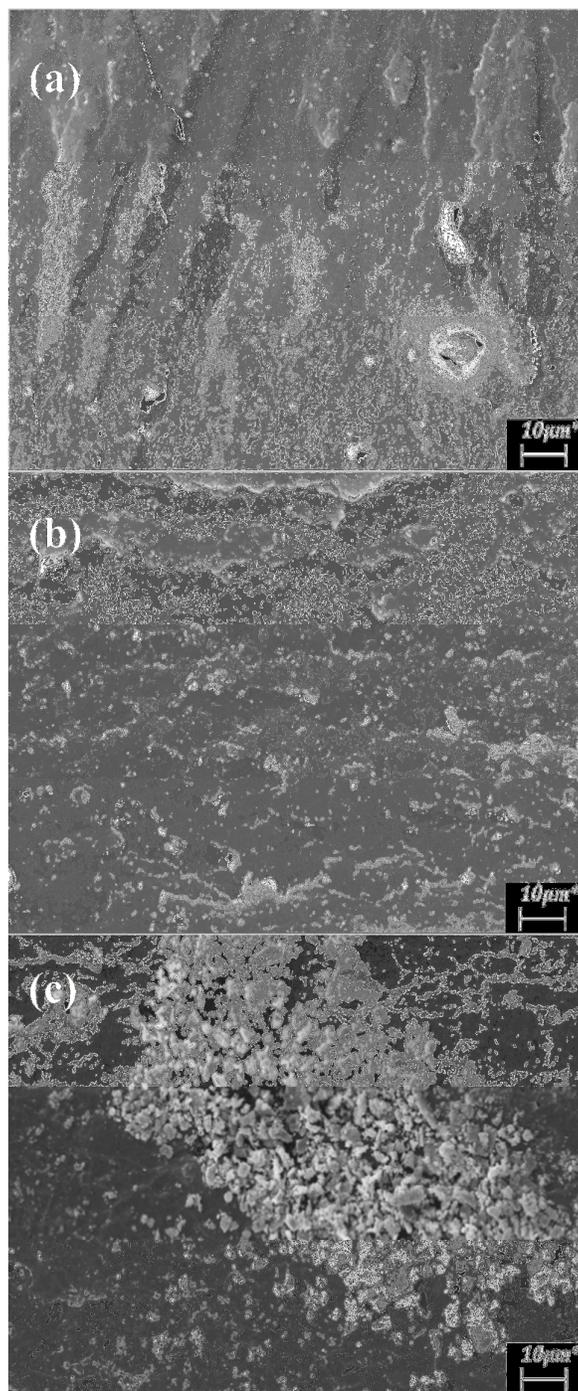
### 3.4 Morphological Analysis

Figure 6(a) illustrates the SEM micrograph taken from the tensile fractured surfaces of control sample of NR/EPDM blends without thermal cycles. It exhibited a relatively rough with apparent shear yielding mechanism. The samples shown thicker tearing line as the rubber matrix was hardly deformed from shear yielding.

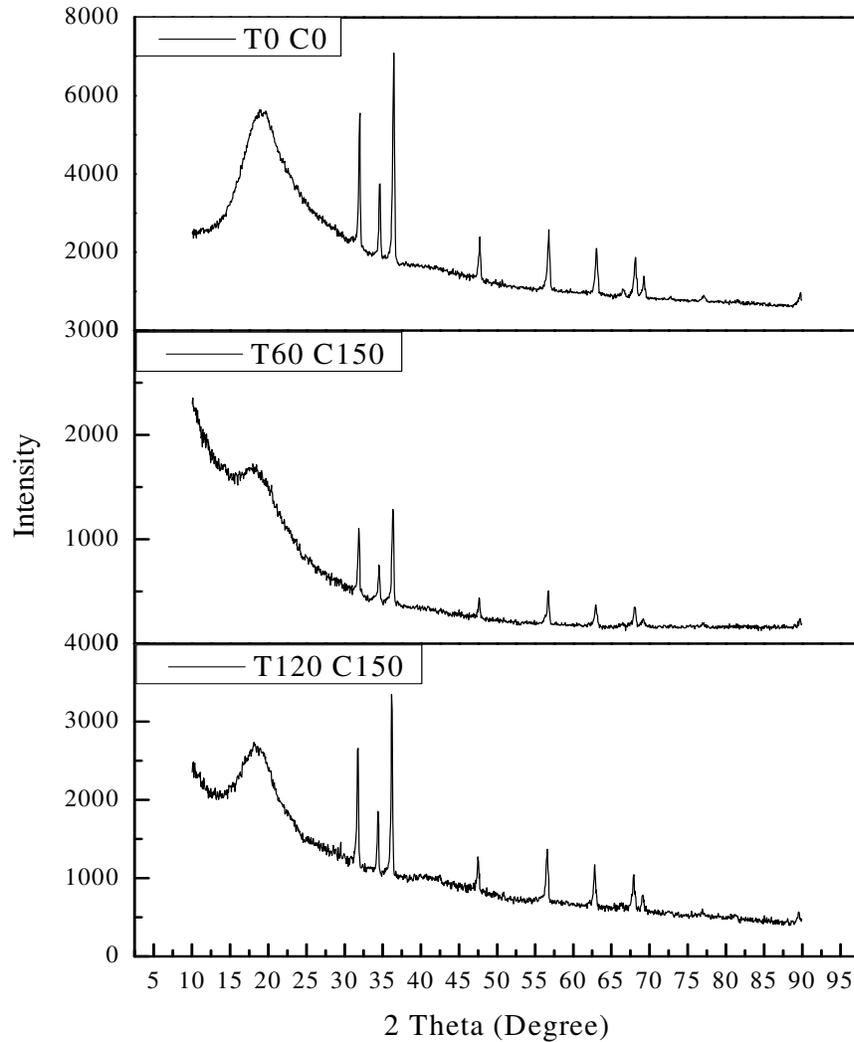
Figure 6(b) and (c) depict the tensile fracture morphologies for NR/EPDM blends under thermal cycles at 60 and 120°C, respectively. It is noted that samples at 60°C showed a rather smoother fracture surface with thinner tearing lines due to matrices shear yielding indicated lesser ductile fracture behavior. In contrast, unique morphological characteristics were observed for blends exposed to 120°C thermal cycles. The surface is dull and full with degraded polymers due to rubber oxidation which resulted in chain scissions under thermal exposure [15]. Scission of the larger molecular chains increased the number of shorter chains of the NR/EPDM blends and led to fewer entanglements and reduce the ability of the strain-crystallization process, hence decreased the tensile properties of the rubber material.

### 3.5 X-Ray Diffraction Analysis

XRD analysis was conducted to investigate the effect of thermal cycles on the structure of NR/EPDM blends. Broad diffraction peak in Figure 7 indicates the amorphous structure of vulcanized NR/EPDM blends [16] whereas sharp peaks indicate the crystalline regions of the blend. When the thermal cycle effect introduced to the NR/EPDM blends, the intensity of the sharp peaks was observed to decrease for almost 60% as compared to samples without thermal cycles. This observation suggests the increment of amorphous state or chain scissions (chain breakage) in the NR/EPDM matrix, which certainly resulting from the effect of thermal cycles.



**Fig. 6.** SEM micrographs of the tensile fracture surface of (a) NR/EPDM blends control sample, (b) NR/EPDM blends experienced thermal cycles at 60°C and (c) NR/EPDM blends experienced thermal cycles at 120°C at 500X magnification



**Fig. 7.** XRD graph of NR/EPDM blends at constant thermal cycles of 150 and different temperature of 0°C, 60°C and 120°C

#### 4. Conclusion

In conclusion, the tensile strength of newly modified NR/EPDM blend decreases at 120°C as the number of thermal cycles increases. This blend showed a drastic drop in tensile strength started at 35 thermal cycles if compared to tensile properties degradation at a lower temperature of 0°C and 60°C. The tensile fracture surfaces indicated transformation from ductile to brittle fracture behavior as the thermal cycle changed from 60°C to 120°C. The modulus at 100% and 300% elongation show the same decreasing trend for 120°C and trivial trend for 60°C as the thermal cycle is increased. The XRD results validate the ductile to brittle failure transformation and molecular degradation from the reduction of crystalline peak observed for modified NR/EPDM blends exposed to thermal cycles compared to the blend without thermal cycles. The finding is significant to verify the extent of property degradation under the influence of thermal cycles at the temperature of 60°C and 120°C.

## Acknowledgements

We would like to acknowledge the Carbon Research Technology Research Group and Universiti Teknikal Malaysia Melaka for the financial support under a high impact short term grant of PJP/2016/FKP/HI6/S01484.

## References

- [1] Hoffman, Werner. "Vulcanization and vulcanizing agent." Maclaren, 1967.
- [2] Razak, Jeefferie Abd, Sahrim Haji Ahmad, Chantara Thevy Ratnam, Mazlin Aida Mahamood, Juliana Yaakub, and Noraiham Mohamad. "Effects of EPDM-g-MAH compatibilizer and internal mixer processing parameters on the properties of NR/EPDM blends: An analysis using response surface methodology." *Journal of Applied Polymer Science* 132, no. 27 (2015).
- [3] Shanks, Robert A. "General purpose elastomers: structure, chemistry, physics and performance." In *Advances in Elastomers I*, pp. 11-45. Springer, Berlin, Heidelberg, 2013.
- [4] Alipour, Abdolmajid, Ghasem Naderi, and Mir HamidReza Ghoreishy. "Effect of nanoclay content and matrix composition on properties and stress-strain behavior of NR/EPDM nanocomposites." *Journal of Applied Polymer Science* 127, no. 2 (2013): 1275-1284.
- [5] Deepalekshmi, P., P. M. Visakh, Aji P. Mathew, Arup K. Chandra, and Sabu Thomas. "Advances in Elastomers: Their Blends and Interpenetrating Networks-State of Art, New Challenges and Opportunities." In *Advances in Elastomers I*, pp. 1-9. Springer, Berlin, Heidelberg, 2013.
- [6] Parameswaranpillai, Jyotishkumar, Sabu Thomas, and Yves Grohens. "Polymer blends: state of the art, new challenges, and opportunities." *Characterization of Polymer Blends* (2014): 1-6.
- [7] Razak, Jeefferie Abd, Sahrim Haji Ahmad, Chantara Thevy Ratnam, Mazlin Aida Mahamood, and Noraiham Mohamad. "Effects of poly (ethyleneimine) adsorption on graphene nanoplatelets to the properties of NR/EPDM rubber blend nanocomposites." *Journal of materials science* 50, no. 19 (2015): 6365-6381.
- [8] Mustafa, W. A., Saidi, S. A., Zainal, M. and Santiagoo, R. "Experimental study of composites based on thermal analysis." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 43, no. 1 (2018): 37-44.
- [9] Juliana, Yaakub, Mohamad Noraiham, Abd Razak Jeefferie, Jano Zanariah, and Iqbal Shueb Mohammed. "Cure characteristics, tensile and morphological properties of graphene nanoplatelets (GNPs) filled NR/EPDM composites." *American-Eurasian Journal of Sustainable Agriculture* 8, no. 4 (2014): 148-155.
- [10] Rezaeian, Iraj, Payam Zahedi, and Motahareh Sadat Loghmani. "Formulation and curing characteristics of EPDM/NR and EPDM/SBR polyblends used in metallic surfaces rubber lining." *Journal of applied polymer science* 113, no. 2 (2009): 849-854.
- [11] Razak, Jeefferie Abd, Sahrim Haji Ahmad, Chantara Thevy Ratnam, Mohammed Iqbal Shueb, Mazlin Aida Mahamood, Juliana Yaakub, Siti Rahmah Shamsuri, and Noraiham Mohamad. "The effects of covalent treated graphene nanoplatelets surface modification to cure characteristic, mechanical, physical and morphological properties of NR/EPDM rubber blend nanocomposites." *Advances in Environmental Biology* (2014): 3289-3299.
- [12] Jones, K. C., and Andrew Tinker. *Blends of natural rubber: Novel techniques for blending with specialty polymers*. Springer Science & Business Media, 1997.
- [13] Zaharescu, Traian, Viorica Meltzer, and Rodica Vilcu. "Thermal properties of EPDM/NR blends." *Polymer degradation and stability* 70, no. 3 (2000): 341-345.
- [14] Nelson, Cherilyn N., and Norman Henry. "Performance of Protective Clothing: Issues and Priorities for the 21st Century: Seventh Volume." ASTM, 2000.
- [15] Valentini, L., S. Bittolo Bon, Miguel A. López-Manchado, Raquel Verdejo, Lucia Pappalardo, A. Bolognini, A. Alvino, S. Borsini, A. Berardo, and N. M. Pugno. "Synergistic effect of graphene nanoplatelets and carbon black in multifunctional EPDM nanocomposites." *Composites Science and Technology* 128 (2016): 123-130.
- [16] Nabil, H., and H. Ismail. "Enhancing the thermal stability of natural rubber/recycled ethylene-propylene-diene rubber blends by means of introducing pre-vulcanised ethylene-propylene-diene rubber and electron beam irradiation." *Materials & Design (1980-2015)* 56 (2014): 1057-1067.