Digest Journal of Nanomaterials and Biostructures Vol. 10, No. 3, July - September 2015, p. 1067 - 1076

SUPERIOR PROPERTIES OF NATURAL RUBBER ENHANCED BY MULTIWALL-CARBON NANOTUBES/NANOCLAY HYBRID

L. SIKONG[a,b,c*], K. KOOPTARNOND[a,b,c], M. KHANGKHAMANO[a,b,c], W. SANGCHAY[d]
[a]*Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla, Thailand 90112*
[b]*The Center of Excellence in Materials Engineering (CEME), Prince of Songkla University, Hat Yai, Songkhla, Thailand 90110*
[c]*The Center of Excellence in Nanotechnology for Energy (CENE), Prince of Songkla University, Hat Yai, Songkhla, Thailand 90110*
[d]*Faculty of Industrials Technology, SongkhlaRajabhat University, Songkhla, Thailand, 90000.*

Multiwall-carbon nanotubes (MWNT) and Montmorillonite natural clay (MMT) were used as hybrid reinforcing filler to enhance mechanical, electrical and dynamic mechanical properties of natural rubber (NR). The effect of filler loading was verified to gain the optimum properties of the fabricated nanocompounds. The results revealed that modulus, tear strength, hardness, storage modulus and damping factor of hybrid filler nanocomposites were greatly enhanced when 20 and 30 phr of MWNT and MMT, respectively, were used. Glass transition temperature (Tg) of the composite materials was also increased by 10°C even at low loading level (5 phr) of the nanofillers.Tensile strength and swelling resistance of the nanocompounds were superior to those of base NR. Electrical conductivity of the nanocompounds increased extremely with the increased MWNT loading but decreased obviously with increasing MMT concentration. Good interaction between the rubber matrix and the nanofillers was believed to be responsible for overall enhancement in mechanical properties of the fabricated rubber nanocompounds.

(Received July 14, 2015; Accepted September 14, 2015)

*Keywords:*Multiwall-carbon nanotubes, Montmorillonite, Hybrid filler,
Rubber nanocomposites, Reinforcement, Properties

1. Introduction

Although natural rubber (NR) provides an excellent flexibility, improvement in mechanical, thermal and electrical properties is needed to meet the requirement of a particular application. To enhance such desirable properties, inorganic fillers are normally added into the rubber matrix. A number of fillers are used in the rubber industry for various purposes including reinforcement, property enhancement, cost reduction and processing improvement. Among them, silica (SiO_2) and carbon black (CB) are the conventional reinforcing-fillers used to improve mechanical properties of various rubbers[1-4]. In general, CB filler provides an enhancement in tensile strength, tear strength, elastic modulus and abrasion resistance [5], whereas silica filler gives a unique combination of tear strength, abrasion resistance, aging resistance and adhesion properties [6]. Recently, carbon nanotubes (CNTs) and graphene have been used as reinforcing fillers fabricating various polymer-nanocomposites to gain improvement in not only physical, mechanical, thermal and electrical properties but also photonic and electronic properties of the materials[7-9]. The application of both CNTs and graphene in this aspect, however, is limited due

---

[*]Corresponding author: lek.s@psu.ac.th

to high cost of the materials, quality of the materials and poor dispersion in the rubber matrix[10, 11]. The extent of the improvement is directly related to the degree of the nanofiller dispersion in the polymer matrix [5]. For large scale production of the rubber based nanocomposites, nevertheless, only achievement in enhancing the material properties is insufficient, low processing cost and inexpensive raw materials are also taken in account. Apart from those fillers, natural clays such as montmorillonite (MMT), which are inexpensive and substantially available, make interesting reinforcing agents due to their high aspect ratio and large surface area of layered silicates (~1 nm in thickness and 100 - 1000 nm in lateral dimensions) consisting in its structure [12]. In addition, these nanoplatelets align easily in an ordered manner and possess an exceptionally high stiffness and strength as well as low gas permeability[13, 14]. Theoretically, therefore, as compared to those particulate fillers such as carbon black, exfoliated clay nanoplatelets exhibit a much greater enhancement in elastic modulus even at very low nanoclay loadings[13]. All these contribute the MMT nanoclay being as a good candidate for producing low cost rubber-based nanocomposites. Poor electrical and thermal conductivity of the rubber-clay nanocomposite, however, is its limitation for a particular application requiring this property.

In this study, rubber based nanocomposites were fabricated using hybrid filler of cheap MMT nanoclay and electrically conductive CNTs to effectively enhance mechanical, thermal and electrical properties of the materials. Loading concentration of the nanofillers was varied and its effect on swelling resistance, crosslink density, tensile strength, elongation at break, elastic modulus, tear strength, hardness and hysteresis of the rubber compounds were evaluated. An optimum mixing ratio of the nanofillers giving rise to the optimum properties of the nanocomposites was also investigated.

2. Materials and Experimental Procedures

2.1 Materials

Natural rubber (NR latex) with the total solid content of 60% obtained from Chalong Latex Industry Co., Ltd (Thailand) was used as a matrix. Multi walled carbon nanotubes (MWNT) purchased from physics department, faculty of science, Chiang Mai University, and Montmorillonite (MMT) nanoclay were employed as hybrid reinforcing filler. Chemical compositions of the starting MMT and the detail of MWNT characteristics are listed in table 1 and 2, respectively. A micrograph of as-received MWNT is illustrated in Fig. 1.

Table 1. Chemical compositions of the as-received MMT

Chemical composition	%	Chemical composition	%
MgO	1.82	CaO	2.69
Al_2O_3	12.29	TiO_2	0.15
SiO_2	69.56	Fe_2O_3	3.16
SO_3	0.62	ZnO	0.03
K_2O	2.13	SrO	0.04

Table 2. Characteristics of as-received MWNT

Materials properties	
Purity (%)	> 95
Length (μm)	> 10
Diameter (nm)	20-50
Resistivity (Ωm)	0.5-0.8
Specific surface area (m^2/g)	150-400
Electrical conductivity $(\Omega cm)^{-1}$	65
True density (g/cm^3)	2.1
Ash content (%wt)	< 0.5

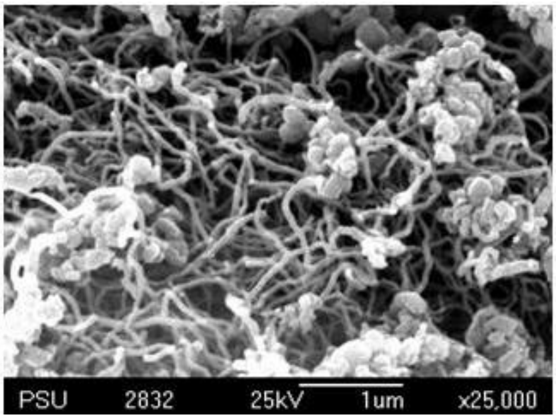

Fig. 1 SEM image of as-received MWNT used as a filler.

2.2 Preparation of hybrid filler nanocomposites

2.2.1 Preparation of clay slurry

As-received MMT was subjected to wet milling process for 100 h to reduce its particle size from ~10 μm to ~100 nm as shown in Fig. 2. The milled clay was then oven-dried overnight at 100°C and grinded in a mortar for a certain time to gain fine clay powder. The powder was pre-dispersed in distilled water using a motor stirrer for 5 h to produce a product of homogeneous clay slurry.

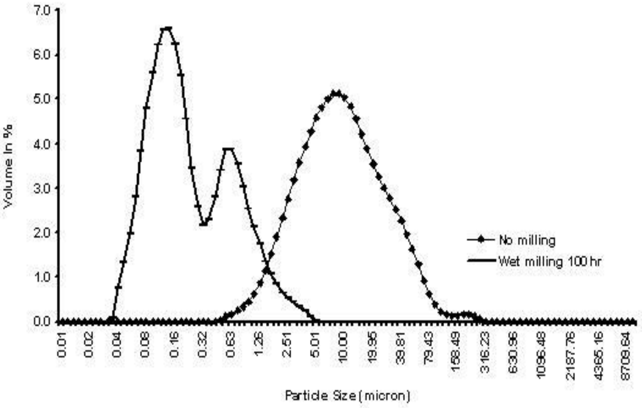

Fig. 2 Particle size analysis of MMT clay before and after 100 h wet milling.

2.2.2 Preparation of hybrid filler nanocomposites

While stirring, the clay slurry was added to the latex and further stirred for another 10 min to gain an homogeneous mixture. Loading concentrations of the slurry were 5, 10, 15, 20, 25 and 30 phr. The latex-clay mixture was then co-coagulated in a dilute acetic acid, washed with distilled water and oven-dried at 80°C for 16 h. The dried nanocomposites were further mixed with MWNT and additives at room temperature using two-roll mill to produce a nanocomposite sheet with 1 mm-thick.

2.3 Characterization

2.3.1 Swelling behaviour

Disk-like samples with the dimension of 12.7 x 6 mm^2 were prepared to measure swelling resistance in toluene and oil. To conduct the experiment, an initial mass (m_i) of the sample at dry condition was weighed and soaked in toluene and oil at room temperature for 3 and 7 days, respectively. Mass of the sample in the swollen state (m_s) was measured after a slight removal of the solvent on the sample surfaces.Three samples were tested for each solvent. Percentage of the swelling was calculated using eq. (1).

$$\%Swelling = \frac{m_s - m_i}{m_i} x100 \tag{1}$$

Where m_i and m_s are the mass (g) of a specimen before and after, respectively, immersion.

2.3.2 Crosslink density

Crosslink density, the number of active network chain segments per unit of volume, of the samples containing various mixing ratios of the nanofillers was determined on the basis of the rapid solvent-swelling measurement using the Flory–Rehner equation[15, 16].

2.3.3 Mechanical properties

Tensile strength and tear resistance of the as-preparednanocompounds were determined using an Instron universal testing machine (5655 series) and the testing procedures were performed according to the standard practice ISO 37 (type 1) and ISO 34, respectively. The stretching force (F) was measured and the force value was converted to stress (σ) unit using the relation expressed in eq. (2) with the assumption that the cross section (A) is unchanged during testing. Strain (ε) of the tested material was calculated using eq. (3). Curves of the stress versus strain were plotted and the tensile or elastic modulus (E) of the material was evaluated from the initial linear part of the stress-strain curves (Hooke's region). Five samples were tested for each composition and an averaged value was taken for further analysis.

$$\sigma = \frac{F}{A} \tag{2}$$

$$\varepsilon = \frac{\Delta l}{l_0} \tag{3}$$

Where σ is stress (N/m^2), F is the applied force (N), and A is the cross section area (m^2), ε is strain (dimensionless), Δl is the elongated length (m), l_0 is the original length of the sample (m). *Hardness* of the samples was measured using a durometer type A according to ASTM D2240.

2.3.4 Dynamic mechanical analysis

Dynamic mechanical-thermal analysis (DMTA) was performed on a DMTA measurement system (Rheometric Scientific Company) using a constant frequency of 1.0 Hz with a wide temperature range from -100°C to +60°C. Samples were analyzed in tension mode. To evaluate the complex modulus E* (storage modulus E'+ viscous or loss modulus E") and damping factor (tan δ), which is a ratio of E"/ E', a static load of 1% pre-strain was applied. The samples were then oscillated to a dynamic load of 0.5% strain. The measurements were conducted under liquid nitrogen flow with a heating rate of 3°C /min. A pre-strain of magnitude 40% was chosen to hold a sample size of 10x25x1 mm^3.

2.3.5 Electrical conductivity measurement

Electrical conductivity measurements were carried out at room temperature with a low resistance meter (LCR meter) using a constant frequency of 100 kHz. The diameter and thickness of the rubber samples for this experiment were 12 and 1 mm, respectively.

3. Results and Discussion

3.1 Swelling resistance and crosslink density

Fig. 3 presents the relationship between %swelling and MWNT loading in MMT/NR nanocompounds. All samples exhibited a larger degree of %swelling in toluene than oil revealing lower swelling resistance of the samples in the solvent. Swelling resistance, which is inversely proportional to %swelling, of samples in both solvents increased obviously with the increased loading level of the nanofillers suggesting an enhancement in crosslink density of the rubber nanocompounds at high loading levels[17]. This suggestion is well supported by the results illustrated in Fig. 4 that crosslink density of the nanocomposites increased gradually with MWNT loading.

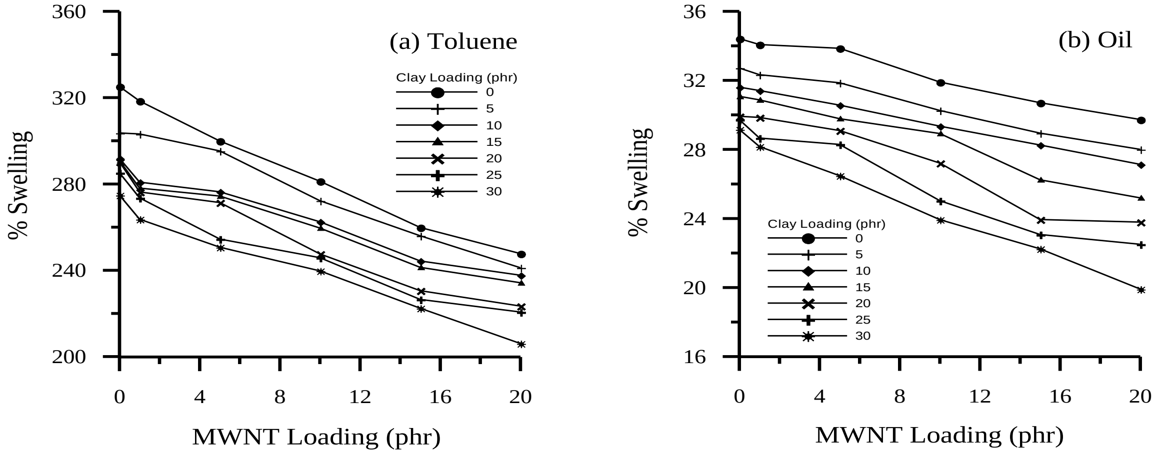

Fig.3 Swelling behavior of rubber nanocomposites varied with MMT and MWNT loadings; (a) and (b) immersed in toluene and oil, respectively.

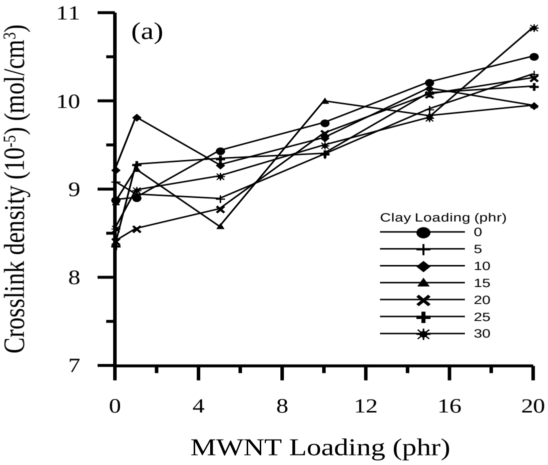

Fig. 4 Crosslink density of the hybrid filler nanocomposites increased with MWNT loading.

3.2 Tensile strength and elongation at break of hybrid filler nanocomposites

As shown in Fig. 5a, tensile strength of pure NR is considerably improved when either single or hybrid filler were added into the rubber matrix. Using single filler of either MWNT or MMT at a very low content of 5 phr resulted in an enhanced tensile strength from 16.7 MPa to 25.8 or 26.2 MPa, respectively, indicating a significant effect of loading level on the composite strength.

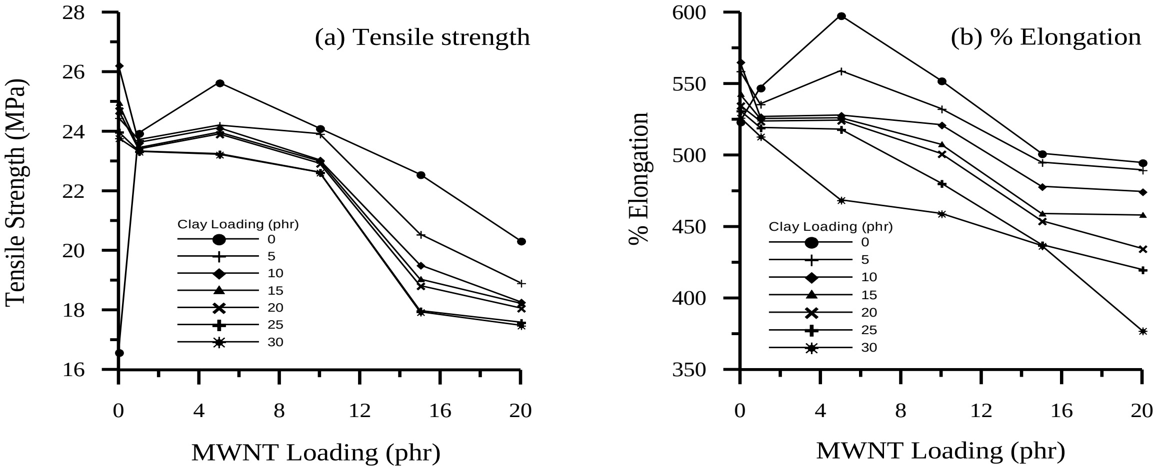

Fig.5 (a) tensile strength and (b) elongation at break of hybrid filler nanocomposites changes with loading level of the nanofillers.

However, as compared to single filler nanocomposites (either MMT/NR or MWNT/NR), hybrid filler nanocomposites exhibited lower tensile strength depending on loading level of the second filler. Similar phenomena were observed in Fig. 5b that elongation at break of single filler nannocomposites was much higher than that of base NR. The highest elongation at break of 600% was found in MWNT/NR nanocompounds when 5 phr of MWNT was added. Although single filler nanocomposites showed higher tensile strength and elongation at break than those hybrid filler ones, a dramatic improvement in tensile strength was achieved in all hybrid filler samples in comparison with base NR. This represents that the reinforcing effect of the nanofillers is very apparent. At high loading levels of both fillers, however, tensile strength and elongation at break of all nanocomposite samples reduced obviously.This could be due to the effect of poor dispersion of the nanofillers in the rubber matrix when high loading levels of the fillers were introduced[18]. The optimum loading level of both MWNT and MMT giving rise to the highest tensile strength (24.21 MPa) and elongation at break (559%) was 5 phr. As compared to those of base NR, these values are enhanced by 46% and 30%, respectively. The significant increase in tensile strength, when low levels of the nanofillers were added into the matrix, is attributed to a high degree of the polymer-MWNT-MMT surface interaction due to high aspect ratios of the nanofillers and their well dispersion in the composite structure[18-21].

3.3 Elastic modulus, tear resistance and hardness of the nanocomposites

Figs. 6a, 6b and 6c present the effect of various filler loadings on elastic modulus, tear resistance and hardness, respectively, of the nanocomposites. As compared to base NR, a considerable increase in elastic modulus, tear resistance and hardness of the nanocompounds was evident at high loading levels of the nanofillers. The optimum composition providing the highest values of the modulus (12.5 MPa), tear resistance (45 N/mm) and hardness (55 Shore) is that composing of MWNT 20 phr and MMT 30 phr. These values are 4.5, 1.8 and 1.3 times, respectively, higher than those of base NR. The dramatic increase in elastic modulus of hybrid filler nanocomposites, when high loading levels of the fillers were applied, implies clearly an evident reduction of elongation at break as demonstrated in Fig. 3b.

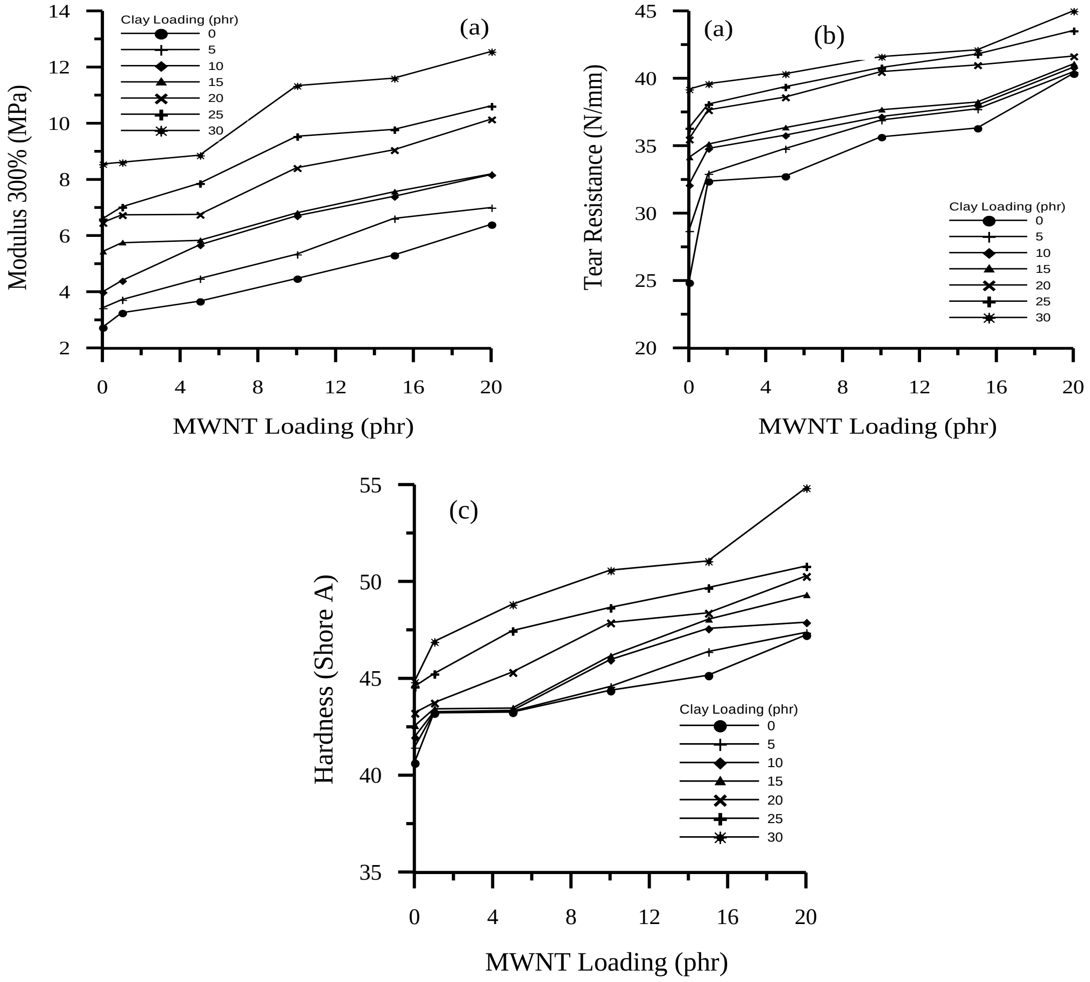

Fig.6(a) Elastic modulus,(b) tear resistance and (c) hardness of the rubber compounds altered with filler loading.

Furthermore, the obvious increase in modulus and tear resistance indicates a good interaction between the fillers and the rubber matrix. Besides, addition of the nanofillers affected directly hardness of the nanocompounds that the hardness increased with increasing loading concentration of the reinforcing agents. This is because, when a harder material is added into the softer one (NR), the total hardness of the composite increases proportionally with the loading amount of the harder material. The result is in a good agreement with the study of Yue et al. [22].

3.4 Electrical conductivity of the rubbernanocompounds

Fig. 7 demonstrates the alteration in electrical conductivity of the fabricated nanocompounds when various loading levels of MWNT and MMT were introduced. The rubber base exhibited poor electrical conductivity of 1.8 x 10^{-10} s/cm. This property, however, is extremely enhanced when electrically conductive MWNT was solely used as a reinforcing material. This is consistent with the results reported by Sharif et al. [22] and Shankar et al. [23]. Addition of only MMT in the rubber matrix, on the other hand, resulted in a significant reduction of electrical conductivity of the nanocomposites. This is due to the fact that the base NR is very poor electrical conductivity and the natural clay-MMT is a good electrical insulator. Therefore, when the MMT was loaded into the rubber matrix, the total electrical conductivity decreased with the increased nanoclay loading.

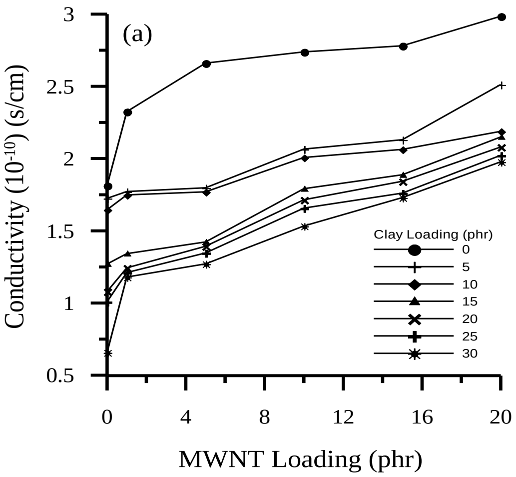

Fig. 7 Electrical conductivity of the as-prepared rubber nanocomposites at various loadings of the hybrid fillers.

The degree of improvement or reduction in electrical conductivity of the according nanocompounds depends strongly on the filler type used and its loading level. Once, MWNT and MMT nanoclay were blended, electrical conductivity of the hybrid filler nanocompounds are hence in between that of MWNT/NR and MMT/NR nanocomposites.

3.5 Dynamic thermal and mechanical analysis of hybrid filler nanocomposites

Dynamic thermal and mechanical properties of the rubber nanocomposites were evaluated in comparison with those of base NR. The presence of MWNT and MMT in the rubber structure enhanced greatly the storage modulus (Fig. 8) and the damping factor or tan δ (Fig. 9) of the nanocomposites. Loading concentration of the hybrid filler, however, affected significantly the magnitude of these two factors. Storage modulus and tan δ increased visibly with the fillers loading. By using 20 phr MWNT and 30 phr MMT, storage modulus increased to a large extent from 3 to 20 MPa at -60 °C and the damping factor raised from 0.2 to 0.35 at an identical temperature indicating a better energy absorber of the material than the base NR under an acute strain environment [24]. Glass transition temperature (Tg) of the hybrid filler compounds, corresponding to the peak temperature of the curves illustrated in Fig. 9, was shifted towards from -60 °C to -50 °C even at a such low loading level (5/5 phr) of the hybrid filler. Similar phenomenon was observed by Peng et al. [25] when MWNT was used as a filler in rubber compounds. The improvement in the storage modulus and Tg suggested an enhanced interfacial adhesion between the polymer chains and the nanofillers (silicate nanoplatelets and MWNT) [25, 26] due to the exfoliated or at least intercalated morphology of the dispersed clay nanoplatelets and MWNT [26]. It is worth to note that, as compared to base NR, the increase in Tg of the hybrid filler nanocomposites is beneficial for an application requiring a higher temperature.

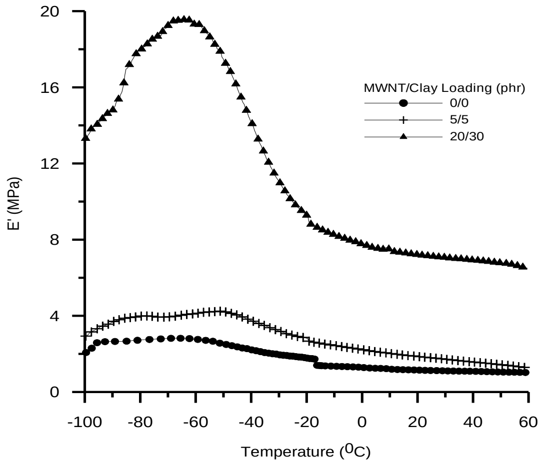

Fig.8 Storage modulus as a function of temperature for base NR and the MWNT/MMT nanocompounds at low and high loading levels of the nanofillers.

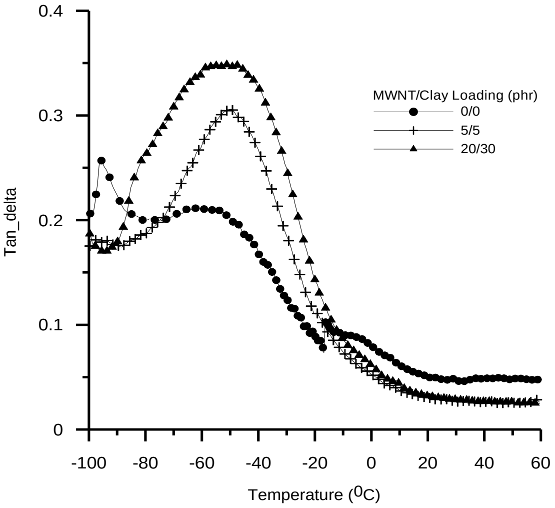

Fig.9 The temperature dependent damping factor for base NR and the MWNT/MMT nanocompositesat low and high loading levels of the nanofillers.

4. Conclusions

Rubber nanocomposites were fabricated at various loadings of hybrid filler MWNT and MMT. The results confirmed an achievement in the improved mechanical, electrical and dynamic thermal and mechanical properties of the hybrid filler nanocompounds that their swelling resistance, modulus, tear strength, hardness, storage modulus and damping factor are superior to those of base NR. Those properties were noticeably enhanced when 20 and 30 phr of MWNT and MMT, respectively, were added into the rubber matrix. The evident improvement in swelling resistance of the hybrid filler materials is believed to be a consequence of the enhancement in crosslink density when the nanofillers were introduced. A significant increase in the elastic modulus, tear resistance, storage modulus and damping factor of hybrid filler nanocomposites suggested an enhanced interaction between polymer chains and the nanofillers as a result of high aspect ratio of the clay nanoplatelets and MWNT consisting in the composite structure. Furthermore, although tensile strength and electrical conductivity of the hybrid filler nanocompounds are considerably increased, the rubber compounds reinforced with only MWNT offered the best tensile strength and electrical conductivity. The presence of the hybrid filler resulted in an increased glass transition temperature (Tg) of the nanocomposites which is useful for a function requiring a higher temperature.

Acknowledgments

The authors are pleased to acknowledge Center of excellence nanotechnology for energy (CENE) and Center of excellence in materials engineering (CEME), Prince of Songkla University, Thailand for their financial supports.

References

[1] N. Rattanasom, S. Prasertsri, T. Ruangritnumchai, Polym. Test **28**, 8(2009).
[2] J.W.t.Brinke, S.C. Debnath, L.A.E.M. Reuvekamp, J.W.M. Noordermeer, Compos. Sci. Tecnol. **63**, 1165(2003).
[3] Q. Liu , Y. Zhang, H. Xu, Appl. Clay Sci. **42**, 232(2008).
[4] A. Ansarifar, A. Azhar, N. Ibrahim, S.F. Shiah, J.M.D. Lawton, Int. J. Adhes. Adhes. **25**, 77(2005).
[5] N. Rattanasom , T. Saowapark, C. Deeprasertkul, Polym. Test26, 369(2007).
[6] A.S. Hashim, B. Azahari, Y. Ikeda, S. Kohjiya, Rubber Chem. Technol. **71**, 289(1998).
[7] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, J. H. Lee, Prog. Polym.Sci. **35**, 1350 (2010).
[8] E.Dervishi, F.Hategekirmana, L. Boyer, F. Wtanabe, M. Fumiya, T. Mustafa, A. Biswas, A.R. Biris, A.S. Biris, Chem. Phys. Lett. **590**, 126(2013).
[9] T. Hasan, V. Scardaci, P.H. Tan, F. Bonaccorso, A.G. Rozhin, Z. Sun, A.C. Ferrari, Nanotube and Graphene Polymer Composites for Photonics and Optoelectronics in Molecular- and Nano-Tubes, Springer US(2011).
[10]L. Ramos-Galicia, L. N. Mendez, Ana Laura Martínez-Hernández, A. Espindola-Gonzalez, I. R. Galindo-Esquivel, R. Fuentes-Ramirez, C. Velasco-Santos, J. Mater. Chem. **21**, 3301(2011).
[11]J. Liang, Y. Wang, Y. Huang, Y. Ma, Z. Liu, J. Cai,C. Zhang, H. Gao, Y. Chen, Carbon **47**, 922(2009).
[12]J.-J. Luo and I. M. Daniel, Compos. Sci. Technol. **63**, 1607(2003).
[13]Y.-P. Wu, Q.-X. Jia, D.-S.Yu, L.-Q. Zhang, Polym. Test **23**, 903(2004).
[14]P. Liu, Appl. Clay Sci.**3 8**, 64(2007).
[15] M. Arroyo, M.A. López-Manchado, J.L. Valentín, J. Carretero, Compos. Sci. Technol. **67**, 1330(2007).
[16]C. Kumnuantip and N. Sombatsompop,Mater. Lett. **57**, 3167(2003).
[17]M. B. a. C. Hepburn, Iran J. Polym. Sci. Technol.**1**, 5(1992).
[18]T.G. Gopakumar, J.A. Lee, M. Kontopoulou, J.S. Parent, Polym. **43**, 5483(2002).
[19]C. Ihemouchen, H. Djidjelli, A. Boukerrou, F. Fenouillot, C. Barres, J.Appl. Polym. Sci. **128**, 2224(2013).
[20]J. Sharif, W. M. Z. W. Yunus, K. Z. Hj. M. Dahlan, M. Hj Ahmad, Polym. Test **24**, 211(2005).
[21]M. Lu, J. Zhou, L. Wang, W. Zhao, Y. Lu, L. Zhang, Y. Liu, Compos. Sci. Technol.

65, 1195(2005).
[22] D. Yue, Y. Liu, Z. Shen, L. Zhang, J. Mater. Sci. **41**, 2541(2006).
[23]R. D. S.S. V. Shankar, B. Vinoth, T. O. Thomas, Int. J. Environ. Sci. Dev. **1**, 181(2010).
[24] Z. Peng, L. X. Kong, S. D. Li, Synth. Met. **152**, 25(2005).
[25]Q. Wang, Y. Luo, C. Feng, Z. Yi, Q. Qiu, L. X. Kong, Z. Peng, Carbon **48**, 4497(2010).
[26] F. Zaïri, J.M. Gloaguen, M. Naït-Abdelaziz, A. Mesbah, J.M. Lefebvre, Acta Mater. **59**, 3851(2011).