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Comparison of two compounding techniques for carbon nanotubes filled natural rubbers through microscopic and dynamic mechanical characterizations

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ABSTRACT

Natural rubber used in wave energy converters requires higher fatigue life and better energy harvesting efficiency to make it inexpensive compared to other renewable energy resources. Carbon nanotubes (CNTs) were extensively used to enhance the mechanical properties of natural rubber, however, its performance in a double-bonded shear condition was rarely investigated. In addition, the state of CNT dispersion was a critical factor for better energy harvesting efficiency and fatigue life. Therefore, this study was aimed to compare two different dispersion approaches in CNT synthesis so that better dynamic mechanical properties and lower hysteresis loss were achieved. One approach was done in the liquid state whereas the other one was carried out in dry condition. Although the former manifested a better CNT dispersion, no significant differences in terms of dynamic mechanical properties and dissipation losses compared to the latter compounding were obtained.

1. Introduction

Natural Rubber (NR) is widely used as a working surface i.e. a pneumatic cell device in Wave Energy Converters (WECs) due to its low cost and outstanding mechanical properties [1–3]. Enhancement of the efficiency of a WEC is largely related to its elastic stiffness, stretchability, and amount of hysteresis when subject to a cyclic loading [4]. A suitable elastomer for WECs should possess low hysteresis loss and good mechanical and fatigue properties. However, further enhancement of its fatigue life and energy harvesting efficiency are still required to make wave energy harvesting more economically valuable. A significant amount of works has been conducted on tailoring mechanical properties of NR reinforced with CNTs [5]. Crack branching and crack deflection i.e. formation of secondary cracks were the main mechanism in improving fatigue crack propagation of CNTs-filled rubber [6,7]. This resulted in more energy dissipation and a reduction of stress in the crack-tip [7,8]. Nevertheless, it was severely related to the state of CNT dispersion, in particular for a higher fatigue life, energy dissipation and energy harvesting efficiency [6,8–10]. It is worth noting that CNT has a high tendency to bundle due to the large surface energy and intensive van der Waals forces [11], thus, achieving a homogenous CNT dispersion is quite challenging. Different dispersion approaches were used for CNT dispersion into rubber including latex mixing, solution method, and mechanical/melting technology which each have their own advantages and disadvantages [12]. Latex compounding cannot be an ideal technique for membrane application as it was mainly used for dipping products such as gloves and surgical products. Although, a better nanofiller dispersion can be achieved in solution mixing, removing the solvent is quite difficult [13,14]. Improper dispersion of CNTs were also the main disadvantages of the mechanical/melt technique.

Therefore, this study was aimed to compare two different compounding approaches in terms of CNT dispersion and related dynamic mechanical properties. One batch was prepared using only mechanical mixing whereas the other one undergoes further processing using solution mixing assisted by ultrasonication in the initial stage of compounding, accompanied with further compounding using twin roll mill to remove the entrap bubbles efficiently. The CNTs dispersion was studied using TEM while the dynamic mechanical properties were examined through a double bonded shear test piece in a cyclic condition to mimic the sea environment for a WEC. Finally, the performance of both approaches is examined in terms of storage and loss moduli, hysteresis behaviour and energy dissipation to identify the enhancing effect of CNTs on NR properties.

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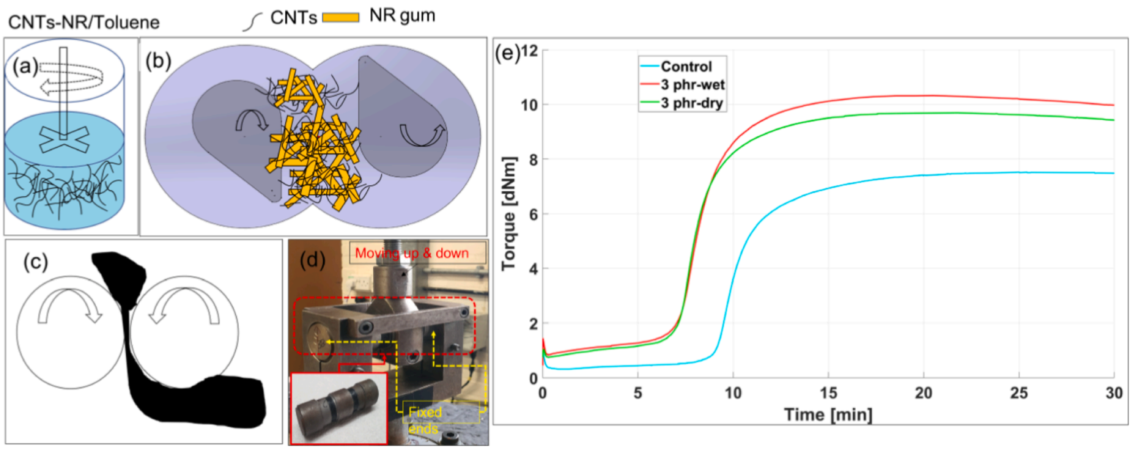

Fig. 1. (a-b) wet and dry dispersion techniques respectively, (c) two-roll mill, (d) double bonded shear test, (e) rheometry test.

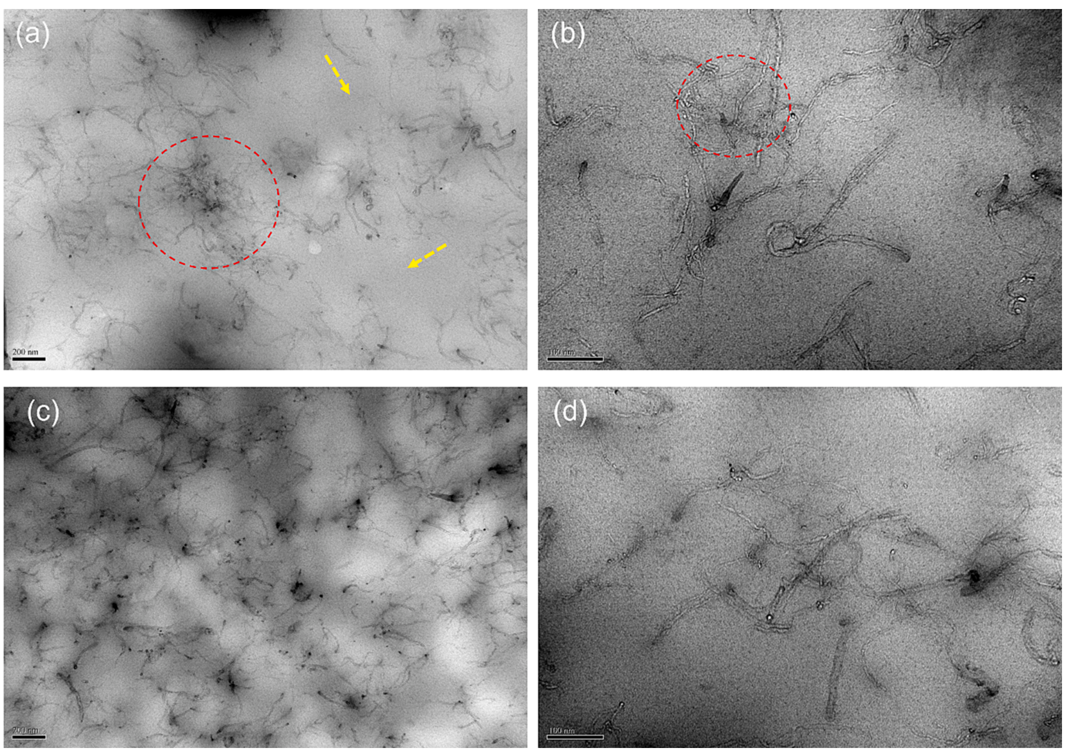

Fig. 2. TEM image of dispersion of CNTs with NR matrix: (a-b) dry dispersion, (c-d) Wet dispersion.

2. Experiment

MWCNTs (NC7000TM) with 10 nm diameter and 1.5 μm length were purchased from *Nanocyl* while natural rubber bales, SMR CV60 gum, were provided from *Malaysian rubber company*. Two different processing approaches were used for CNT addition to achieve better CNTs dispersion (Fig. 1a-b). 3 phr CNT was used for the nanocomposites while a control sample was also prepared for comparison. The first approach hereinafter called wet is as follows: (i) the initial gums were dissolved into toluene and left for 4 days to turn into a liquid state, (ii) the MWCNTs was bath-sonicated for 30 min in toluene using 40 % energy output and 50 % duty cycle, (iii) CNTs/toluene mixture was added to NR/toluene solution and vigorously stirred for 1 h (Fig. 1a), (iv) the CNT-NR/ toluene mixture was poured in a tray and dry for three days, (v) the dried CNT/NR compound was further homogenized by two-roll mill at 30 rpm (Fig. 1c). On the other hand, the MWCNTs were directly added to the NR in an internal mixer at 50 rpm hereinafter called dry method (Fig. 1b). The rubber formulation was zinc oxide (5 phr), stearic acid (2 phr), 6PPD (3phr), and Sasol wax (2 phr) added in the internal mixer, whereas Sulfur (1.5 phr) and CBS (1.5 phr) added on the two-roll mill. Based on the rheometry test data, samples were hot pressed at 150 °C for 13 min (17 min for control) for final curing where a square sample of 9″x9″x2 mm were produced. The dispersion state of CNTs was characterized by TEM *Jeol JEM-1400* in which an ultra-thin section of sample in the range of 60–70 nm was prepared using ultra-microtome at −120 °C. The volumetric electrical conductivity of the nanocomposites was also measured according to ASTM D257 to quantitatively verify the TEM results based on the CNT dispersion. Dynamic mechanical characterization was conducted in a cyclic condition (sinusoidal wave form at − 1 Hz) using a double bonded shear test piece with 25 mm in diameter and 6 mm in thickness at various strain amplitudes, each 6 consecutive cycles, and 1 min rest between each 6 cycles

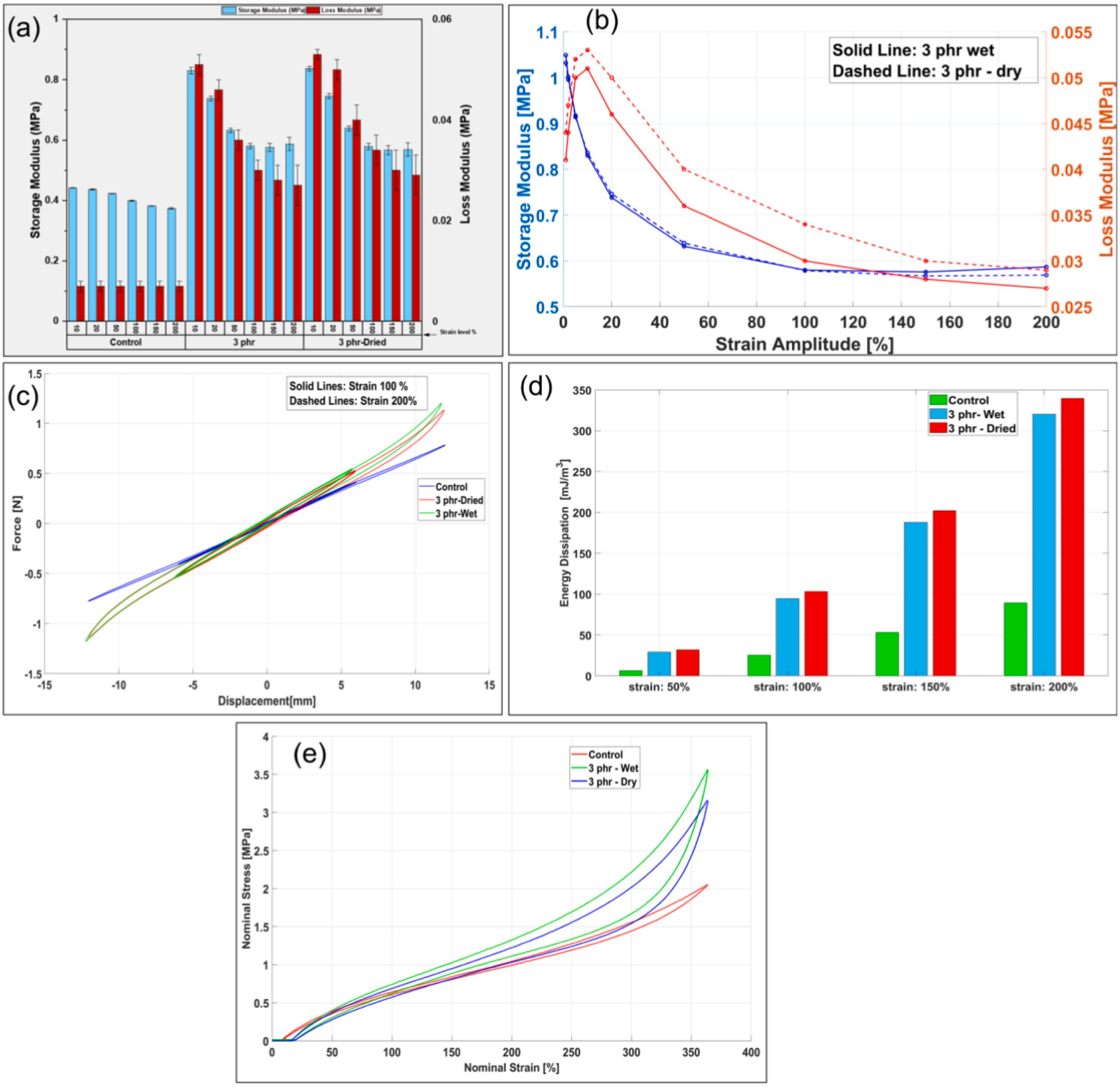

Fig. 3. Comparison of the control, 3 phr wet and 3 phr dry: (a-b) storage and loss moduli, (c) loading–unloading curves at two different strain amplitudes, (d) Energy dissipation corresponding to the hysteresis curves shown in (c); (e) Tensile properties.

(Fig. 1d). Storage and loss moduli, hysteresis behaviour and energy dissipation (the area of hysteresis) were compared. Finally, uniaxial quasi-static tensile properties of the samples were probed using ADMET *eXpert 8000* in which samples were preconditioned for 50 cycles to remove the Mullins effect; then the tensile test (loading–unloading test for 5 cycles) was conducted and the mechanical properties at cycle No. 5 was reported.

3. Result and discussion

3.1. Dispersion analysis

The dispersion state of CNTs within the NR for dry and wet conditions are shown in Fig. 2 a-b and c-d, respectively. The presence of CNT agglomerations and poor CNTs-regions can be seen in the dry sample as highlighted by a red dashed circles and dashed yellow arrows in Fig. 2a-b, respectively. In contrast, a homogenous CNTs dispersion is achieved in the wet condition i.e., CNTs are uniformly dispersed throughout the matrix. This can be attributed to the combined effect of sonication in debundling CNTs aggregates assisted by the addition of toluene. Both dry and wet methods manifest quite proper interfacial bonding between CNTs and NR. As for the electrical conductivity, the solution method (3.7×10^{-4} S/m) leads to a huge increase with respect to dry route (8.52×10^{-6} S/m), almost two orders of magnitude which is in line with TEM results.

3.2. Dynamic shear properties

Fig. 3 shows the storage and loss moduli in which incorporation of CNTs significantly enhances the dynamic shear properties of the NR nanocomposites compared to the control (Fig. 3a). This can be attributed to the reinforcing effect of CNTs in improving mechanical properties resulting from appropriate shear-loading transfer between CNT and NR. Moreover, increasing strain amplitude reduces storage modulus, though the reduction in the control compared to CNTs filled rubber is quite negligible. This can be attributed to the Payne effect which is one of the typical phenomena in filled rubber, especially at relatively low strain levels (Fig. 3b) [15]. Although both wet and dry approaches manifest quite the same storage modulus at different strain levels, the latter presents a higher loss modulus compared to the former which can be ascribed to the presence of CNTs aggregates. In fact, the agglomerated CNTs (Fig. 2a) possess a weak interfacial bonding with the matrix, thus, acting as a crack which results in further energy dissipation.

The hysteresis behaviour and energy dissipation at different strain amplitudes are shown in Fig. 3c-d respectively. The control manifests the lowest hysteresis loss and energy dissipation due to its less visco-elastic properties. In contrast, with the addition of CNTs, hysteresis loss and energy dissipation increase (Fig. 3c-d), due to the destruction and reorientation of CNTs aggregates during stretching and their weak-interfacial bonding [8]. Furthermore, the dry condition demonstrates relatively higher hysteresis and energy dissipation with respect to the wet sample arising from its higher heterogeneity compared to the latter, i.e.,more energy is dissipated into heat when a poor CNTs dispersion is obtained indicating less energy harvesting efficiency as well as shorter loading–unloading life in WECs. It is worthy to note that the higher the energy dissipation the lower the fatigue life of the elastomer [16]. Comparing trivial hysteresis of the control with high hysteresis loss in the CNTs filled rubbers, one can say that CNTs might have a detrimental effect on wave energy harvesting due to higher hysteresis in CNTs filled rubber. However, a balanced fatigue life and energy harvesting capability should be met to assure efficient energy harvesting can be achieved, thus, improving CNTs dispersion within the NR is critical for WECs. Tensile properties of the sample are also shown in Fig. 3e indicating a substantial enhancement in tensile properties by CNTs. The solution method manifests relatively a higher tensile property with respect to the dry technique due to better state of CNT dispersion. In addition, the presence of hysteresis during loading–unloading is notable in the filled and unfilled rubbers, though the control manifests relatively a lower hysteresis. This can be related to Mullins's effect resulting from disruption of the polymer chains, debonding of filler from the interface (matrix) and filler-filler interaction [17].

4. Conclusion

MWCNTs were successfully incorporated into NR to enhance its dynamic shear properties. Two different compounding approaches were used to reach a better CNT dispersion. TEM images proved that the wet condition reached less heterogeneity in CNTs dispersion compared to the dry method resulted in two orders of magnitude increase in its electrical conductivity. The wet condition possessed better dynamic shear properties and less hysteresis compared to the dry method. Nevertheless, the difference achieved were not significant amongst them; besides, solvent free nature of the mechanical mixing and its low cost made it ideal approach for compounding CNT/NR.

CRediT authorship contribution statement

Ali Esmaeili: Methodology, Investigation, Funding acquisition. **Mokarram Hossain:** Conceptualization, Funding acquisition, Project administration, Supervision. **Ian Masters:** Conceptualization, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] Collins, et al., Renew. Sustain. Energy Rev. 151 (2021), 111478.
[2] Ojlh et al. , (2016) 978–981. https://doi.org/10.3850/978-981-11-0782-5.
[3] Greaves et al. , Int. Conf. Offshore Renew. Energy. (2016).
[4] Kaltseis, et al., RSC Adv. 4 (2014) 27905–27913.
[5] Ji, et al., Int. J. Fatigue 163 (2022), 107094.
[6] Zhan, et al., J. Appl. Polym. Sci. 137 (2020) 1–9.
[7] Guo, et al., Materials (Basel). 13 (2020) 1–12.
[8] Xu, et al., Int. J. Fatigue 131 (2020), 105388.
[9] Dong, et al., J. Appl. Polym. Sci. 132 (2015) 1–8.
[10] Wei, et al., RSC Adv. 8 (2018) 10573–10581.
[11] Esmaeili, et al., Compos. Sci. Technol. 200 (2020) 1–11.
[12] Gao, et al., Results Phys. 15 (2019), 102720.
[13] Ismail, et al., Polym. - Plast. Technol. Eng. 49 (2010) 260–266.
[14] Kueseng, et al., Eur. Polym. J. 42 (2006) 220–227.
[15] Yang, et al., Polymer (Guildf). 244 (2022), 124661.
[16] Dong, et al., Polym. Test. 63 (2017) 281–288.
[17] Tang et al. , Elsevier Inc., 2019. https://doi.org/10.1016/B978-0-12-817342-8.00012-3.