Fatigue and Mechanical Properties of Graphene Nanoplatelets Reinforced Nr/Epdm Nanocomposites

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Abstract. Engine mounting suffers from fluctuating forces which may results in sudden failure due to fatigue. Graphene nanoplatelets have attracted great interest due to their exceptional physical, mechanical and thermal properties. Natural rubber/ethylene propylene diene monomer (NR/EPDM) reinforced with graphene nanoplatelets (GNPs) were investigated to improve the properties of NR/EPDM blend prior to fatigue and mechanical properties for engine mounting service. Firstly, the NR/EPDM blends and nanocomposite were tested for tensile properties and followed by the fatigue properties (tensile mode) using displacement controlled. Tensile plot shows that the NR/EPDM nanocomposite has higher tensile value of 95% compared to NR/EPDM blend. The S-N curve illustrates that NR/EPDM blend and NR/EPDM nanocomposite break by the same cycle which is 100 000 cycles. The fracture behaviour of loading conditions was supported via morphological analysis using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis.

1. Introduction

Nowadays, multiple studies reported the enhanced strength of rubber composite using graphene as reinforcement [1]. Nanomaterials like graphene are well known to have exceptional properties in mechanical, thermal and electrical [2]. NR/EPDM blend have been explored over three decades because NR/EPDM could possess good physical properties with adequately high aging and ozone resistance [3]. Combining NR/EPDM blend with nanofiller (GNPs) is not a new brand material. It has been studied by several researchers on mechanical properties [4], damping properties [5], processing parameters [6], cure characteristics [7] and etc. However, study on fatigue properties (dynamic behaviour) relative to tensile properties (static behaviour) of NR/EPDM filled GNP's are still scarce.
This paper is focusing on fatigue and mechanical properties of graphene nanoplatelets reinforced NR/EPDM nanocomposites.

Fatigue is one of the major failure mechanisms in engineering structures [8]. Due to Araham et al. [9], mechanical fatigue of elastomers is manifested in a progressive reduction of the physical properties as a result of a crack propagation during continuous dynamic excitation. Though there are levels of stress or strain below each elastomer will suffer fatigue damage, such limits are not well established. Typically, the fatigue process involves a period during which cracks nucleate in regions that were initially free of observed cracks, followed by a period during which nucleated crack grow to the point of failure. Analysis approaches that are currently available for predicting fatigue life in rubber, including both crack nucleation as well as crack growth approaches, are reviewed by Mars and Fatemi [10].

2. Experimental study

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). GNPs was treated using 70/30 of ethanol/water using vibration sonicator for 2 hours before dried in the oven at 60 °C until it reaches the moist bulk form. The compounding process was performed using a Haake internal mixer. 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 and nanocomposite were summarized in Table 1. Firstly, formulation recipe in Table 1 were mixed accordingly. The blend and nanocomposites were filled into mold cavity. NR/EPDM blends and nanocomposites then were compressed using GT7014-A hot press from Gotech. The samples were prepared under compression of 1800 kg/cm². From this stock, sheets for both NR/EPDM blend and nanocomposite was vulcanized approximately 2 mm thick with a semi-efficient vulcanization system with a hot press at 150 °C. The samples were cut into 64 mm x 10 mm dog bone sample size. Then the samples were tested for tensile and fatigue properties according to ASTM D1822 using Universal Tensile Machine (Toyoseiki Strograph) and ASTM D7791 using Fatigue Machine (5 kN Shimadzu 4830) testing machine. The sample were subjected under prescribed sinusoidal displacement with stretch ratio of 20. The stretch rate of the material is about 2 s⁻¹ with the frequency imposed for all loading conditions was 2 Hz. For each test the number of cycles required for the complete rupture of each specimen. The test was stopped at 2 million cycles if no crack or rupture is observed in the specimen.

Table 1. NR/EPDM Formulation Recipe

| Ingredients       | Rubber blend (phr)* | Rubber nanocomposite (phr)* |
|-------------------|---------------------|----------------------------|
| NR (SMR 20)       | 70                  | 70                         |
| EPDM              | 30                  | 30                         |
| GNP              | 0                   | 3                          |
| ENR-50            | 10                  | 10                         |
| Zinc oxide        | 5.0                 | 5.0                        |
| Stearic acid      | 2.0                 | 2.0                        |
| Sulphur           | 1.5                 | 1.5                        |
| MBTS              | 1.0                 | 1.0                        |
| TMTD             | 0.3                 | 0.3                        |
| 6PPD             | 2.0                 | 2.0                        |
After that, the fatigue fractured surface morphologies were investigated using a scanning electron microscopy, model EVO-50 from Zeiss. The samples were placed onto aluminium stubs and sputter coated with thin layer of gold, about 20 mm thickness. All samples were examined with secondary electron imaging mode. Meanwhile, XRD analysis was performed to analyse the crystallinity of the rubber using PANalytical X’Pert PRO diffractometer and the data was analysed using X’pert PRO software. The x-ray source used was CuKα radiation with λ = 1.5418 nm and all samples were characterized under conditions of 20 scanning range (5 to 40°), 1 sec of dwell time, and step size of 2° in 20 min. Finally, the samples with 1mm thickness were analysed using DMTA to measures the stiffness and damping behaviour of sample, which are reported as storage modulus. Dynamic mechanical thermal analysis was performed using a Perkin Elmer DMTA-7e in the temperature scan mode with a parallel plate. The measurement was carried out at a heating rate of 10ºC min-1 over a temperature range of -100ºC to 100ºC.

3. Results and discussion

3.1 Uniaxial test

Figure 1 shows the tensile graph for both blend and nanocomposite. The additional of GNPs filler in NR/EPDM blend had cause an increased in pattern of tensile strength and elongation at break. About 95% and 60% of drastic improvements were observed for tensile strength (TS) and $E_b$ respectively. The increment of elongation at break ($E_b$) with the additional of GNPs with two-dimensional multilayer structures have a unique frictional interlayer sliding that usually exist because of the weak Van Der Waals forces bonded in the GNPs layers which may assist the elongation of produced nanocomposite blends [11]. Thus, the additional of GNPs may serve as dual functions as and reinforcing agent to the NR/EPDM blend due to the TS increment, as well as an elasticity enhancer due to the increment in $E_b$[12].

![Figure 1. Stress vs Strain for NR/EPDM blend and nanocomposite.](image)

Table 2 shows the comparison of tensile properties and fatigue properties of NR/EPDM blend and nanocomposite. For modulus at 100% (M100) and modulus at 300% (M300), the increasing value of NR/EPDM nanocomposite for both M100 and M300 compared to NR/EPDM blend attributes the stiffness properties. The additional of GNPs loading producing higher M100 and M300. The percentage of improvement in modulus values was about 18% and 32% for M100 and M300, respectively. Increased modulus at M100 and M300 of rubber elongation indicated a good rubber-filler
interaction between the NR/EPDM rubber blend and GNPs nanofiller. Furthermore, lamellar structure of the graphene allowed better surface wetting and enhanced polymer-matrix interactions between the nanofiller and rubber matrix, thereby led to better stress transfer that yield better reinforcements effects on the GNPs [13].

NR/EPDM blend and nanocomposite having the same number of fatigue life however NR/EPDM blend sample breaks without having the initial crack compared to NR/EPDM nanocomposites which rapidly propagated after initiation of crack at around 30,000 cycles until it reaches a complete rupture. The additional of GNPs to rubber compounds can have a pronounced strengthening effect, depending on the volume fraction used. It can be seen that, by adding GNPs to NR/EPDM generally crack before it fully ruptured due to pull out of fillers which is in good agreement with the fracture surface morphology shows in Figure 2. NR/EPDM nanocomposite indicate thicker shear yield of matrix. The thicker the shear yield of matrix, the higher the crack resistance. Besides, in displacement control, the utilization of GNPs, maximizing the compound stiffness will maximize the energy release rate, resulting in maximum fatigue life compared to NR/EPDM blend.

| Table 2. Uniaxial test results of NR/EPDM blend and nanocomposite. |
| --- | --- | --- | --- | --- |
| Formulation | Tensile properties | Fatigue properties |
|             | TS (MPa) | M100 (MPa) | M300 (MPa) | E_B Peak Stress (MPa) | Fatigue life, N_f (cycles) |
| NR/EPDM blend | 13.46±4.8 | 1.29±0.13 | 3.08±0.42 | 200±44 | 1.51±0.56 | 100,000 |
| NR/EPDM nanocomposite | 26.24±2.6 | 1.52±0.08 | 4.07±0.22 | 320±31 | 1.60±0.78 | 100,000 |

### 3.2 Morphological Analysis

Figure 2 shows the fatigue fracture surfaces of NR/EPDM blend and nanocomposite at small-scale with 300x magnification. Figure 2 (a) shows a flaw located on the fatigue crack surface. Crack growth of rubber is assumed to start from very small flaws [14]. Figure 2 (b) and (c) illustrate the fracture surface of NR/EPDM blend and nanocomposite after fatigue failure. Both materials producing two zones of crack which illustrated by the rough and smooth region. The rough region (Zone 1) was a result from the cracks that initiated from mechanism of the pulled-out particle around 10 µm and propagate slowly under cyclic loading [15]. Meanwhile, the smoother fracture surface (Zone 2) was attribute to the catastrophic failure that occurred as a result from the lack of ability of NR/EPDM nanocomposite to resist the growth of cracks as the cyclic loading increases. The incapability to resist crack propagation is due to the filler sheets that are no longer able to transfer the stress more evenly to the neighbouring matrix as the fatigue test progress. The increase in surface roughness indicates that the additional of graphene nanoplatelets resulted in the increase in rubber stiffness which consequently cracks to occur rapidly compared to rubber blend [16]. Figure 2 (d) and (e) show larger number of humps appear on the fracture surface of NR/EPDM nanocomposite compared to NR/EPDM blend which has smaller number of humps. In other words, the NR/EPDM blend has smoother surface than NR/EPDM nanocomposite.
3.3 X-Ray Diffraction Analysis

XRD patterns for NR/EPDM blend and nanocomposite depicted in Figure 3. The existence of broad diffraction peak in NR/EPDM blend can be referred as amorphous structure which remains unchanged in both pictograms upon blending with GNPs [17]. NR/EPDM nanocomposite exposed the [002] diffraction at $2\theta = 26.6^\circ$ corresponding to an interlayer d-spacing (0.34 nm) of C in graphene platelets [18]. It is attributed to the layered crystalline GNPs weakly with an increment in GNPs loading up to 3 wt%. Crystalline phase is arranged in ordered with high cohesion. Therefore, the higher the crystallinity, the greater the strength of rubber thus reducing the degree of freedom for the molecular chain to move. Peak at $2\theta = 34.3^\circ$ in the spectrum was originated from the (002) plane of ZnO which appeared as the vulcanization agent [19].

Figure 3. XRD of NR/EPDM blend and nanocomposite
Conclusion
As the conclusions, the NR/EPDM blends and nanocomposite were successfully produced and tested for tensile properties and followed by the fatigue properties (tensile mode) using displacement-controlled. NR/EPDM nanocomposite exhibits superior tensile properties with 95% than its host NR/EPDM blend. Furthermore, it shows compatible dynamic properties where both NR/EPDM nanocomposite has higher peak stress with 6% compared to NR/EPDM blend and had similar fatigue life of about 100000 cycles. The properties were in line with the morphological analysis on its fracture surfaces observed via scanning electron microscopy (SEM) as well as structural, compositional and thermal properties. Therefore, NR/EPDM nanocomposite has advantage on engine mounting industry due to its significant properties of tensile and fatigue.

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