

PREPARATION AND CHARACTERIZATION OF AN EPOXY NANO-COMPOSITE TOUGHENED BY A COMBINATION OF LIQUID EPOXIDIZED NATURAL RUBBER, CARBON NANO-TUBE AND NANO-CLAY USING TAGUCHI ANALYSIS METHOD

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ABSTRACT

This paper addressed the effects of operating variables on mechanical properties of epoxy/liquid epoxidized natural rubber (LENR)/ carbon nano-tube/nano-clay nano-composite including tensile strength, impact strength and fracture toughness. The variables were pre-cure temperature, cure temperature, nano-clay content and carbon nanotube content. The experiments were executed based on the design of experiments using Taguchi methods. It is observed that the tensile strength, impact strength and fracture toughness can be optimized with 1.0% of nano-clay loading, 0.6% nano-tube loading, pre-cure at 50°C and cure at 130°C. Confirmation experiments were performed with the optimum parameter settings for each mechanical property. The mechanicals and morphology of the optimum sample were examined by dynamic mechanical analyzer, field emission scanning electron microscopy and transmission electron microscopy. Morphologically, it was observed that fillers of different shapes provide different features on the fracture surface due to different mechanisms in their toughening action. The state of dispersion from morphology and chemical structure results show that the optimum nano-composite obtained in different conditions have an intercalated structure.

Epoxy resins are considered as one of the most important types of thermosetting polymers. They are widely used in coating and structural applications such as electrical laminates, castings, encapsulations, fibre reinforced composites, as tooling components and as adhesives. This is due to its excellent mechanical, thermal and electrical properties [1]. Even so, the usability of epoxy resins are limited because it is brittle and rigid in nature, have poor resistance to crack propagation and low impact strength. Hence, many applications have been performed with the aim of toughening of epoxy polymers. The addition of nano-materials results in an impressively efficient reinforcement without sacrificing the ductility, impact strength, heat stability or other important characteristics. Most structural applications require a balance between stiffness and impact, which has been achieved by using nano-clays or nano-silicates at loadings of less than 10%. This inclusion improves the mechanical, thermal, dimensional and barrier properties. In most of the epoxy/clay nano-composites research, clay minerals have been fully used because of the low cost and availability compared to other layered materials [2-4]. The optimization of epoxy/LENR/nano-clay/carbon nano-tube has been studied in our previous work [5]. Addition of the combination of LENR, nano-clay and carbon nano-tube to epoxy has improved the impact strength, fracture toughness and tensile strength considerably. In the current work, the morphology of the optimized specimens were investigated using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

Materials The epoxy used in this study was Morcote BJC 39, which contains epoxy resin and hardener amines supplied by Vistec Technology Sdn. Bhd. MMT Na⁺ is an untreated montmorillonite which is a natural montmorillonite from Southern Clay Products. The MWNTs manufactured by Arkema (GraphistrengthTM C100) with the following specifications: purity > 90%, length 0.1-10 nm, diameter 10-15 nm.

Experiment design using the Taguchi method. In this design, four factors have been chosen which are composition of clay and MWNT, pre-cure temperature and cure temperature. All independent factors were considered at three predetermined levels (Table 1). The practical aspects and some screening experimental work have been considered.

Table 1. Parameter and their variation levels

Parameter and level	Level		
	1	2	3
Pre-cure temperature (°C)	Room temperature	50	70
Cure temperature (°C)	120	130	140
Nanoclay content (wt %)	0.5	1.0	1.5
Carbon nanotube content (wt%)	0.2	0.6	1.0

Sample preparation and characterization. First, nano-clays and carbon nano-tubes were ground appropriately in an agate mortar and pestle. The clay-MWNT hybrids were prepared according to an L9 array. After mixing, clay-MWNT was dispersed in the mixture of methanol and LENR and sonicated using an ultrasonic bath. The solution was then introduced into the epoxy resin and sonicated for 3 hours. Later, the hardener with ratio 1:3 were added with gentle mixing and degassed again. The mixture was then poured into a steel mold for the pre curing and curing process. The tensile test was performed at room temperature according to ASTM D638-91. A gauge length of 100 mm was employed with a cross-head speed of 5 mm/min using Testometric 350 model M350-10CT. The Izod impact strength was determined using the Ray Ran Pendulum Impact System according to ASTM D256-88. The fracture toughness test was executed at room temperature according to ASTM D5045 using Testometric 350 model M350-10CT.

Determination of optimum conditions. The effects of each parameter on the tensile strength, impact strength and fracture toughness are shown in Figure 1 and 2. The optimum parameter to attain an epoxy/clay/MWCNT hybrid nano-composite with maximum properties can be determined by maximum points in the main effects plots in Figure 1 and 2. The optimum sample for verification was prepared and exposed to tensile, impact and fracture toughness test. The verification study results showed that the proposed optimum parameter corresponds well with results obtained by the Taguchi approach.

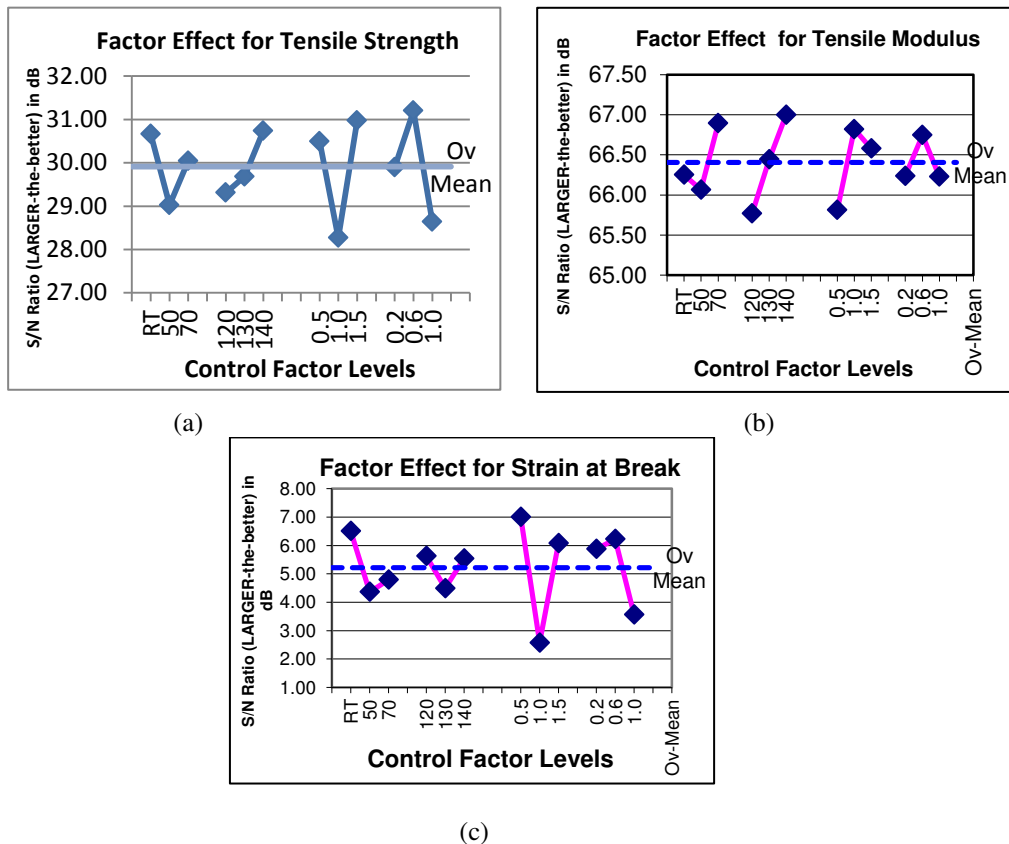


Figure 1. Main effect for (a) tensile strength (b) tensile modulus (c) strain at break

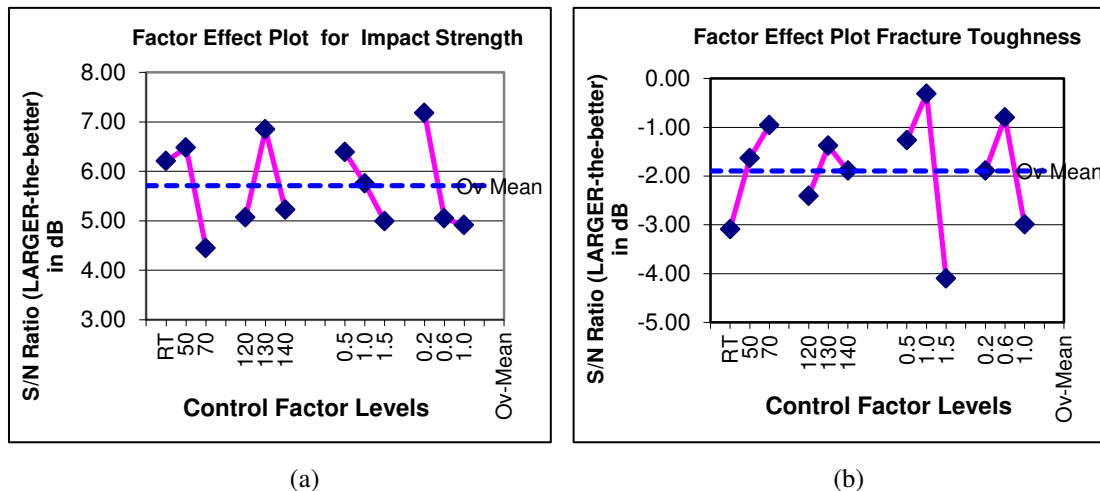


Figure 2. Main effect for (a) impact strength and (b) fracture toughness

Mechanical properties. To compare the effects of nano-clay, nano-tube and LENR in optimum setting parameter, other samples were fabricated. Figure 3 shows the comparison of tensile strength, failure strain and tensile strain of the optimum sample obtained from the Taguchi method compared to the neat epoxy (NE), epoxy/LENR (EL), epoxy/LENR/nano-clay (ELNC), epoxy/LENR/nano-tube (ELNT), epoxy/nano-clay/nano-tube (ENCNT), epoxy/LENR/nano-clay/nano-tube (optimum). Referring to Figure 3, the addition of nano-clay and nano-tube has increased the tensile strength of nano-composite system compared to neat epoxy. The same trend was observed for the tensile modulus of the modified specimens except for EL. Strain at break was tremendously enhanced with the addition of LENR due to the modification of the ductility in the matrix but it decreased the tensile modulus of the system. The epoxy composites embedded with nano-clay, nano-tube and LENR has shown the best combination of the tensile strength, tensile modulus and strain at break. The positive properties of this specimen are the result of better dispersion of LENR and filler in the matrix [6, 7].

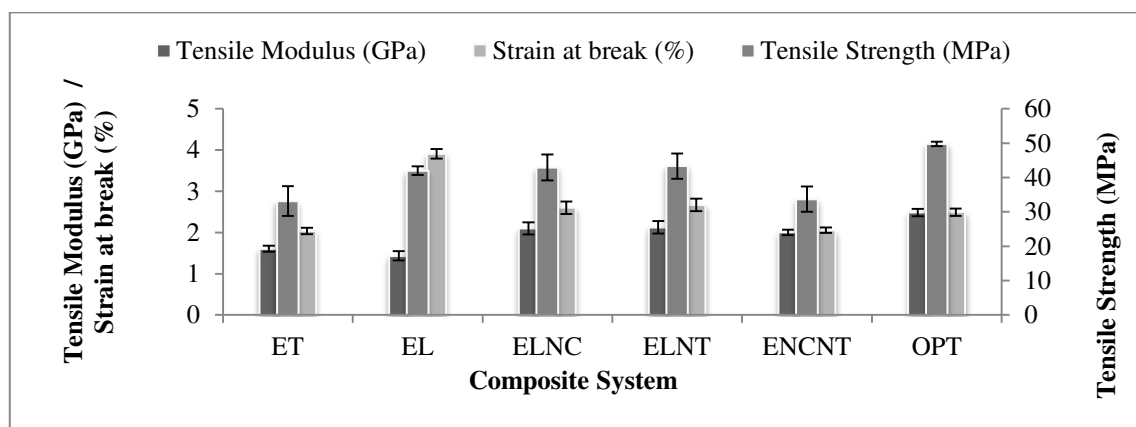


Figure 3. Comparison of tensile modulus, strain at break and tensile strength among nanocomposites system

The addition of LENR has shown a dramatic increase nearly 27% in impact strength compared to neat epoxy (Figure 4a). However, dual addition of nano-clay and nano-tube has a drawback on the impact strength. The enhancement of impact strength in EL specimens is the effect of LENR acting as a component that absorbs shock when loads are applied to the specimen during testing. The same observation was also reported by many other researchers [8-10]. There are a variety of proposed mechanisms exist that cause the occurrence of increased impact strength in nano-composites. However, the validity of the existence of this mechanism is still discussed in the field

of research to date. There is a similarity in all the mechanisms which is the existence of a rubber phase in the epoxy matrix. In addition, Ratna & Banthia [11] also stated that the presence of the rubber phase in the epoxy matrix have increased impact strength.

The presence of the fillers, either nano-clay or nano-tube, has affected the impact strength of the nano-composite system. ELNC specimens showed a reduction of 17% while ELNT specimens indicated a reduction of 30% compared to neat epoxy specimens. The presence of rigid fillers increases the brittleness of epoxy matrix. Therefore, the addition of nano-tubes plays a more significant role on impact strength compared to nano-clays. Despite the presence of the LENR, the effects of fillers in epoxy matrices were not encountered. The strength of impact specimens is reduced as a result. Dispersion of non-uniform fillers affects the interaction of filler and matrix interface causing an imperfection in morphology between the two phases present.

Based on Figure 4(b), fracture toughness properties show the same trend of impact strength in Figure 4 when reinforced with LENR. The addition of LENR increased the fracture toughness by 67%. In reinforced LENR epoxy, the addition of the filler increases the fracture toughness of specimens. ELNC specimens obtained an increment of 95% whilst the ELNT specimens showed a smaller increase of 44%. Specimens with nano-clay (ELNC) and nano-tube (ENCNT) recorded a decline percentage compared to epoxy specimens reinforced with LENR (EL). OPT specimens has shown a remarkable increase of fracture toughness by 146%. Specimens without LENR have shown poor interface interaction between matrix and fillers. This morphology can be proved by the FESEM micrograph indicated the presence of nano-tube pull-out mechanism. When the load is applied, the stress is not transferred on the matrix; instead it is transferred to the nano-tubes resulting in catastrophic failure of the specimens.

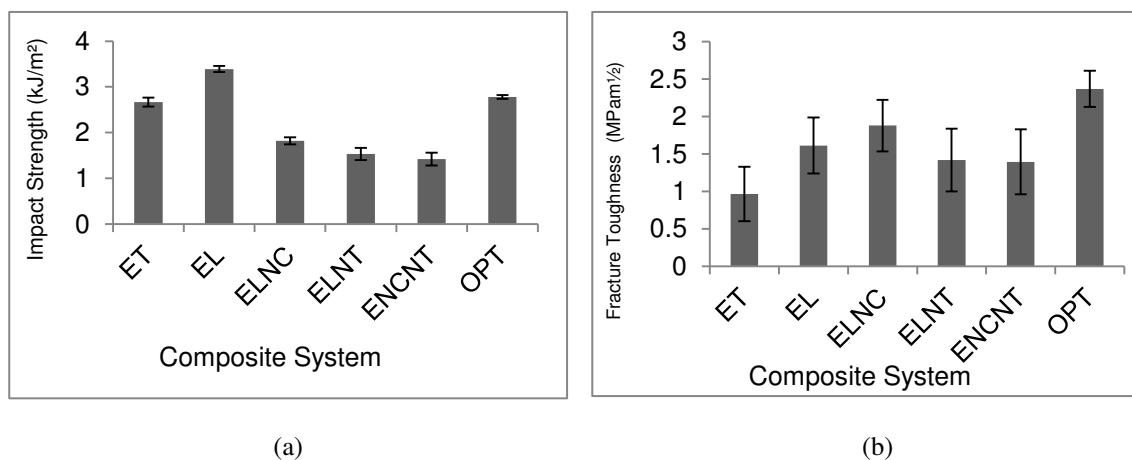


Figure 4. (a) Impact strength of neat epoxy and epoxy nanocomposite system (b) Fracture toughness of neat epoxy and epoxy nanocomposite system

The DMA analysis for storage modulus and $\tan \delta$ are shown in Figures 5 and 6. Figure 5 shows all specimens display the existence of significant cross linking of epoxy network as indicated by the horizontal curve. After glass transition temperature, the sudden fall of storage modulus is observed with the increment of temperature. Sudden drop of storage modulus is related to the emission phenomenon due to the movement energy of polymer network when the temperature is increased [12]. Specimens display a rigid behaviour before glass transition temperature whereas, above that temperature specimens are flexible. Based on the storage modulus plot, all specimens, except for EL specimens showed an increase in value compared to neat epoxy.

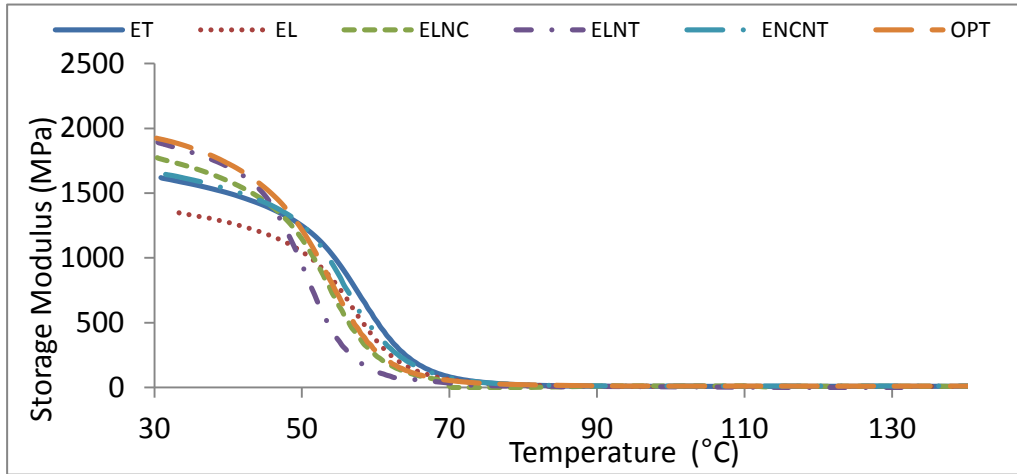


Figure 5. Storage modulus for neat epoxy and epoxy nanocomposite system

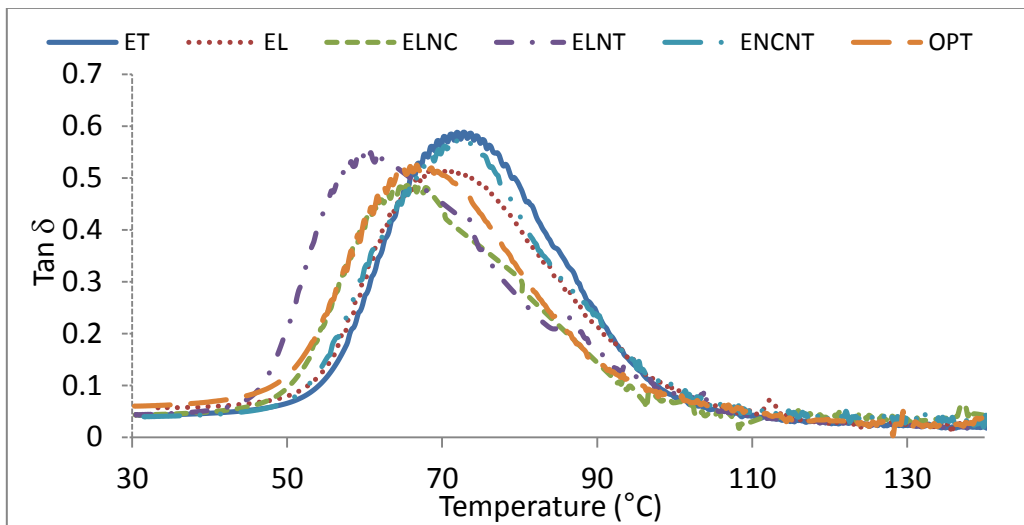


Figure 6. Tan δ for neat epoxy and epoxy nanocomposite system

The peak factor is defined as the full width at half maximum of the tan δ peak divided by its height, and it can be qualitatively used to access the homogeneity of the epoxy network [12 - 15]. Based on Figure 7, neat epoxy had a low peak factor which indicated a high homogeneity in the epoxy network while other specimens showed an increase in peak factor resulting from greater heterogeneity due to the addition of filler. In addition, increased of peak factor are also contributed by the inclusion of liquid epoxidized natural rubber into the epoxy matrix network.

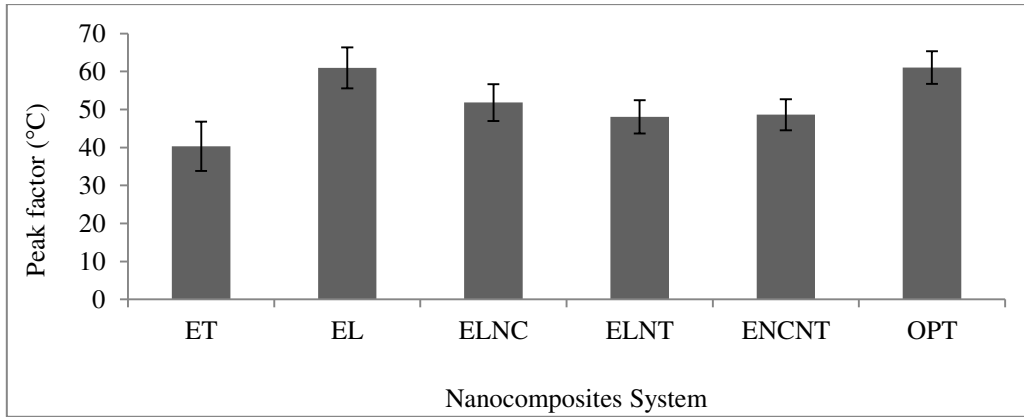


Figure 7. Peak factor for neat epoxy and epoxy nanocomposite system

As shown in Fig 8(a), neat epoxy shows smooth and some voids' existence due to its brittle nature. On the contrary, Fig 8(b) shows rougher surface suggesting the improvement on the fracture toughness. Based on that figure, this morphology suggests an excellent bonding between nano-tube, nano-clay and epoxy matrix. Different microstructures are observed on the fracture surfaces of different nano-composites (Figure 9). The observed difference can be due to the presence of fillers having different shapes. In ELNT specimens, the main energy dissipating mechanism is crack bridging. Hence crack deviation might be the second mechanism due to high aspect ratio of nano-tubes [16]. However, in ELNC specimens, when a crack reaches nano-clay particles, it has to travel a longer path along the surface area of nano-clay layers before it starts to propagate. Therefore, crack deviation is the main energy dissipation in nano-clay nano-composites.

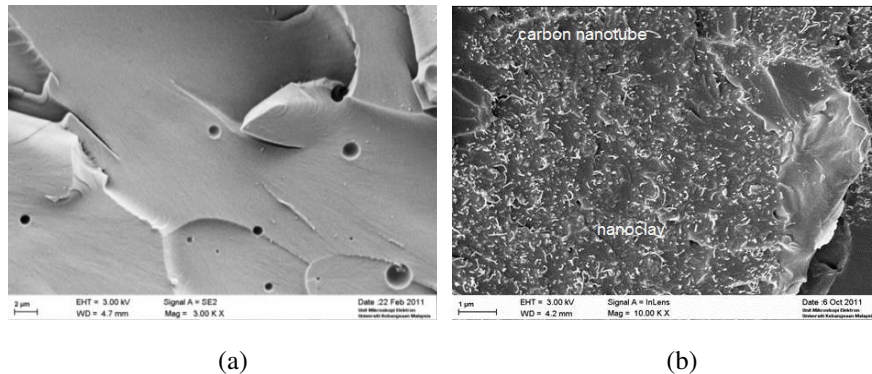


Figure 8. The FESEM micrographs taken from fracture surface of: (a) neat epoxy (NE), (b) epoxy/LENR/nanoclay/nanotube (OPT)

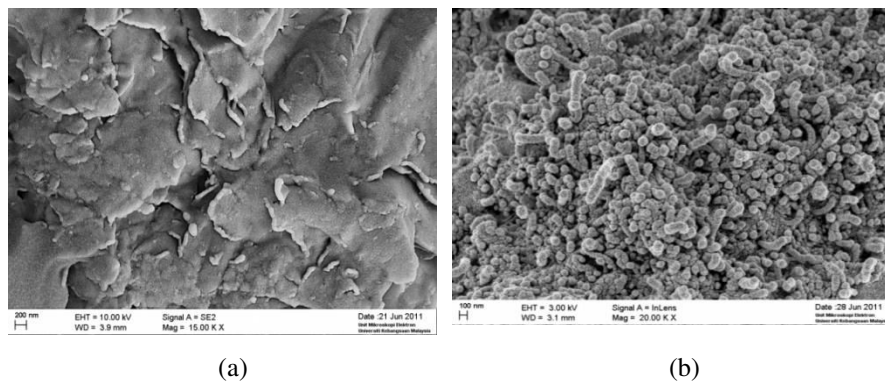


Figure 9. The FESEM micrographs taken from fracture surface of: (a) ELNC; (b) ELNT

A TEM micrograph for ELNT (Figure 10 (a)) shows the poor dispersion of nano-tubes in the epoxy matrix. Aggregation and tubes with a curled, entangled structure were clearly observed. Figure 10(b) shows that the clay platelets for large aggregates consist of highly multi-layered platelets. For the optimum specimen (Figure 11), it is deduced that some nano-tubes were intercalated into the nano-clay galleries and the nano-composites formed an intercalated morphology. Based on this micrograph, a better dispersion of nano-tubes (Figure 11) resulted from the presence of nano-clays. This is due to different forms and shapes of these nano-fillers.

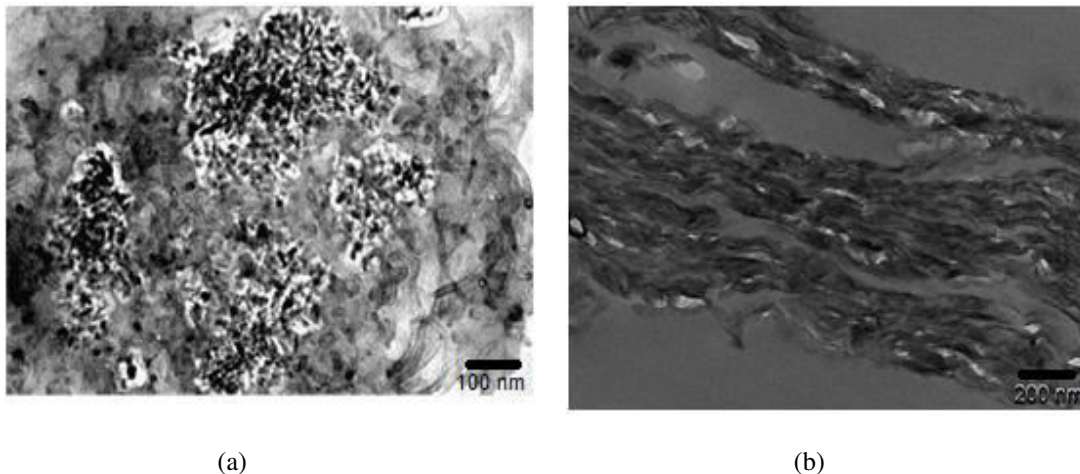


Figure 10. TEM micrograph of (a) ELNT (b) ELNC specimen

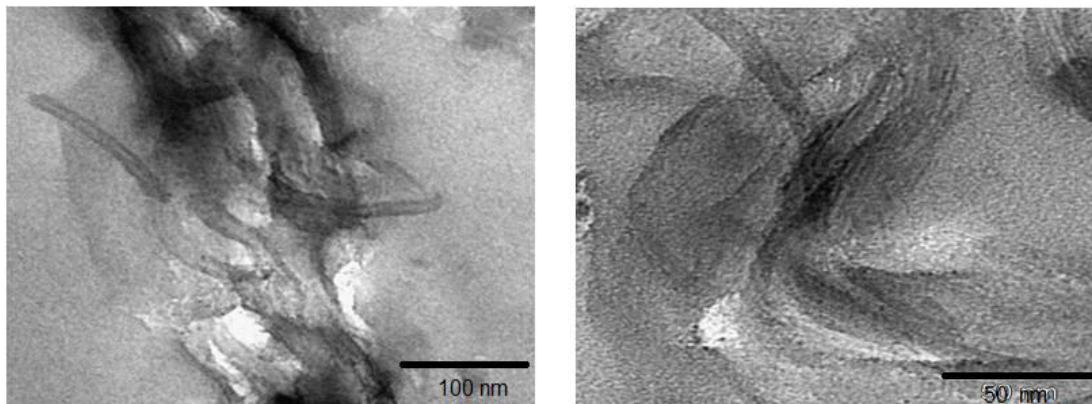


Figure 11. TEM micrograph of OPT specimen

As a conclusion, the effects of operating variables on mechanical properties of epoxy/liquid epoxidized natural rubber (LENR)/ carbon nano-tube/nano-clay nano-composite including tensile strength, impact strength and fracture toughness are well understood.

REFERENCES

- [1] JW Muskopf, SB. Mccollister, (2000). New York: Wiley.
- [2] S. R. Ha, S. H. Ryu, S. J. Park, K. Y. Rhee, (2007). *Mater. Sci. Eng.: A*. 448 (1-2), 264-268.
- [3] W. Liu, S. V. Hoa, M. Pugh, (2005). *Compos. Sci. Technol.* 65 (15-16), 2364-2373.
- [4] W. Liu, S. V. Hoa, M. Pugh, (2005). *Compos. Sci. Technol.* 65 (2), 307-316.
- [5] K. Z. K. Ahmad, S.Hj. Ahmada, M.A.Tarawneha, P.R. Apte. (2012). *Procedia Chemistry*. 4, 80 – 86
- [6] L. Ci, and J. B. Bai, (2006). *Composites Science and Technology*. 66 (3-4), 599-603.

- [7] Kim, B. Chul, S. W. Park, and D. G. Lee, (2008). *Composite Structures*. 86 (1-3), 69-77.
- [8] J.F.Hwang, J. A. Manson, R. W. Hertberg, G.A. Miller, & L.H. Sperling (1989) *Polymer Engineering and Science*. 29 (20),1466-1476.
- [9] P. Saadati, H. Bahrvand, A. Rahimi, & J. Morshedian, (2005). *Iranian Polymer Journal*. 14 (7), 637-646
- [10] Thomas, Raju, D. Yumei, H. Yuelong, Y. Le, P. Moldenaers, Y. Weimin, T. Czigany, and S. Thomas, (2008). *Polymer*. 49 (1),278-294.
- [11] D. Ratna, & A. K. Banthia, (2004). *Macromolecular Research*. 12(1),11-21
- [12] Zhou, Yuanxin, F. Pervin, L. Lewis, and S. Jeelani, (2007). *Materials Science and Engineering: A*. 452-453, 657-664.
- [13] M. Hosur, R. Barua, S. Zainuddin, S. Jeelani, A. Kumar, J. Trovillion, & J. Pereza, (2010). *Matéria*. 15 (2).
- [14] F. Pervin, Y. Zhou, M.A. Biswas, V. Rangari & S. Jeelani, (2005). *Proceeding of 5th annual Automotive Composites Conference and Exhibition*. Sept 12-14,Tory MI.
- [15] Y. Zhou, F. Pervin, M. A. Biswas, K. Vijaya, S. Jeelani, (2006). *Materials Letter*. 60, 869-873
- [16] M. R. Ayatollahi, M. M. Shokrieh, S. Shadlou, A. R. Kefayati, & M. Chitsazzadeh, (2011). *Iranian Polymer Journal*. 20 (10), 835-843.