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Mechanical and Thermal Properties of Single-Walled Carbon Nanotube Filled Epoxidized Natural Rubber Nanocomposite

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Abstract: The use of Single-Walled Carbon Nanotube (SWCNT) as a reinforcement in rubber nano composite nowadays attracts a great deal of attention. Rubber used in this study was Epoxidized Natural Rubber (ENR) and was incorporated with SWCNT as nano filler. The influence of SWCNT nanofiller on mechanical and thermal properties of the produced nanocomposite was studied. The nanocomposite were prepared by using Haake internal mixer with 0, 5, 10 and 15 parts per hundred rubber of the SWCNT and the detailed preparation method is presented. Mechanical properties were evaluated by means of tensile and hardness tests under different SWCNT composition. As results, the strength and elongation at break of the nanocomposite decreased and simultaneously, the strength modulus and hardness increased. Moreover, from the differential scanning calorimetry analysis, the value of melting temperature (T_m), crystalline temperature (T_c) and heat transition (ΔH) were found increased with the increasing ratio of SWCNT.

Key words: Epoxidized natural rubber, Single-walled carbon nanotube, Nanocomposite, Mechanical properties, Thermal properties

INTRODUCTION

Nanocomposite can be defined as composites filled with nanofiller such as nanoparticles and recently are gaining significant attention from scientists and engineers. Comparing to the conventional fiber or particle reinforced composites, it is well-known that nanocomposite has superior physical properties, due to the high surface-to-volume ratio of nanoscale reinforcing fillers embedded in the matrix.

Single-Walled Carbon Nanotube (SWCNT) has been widely used with different kinds of polymers, yet, very little work involving one of the natural resource- rubbers. Owing to their unique structure, electrical and mechanical properties, one of the most important future opportunities is the emergence of new composite materials. Usually, elastomeric materials reinforced with carbon black or silica, although the full effect of these fillers is diminished due to their agglomeration (Kueseng and Jacob, 2006; Mohamad *et al*., 2008; Bhattacharyya *et al*., 2008). Further, one of the advantages of SWCNT as nanofiller is it has many remarkable properties such as electrical conductivity; six orders of magnitude higher than the copper, high current carrying capacity (Abdul-Lateef *et al*., 2010), excellent field emitter (Ye *et al*., 2007), high aspect ratio and small tip radius of curvature are ideal for field emission. Relatively low CNT loading (<10 wt.%) within polymeric matrices, are good for various applications (Ajayan *et al*., 2000).

In our previous works, the production and applications of CNTs have been extensively investigated (Azam *et al*., 2011, 2013a). For advanced applications, SWCNT have been used in many types of devices such as electrochemical capacitors (Azam *et al*., 2011, 2012a, b), batteries (Kawasaki *et al*., 2008; Lee *et al*., 2009) and field-effect transistors (Azam *et al*., 2010, 2013a). SWCNT is being considered excellent for energy production and storage because of their small dimensions, smooth surface topology and perfect surface character. Most of the applications were focusing on the large surface area of SWCNT to store electrical charge (Azam *et al*., 2013a, b; Manaf *et al*., 2013).

The concept of nano-sized filler filled material was recently demonstrated by the incorporation of nanoparticles in a rubber polymer matrix such as clay into natural rubber and SWCNT into silicone rubber (Mohamad *et al*., 2010). As known, rubber is a thermal and electrical insulator. Thus, incorporation of conductive fillers into this material may produce composite material with better mechanical and physical properties. Rubber nanocomposite may suit various industrial applications such as tire component, electrical sensors, vibration-proof, shock dampener and electrical shielding (Das *et al*., 2008; Ratnam *et al*., 2000).

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Epoxidized Natural Rubber (ENR) was produced by chemical modification of NR by using peroxy formic acid. Chemical modification of ENR caused the formation of high polarity, degree of crystallinity and branching and morphology. This modification can interchange a plastic to fiber to rubber and vice versa. Also, ENR was used as a matrix because it offering unique properties such as good oil resistance, low gas permeability, higher wet grip, rolling resistance and high strength.

The development of polymer nanocomposite has created a number of technologies and opportunities that can be applied to ENR. Although, rubbers are known to be a thermal and electrical insulator, incorporation of conductive fillers into them could produce composite material with some electrical conductivity. Also, differences in mechanical properties are also important to suit any application. It correlates to the aspects of toughness, hardness (Bokobza, 2007), elastic (Fakhru'l-Razi *et al.*, 2006) and thermal conductivity (Thostenson *et al.*, 2009; Motamedi and Mashhadi, 2010).

As one of the rarely-explored studies, ENR filled with SWCNT was prepared with a filler content of 5, 10 and 15 by phr. Present study focused on the preparation of four different samples; ENR unfilled and filled SWCNT with various weights. The results to be discussed are not only for characterizing the mechanical properties, but also analyzing the melting temperature and crystalline temperature of the as-prepared nanocomposite by using Differential Scanning Calorimetry (DSC).

MATERIALS AND METHODS

Materials: Two main materials were used in this work are as follows:

- **ENR:** Purchased from Mentari Equipment Sdn. Bhd. under the trade name ENR 50 with 50% epoxidization
- **SWCNT:** Commercial CNT purchased from Sigma-Aldrich, product of USA with >75% purity level and 0.7-1.3 nm of diameter

Table 1 tabulates the formulation used in this study. From this formulation recipe, the contents of SWCNT were varied as 5, 10 and 15 phr, whereas, rubber and other ingredients were kept constant.

Composite mixing formulation: According to ASTM D-3192, the compounding process was performed and carried out using a Haake internal mixer working at 150°C and a rotor speed at 60 rpm for 12 min. First, rotor will be started and ENR was blended for 1 min and mixed with all ingredients except sulphur for another 8 min. Finally, sulphur was added and blended for 1 min before the mixture was dumped onto two roll mill (procedure flow in Fig. 1). Next, the blended materials were crushed the last process was vulcanization.

Table 1: SWCNT/ENR compound formulation

Ingredients	Parts per hundred (phr)
ENR	100
Zinc oxide	3.75
Sulphur	1.50
Stearic acid	1.88
SWCNT	5/10/15

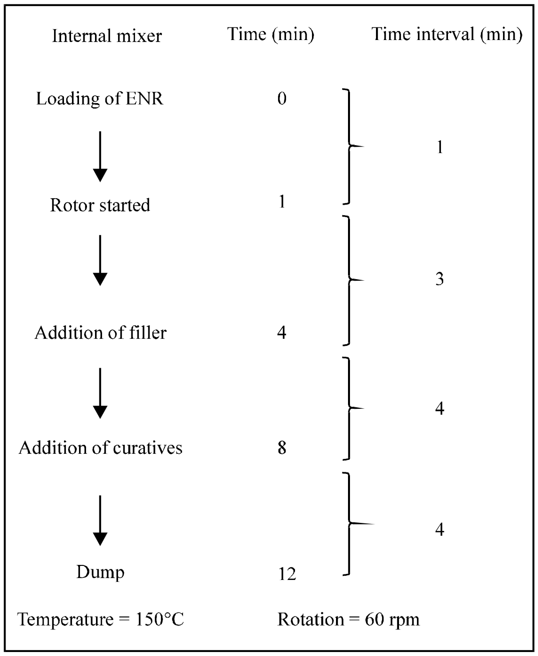

Fig. 1: Flow chart of blending process using internal mixer

The vulcanization was carried out at 150°C for 20 min by using a hot press machine. The pressure for the hot press was adjusted at 300 KPa to obtain the thickness (200~300 μm) of rubber composite sheet. Upon completion, all fabricated SWCNT/ENR nanocomposites were gray and black in color and the unmixed ENR was yellow (Fig. 2 and 3).

Mechanical testing: Tensile properties of vulcanized samples were carried out according to D-412 using an Instron 4301 Universal Testing Machine (UTM) at room temperature and the prepared samples are as shown in Fig. 3. The sample of gauge length 10 mm were stretched at 500 mm min^{-1} until failure. Three samples of each composition were tested for statistical accuracy. Additionally, hardness test for similar samples was carried out using the Shore type A Zwick/Roell Durometer according to ASTM D-2240 at room temperature.

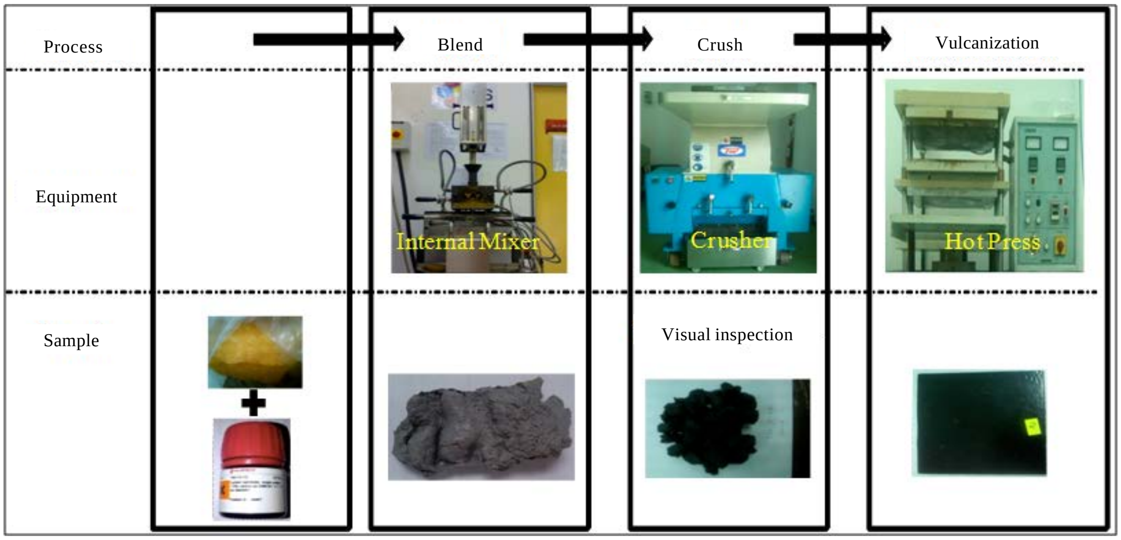

Fig. 2: Fabrication process of SWCNT/ENR nanocomposite

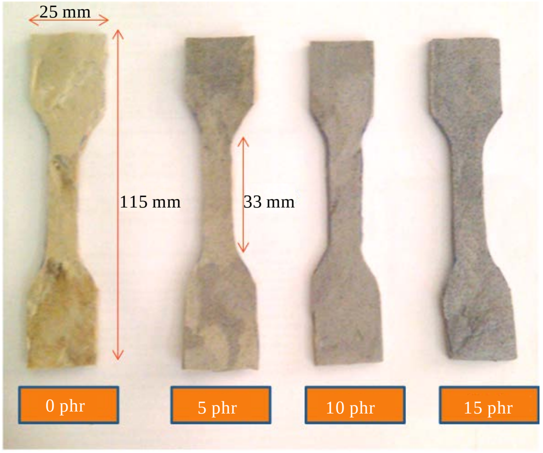

Fig. 3: Digital images of samples prepared for tensile test

Thermal testing: Thermal properties of the composites were tested using Differential Scanning Calorimeter (DSC2910; TA Com). The measurement was performed in temperatures varying from -100 to 250°C with a heating rate of 10°C min^{-1}. The specimen weight used was around 0.5-5.0 mg. This testing is to find the melting temperature (T_m), crystalline temperature (T_c) and heat transition (ΔH).

RESULTS AND DISCUSSION

Mechanical properties of SWCNT/ENR composite: First, the results of the tensile properties and hardness test of ENR unfilled and filled with SWCNT are tabulated in Table 2 and also depicted in Fig. 4. Tensile strength and Elongation at Break (EB) decreasing with the increasing SWCNT filler loading. The decreasing values ranging from 20.71-16.68 MPa in tensile strength and from 635-497% for EB, confirming that the decreasing percentages are around 19.46 and 21.73%, respectively.

Table 2: Summarized results of the tensile properties

	SWCNT (phr)			
Properties	0	5	10	15
Tensile strength (MPa)	20.71	17.53	17.15	16.68
Tensile modulus (MPa)				
100% elongation	0.66	0.71	0.93	1.13
300% elongation	2.49	2.75	3.40	4.02
Elongation at break, EB (%)	635	541	513	497

Generally, in the case of conventional composites, the tensile strength will increase with increasing filler loading until maximum point is reached. It is suggested that reduction in tensile strength as shown in Fig. 4a was occurred due to the agglomeration of filler particles (Yoksan, 2008) and/or as a result of physical contact between adjacent agglomerates. The agglomerate acted like a foreign body in the composites. Figure 4b also shows the EB decreased with increasing filler loading (similar trend with tensile strength). Since there was a high amount of agglomerates in the higher filler loading composites, these agglomerates acted as obstacles to chains movement and could initiate failure under stress. Agglomerates will become stress concentrator and building up stresses (Ciesielski, 1999) in composites quicker than usual and caused earlier rupture when compared to unfilled samples. Hence, the ability

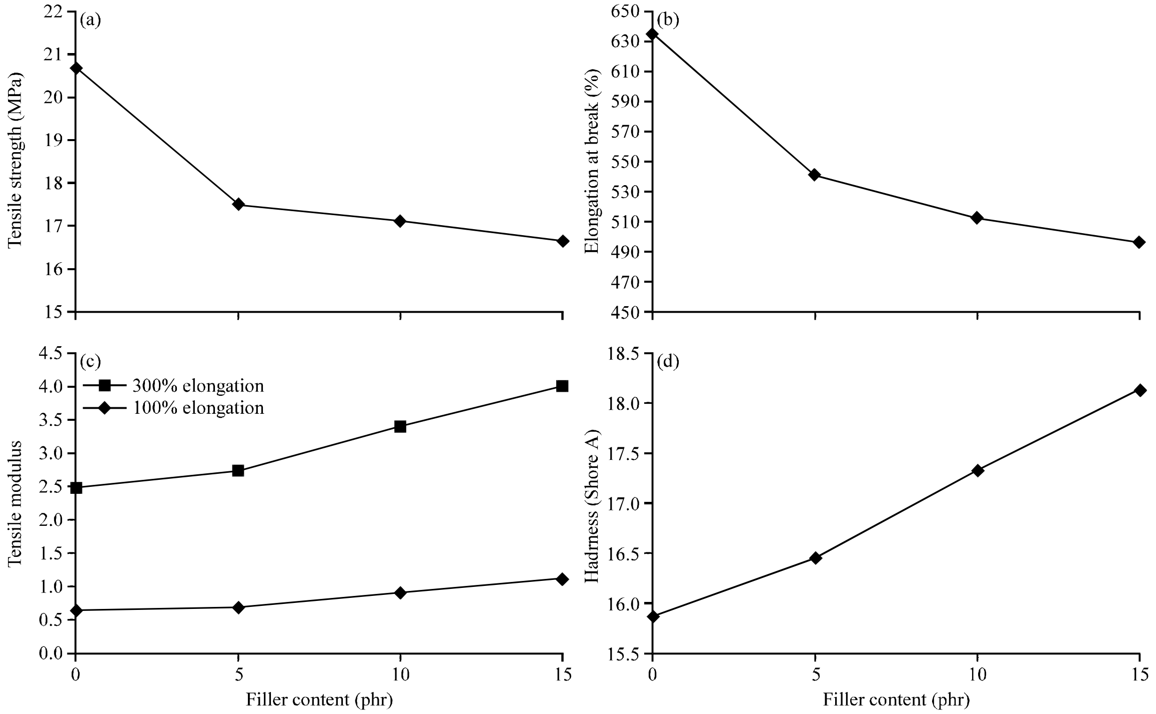

Fig. 4(a-d): Comparison of (a) Tensile strength, (b) Elongation at break, (c) Tensile modulus and (d) Hardness with various filler contents of SWCNT/ENR

of the composites to withstand the tensile stresses during deformation decreased with decreasing ratio of rubber matrix to alumina fillers.

Comparing to the tensile strength and EB, the modulus at 100 and 300% elongation as shown in Fig. 4c were increased with increasing filler loading. For 100% of elongation, the increasing of tensile modulus from 0.66-1.13 MPa, thus the calculated difference is 47% increase. Moreover, for 300% of elongation is increased from 2.49-4.02 MPa and the difference is 61.77% increase.

The increase of tensile modulus may be attributed to the higher cross-link density (Balakrishnan and Saha, 2011) and good distribution (Likozar and Major, 2010) of fillers in ENR matrices. Also, the contribution of electrostatic adsorption from polar group (Fu *et al*., 2009) in ENR (epoxide group) between matrix and filler. This phenomenon was driven by different charges acting on the matrix or filler surfaces which depends on the filler's type. This mechanism would strengthen the nano composite interface. It would hold them together and increased their resistance to deformation. This helped in improving the modulus of the nanocomposite. The uniformity of the filler distribution also efficiently hindered the chain movements during deformation. This would increase the stiffness of the nanocomposite as well as the tensile modulus.

The tensile modulus result is reliable with the result obtained from the analysis of the hardness test (refer to Fig. 4d). The ENR with various filler content was enhanced from 15.88-18.13; an increasing percentage of 12.41%. It can be suggested that the increase in hardness is due to the increase of tensile modulus and corresponding to the amount of SWCNT in the ENR matrices. Theoretically, the trend of hardness and tensile modulus of materials will be in the same direction. This is consistent with the previous work done by Zhou *et al.* (2006) which claimed that the increase gradually in hardness might be attributed to the reinforcement of the well-dispersed of CNT (Le *et al.,* 2012).

Thermal properties of SWCNT/ENR composite: The heating and cooling scan of DSC were used to determine the melting temperature (T_m), crystalline temperature (T_c) and crystalline level from the heat of crystallization of SWCNT/ENR nanocomposite. The plots of DSC analysis of varying SWCNT/ENR contents are shown in Fig. 5. The endothermic melting peak displayed the melting temperature, whereas, the exothermic curves of the samples displayed the crystallization temperature. The area under the curves indicates the heat of crystallization (ΔH_c) values which depend on the crystallinity of the

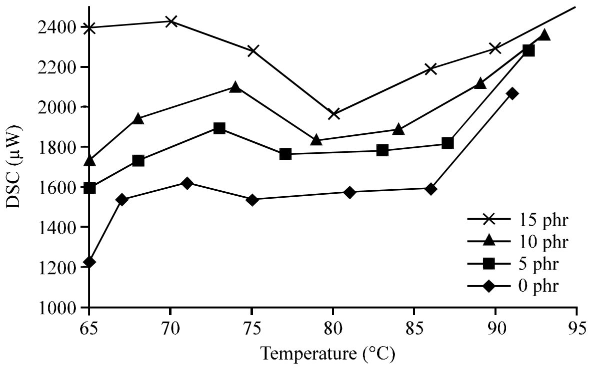

Fig. 5: Endothermic curves of SWCNT/ENR nanocomposite

material. The degree of the crystalline of these samples can be calculated as the ratio of ΔH_c of the samples with ΔH_c of the unmixed.

In the present study, DSC measurements were performed at a temperature range of -100-250°C. From the curves, it was confirmed that T_c, T_m and ΔH_c for SWCNT/ENR nanocomposite were increased with the addition of SWCNT. The T_m and T_c were observed to increase from 75.13-80.69°C and from 81.36-86.36°C, respectively. Moreover, ΔH_c of the sample also increased from 4.36 to 10.32 J g^{-1} with increasing filler content.

The increase of T_c, T_m and ΔH_c may be attributed to the physical adsorption and chemical interaction between SWCNT and rubber molecules. In the case of polymer nanocomposite, DSC measurement is useful for the identification of the extent of intercalation/exfoliation of the nanoparticles in the polymer matrix. The segmental mobility of the polymer matrix is greatly affected by the interactions of the intercalated/exfoliated polymer chains with the nanofiller (Spitalsky *et al.*, 2010), thereby enhance the T_c, T_m and ΔH_c for SWCNT/ENR nanocomposite.

CONCLUSIONS

SWCNT filled ENR nanocomposite were synthesized using Haake internal mixer with 0, 5, 10 and 15 phr. The vulcanization process was performed by using hot press to form physical cross-link between the polymer chains. It was found that tensile strength and EB were decreased about 19.46 and 21.73%, respectively with increasing SWCNT loading in the nanocomposite. However, in contra, increasing SWCNT increased the tensile modulus (100% and 300% elongation) and hardness by 71.21% and 14.17%, respectively.

Besides, DSC analysis confirmed the increase of T_c (from 81.36-86.36°C), T_m (from 75.13-80.69°C) and ΔH_c (from 4.36 to 10.32 J g^{-1}) with increasing filler contents. The results may be attributed to the cross-link and distribution of SWCNT in ENR matrices. One possible suggestion is that, it could be caused by physical contact between adjacent agglomerates.

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REFERENCES

Abdul-Lateef, A.A., M. Al-Harthi and M.A. Atieh, 2010. Effect of multi-walled carbon nanotubes on the mechanical and thermal properties of natural rubber. Arab J. Sci. Eng., 35: 49-56.

Ajayan, P.M., L.S. Schadler, C. Giannaris and A. Rubio, 2000. Single-walled carbon nanotube-polymer composites: Strength and weakness. Adv. Mat., 12: 750-753.

Azam, M.A., M.A. Mohamed, E. Shikoh and A. Fujiwara, 2010. Thermal degradation of single-walled carbon nanotubes during alcohol catalytic chemical vapor deposition process. Jpn. J. Appl. Phys., Vol. 49. 10.1143/JJAP.49.02BA04

Azam, M.A., A. Fujiwara and T. Shimoda, 2011. Direct growth of vertically-aligned single-walled carbon nanotubes on conducting substrates using ethanol for electrochemical capacitor. J. New. Mat. Elect. Syst., 14: 173-178.

Azam, M.A., A.R.M. Warikh, K. Isomura, A. Fujiwara and T. Shimoda, 2012a. X-ray and morphological characterization of Al-O thin films used for vertically aligned single-walled carbon nanotube growth. Adv. Mater. Res., 620: 213-218.

Azam, M.A., K. Isomura, A. Fujiwara and T. Shimoda, 2012b. Direct growth of vertically aligned single-walled carbon nanotubes on conducting substrate and its electrochemical performance in ionic liquids. Phys. Status Solidi A, 209: 2260-2266.

Azam, M.A., A. Fujiwara and T. Shimoda, 2013a. Significant capacitance performance of vertically aligned single-walled carbon nanotube supercapacitor by varying potassium hydroxide electrolyte concentration. Int. J. Electrochem. Sci., 8: 3902-3911.

Azam, M.A., N.S.A. Manaf, E. Talib and M.S.A. Bistamam, 2013b. Aligned carbon nanotube from catalytic chemical vapor deposition technique for energy storage device: A review. Ionics, 19: 1455-1476.

Balakrishnan, A. and M.C. Saha, 2011. Tensile fracture and thermal conductivity characterization of toughened epoxy/CNT nanocomposites. Mater. Sci. Eng.: A, 528: 906-913.

Bhattacharyya, S., C. Sinturel, O. Bahloul, M.L. Saboungi, S. Thomas and J.P. Salvetat, 2008. Improving reinforcement of natural rubber by networking of activated carbon nanotubes. Carbon, 46: 1037-1045.

Bokobza, L., 2007. Multiwall carbon nanotube elastomeric composites: A review. Polymer, 48: 4907-4920.

Ciesielski, A., 1999. An Introduction to Rubber Technology. Rapra Technology Limited, New York.

Das, A., K.W. Stockelhuber, R. Jurk, M. Saphiannikova and J. Fritzsche *et al*., 2008. Modified and unmodified multiwalled carbon nanotubes in high performance solution-styrene-butadiene and butadiene rubber blends. Polymer, 49: 5276-5283.

Fakhru'l-Razi, A., M.A. Atieh, N. Girun, T.G. Chuah, M. El-Sadig and D.R.A. Biak, 2006. Effect of multi-wall carbon nanotubes on the mechanical properties of natural rubber. Compos. Struct., 75: 496-500.

Fu, S.Y., Z.K. Chen, S. Hong and C.C. Han, 2009. The reduction of carbon nanotube (CNT) length during the manufacture of CNT/polymer composites and a method to simultaneously determine the resulting CNT and interfacial strengths. Carbon, 47: 3192-3200.

Kawasaki, S., T. Hara, Y. Iwai and Y. Suzuki, 2008. Metallic and semiconducting single-walled carbon nanotubes as the anode material of Li ion secondary battery. Mater. Lett., 62: 2917-2920.

Kueseng, K. and K.I. Jacob, 2006. Natural rubber nanocomposites with SiC nanoparticles and carbon nanotubes. Eur. Polym. J., 42: 220-227.

Le, H.H., X.T. Hoang, A. Das, U. Gohs and K.W. Stoeckelhuber *et al*., 2012. Kinetics of filler wetting and dispersion in carbon nanotube/rubber composites. Carbon, 50: 4543-4556.

Lee, J.H., B.S. Kong, S.B. Yang and H.T. Jung, 2009. Fabrication of single-walled carbon nanotube/tin nanoparticle composites by electrochemical reduction combined with vacuum filtration and hybrid co-filtration for high-performance lithium battery electrodes. J. Power Sources, 194: 520-525.

Likozar, B. and Z. Major, 2010. Morphology, mechanical, cross-linking, thermal and tribological properties of nitrile and hydrogenated nitrile rubber/multi-walled carbon nanotubes composites prepared by melt compounding: The effect of acrylonitrile content and hydrogenation. Applied Surf. Sci., 257: 565-573.

Manaf, N.S.A., M.S.A. Bistamam and M.A. Azam, 2013. Development of high performance electrochemical capacitor: A systematic review of electrode fabrication technique based on different carbon materials. ECS J. Solid State Sci. Technol., 2: M3101-M3119.

Mohamad, Z., H. Ismail and R.C. Thevy, 2008. Tensile properties and morphology of dynamic vulcanized ENR-5/EVA blends: Different vulcanization system. J. Chem. Nat. Res. Eng., 2: 91-98.

Mohamad, N., A. Muchtar, M.J. Ghazali, D.H. Mohd and C.H. Azhari, 2010. Epoxidized natural rubber-alumina nanoparticle composites: Optimization of mixer parameters via response surface methodology. J. Applied Polymer Sci., 115: 183-189.

Motamedi, M. and M.M. Mashhadi, 2010. Rubber/carbon nanotube nanocomposite with hyperelastic matrix. J. Solid Mech., 2: 43-49.

Ratnam, C.T., M. Nasir, A. Baharin and K. Zaman, 2000. Electron beam irradiation of epoxidized natural rubber. Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. Atoms, 171: 455-464.

Spitalsky, Z., D. Tasis, K. Papagelis and C. Galiotis, 2010. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. Prog. Polymer Sci., 35: 357-401.

Thostenson, E.T. S. Ziaee and T.W. Chou, 2009. Processing and electrical properties of carbon nanotube/vinyl ester nanocomposites. Compos. Sci. Technol., 69: 801-804.

Ye, Y., H. Chen, J. Wu and L. Ye, 2007. High impact strength epoxy nanocomposites with natural nanotubes. Polymer, 48: 6426-6433.

Yoksan, R., 2008. Epoxidized natural rubber for adhesive applications. Kasetsart J. Nat. Sci., 42: 325-332.

Zhou, X., Y. Zhu, Q. Gong and J. Liang, 2006. Preparation and properties of the powder SBR composites filled with CNTs by spray drying process. Mater. Lett., 60: 3769-3775.