Fabrication and Characterization 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 nanocomposite nowadays attracts a great deal of attention. The rubber used in this study was Epoxidized Natural Rubber (ENR) with SWCNT as nanofiller. The influence of nanofiller on the mechanical and thermal properties of the produced nanocomposite was studied. In this study, 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 methodology is presented. The mechanical properties were evaluated by tensile and hardness tests and presented with the addition of SWCNT, the strength and elongation at break of the ENR decreased and simultaneously, the strength modulus and hardness increased. The surfaces of the fractured specimens were examined in order to assess the fracture mechanisms. The nanocomposite was evaluated by scanning electron microscopy and thermal analysis. Moreover, from the differential scanning calorimetry analysis, the increase of melting temperature (T_m), crystalline temperature (T_c) and heat transition (ΔH) with the increasing ratio of CNT.

Key words: Epoxidized natural rubber, single-walled carbon nanotubes, nanocomposites, 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. It is well-known that nanocomposite has superior physical properties because of the high surface to volume ratio of nanometer scale reinforcing fillers embedded in the matrix, compared to the conventional fiber or particle reinforced composites. Despite SWCNT has been widely used with different kinds of polymers yet very little work involving one of the natural resource-rubbers. 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; Bhattacharyya et al., 2008). It elaborates a key to incorporate well-blended nanofiller into rubber to obtain beneficial mechanical and physical properties.

Further, the advantages of SWCNT as nanofiller is because 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. For advanced applications, SWCNT have been used in many types of devices such as electrochemical capacitors (Azam et al., 2011; 2013a, b), batteries (Kawasaki et al., 2008; Lee et al., 2009) and field-effect transistors (Azam et al., 2012a).

Owing to their structural characteristics and their electrical and mechanical properties, one of the most important opportunities in the future is the emergence of a new generation of composite materials since, relatively low carbon nanotube loading (<10 wt.%) within polymeric matrices are required for various applications (Ajayan et al., 2000).

The production and applications of CNTs have been extensively investigated during the last 15 years (Azam et al., 2011, 2013a). The most popular applications are super capacitors, gas storage, drug delivery and battery electrodes. All the applications were focused on the surface area of SWCNT which known that SWCNT has large surface area to store energy (Azam et al., 2012b). SWCNT is being considered for energy production and storage because of their small dimensions, smooth surface topology and perfect surface character since only the basal graphite planes are exposed in their structure. The rate of electron transfer at carbon electrodes ultimately

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determines the efficiency of fuel cells and this depends on various factors such as the structure and morphology of the carbon material used in the electrodes.

The concept of nano-sized filler filled material was recently demonstrated by the incorporation of nanoparticles in a rubbery 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 could 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).

Epoxidized Natural Rubber (ENR) was produced by chemical modification of NR by using peroxy formic acid. The chemical modification of ENR caused the formation of high polarity, degree of cristallinity, degree of branching and morphology. This modification can interchange a plastic to fibre to rubber and vice versa. Since, the study of ENR was used as a matrix because 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. Its potential as a substitute to many synthetic elastomers is a subject of investigation. Although, rubbers are known to be a thermal and electrical insulator, incorporation of conductive fillers into these materials could produce composite material with some electrical conductivity. The properties of these composites vary as a function of volume fraction of the conductive fillers. Also, differences in mechanical properties and applications can be considered to ensure that the objectives of learning are successful. 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 a pilot study of rarely-explored studies, ENR filled with SWCNT was prepared with a filler content of 5, 10 and 15 by phr. The present study focused on the preparation of four samples; ENR unfilled and filled SWCNT with various weights. The results to be discussed are not only for characterizing the mechanical properties (Universal Testing Machine (UTM); Instron) but also analyzing the melting temperature and crystalline temperature of the as-prepared nanocomposite by using Differential Scanning Calorimetry (DSC).

MATERIALS AND METHODS

The two main materials were used in this research are as follows:

- ENR was purchased from Mentari Equipment Sdn. Bhd. under the trade name ENR 50 with 50% epoxidization
- The SWCNT used is commercialized 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 recipe, the contents of SWCNT were varied as 5, 10 and 15 phr whereas rubber and other ingredients were kept constant.

Composite 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.

Firstly, rotor will be started and ENR was blended for 1 min and followed by all ingredients were added except sulphur and mixed for another 8 min. Finally, sulphur was added and blended for 1 min before the mixture was dumped onto two roll mill. The flow chart of blend processing was shown in Fig. 1.

Table 1: SWCNT/ENR compound formulation

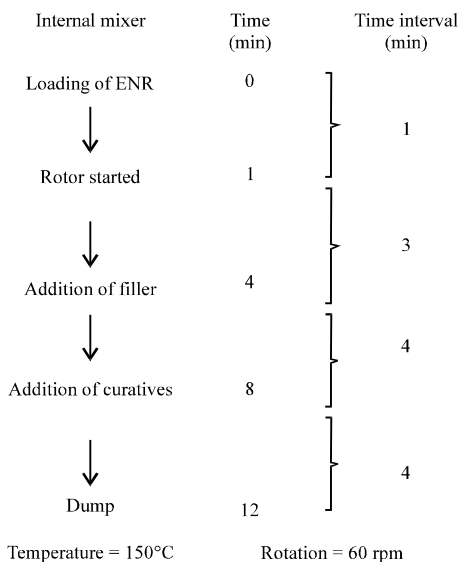| Ingredients	Parts per hundred (phr)
ENR	100
Zinc oxide	3.75
Sulphur	1.50
Stearic acid	1.88
SWCNT	5/10/15

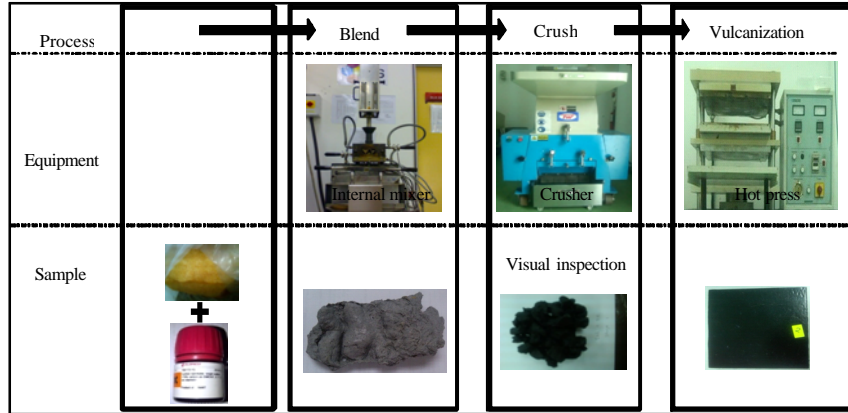Fig. 1: Flow chart of the blend process using internal mixer

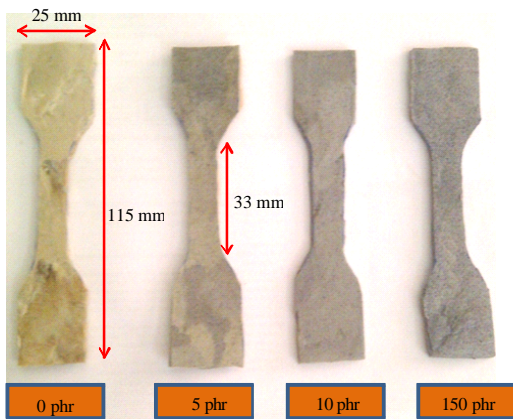Fig. 2: Fabrication process of SWCNT/ENR nanocomposite

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

Next, the blended material will go for the crusher machine and the last process is vulcanization. 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. The SWCNT nanocomposite were black and unmixed was yellow. Figure 2 shows the fabrication process of SWCNT/ENR nanocomposite.

Mechanical testing: Tensile properties of vulcanized samples were carried out according to D-412 using an Instron 4301 UTM at room temperature 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.

For the hardness test was carried out using the Shore type A Zwick/Roell Durometer according to ASTM D-2240 at room temperature. Also, three samples of each composition were tested.

Thermal testing: The thermophysical properties of the composites were tested on DSC 2910 Differential Scanning Calorimeter produced by TA Com. USA. The measure was performed in temperatures varying from 100-250°C with a heating rate of 10°C min^{-1}. The compounds were vulcanized at 150°C with a proper pressure. The specimen size was used 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: The summarized results of the tensile properties and hardness test of ENR unfilled and filled with SWCNT were shown in Table 2. Tensile strength and Elongation at Break (EB) decreases, respectively with the SWCNT filler loading increases. The decreasing from 20.71-16.68 MPa in tensile strength and for EB is from 635-497%, these mean the decreasing are around 19.46 and 21.73%, respectively.

Generally, in the case of conventional composites, the tensile strength will increase with increasing filler loading until maximum point is reached. Reduction in tensile strength as shown in Fig. 4a occurred due to the agglomeration of filler particles (Yoksan, 2008) and/or it can be suggested simply the result of physical contact between adjacent agglomerates. The agglomerate acted like a foreign body in the composites. Figure 4b also shows the EB decrease with increasing amounts of filler loading (same 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

Table 2: Results of the tensile properties

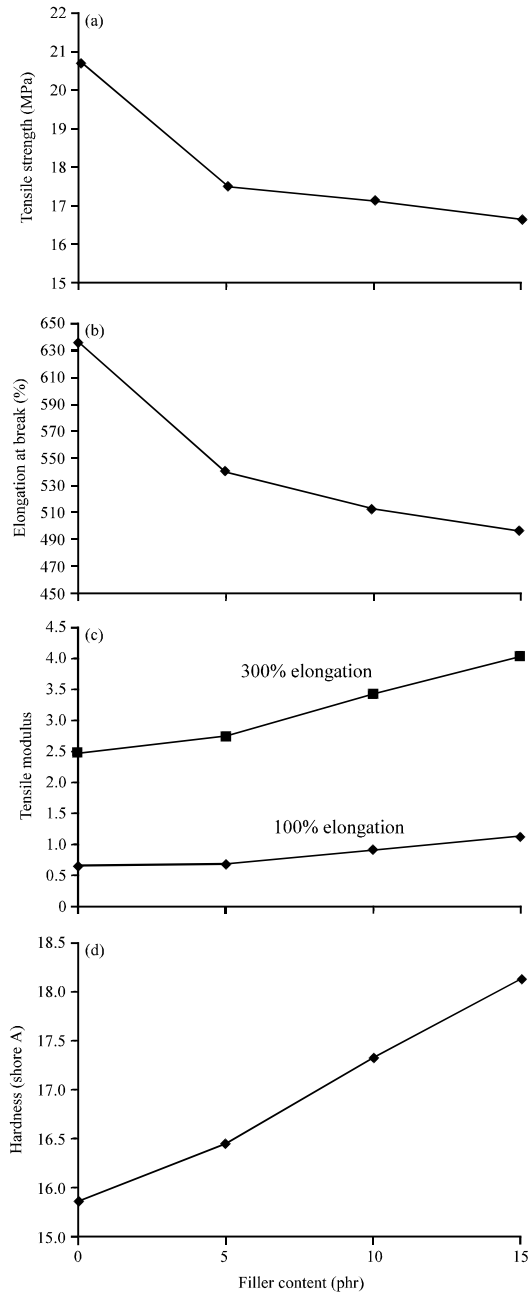| Properties	SWCNT (phr)			
	0	5	10	15
Tensile strength (MPa)	20.71	17.53	17.15	16.68
Tensile Modulus (MPa)				
100% elongation	0.66	0.71	0.93	1.13
300% elongation	2.49	2.75	3.40	4.02
Elongation at Break (EB) (%)	635.00	541.00	513.00	497.00

Fig. 4: Comparison of a) tensile strength; b) elongation at break; c) tensile modulus and d) hardness with various filler contents of SWCNT/ENR

composites quicker than usual and caused earlier rupture when compared to unfilled samples. Hence, the ability 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 nanocomposite 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 (Fig. 4d). The ENR with various filler content was enhanced from 15.88-18.13 which 12.41% increased. It can be suggested 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 earlier research 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: The heating and cooling scan of Differential Scanning Calorimetry (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
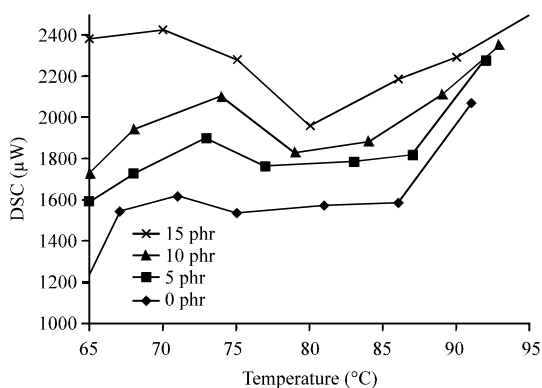
Fig. 5: The endothermic curves of SWCNT/ENR nanocomposite

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° to 250°C. From the table, 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 4.36-10.32 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, the 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 nanofillers (Spitalsky *et al.*, 2010) thereby enhance the T_c, T_m and ΔH_c for SWCNT/ENR nanocomposite.

CONCLUSION

SWCNT filled ENR nanocomposite were synthesized and blend processed using Haake internal mixer with 0, 5, 10 and 15 phr. The vulcanization process is by using hot press machine to form cross-link between the polymer chain. Increasing amount of SWCNT as filler did not cause an obvious effect to the tensile properties. It was found that the tensile strength and EB were decreased about 19.46 and 21.73%, respectively with increasing SWCNT content in the nanocomposite but increased the tensile modulus (100% elongation and 300% elongation)

and hardness around 71.21 and 14.17%, respectively. According to the DSC also showed the increase of T_c (from 81.36-86.36°C), T_m (from 75.13-80.69°C) and ΔH_c (from 4.36-10.32 J g⁻¹) with increasing filler content. The results show the attribute of cross-link and distribution of SWCNT in ENR matrices. Also, it can be suggested that it caused by physical contact between adjacent agglomerates. Regarding to the properties of the SWCNT/ENR nanocomposite, the recommended application for the nanocomposite is one of polymer component part in a battery or capacitor. Further, studies are required for better understanding of structural properties and morphology of the nanocomposite.

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

Azam, M.A., A. Fujiwara and T. Shimoda, 2013b. Significant capacitance performance of vertically aligned single-walled carbon nanotube supercapacitor by varying potassium hydroxide electrolyte concentration. Int. J. Electrochem. Sci., 80: 3902-3911.

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.

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.

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.