Applied Polymer
JOURNAL OF · SCIENCE

Fatigue and Hysteresis Behavior of Halloysite Nanotubes-Filled Natural Rubber (SMR L and ENR 50) Nanocomposites

H. Ismail, S. Z. Salleh, Z. Ahmad

Polymer Engineering Division, School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
Correspondence to: H. Ismail (E-mail: hanafi@eng.usm.my)

ABSTRACT: The effect of various halloysite nanotubes (HNTs) loading on fatigue life, stress–strain behavior, and hysteresis of HNTs/Standard Malaysian Rubber (SMR) L and HNTs/epoxidized natural rubber (ENR) 50 nanocomposites were studied. The addition of HNTs caused decrement in fatigue life for both nanocomposites at any extension ratio. Generally, HNTs/SMR L nanocomposites showed higher fatigue life than ENR 50 nanocomposites. Addition of more HNTs caused decrement of stress for HNTs/SMR L nanocomposites, whereas HNTs/ENR 50 nanocomposites showed vice versa at any strain. This result was supported by the graph of accumulated strain energy against extension ratio. Hysteresis values increased with addition of HNTs in both nanocomposites where of HNTs/ENR 50 nanocomposites exhibited higher hysteresis than HNTs/SMR L nanocomposites at any HNTs loading. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

In the past of few years, polymer nanocomposites have been widely explored. The field of nanocomposites is still more focused on exploration rather than application.[1] The production of nanocomposites on a commercial scale has yet to be fully realized, because their performance characteristics are still being evaluated.[2] Many researchers investigated the effect of new types of filler which generally in nanosize toward mechanical, electrical, and thermal properties of rubbers. For example, Ismail et al.[3] and Sui et al.[4] investigated the effect of multiwalled carbon nanotubes (MWCNTs), whereas Ismail et al.,[5,6] Pasbakhsh et al.,[7–9] Due et al.,[10] and Rooj et al.[11] used halloysite nanotubes (HNTs) in various types of rubbers.

However, less investigation regarding the effect of nanosize filler in fatigue properties has been done. Previously, many researchers have been used micrometer size of fillers such as paper sludge,[12] white rice husk ash (WRHA),[13,14] feldspar,[15] and oil palm wood flour[16] to study the fatigue properties of rubber. From these investigations, all researchers stated that the addition of filler in rubber only caused reduction in fatigue life and increment in hysteresis. Hence, by replacing microsized filler to nanosized filler probability may produce inverse results due to better filler dispersion. This is because a fine dispersion of filler resulting in a good adhesion at the polymer/filler interface is the basic requirement for attaining optimum reinforcement and low hysteresis in elastomers.[17]

In this article, HNTs is used as filler with various HNTs loading for determination of fatigue properties in natural rubber (NR). Generally, HNTs can be described as hollow tubular structure in the submicron range and chemically similar to kaolin[11,18] and most of HNTs are nanotubes.[19] In addition, HNTs is composed of siloxane and has only few hydroxyl groups, which indicates that HNTs possess much better dispersion property than other natural silicate.[10] These characteristics showed interesting effect in rubber as shown by Ismail et al.[5] where addition of HNTs increased the tensile strength and elongation at break up to 100 phr of HNTs loading in ethylene propylene diene monomer (EPDM) nanocomposites. We[20] also reported the increment in tensile strength up to 20 phr loading of HNTs in Standard Malaysian Rubber (SMR) L nanocomposites. Besides, we[21] also reported that replacement of carbon black (CB) with HNTs able to increase fatigue life of CB/HNTs/SMR L nanocomposites.

In this work, two types of NR, i.e., unmodified (SMR L) and modified epoxidized natural rubber (ENR 50) was used. Further investigation regarding the effect of HNTs loading toward fatigue life with various extension ratio, stress–strain behavior, and hysteresis was done.

EXPERIMENTAL

Materials and Chemicals

SMR L was obtained from Rubber Research Institute, Malaysia (RRIM). While ENR 50 was purchased from Kumpulan Guthrie Sdn. Bhd. HNTs were purchased from Imerys Tableware Asia Limited, New Zealand. The other ingredients such as zinc oxide, stearic acid, sulfur, *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), and 2,2-methylene-bis-(4-methyl-6-*tert*-butylphenol) (BKF) were obtained from Bayer (M) Sdn. Bhd.

Sample Preparation

The formulation used for both nanocomposites is shown in Table I and two-roll mill model XK-160 with the size of 160 × 320 mm^2 was used for mixing process. The cooling water was ensured to flow continuously to maintain the temperature of two-roll mill to avoid crosslinking occurred during the mixing process.

Monsanto Moving Die Rheometer (MDR 2000) was used to investigate the curing characteristics for each HNTs/SMR L and HNTs/ENR 50 nanocomposites at 150°C. Then, the cure time (t_{90}) obtained from this test was used in compression molded at 150°C and turned both nanocomposites into rectangular sheets with the dimension of 22.9 × 7.6 × 0.15 cm^3 and beaded edges.

Measurements

Fatigue Life. The rectangular sheets were cut into dumbbell shaped by using a BS type E dumbbell cutter and were cut at right angles to the grain. Monsanto fatigue-to-failure tester (FTFT) is used for fatigue test where the samples were subjected to repeated cyclic strain at 100 cpm with extension ratio 1.61 ± 0.04, 1.78 ± 0.04, 2.01 ± 0.05, and 2.36 ± 0.08. For each nanocomposites, six samples were examined for the fatigue life while only the first four samples with the highest cyclic were chosen to be used in JIS average. The calculated data were fatigue life in kilocycles (kc). The JIS average formulation was calculated by the eq. (1):

$$\text{JIS average} = 0.5A + 0.3B + 0.1(C + D) \tag{1}$$

where *A* is the highest value of cyclic followed by *B*, *C*, and *D*, respectively.

Strain Energy Measurement. The equipment used consisted of a stand incorporated upper clamp, pan incorporating lower clamp (weight 50 g) plus various weights as supplied with a FTFT.[16]

Table I. The Experimental Formulation of the HNTs/NR Nanocomposites

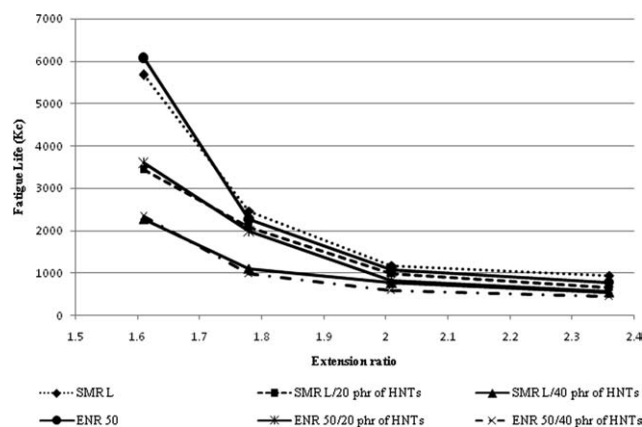| Ingredients	Content (phr)
NR	100
Zinc oxide	5
Stearic acid	3
CBS	0.5
BKF	1.0
Sulfur	2.5
HNT	0, 20, 40

Figure 1. Fatigue life with various HNTs loading for HNTs/SMR L and HNTs/ENR 50 nanocomposites.

Width and thickness of the samples were measured. Then, a horizontal line was drawn on the sample surface with 2.5 cm apart. The sample must be cycled for at least 30 cycles at the maximum extension ratio that has been used in determined the fatigue life. Next, the sample was hanged at upper clamp's stand, whereas the other end was clamped with lower clamp which was 50 g in weights. The total weights with 100 g were loaded at the sample. Horizontal chalk lines were drawn on the sample in the linear region when fully extended. After 1 min, the weights were detached. The distances between the marks are measured. Then, these steps were repeated by additional weights used are 200 g until extension ratio of about 25 was attained.

Stress (obtained from manual calculation of load/area) is plotted against extension ratio curve where from this graph, the values of stress reading (h) at the intervals of extension ratio 0.1 ranging from 1.0 to 2.5 was gathered. Strain energy values were obtained by applying the Simpson rule (2) to sets of three consecutive results to give area *A* of sections of the curve and subsequently the total area of the curve at extension ratio increments of 0.2:

$$\text{Area} = (1/3)a[h_x + 4h_{(x-1)} + h_{(x-2)}] \tag{2}$$

where $a = 0.1$ (strain interval).

Scanning Electron Microscopy. The morphology of tensile and fatigue fracture surfaces of nanocomposites were observed under a Supra-35VP field emission scanning electron microscope (SEM). The fracture end surfaces were cut and mounted on aluminum stubs. All the samples were coated with a thin layer of Pd-Au prior the test to avoid electrostatic charging during the examination process.

RESULTS AND DISCUSSION

Fatigue Life

Figure 1 shows the effect of various HNTs loading against fatigue life for both nanocomposites. It can be seen that addition of HNTs into both nanocomposites caused reduction of fatigue life at any extension ratio. The addition of filler causes

heterogeneous nature in rubber vulcanizates[22] and also increases the stiffness[23] which shortens the fatigue life eventually. When more HNTs are added into both nanocomposites, the dispersion of HNTs became worst. Lack of wetted efficiency by rubber at higher loading of filler worsens the filler distribution in matrix. These inherent defects act as stress concentration and reduce the fatigue life.[13,14]

The pattern in Figure 1 has been expected based on our previous result[20] which showed that addition of HNTs caused decrement in fatigue life for SMR L nanocomposites where the extension ratio used was 2.01. Similar expectation for HNTs/ENR 50 nanocomposites is observed as shown in Table II. It can be noticed that fatigue life decreased with addition of HNTs.

Besides, Figure 1 also shows reduction of fatigue life for both nanocomposites with increasing extension ratio. This indicates that larger deformation undergo by nanocomposites also can be a factor that affect the fatigue life. Poh et al.[24] explained that reduction of fatigue life at higher extension ratio is due to the higher cyclic tensile stress and more pronounce in noncrystallizing nature of rubber.

As can be seen in Figure 1 and Table II, generally the fatigue life of HNTs/SMR L nanocomposites is higher than HNTs/ENR 50 nanocomposites. This is because HNTs unable to make interaction in SMR L as efficient as in ENR 50 nanocomposites because HNTs able to form hydrogen bonds with epoxide groups in ENR 50 nanocomposites. Similar explanation has been reported by Franco[25] on the interaction between silica and ENR. Silica show strong filler–rubber interaction due to hydrogen bonding between silanol groups of silica and epoxy groups of polyisoprene. Similar interaction is expected which happened between HNTs and ENR because HNTs also have same chemical groups as silica. HNTs have two different interlayer surfaces;[26] aluminol (Al-OH) group located inside the tubes while the outer surface primarily is covered by siloxane (Si—O) group, and a few silanol and aluminol which are exposed on the edges of the rolled sheets of the tubes.[27]

This interaction cause lower strain crystallization in ENR 50 nanocomposites due to more chains restriction compared to SMR L nanocomposites. Besides, strain-induced crystallization is better in SMR L compared to ENR 50 matrix because stereoregularity in the backbone chains of SMR L. Ismail et al.[15] stated that the order of NR in strain-crystallizing nature is SMR

Table II. Fatigue Life for Both Nanocomposites with Extension Ratio 2.01 ± 0.05

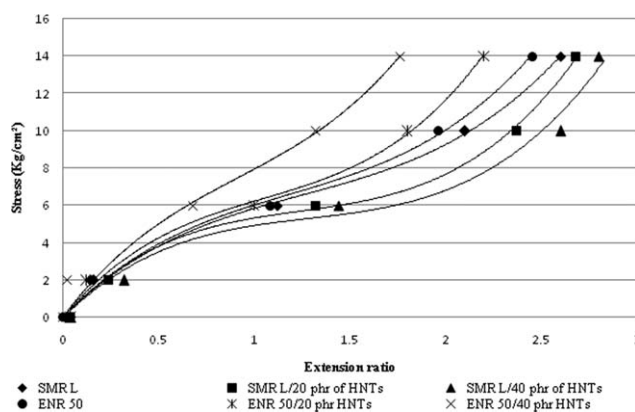| HNTs loading (phr)	Fatigue life (Kc)	
	SMR L	ENR 50
0	1264	1211
10	1039	1012
20	987	833
30	824	687
40	771	586

Figure 2. Stress for HNTs/SMR L and HNTs/ENR 50 nanocomposites with various HNTs loading.

L > ENR 25 > ENR 50. Thus, higher fatigue life can be observed for HNTs/SMR L nanocomposites than HNTs/ENR 50 nanocomposites.

Stress–Strain Behavior and Strain Energy

The stress–strain behavior of HNTs filled both nanocomposites is shown in Figure 2. The addition of HNTs in SMR L nanocomposites caused reduction of stress at any strain whereas HNTs/ENR 50 nanocomposites showed vice versa. This indicates poor interaction of HNTs in SMR L nanocomposites. Similar observation was obtained by Ismail et al.[16] for WRHA-filled NR (SMR L). However, as explained before, HNTs able to make interaction with ENR 50 which cause extra chain restriction. Hence, this making higher stress required for higher HNTs loading in ENR 50 nanocomposites at any strain. Ismail et al.[14] reported that the increment loading of CB, silica, and WRHA in ENR 50 vulcanizates caused increment in stress at any strain.

Figure 3 shows the accumulated strain energy versus extension ratio at any HNTs loading for both matrixes. It can be seen that HNTs/SMR L nanocomposites showed reduction of accumulated strain energy as HNTs loading increased while contrary results were obtained for HNTs/ENR 50 nanocomposites. This indicates that less work is required to deform HNTs/SMR L
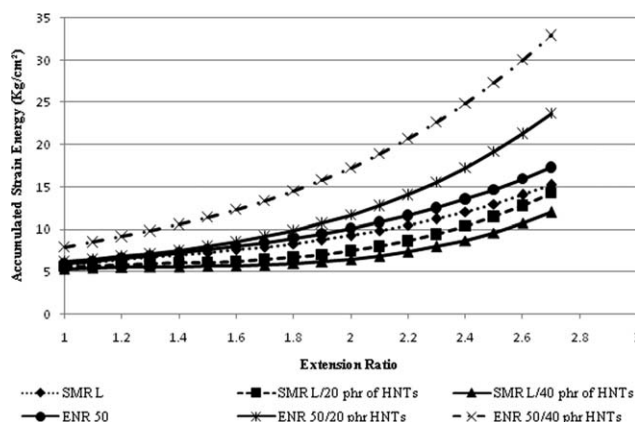

Figure 3. Accumulative strain energy of HNTs/SMR L and HNTs/ENR 50 nanocomposites with various HNTs loading.

nanocomposites when more HNTs added. Ismail et al.[16] explained that increment of filler loading weakens the interfacial interaction between filler and rubber matrix which would decrease the effectiveness of stress transferred from rubber matrix and consequently reduce the work required to deform the composites. This supports the previous data where addition of HNTs reduced the stress at any strain. On the other hand, HNTs/ENR 50 nanocomposites needs more work to deform when more HNTs added into system. As stated before, it is due to the interaction of HNTs and ENR 50.

Hysteresis Effect on Fatigue Life

Hysteresis is an important aspect of studying the fatigue properties of vulcanizates because it is a measurement of the energy loss when elastomerics are subjected to dynamic deformation.[22] Hysteresis is the differences between the amount of energy absorbed when rubber is stretched and the amount of energy released when the rubber was relaxed.[28] Hence, it is important for rubber to release energy at higher rate to prevent heat build-up in vulcanizates and cause chain scission.

The fatigue life against strain energy for both nanocomposites is plotted as shown in Figure 4 where the slope of each graph is determined to find the hysteresis value. The hysteresis value which indicated by the strain exponent (n) is equal to the slope for that graph according to the following equation:[29]

$$N = [G'/(n-1)W^n][1/C_0(n-1)]$$

where N is the number of cycles to failure, G' the modified cut growth constant, C_0 the effective critical flaw size, and W the strain energy per unit volume. The higher value of n indicates higher sensitivity toward the changes in strain energy as exhibited by the highest filled vulcanizates.

Table III shows the values of strain exponent (n) for both nanocomposites with various HNTs loading. As higher addition of HNTs into both matrixes, the value of n is increased. This indicates higher hysteresis for higher HNTs loading. This has been mentioned before that addition of HNTs cause increment in stiffness of nanocomposites which cause reduction of resilience. Both nanocomposites unable to return back to its original
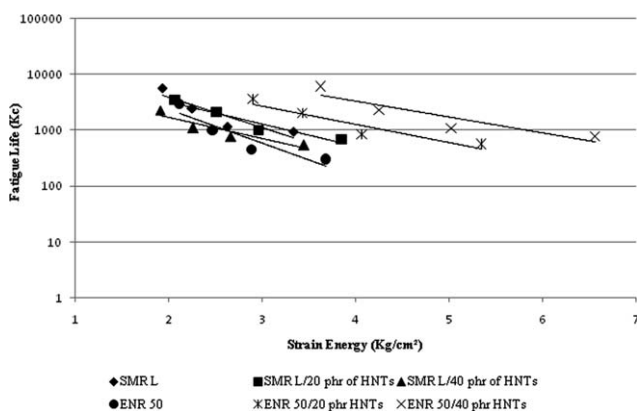
Table III. Strain Exponent Values (n) for Both Nanocomposites with Various HNTs Loading

HNT loading (phr)	Strain exponent values (n)	
	SMR L	ENR 50
0	0.29	0.25
20	0.40	0.47
40	0.42	0.52

shapes when unloaded. Consequently, more heat build up in nanocomposites which cause chain scission and thus shorten the fatigue life.

Strain-induced crystallization play the primary considerations in comparing hysteresis of SMR L and ENR 50 nanocomposites. Young[30] stated that rubber that show strain crystallization is able to release energy at superior rate. Besides, Poh et al.[24] mentioned that increasing epoxidation increases results in decreasing the resilience (more damping), reduce air permeability, higher hysteresis, and better wet traction. Hence, hysteresis of HNTs/ENR 50 nanocomposites is higher than HNTs/SMR L nanocomposites.

Scanning Electron Microscope

Figures 5 and 6 separately show SEM images for fatigue-fractured surface of HNTs/SMR L and HNTs/ENR 50 nanocomposites with three different HNTs loading, i.e., 0, 20, and 40 phr. Fatigue-fractured surfaces have two distinct zones on its surface. Generally, Zone 1 represents the initial stage of failure. This zone is known for ductile failure with rough surface which is responsible to slow down the fatigue life failure. While Zone 2 is the last stage of failure. It represents brittle failure with smooth surface. Nanocomposites with longer fatigue life would show rougher surface than smooth surface. These zones are dependent on several factors such as amount and dispersion of filler in nanocomposites.
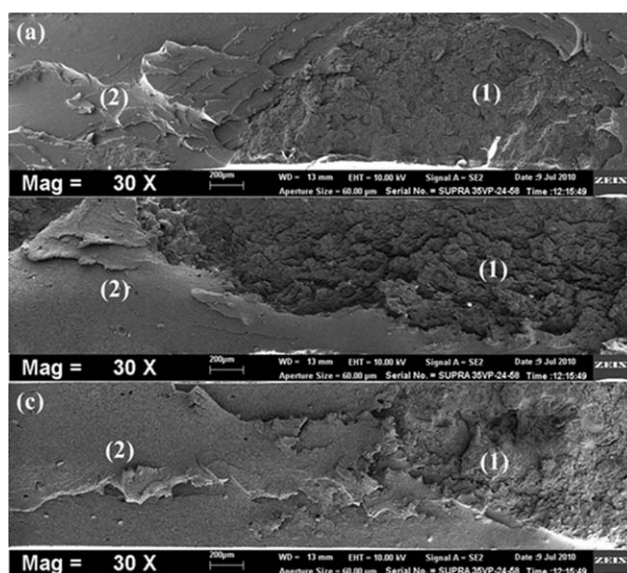

Figure 4. Relationship between fatigue life and strain energy of HNTs/SMR L and HNTs/ENR 50 nanocomposites with various HNTs loading.

Figure 5. SEM images for HNTs/SMR L nanocomposites with 0, 20, and 40 phr (at 30× magnification).
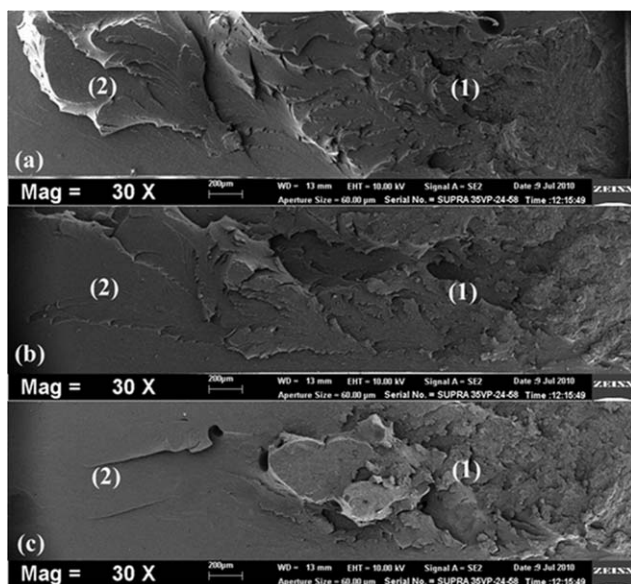
Figure 6. SEM images for HNTs/ENR 50 nanocomposites with 0, 20, and 40 phr (at 30× magnification).

The area for both zones changes with addition of HNTs into both nanocomposites. Figures 5(a) and 6(a) in which nanocomposites without any HNTs loading show larger rough surfaces with less smooth surfaces than others figures (b and c). However, lesser rough surface with larger smooth surface can be noticed with addition of HNTs as shown in (b and c) for both figures.

This indicates nanocomposites with lower filler loading show higher fatigue life than nanocomposites with higher filler loading. More tearing surface appeared to delay fatigue life failure. However, at higher loading, fast crack propagation is observed as proven with the appearance of smooth surface. This can be related to the increment of stiffness and bad dispersion of HNTs in nanocomposites. We[18] reported that the addition of HNTs caused increment in maximum torque indirectly correlated with increment in stiffness of nanocomposites. Addition of HNTs which is nondeformable material would reduce the ductility of nanocomposites hence consequently increase the possibility for brittle failure rather than ductile failure.
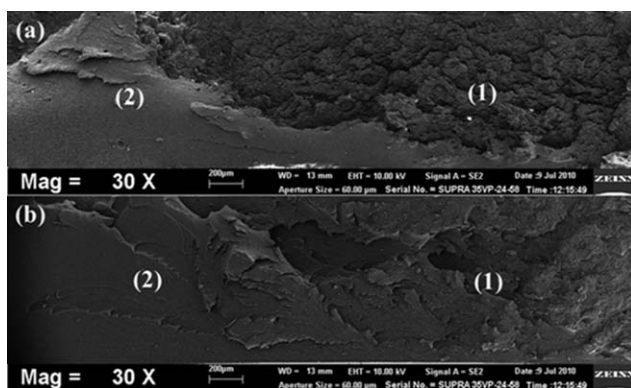

Figure 7. SEM images for both nanocomposites: (a) SMR L and (b) ENR 50 nanocomposites with 20 phr of HNTs (at 30× magnification).

Besides that higher HNTs loading leads to lack of wetted efficiency of rubber. As explained earlier, these may cause inherent defects which act as stress concentration in nanocomposites. This definitely weakens the strength of nanocomposites and unable to undergo longer dynamic deformation. Bad dispersion in matrix causes heterogeneous nature that becomes worst. Consequently, stress is unable to distribute uniformly in nanocomposites with higher filler loading.

The comparison fatigue-fractured surfaces between different matrixes can be seen in Figure 7 which is loaded with 20 phr of HNTs. It can be seen that rough surface in Figure 7(a) is larger than in Figure 7(b). As aforementioned, this tearing surface is able to withstand longer force applied than smooth surface. This is proved for longer fatigue life occurred in HNTs/SMR L nanocomposites than in HNTs/ENR 50 nanocomposites.

CONCLUSIONS

Fatigue life for both nanocomposites decreased with addition of HNTs at any extension ratio. HNTs/SMR L nanocomposites showed higher fatigue life than in ENR 50 nanocomposites. HNTs/SMR L nanocomposites showed reduction of stress, whereas HNTs/ENR 50 nanocomposites showed vice versa at any strain. The graph of accumulated strain energy against extension ratio supported this result. Hysteresis values increased with addition of HNTs in both nanocomposites and HNTs/ENR 50 nanocomposites demonstrated higher hysteresis than HNTs/SMR L nanocomposites at any HNTs loading.

ACKNOWLEDGMENTS

REFERENCES

1. Ray, S.; Easteal, A. *J. Mater. Manufact. Process* **2007,** *22,* 741.

2. Bhattacharya, S. N.; Gupta, R. K.; Kamal, M. R. Polymeric Nanocomposites: Theory and Practice; Carl Hanser Verlag: Munich, **2008,** p 233.

3. Ismail, H.; Ramly, F.; Othman, N. *Polym.-Plast. Tech. Eng.* **2010,** *49,* 260.

4. Sui, G.; Zhong, W. H.; Yang, X. P.; Yu, Y. H. *Mater. Sci. Eng.* **2008,** *485,* 524.

5. Ismail, H.; Pasbakhsh, P.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Polym.-Plast. Tech. Eng.* **2009,** *48,* 313.

6. Ismail, H.; Pasbakhsh, P.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Polym. Test.* **2008,** *27,* 841.

7. Pasbakhsh, P.; Ismail, H.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Appl. Clay Sci.* **2010,** *48,* 405.

8. Pasbakhsh, P.; Ismail, H.; Ahmad Fauzi, M. N.; Abu Bakar, A. *J. Appl. Polym. Sci.* **2009,** *113,* 3910.

9. Pasbakhsh, P.; Ismail, H.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Polym. Test.* **2009,** *28,* 548.

10. Du, M.; Guo, B.; Lei, Y.; Liu, M.; Jia, D. *Polymer* **2008,** *49*, 4871.

11. Rooj, S.; Das, A.; Thakur, V.; Mahaling, R. N.; Bhowmick, A. K.; Heinrich, G. *Mater. Design.* **2010,** *31*, 2151.

12. Ismail, H.; Arjulizan, R.; Azura, A. R. *J. Polym. Environ.* **2007,** *15*, 67.

13. Ismail, H.; Ishiaku, U. S.; Lu, E. S.; Mohd Ishak, Z. A. *Int. J. Polym. Mater.* **1997,** *38*, 275.

14. Ismail, H.; Ishiaku, U. S.; Lu, E. S.; Mohd Ishak, Z. A. *Int. J. Polym. Mater.* **1998,** *39*, 45.

15. Ismail, H.; Osman, H.; Ariffin, A. *Polym.-Plast. Tech. Eng.* **2007,** *46*, 579.

16. Ismail, H.; Jaffri, R. M.; Rozman, H. D. *Polym. Int.* **2000,** *49*, 618.

17. Thomas, S; Stephen, R. Rubber Nanocomposites: Preparation, Properties and Applications; Thomson Digital: Noida, **2010, p 1.**

18. Liu, M.; Guo, B.; Lei, Y.; Du, M.; Cai, X.; Jia, D. *Nanotechnology* **2007,** *18*, 455703.

19. Jia, Z-X.; Luo, Y-F.; Yang, S-Y.; Guo, B-C.; Du, M-L.; Jia, D-M. *Chin. J. Polym. Sci.* **2009,** *27*, 857.

20. Ismail, H.; Salleh, S. Z.; Ahmad, Z. *Polym.-Plast. Tech. Eng.* **2011,** *50*, 681.

21. Salleh, S. Z.; Ismail, H.; Ahmad, Z. *Key Eng. Mater.* **2011,** *471*, 957.

22. Mohd Ishak, Z. A.; Abu Bakar, A.; Ishiaku, U. S.; Hashim, A. S.; Azahari, B. *Eur. Polym. J.* **1997,** *33*, 73.

23. El-Sabbagh, S. H.; Ismail, M. N.; Yehia, A. A. *J. Elast. Plast.* **2001,** *33*, 263.

24. Poh, B. T.; Ismail, H.; Quah, E. H. *Polym. Test.* **2001,** *20*, 389.

25. Franco, C. *Macromol. Mater. Eng.* **2002,** *287*, 348.

26. Pasbakhsh, P.; Ismail, H.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Appl. Clay Sci.* **2010,** *48*, 405.

27. Liu, M.; Guo, B.; Zou, Q.; Du, M.; Jia, D. *Nanotechnology* **2008,** *19*, 205709.

28. Definition of Hysteresis. Available at: http://www.engineeringdictionary.org/Rubber-Dictionay/Hysteresis. Accessed April 14, 2011.

29. Payne, A. R.; Whittaker, R. E. *J. Appl. Polym. Sci.* **1971,** *15*, 1941.

30. Young, D. G. *Rubber Chem. Technol.* **1985,** *58*, 785.