

Syntheses and experimental characterisations of carbon nanotubes-enhanced natural rubbers for wave energy harvesting applications

Mokarram Hossain*,1, Ali Esmaili*, Ian Masters*

*Zienkiewicz Centre for Computational Engineering, Faculty of Science and Engineering, Swansea University, SA1 8EN, United Kingdom

1, corresponding author : mokarram.hossain@swansea.ac.uk

Abstract: Flexible membrane used in wave energy convertors (mWECs) are typically rubbers that require higher fatigue life and better energy harvesting efficiency for making them inexpensive compared to other renewable energy resources. Carbon nanotubes (CNT) were extensively used to enhance the mechanical properties of natural rubbers. This study was aimed to develop a novel compounding approach in CNTs dispersion within the natural rubber to improve both dynamic mechanical properties and hysteresis loss. One approach was done in the liquid state whereas the other one was carried out in a dry condition. This finding is crucial for a wave energy converter, which, is subjected to a complex dynamic loading scenario, as further energy can be harvested upon each deformation while the membrane possesses a better lifetime simultaneously.

Introduction:

Carbon nanotube (CNT) manifests excellent performance in enhancing multi-functional properties of natural rubbers (NR) owing to its outstanding mechanical, electrical, and thermal properties[1]. Since a flexible wave energy convertors (mWEC) is subjected to a harsh sea-water environment as well as highly repetitive loading conditions, the performance of the elastomer in WECs, must be well studied when subjected to alternating loading conditions [2]. In addition, one of the main factors affecting the fatigue life, energy dissipation and energy harvesting efficiency of a WECs device is a relatively good CNT dispersion as well as proper interfacial bonding between CNTs and NR. Therefore, this study was aimed to develop a combined compounding approach using both solution and mechanical mixing techniques to guarantee that a proper CNT dispersion can be achieved.

Experiments:

Multi-walled CNTs (MWCNTs) possessing an average of 10 nm diameter and 1.5 μm length were used. Two different processing approaches were used for CNT addition to find out an optimum method achieving better CNTs dispersion. The nanocomposites contained 3 phr CNT 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 few days to turn into a liquid state i.e. NR/toluene solution, (ii) the MWCNTs was bath-sonicated for 30 min in toluene, (iii) CNTs/toluene mixture was added to NR/toluene solution and vigorously stirred for 1 h, (iv) the CNT-NR/ toluene mixture was poured in a tray and dry, (v) the dried CNT/NR compound was further homogenised by two-roll mill. On the other hand, the MWCNTs were directly added to the NR using an internal mixer in the solid state hereinafter *called dry*. The dispersion state of CNTs was characterized by TEM. Dynamic mechanical characterization was conducted in cyclic condition (sinusoidal wave form - 1 Hz) using a double bonded shear test piece. Storage and loss moduli, hysteresis behaviour and energy dissipation (the area of hysteresis) of the samples were compared.

CNT Dispersion analysis:

The dispersion state of CNTs within the NR for dry and wet conditions are shown in Fig. 1 (left, a-d). The presence of CNT agglomerations and poor CNTs-regions can be seen in the dry sample as highlighted by red dashed circles and dashed yellow arrows, Fig. 1(left, a-b). In contrast, a homogenous CNTs dispersion is achieved in wet dispersion technique, i.e., CNTs are uniformly dispersed throughout the matrix Fig. 1(left, c-d). Apart from the dispersion state, both dry and wet methods manifest quite proper interfacial bonding between CNTs and NR. It can be concluded that dispersing CNTs within NR should be carried out in the liquid state to reach less CNTs aggregates which most likely enhance fatigue life and energy harvesting efficiency of the rubber nanocomposites [3,4].

Dynamic shear properties :

Fig.1 (right, a) shows storage and loss moduli of the NR nanocomposites along with the control. Incorporation of CNTs significantly enhance dynamic shear properties of the NR with respect to the control when compared at the same strain amplitude Fig 1(right, a). This can be attributed to reinforcing effect of CNTs in improving mechanical properties resulting from appropriate shear-loading transfer between CNT and NR. Although both wet and dry approaches manifest quite the same storage modulus at different strain levels, the latter presents higher loss modulus compared to the former which can be ascribed to presence of CNTs aggregates in the dried condition. In fact, the agglomerated CNTs possess a weak interfacial bonding with matrix, thus, acting as a crack which results in further energy dissipation.

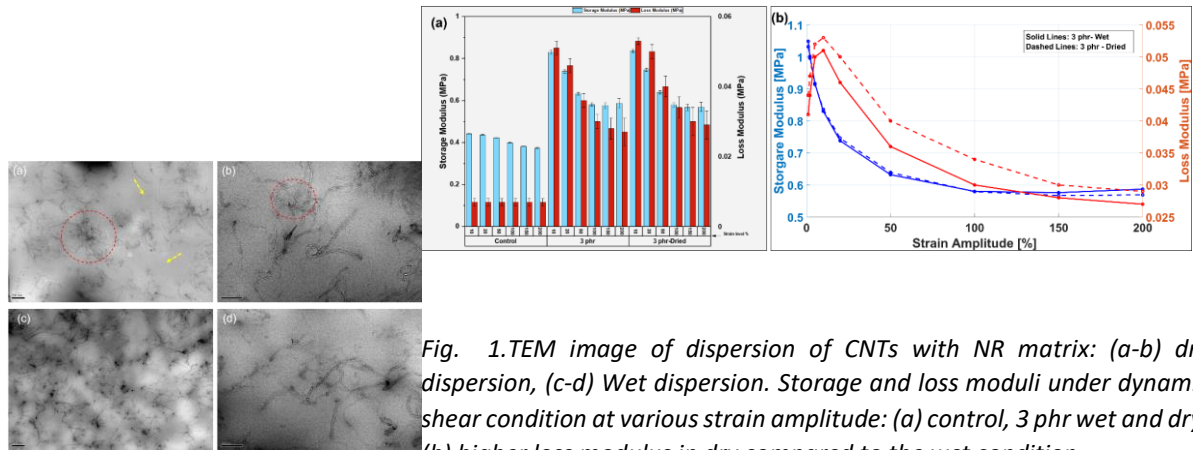


Fig. 1. TEM image of dispersion of CNTs with NR matrix: (a-b) dry dispersion, (c-d) Wet dispersion. Storage and loss moduli under dynamic shear condition at various strain amplitude: (a) control, 3 phr wet and dry, (b) higher loss modulus in dry compared to the wet condition.

Conclusion:

MWCNTs was successfully incorporated into NR to enhance its dynamic shear properties. A novel method in improving CNTs dispersion within NR was developed in this study to guarantee better energy harvesting efficiency and better cyclic performance in shear mode can be achieved [5]. TEM images proved that the wet approach could reach less heterogeneity with respect to the dry method. It was concluded that the state of CNTs dispersion was a critical parameter in optimizing performance of a flexible membrane in a WEC device through enhancing cyclic shear performance and lower energy hysteresis loss.

References:

- [1] A.S.S. Sethulekshmi, A. Saritha, K. Joseph, A comprehensive review on the recent advancements in natural rubber nanocomposites, *Int. J. Biol. Macromol.* 194 (2022) 819–842. <https://doi.org/10.1016/j.ijbiomac.2021.11.134>.
- [2] I. Collins, M. Hossain, W. Dettmer, I. Masters, Flexible membrane structures for wave energy harvesting: A review of the developments, materials and computational modelling approaches, *Renew. Sustain. Energy Rev.* 151 (2021) 111478. <https://doi.org/10.1016/j.rser.2021.111478>.
- [3] R. Kaltseis, C. Keplinger, S.J. Adrian Koh, R. Baumgartner, Y.F. Goh, W.H. Ng, A. Kogler, A. Tröls, C.C. Foo, Z. Suo, S. Bauer, Natural rubber for sustainable high-power electrical energy generation, *RSC Adv.* 4 (2014) 27905–27913. <https://doi.org/10.1039/c4ra03090g>.
- [4] P. Bernal-Ortega, M.M. Bernal, A. González-Jiménez, P. Posadas, R. Navarro, J.L. Valentín, New insight into structure-property relationships of natural rubber and styrene-butadiene rubber nanocomposites filled with MWCNT, *Polymer (Guildf)*. 201 (2020). <https://doi.org/10.1016/j.polymer.2020.122604>.
- [5] Y. Zhan, N. Yan, G. Fei, H. Xia, Y. Meng, Crack growth resistance of natural rubber reinforced with carbon nanotubes, *J. Appl. Polym. Sci.* 137 (2020) 1–9. <https://doi.org/10.1002/app.48447>.