

A STUDY OF THE MECHANICAL PROPERTIES OF CNT/UHMWPE NANOCOMPOSITES

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ABSTRACT

The present paper reports a proposed approach to fabricate CNT/UHMWPE nanocomposites and the associated mechanical test results including tensile and dynamic mechanical analysis. Carbon nanotubes were first dispersed in toluene and further dispersed in a certain amount of low molecular weight polyethylene. A series of nanocomposite samples with various ratios of LMWPE and UHMWPE were successfully fabricated using the compression moulding process. The uniaxial tensile test results showed that the strength and toughness of the nanocomposites were comparable to the pure UHMWPE except for those with a very high amount of LMWPE (>25%). Moreover, in contrast to the brittle failure mode of the samples without CNT, it was observed that nanocomposites with a relatively high content of LMWPE (up to 25%) failed in ductile modes. The CNT/UHMWPE nanocomposite developed in this study provides a solution for improving the processability of UHMWPE for practical applications.

Keywords: *Nanocomposites, CNT, UHMWPE*

1 INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) refers to as polyethylene having a molecular weight in excess of about a million and commonly above 2 or 3 million [1]. It is well recognized for its outstanding physical and mechanical properties and has been widely employed in many industrial, military, and medical applications. Carbon nanotube (CNT) is among the strongest materials mankind has produced to date [2], with exceptionally high strength and elastic modulus, unique electrical conductivity, as well as relatively high thermal stability and conductivity; nevertheless, with a low density due to its hollow, one-dimensional structure. Consequently, it is highly beneficial to employ CNT as a nano-filler for reinforcement in structural and multi-functional nanocomposites. It is desirable to integrate CNTs into a UHMWPE matrix to introduce a nanocomposite which takes advantage of the high mechanical performance of both constituents [3].

UHMWPE provides a number of technically important properties including notched impact strength, energy absorption capacity at high loading rates (critical to ballistic protection applications), tensile impact strength at elevated temperature, resistance to stress cracking, and extremely low embrittlement temperatures. Although the extremely high molecular weight has brought superior mechanical properties for UHMWPE, the ultra-high molecular weight also brings great challenges for its processing and forming such as poor dissolution, very high melt viscosity, and poor melt flowability [4-7]. For instance, UHMWPE extrusion products can only be extruded by

large trust extruder with special screw structures, simultaneously adding a large amount of organic compounds as lubricants [4]. It is also very difficult to carry out injection moulding due to the poor fluidity of UHMWPE [4-5]. Although Huang et al. [8] have obtained injection parts of UHMWPE blend containing 90 wt% commercial UHMWPE and 10 wt% low molecular weight polyethylene (LMWPE), pure UHMWPE parts with profiled surfaces still cannot be manufactured directly by injection moulding. Also, the incorporation of LMWPE to improve the processability has a great influence on the mechanical properties. As reported in [5], for instance, the elongation of injection moulded UHMWPE specimens (with the addition of about 20 wt% of LMWPE to facilitate the injection moulding) is only about one-third of the elongation of the pure UHMWPE. Additionally, it is noticed that the processability is also an important topic in the research and development of UHMWPE-based composites [9-11].

Carbon nanotube is a promising fully carbon-based nano-additive owing to its excellent mechanical and transport properties [2-3, 11-12]. While few researchers have explored the use of CNTs in UHMWPE, these studies not only indicate potential for substantial improvement of mechanical performances of the composites such as the Young's modulus, strength, and toughness [11], but also bring in multi-functionality of the nanocomposites such as the electrical conductivity and sensing capabilities [13]. Sreekanth et al. [14] employed chemically functionalized CNTs and have achieved improvements in fracture strain and toughness of 70% and 176%, respectively, with only 2.0 wt% CNT composition in neat UHMWPE. As demonstrated in many studies, properties of CNT/UHMWPE nanocomposites are highly sensitive to synthesis and process parameters, and there is paucity of research in this area [15-16].

This paper reports a proposed approach to fabricate CNT/UHMWPE nanocomposites and the associated mechanical test results including tensile test and dynamic mechanical analysis (DMA). Nanotubes were first dispersed in a solvent and further dispersed in a certain amount of LMWPE. A series of nanocomposite samples with 1 part of CNTs per hundred parts (PPH) of UHMWPE and various ratios (0 to 35%) of LMWPE and UHMWPE were compression-moulded. Uniaxial tensile and DMA test results are discussed and compared with the test results of the pure UHMWPE and those with 25% of LMWPE.

2 NANOCOPOSITES PREPARATION AND TEST METHODS

2.1 Preparations of CNT/UHMWPE Nanocomposites

Our attempt to make a processing-friendly CNT/UHMWPE nanocomposite is illustrated in Figure 1. Nanotubes are first dispersed in toluene and further dispersed in a certain amount of LMWPE in toluene solution with an average molecular weight of $M_w \sim 35K$ and $M_n \sim 7.7K$ by GPC (gel permeation chromatography). The lower molecular weight polyethylene acts as a surfactant for the CNTs and, by wrapping around each CNT and thus dispersing CNTs into small bundles or individual tubes, brings the CNTs into the formulation through the solvent processes. Moreover, the LMWPE also plays the role as a compatibilizer to diminish interface isolation between the CNT and the UHMWPE matrix, which is critical to facilitate the high mechanical performance of the CNT. In addition, such lower molecular weight polyethylene behaves more like a liquid above its melting point and plays as a solvent in the compression moulding of UHMWPE, effectively improving the processability. Finally, the LMWPE solution with dispersed CNTs is mixed with UHMWPE powder, wherein the UHMWPE has a molecular distribution from 3 million to 6 million by weight per molar. After removal of the solvent, the dried mixture is then employed to mould thin nanocomposite samples under controlled temperature and pressure. Figure 2 displays the nanotubes before and after dispersed in the toluene solution.

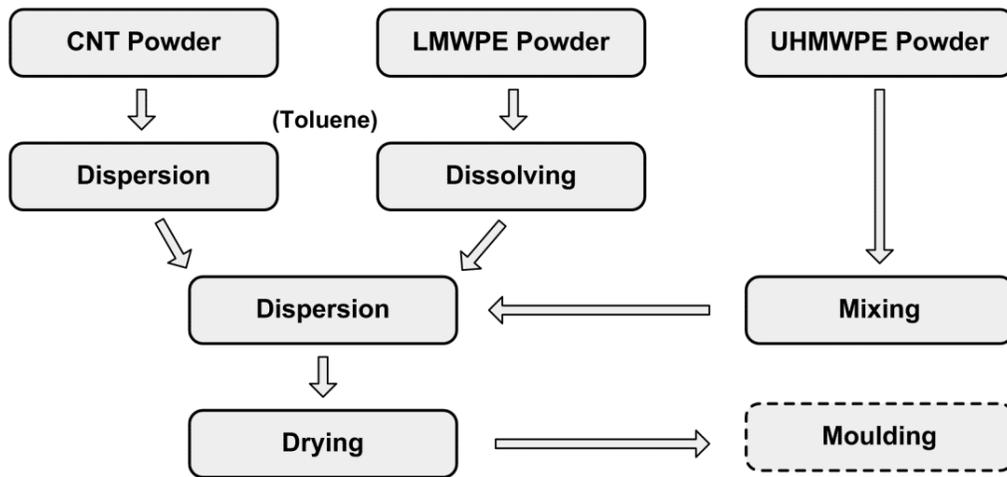


Figure 1. A wet-mixing process for the preparation of CNT/UHMWPE nanocomposites.

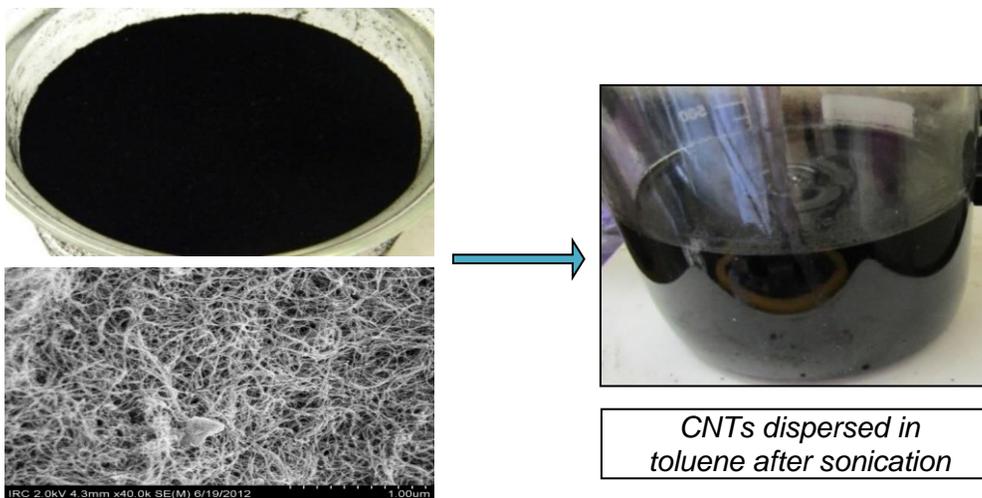


Figure 2. A wet-mixing process for the preparation of CNT/UHMWPE nanocomposites.

2.2 Mechanical Test Methods

In this study, quasi-static tensile tests were carried out to evaluate the elastic modulus, strength, failure strain, and toughness of the nanocomposites using coupon specimens cut from the moulded samples (Figure 1). Extensometers were employed to measure the strain (up to 0.5) thus to characterize the elastic behavior. The toughness is evaluated as the area under the engineering stress versus strain curves, where the engineering strain is estimated using the crosshead displacement due to the limitation of the extensometer. Figure 3(a) shows an image of the tensile test setup.

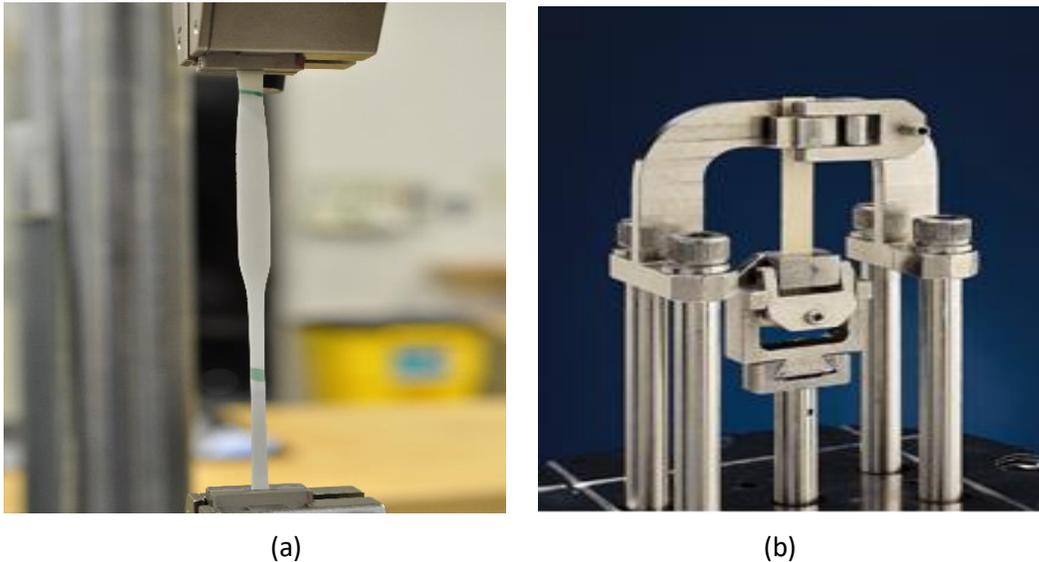


Figure 3. Test setup: (a) Uniaxial tensile test; (b) Tensile film clamp for DMA [17].

DMA tests were also carried out employing the common test method that measures the complex modulus at a low constant frequency while varying the sample temperature, in order to evaluate the viscoelastic behaviour of the nanocomposites at temperatures ranging from 23°C (room temperature) to 100°C and to identify the influences of LMWPE and CNTs on the elastic behaviour. Specimens were cut from the moulded thin samples and six repeats were tested for the nanocomposites with different ratios of LMWPE/UHMWPE. Figure 3(b) displays an image of the DMA tensile film clamp employed in this study [17].

3 RESULTS AND DISCUSSION

3.1 Tensile Test Results

The tested nanocomposites include specimens with various weight percent of LMWPE (0%, 2%, 5% 10%, 15%, 20%, 25%, 30%, and 35%), all with 1 PPH (part per hundred parts) CNT. For comparison, tensile tests were also carried out for specimens of pure UHMWPE and drily mixed powders of LMWPE (25%) and UHMWPE (75%).

Figure 4 compares the tensile test results of yield strength (the first peak of the stress-strain curve), failure strain, and toughness. As can be seen from the bar graphs, compared to pure UHMWPE specimens, specimens with 25% LMWPE (without CNT) have greatly decreased strength, failure strain, and toughness. For specimens with CNT and with 0% to 10% LMWPE, the mechanical properties are essentially not reduced compared to the pure UHMWPE. Moreover, with a higher amount of LMWPE (> 15%), the mechanical properties are significantly reduced. However, up to 25% of LMWPE, the mechanical properties of the nanocomposites are considerably higher than those of the 25% LMWPE specimens without CNT. These results demonstrated that the incorporation of CNTs can maintain the mechanical properties of UHMWPE with a high content of LMWPE. Figure 5 displays the representative stress-strain curves, from which similar observations can also be made.

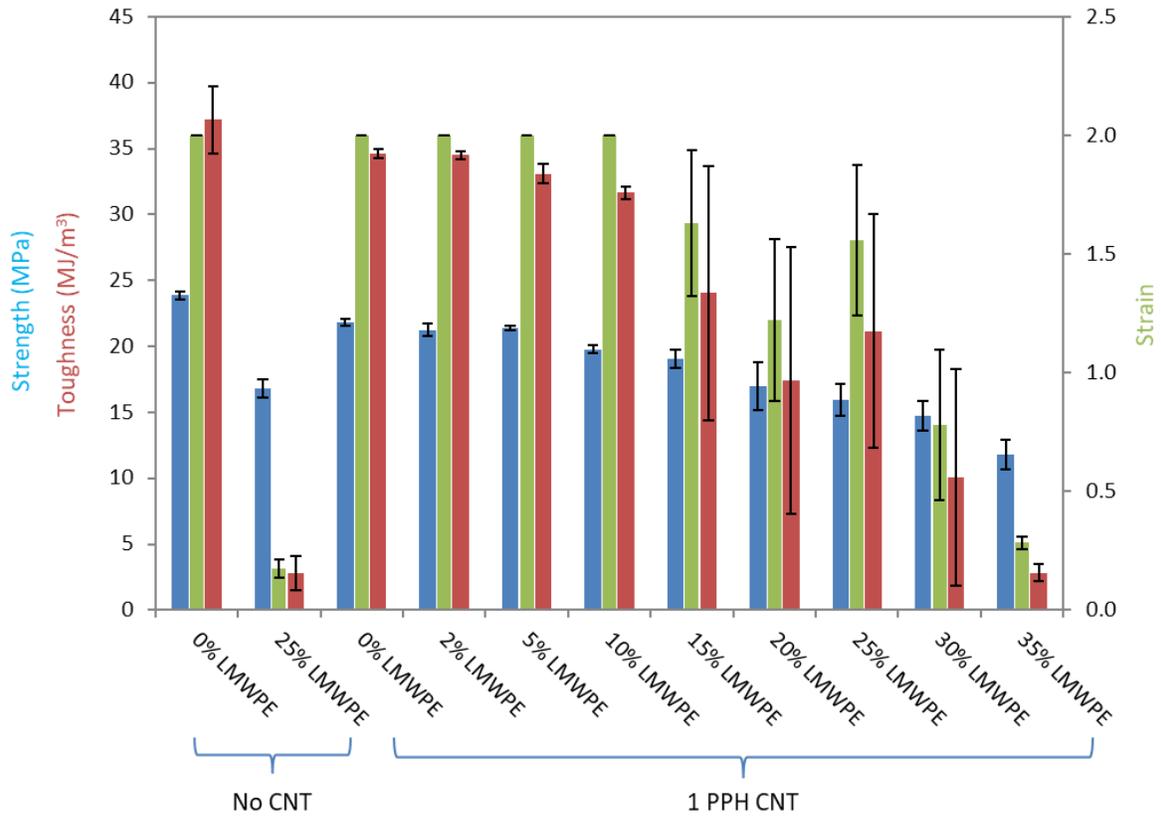
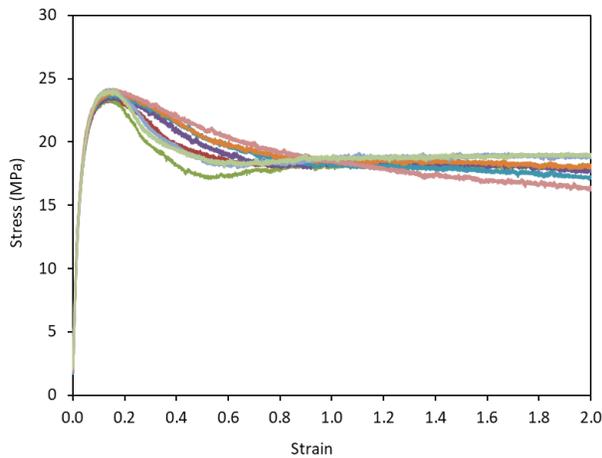
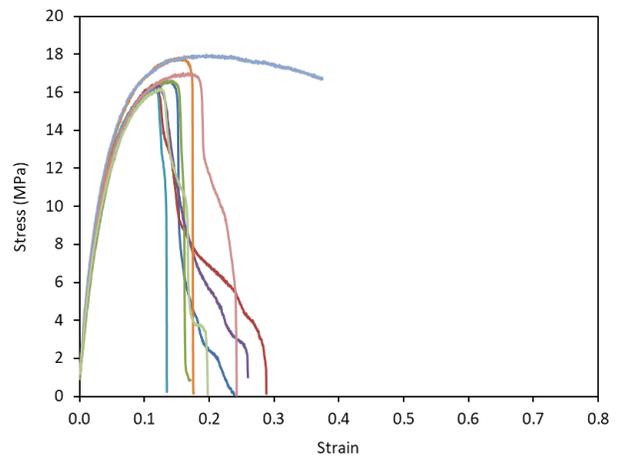


Figure 4. Comparison of the tensile yield strength, failure strain, and toughness.



(a) Pure UHMWPE



(b) 25% LMWPE (No CNT)

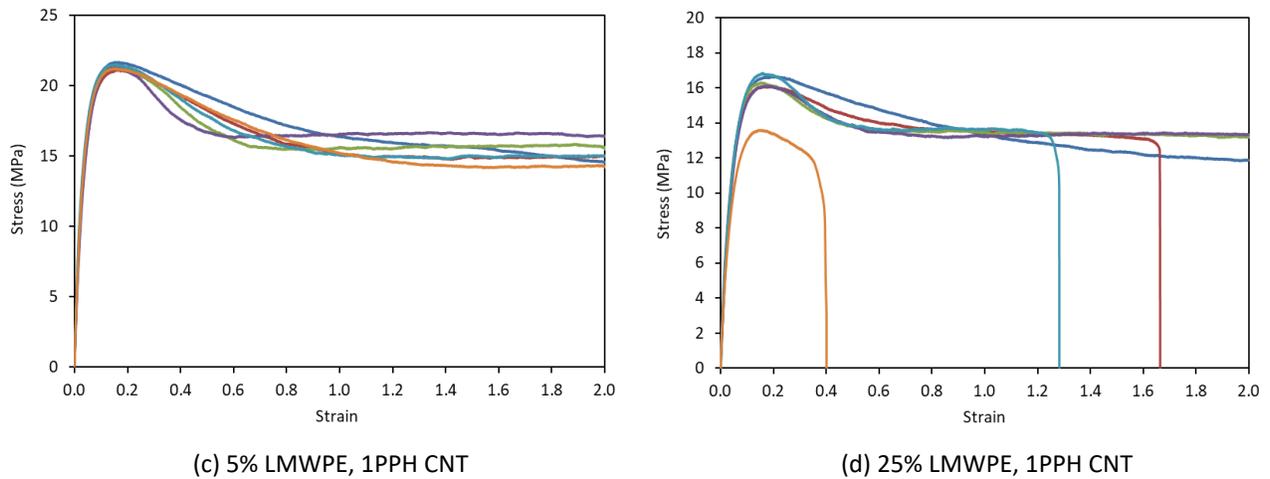


Figure 5. Representative stress versus strain curves.

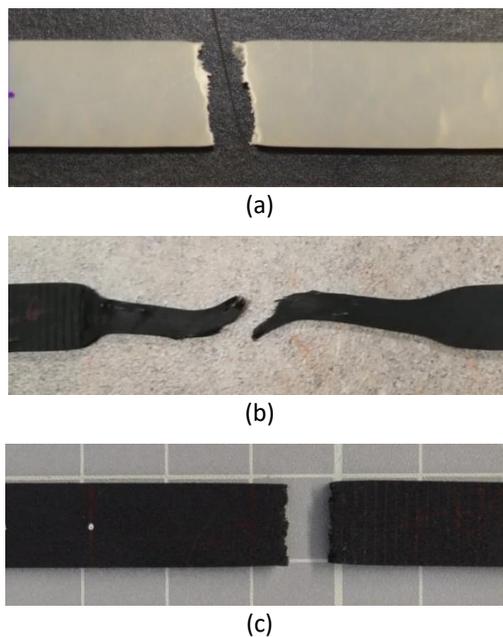


Figure 6. Tensile fracture surface: (a) 25% LMWPE without CNT; (b) 25% LMWPE with 1PPH CNT; and (c) 35% LMWPE with 1 PPT CNT.

It was observed that different failure modes occurred in the different tested nanocomposite specimens. The materials exhibit brittle behavior when a large content of LMWPE is included. However, compared to materials without CNTs, the nanocomposites show a ductile failure mode when the LMWPE content is less than 30%. Figure 6 depicts fracture surfaces of representative specimens of 25% LMWPE without CNT, 25% LMWPE with CNT, and 35% LMWPE with CNT. It is shown that for the specimen without CNT (Figure 6a), the tensile specimen fails in a brittle manner with very little necking before the final failure. This is in consistent with the small failure strain as illustrated in the stress-strain curves in Figure 5(b) and also explains the low toughness of the material (Figure 4).

On the other hand, for the nanocomposites with 25% LMWPE and 1 PPH CNT, it is observed that the fracture surface is ductile with significant necking before the final failure. This is in consistent with the large failure strain in average as indicated in Figure 5(d) and also explains the relatively large toughness of the material (Figure 4). However, as illustrated in Figure 6(c), for nanocomposites with the LMWPE content higher than 35%, the specimen again fails in a brittle manner with very low toughness, as shown in Figure 4 for the nanocomposites with 35% of LMWPE.

3.2 DMA Results

Preliminary DMA tests were carried out to understand the viscoelastic behaviour of the CNT/UHMWPE nanocomposites and the influence of LMWPE and CNT. Figure 7 represents the storage modulus (E') of the nanocomposites at temperatures ranging from 25 to 100°C.

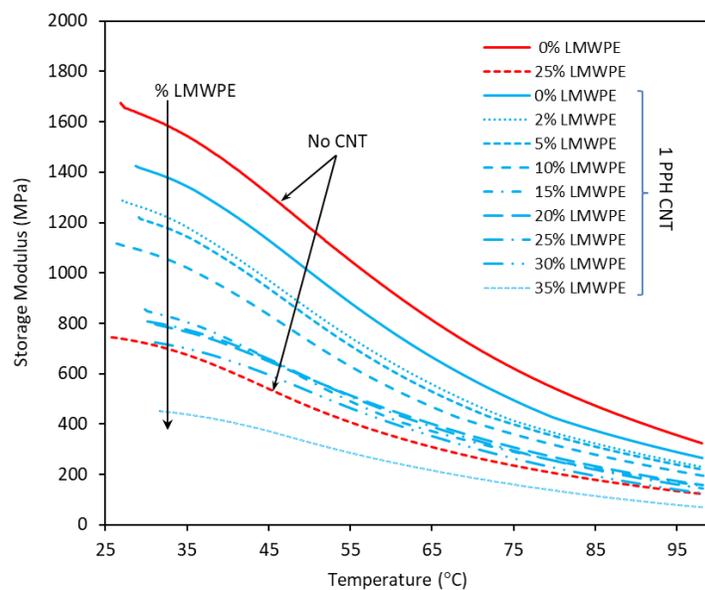


Figure 7. DMA test results: storage modulus.

As can be seen from Figure 7, the modulus of the nanocomposites decreases with the LMWPE content. For the materials with 25% UHMWPE (no CNT), the modulus at room temperature is about 50% of that of the pure UHMWPE. However, the nanocomposite with 25% LMWPE and 1PPH CNT shows a considerably higher modulus, indicating the enhancement effect of CNT on modulus. Finally, it is noticed that the influences of LMWPE and CNT hold at the entire temperature range, but considerably reduced moduli are observed at elevated temperatures.

Figures 8(a) and 8(b) illustrate the loss modulus (E'') and tangent of the phase angle ($\tan \delta = E''/E'$) at temperatures from 25 to 100°C, respectively. As shown in the figures, the influences of the LMWPE on the loss modulus and $\tan \delta$ can be roughly divided into two sets according to their LMWPE contents. For the nanocomposites with $\leq 15\%$ LMWPE, the $\tan \delta$ is close to that of the pure UHMWPE at low temperatures but is higher at elevated temperatures. However, for nanocomposites with $> 15\%$ LMWPE, the $\tan \delta$ is lower than materials with 25% LMWPE (no CNT) at low temperatures but is higher at elevated temperatures. The influence of the LMWPE content on the loss modulus is in a similar trend as that of the storage modulus shown in Figure 7.

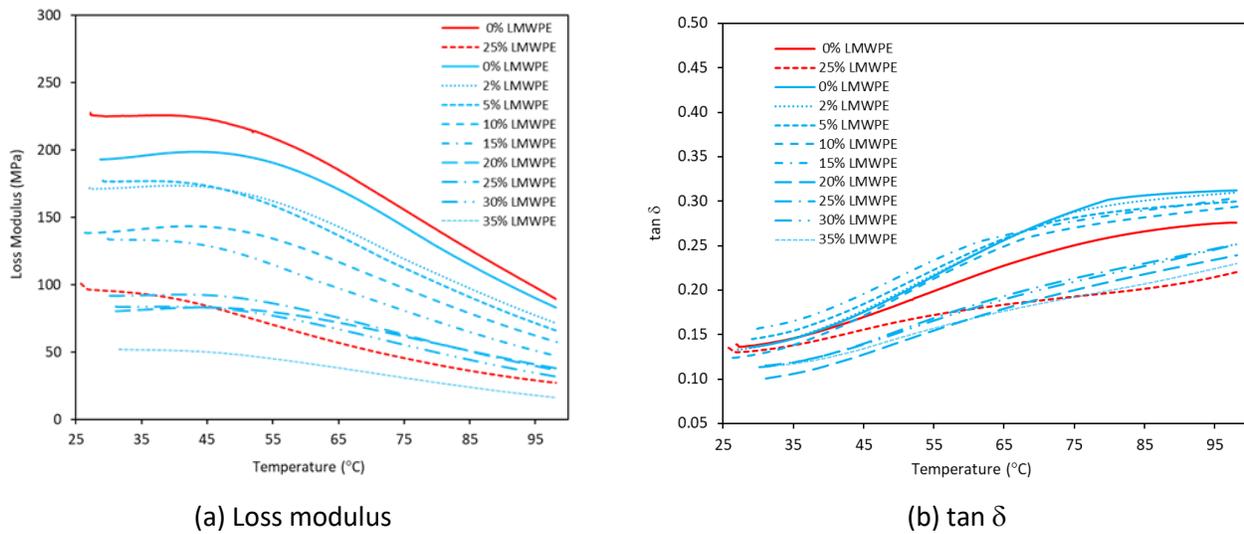


Figure 8. DMA test results for nanocomposites.

4 CONCLUSIONS

An experimental study was carried out to demonstrate the “wet-mixing” approach to make processing-friendly CNT/UHMWPE nanocomposites without significantly decreasing their mechanical properties. Nanotubes were first dispersed in a solvent and further dispersed in a certain amount of low molecular weight polyethylene. A series of nanocomposite samples with 1 PPH of CNT and various ratios (0 to 35%) of LMWPE and UHMWPE were successfully fabricated using the compression moulding process. The uniaxial tensile test results indicated that the strength and toughness of the nanocomposites were comparable to the pure UHMWPE except for those with a very high amount of LMWPE (>25%). Furthermore, it was observed that nanocomposites with a relatively high content of LMWPE (up to 25%) failed in ductile modes, in contrast to the brittle failure mode of the samples with about 25% of LMWPE (without CNT). The preliminary DMA results showed a noticeable enhancement of CNT on the storage modulus. The CNT/UHMWPE nanocomposite developed in this study provides a solution for improving the processability of UHMWPE for practical applications with its critical mechanical properties maintained through the integration of CNTs in the UHMWPE matrix.

5 REFERENCES

- [1] M. B. Turell, A. Bellare. “A study of the nanostructure and tensile properties of ultra-high molecular weight polyethylene”. *Biomaterials*, Vol. 25, No.17, pp 3389–3398, 2004.
- [2] A. D’Alessandro, F. Ubertini. “Advanced applications of carbon nanotubes in engineering technologies”. In: J. Abraham, S. Thomas, N. Kalarikkal (eds). *Handbook of Carbon Nanotubes*, Springer, Cham, 2021.
- [3] A. Iqbal, A. Saeed, and A. Ul-Hamid. “A review featuring the fundamentals and advancements of polymer/CNT nanocomposite application in aerospace industry”. *Polymer Bulletin*, Vol. 78, pp 539–557, 2021.
- [4] H. Zhang, Y. Liang. "Extrusion processing of ultra-high molecular weight polyethylene." In: *Extrusion of Metals, Polymers and Food Products*, pp 165-179, Intech, Croatia, 2018.
- [5] H.A. Scheetz, R.C. Gilles. “Melt processable UHMWPE”. USP 4281070,1981.

- [6] L. Fang, Y. Leng, and P. Gao. "Processing and mechanical properties of HA/UHMWPE nanocomposites". *Biomaterials*, Vol. 27, No. 20, pp 3701-3707, 2006.
- [7] B.P. Rotzinger, H.D. Chanzy, and P. Smith. "High strength/high modulus polyethylene: Synthesis and processing of ultra-high molecular weight virgin powders". *Polymer*, Vol. 30, No. 10, pp 1814-1818, 1989.
- [8] Y. Huang, J. Xu, Z. Zhang, L. Xu, L. Li, J. Li, and Z. Li. "Melt processing and structural manipulation of highly linear disentangled ultrahigh molecular weight polyethylene". *Chemical Engineering Journal*, Vol. 315, pp 132-141, 2017.
- [9] M. Yeager, T. Bogetti. "Single curvature preforming of ultra-high molecular weight polyethylene (UHMWPE) composites". CCDC Army Research Laboratory Aberdeen Proving Ground, United States, 2019.
- [10] D.L.P. Macuvele, J. Nones, J.V. Matsinhe, M.M. Lima, C. Soares, M.A. Fiori, and H.G. Riella. "Advances in ultra high molecular weight polyethylene/hydroxyapatite composites for biomedical applications: A brief review". *Materials Science and Engineering: C Materials for Biological Applications*, Vol. 76, pp 1248-1262, 2017.
- [11] J.A. Puértolas, S.M. Kurtz. "Evaluation of carbon nanotubes and graphene as reinforcements for UHMWPE-based composites in arthroplastic applications: A review". *Journal of the Mechanical Behavior of Biomedical Materials*, Vol. 39, pp 129-145, 2014.
- [12] G. Pal, S. Kumar. "Mechanical properties of isolated carbon nanotube". In: *Carbon Nanotube-Reinforced Polymers*, pp. 173-199, Elsevier, 2018.
- [13] S.K. Reddy, S. Kumar, K.M. Varadarajan, P.R. Marpu, T.K. Gupta, and M. Choosri. "Strain and damage-sensing performance of biocompatible smart CNT/UHMWPE nanocomposites". *Materials Science and Engineering: C Materials for Biological Applications*, Vol. 92, pp 957-968, 2018.
- [14] P.S. Rama Sreekanth, S. Kanagaraj. "Assessment of bulk and surface properties of medical grade UHMWPE based nanocomposites using nanoindentation and microtensile testing". *Journal of the Mechanical Behavior of Biomedical Materials*, Vol. 18, pp 140-151, 2013.
- [15] Y. Wang, R. Cheng, L. Liang, and Y. Wang. "Study on the preparation and characterization of ultra-high molecular weight polyethylene-carbon nanotubes composite fiber". *Composites Science and Technology*, Vol. 65, pp 793-797, 2005.
- [16] S. Park, I.S. Choi. "Production of ultrahigh-molecular-weight polyethylene/pristine MWCNT composites by half-titanocene catalysts". *Advanced Materials*, Vol. 21, pp 902-905, 2009.
- [17] https://www.tainstruments.com/wp-content/uploads/2020_DMA_Online_Training_Part_1.pdf (accessed on Feb. 28, 2022).