

The Effect of Strain in Curing Process on Morphology and Mechanical Properties of Natural Rubber/Organoclay Nanocomposites

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Abstract: - In this paper, two methods were used for the preparation of natural rubber/organoclay nanocomposites including ordinary method and curing under strain. The single networked natural rubber nanocomposites were used as comparison. The effects of organoclay with different extension ratio on mechanical properties, hardness, swelling behaviour and morphology of ordinary and extended natural rubber nanocomposites were studied. The results showed that extended natural rubber nanocomposites exhibit higher physical and mechanical properties. The tensile strength of extended natural rubber nanocomposites increased up to more 4 times than pure natural rubber and then decreased with increasing extension ratio. Modulus and hardness continuously increased with increased extension ratio. The microstructure of the natural rubber/organoclay systems was studied by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Following, the effect of different extension ratios on dispersion of nanoclay layers in nanocomposites were investigated.

Keywords: - Natural Rubber, Organoclay, Curing, Nanocomposite, Microstructure, Mechanical Properties.

I. INTRODUCTION

Natural rubber is used as the most applicable rubber in many engineering applications and need to reinforce it. The fillers such as carbon black, clays, and calcium carbonate are added to rubber formulation in order to optimize properties needed for service application [1]. Achieving a method in which the filler be dispersed adequately in polymer matrix is always a challenge in polymer processing. The most important factor indicating an improvement of properties in rubber by adding nanofiller is dispersion of it in the rubber matrix. The main aspect in preparing nanoclay nanocomposites is the degree of dispersion of nanofiller. This can significantly improve the overall properties of the nanocomposites.

One of the most important phenomena in polymer science is the reinforcement of rubber by nanoclay. Nanoclay is a kind of commonly used nanoscale filler used for polymers due to excellent mechanical, barrier and thermal stability achieved by adding it in polymer composite. Recently, researchers have focused their investigations on rubber-clay nanocomposites due to the significant improvement in physical-mechanical properties [2,3], thermal stability [4,5], gas permeability [6,7] and flammability [8,9]. Layered silicates on nanoscale size are effective reinforcements for rubber materials [10-13].

Recently, the largest number of studies is devoted to production of NR nanocomposite by using Cloisite 10A and Cloisite 15A [14], with aliphatic and aromatic modified montmorillonite [15], octadecylammonium modified montmorillonite [16], modified vermiculite [17], modified montmorillonite [18,19] Cloisite 30B and Nanomer I.30P [20] and bentonite [21]. Based on these reports, the use of organically modified nanoclay could also be noted as an inorganic filler to improve the mechanical performance of NR. Other researchers have investigated the effect of using nanoclay in various rubbers.

An extended structure is formed when the partially crosslinked elastomer is further crosslinked in a state of straining. An extended elastomer refers to rubber crosslinked twice, the second time while in a deformed state. While extended rubbers can be formed inadvertently due to chain scission or strain-induced crystallization, the potential for improved mechanical properties in such materials has elicited much interest

[22]. The modulus and mechanical properties of extended NR increases with extension ratio [22, 23, 24]. Thus, when appropriately prepared, double networks can have higher mechanical properties than single networks of the same modulus.

In this article, two methods were used for the preparation of natural rubber/nanoclay nanocomposites including ordinary method and extended NR nanocomposite. Comparatively many studies have been published on the mechanical behaviour of the single network rubbers. Recently, it has been reported that the ultimate tensile strength of the extended NR is somewhat invariant to residual strain, or even improved in the direction of residual strain notwithstanding the higher tensile modulus [22, 23]. It has also been reported that the mechanical fatigue resistance of the extended NR perpendicular to the cure stretching direction was greatly enhanced, about ten times, compared with that of a conventionally crosslinked one.

NR/nanoclay nanocomposites were prepared by sample shear mixing. The effect of extension ratio on the morphology, mechanical properties and swelling resistance (solvent resistance) of NR was investigated in terms of X-ray diffraction, rheometric and mechanical analysis. The extended natural rubber exhibited enhanced mechanical performance in comparison to single networks. Associated with rubber compounds prepared in common method numerous reports are presented, that these reports was reviewed and summarized. Until today any report of production of extended nanocomposite has not spread. In this regard, there are few reports in relation to traditional composites based on natural rubber, styrene – butadiene rubber (SBR), isoprene rubber (IR) and polybutadiene rubber (BR) is presented. In these systems, reinforcing agent was carbon black but use of nanoclay by nanolayered structure it has remained hidden from the eyes of researchers. In this paper, the effect of nanoclay on morphology and mechanical performance NR nanocomposites prepared by extension are investigated.

II. EXPERIMENTAL

Materials

The commercially available NR used in this study was ribbed smoked sheet (RSS) No. 1 with mooney viscosity ML [1+4,100]=80 from Indonesia. Organically modified montmorillonite (nanoclay) was purchased from Southern Clay Products (Gonzales, TX) under the trade name of Cloisite 15A. This nanoclay was modified by dimethyl dihydrogenated tallow quaternary ammonium with a concentration of 125 mequiv/100 g of clay. The curing additives (zinc oxide, stearic acid, sulfure) were purchased from Iranian suppliers (analytical grade). Dibenzothiazyl disulfide (MBTS) and IPPD 4010NA antioxidant from Bayer Company and toluene for swelling experiment was supplied by Merck.

Preparation of NR nanocomposites

All the rubber nanocomposites were prepared on a two roll mill of 300 mm length, 170 mm diameter with friction ratio 1.4 operated at room temperature.

For mixing the ingredients of the nanocomposites, firstly natural rubber was masticated, and then nanoclay were added and mixed. Then zinc oxide, stearic acid and antioxidant were added to the compound. After mixing, the rubber compounds were left for 8 h and then sulfure, accelerator was added. The extended NR nanocomposite was prepared by a two-step crosslinking method, in which the crosslinking was achieved while the NR was in a stretched condition. In the first step, the rubber sheet was cured partially for 10 min at 150°C under a pressure of 10 Mpa. In the second step, the partially crosslinked rubber sheet was uniaxially stretched to various desired lengths (extension ratio) using a metal holder. The stretched sheet was placed in a vacuum oven for 70 min at 135 °C. The fully cured rubber sheet was then placed in air at room temperature for 24 h. Finally, the extended nanocomposites were obtained by releasing the strain.

III. CHARACTERIZATION

X-ray Diffraction

To study the degree of dispersion of the nanoclay and increase in clay intergallery space in the rubber composites, XRD studies were done using a PHILIPS X-PERT PRO diffractometer in the range of $2\theta = 1-10^\circ$ and using Cu target ($\lambda = 0.154$ nm). In this experiment, acceleration voltages of 40 kV and beam current of 40 mA were used, and the scanning rate was maintained at $2^\circ/\text{min}$. The d -spacing of the nanoclay particles were calculated using the Bragg's law ($\lambda=2d\sin\theta$).

Cure Characteristics

Curing characteristics of nanocomposites were measured according to ASTM D2084-95 [24] by using Oscillating Disc Rheometer (Monsanto Rheometer 100) operated at 150 °C with 3° arc oscillation angle. Scorch time (t_2), optimum cure time (t_{95}), and also the minimum torque (M_L), maximum torque (M_H) and the difference between minimum and maximum torque (ΔM) of rheometry were determined.

Mechanical Properties

The mechanical behavior including the tensile strength, modulus, percentage elongation at break of the NR nanocomposites was investigated by the tensile test. Tensile properties were measured on dumbbell shaped specimens punched out from the molded sheets. The tests were carried out as according to the ASTM D-412 method in a Universal Testing Machine (Zwick-Roel, model Z050, Germany). Tests were carried out at room temperature and cross-head speed of 500 mm/min. Result of tensile test for each sample was recorded as the average of three repeated observations. A Zwick hardness tester was employed according to ASTM D2240 for measuring hardness of the prepared samples.

Swelling Measurements

Swelling test in toluene solvent was conducted for the rubber compounds. Samples of $25 \times 15 \times 2 \text{ mm}^3$ were used to determine the swelling behavior of vulcanized rubber according to ASTM D 471-06. Initially, the dry weight of the samples was measured. Then, the samples were immersed in toluene at 25°C for 72 h; the swollen weight of the samples was recorded for the determination of the swelling ratio and cross link density. The samples were periodically removed from the test bottles, the adhering solvent was cleaned from the surface, and the samples were weighed immediately. The degree of equilibrium can be used to quantify swelling ratio, non-mechanical property, cross linking density, and chemical interaction between the polymer and nanoparticle [24]. The swelling ratio can be calculated by the following equation [25]:

$$\text{Swelling Ratio} = \frac{m_s - m_d}{m_d} \quad (1)$$

Where m_d and m_s are the initial weight of dry rubber and the weight of solvent adsorbed by the sample, respectively.

Field Emission Scanning Electron Microscopy

A Field Emission Scanning Electron Microscope (FE-SEM; Hitachi microscope Model S-4160, voltage 15 kV, Japan) was used to study the morphology of the rubber nanocomposites fractured surfaces. Before the tests, the samples were fractured in liquid nitrogen. Afterward, the fracture surface was coated with gold and observed by FE-SEM.

IV. RESULTS AND DISCUSSION

Morphological Studies on NR Nanocomposites

X-ray diffraction analysis has been utilized for the studying the morphology of produced nanocomposites. The XRD pattern of nanoclay revealed a characteristic diffraction peak at $2\theta = 2.8^\circ$, corresponding to a basal spacing of 3.15 nm. The XRD pattern of pure NR showed any characteristic diffraction peak. The nanocomposite containing 5 phr (parts per hundred parts of rubber) nanoclay has the d-spacing of 3.99 nm. This indicates the penetration of polymeric chains into silicate galleries resulting an increment of d-spacing to about 0.75 nm compared to nanoclay (Fig. 1).

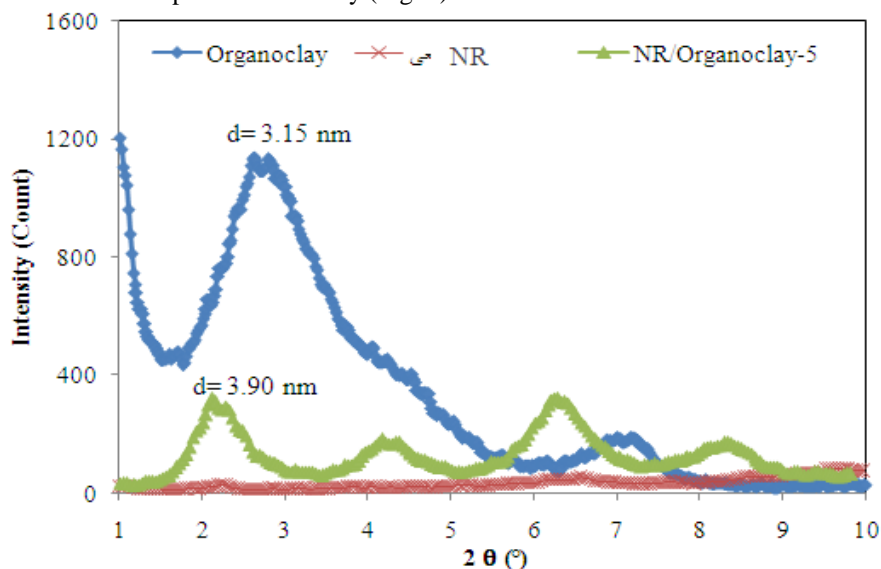


Fig. 1- X-Ray diffraction patterns of nanoclay, pure NR and NR/nanoclay (5 phr) nanocomposites.

The mechanical properties of natural rubber nanocomposites containing 5 phr nanoclay that have been prepared by different extension ratios (α) are presented in figures 2, 3, 4 and 5. Accordingly, the tensile strength of natural rubber would boost considerably (about 3-times) by adding nanoclay. Although the improvement of tensile strength in NR nanocomposites was shown in other papers [22,23,26], its 3 times improvement has been rarely reported. The outcomes of the tensile test are fully compatible with the rheometric findings.

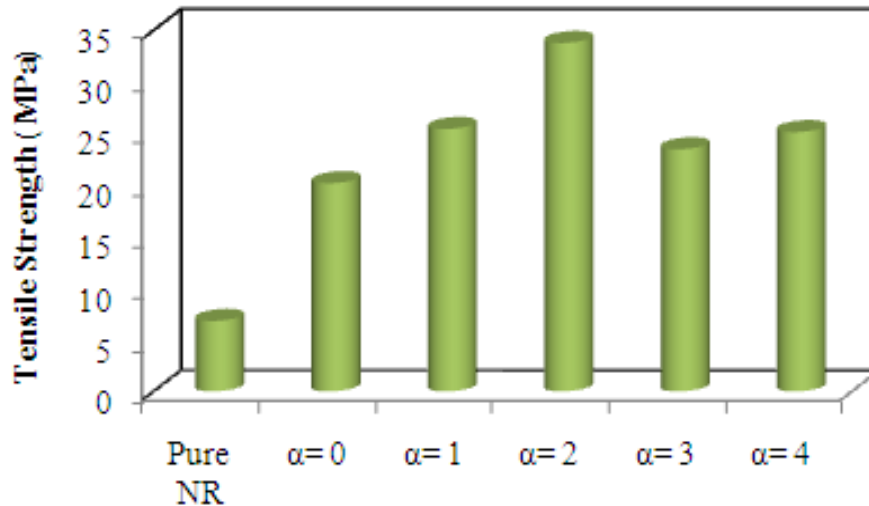


Fig.2- Tensile strength of pure NR and extended NR nanocomposites by different stretching ratios.

The tensile strength would maximise to its highest point (about 33 MPa) by $\alpha=2$, as the extension ratio increases through the cure process of nanocomposites. This amount is about 6 times higher than pure natural rubber. The remarkable improvement of tensile strength in these nanocomposites can be due to the orientation of polymer chains and silicate nanolayers throughout curing process. Also these chains and nanolayers can be more oriented during the tension test and cause remarkable improvement in tensile strength. On this basis the synergistic effect can be realized in these nanocomposites. That would occur because of the reinforcing effect of silicate nanolayers and also the orientation of chains and nanolayers during the cure process.

The tensile strength diminishes by raising the extension ratio for $\alpha=3$ and 4 times. Reduced properties in higher α value can be related to the extra free volume in the system, the separation of chains from the surface and gallery spacing of layers and even to the break off of cross links in network. By adding nanoclay to natural rubber, the modulus that is, somehow, the resistancy of matter against deformation will grow significantly (about 3 times) (Fig. 3). The growing extension ratio can cause a constant and duplex increase in the modulus of produced nanocomposites.

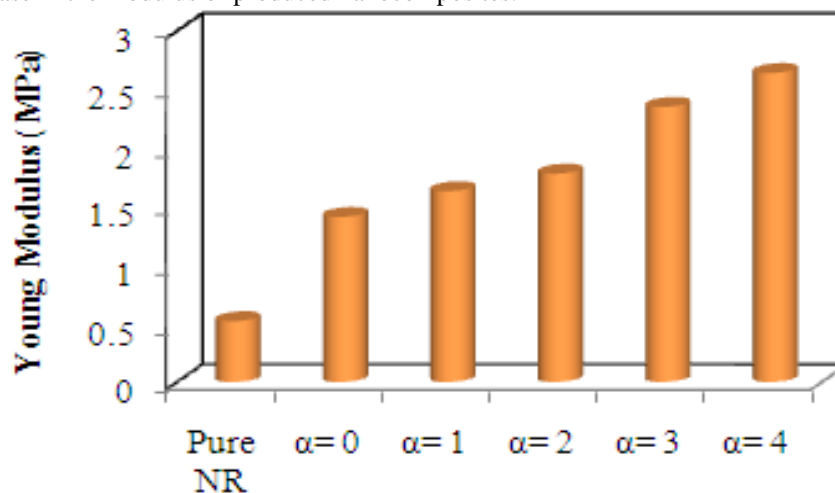


Fig.3- Young Modulus of pure NR and extended NR nanocomposites by different stretching ratios.

The elongation at break of nanocomposite samples is lower than that of pure NR (Fig. 4). A significant rise in the trend of elongation of the extended NR nanocomposites is observed as the extension ratio boosts up to $\alpha=2$.

The greater α values are, the more significantly reduced elongation at break will be obtained. This remarkable reduction in elasticity of nanocomposites (by $\alpha=3$ and 4) is due to the harmful effects of pre-stretching process that causes the loss of chain entanglements, failure of cross links and separation of the chains on surface and gallery spacing of layers. The same trend was observed in the tensile strength of nanocomposite samples.

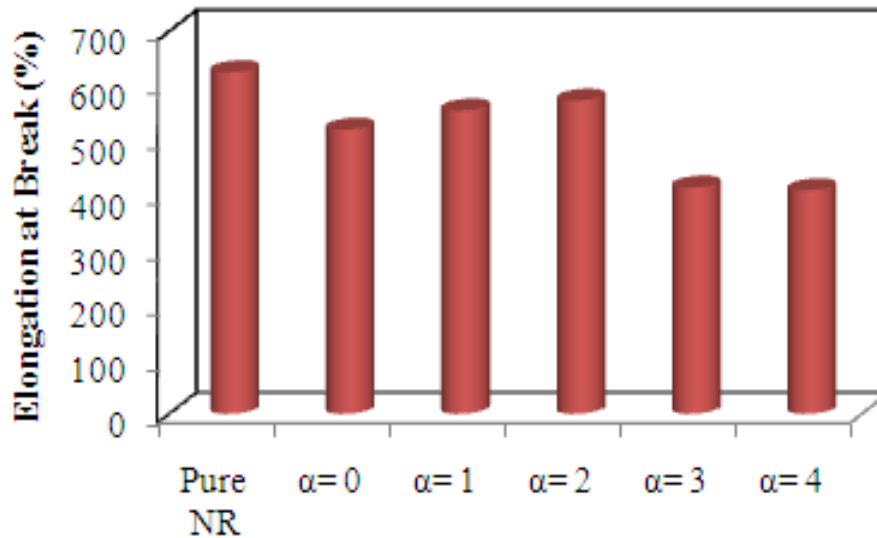


Fig.4- Elongation at break of pure NR and extended NR nanocomposites by different stretching ratios.

The hardness of NR is also significantly incremented by adding nanoclay. Accordingly, by adding 5 Phr nanoclay, its hardness heightens from 43 to 48. Moreover, the hardness of extended nanocomposites will be added uniformly by growing the extension ratio, and this is consistent with other mechanical results (Fig. 5). Further orientation of chains in the vicinity of nano-layers is the reason for the incremented hardness of the nanocomposites.

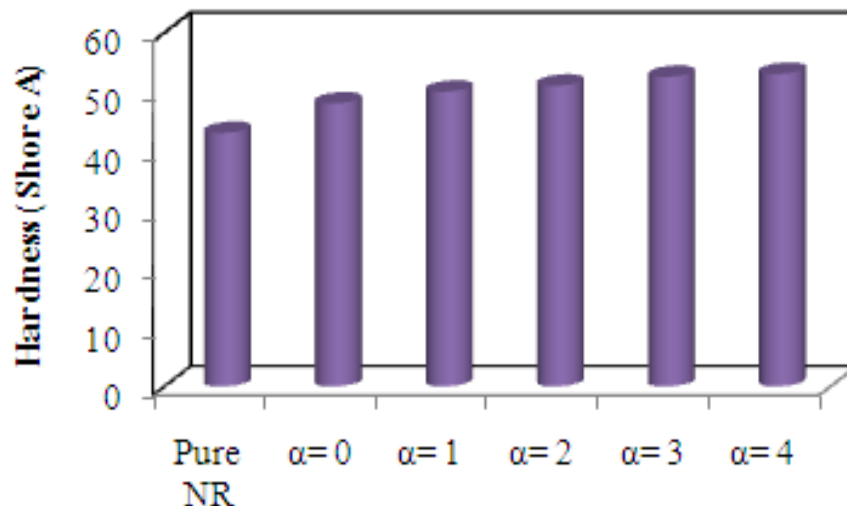


Fig.5- Hardness of pure NR and extended NR nanocomposites by different stretching ratios.

Swelling Behavior of NR nanocomposites

The degree of adhesion between polymer chains and filler particles can be evaluated from equilibrium swelling of the composites in good solvents. The extent of swelling at equilibrium is reduced in the case of adsorption of polymer chains on particle surfaces [27].

The sorption curves of nanocomposites filled with nanoclay versus time obtained by plotting Q_t (the weight-swelling ratio) in toluene at room temperature. The swelling test results for pure NR, ordinary nanocomposite and extended nanocomposites which have different extension ratio are illustrated in Fig. 6. Addition of nanoclay to NR leads to dramatic declines in the swelling ratio and swelling rate. Addition of nanoclay can be greatly increment the rubber swelling resistance against penetration of solvent.

This is due to the favorable interactions and also high surface area of nanoparticles with the polymer chains that prevents swelling and solvent penetration into the matrix. By extension of rubber, significant changes will be led in the swelling rate and the equilibrium swelling ratio of prepared nanocomposites (Fig. 6).

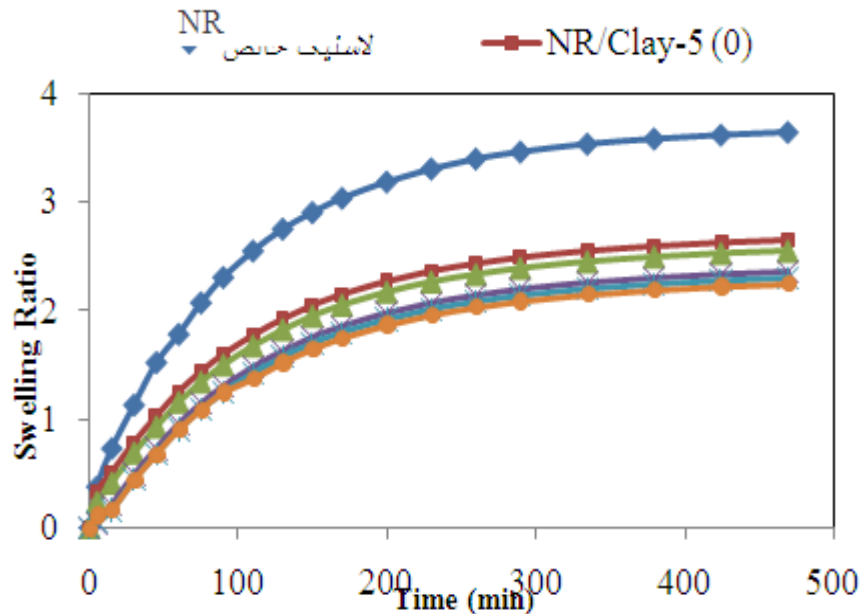


Fig. 6- Swelling behavior of pure NR and extended NR nanocomposites by different stretching ratios (The numbers in parentheses indicate the extension ratio)

Increasing extension ratio in the nanocomposites, the swelling ratio is reduced and this cause a maximum change for $\alpha=2$, where for higher extension ratios, the swelling ratio does not change a bit. You should note that the swelling ratio is a criterion of the degree of cross links in a system. Although this phenomenon shows that the real cross link density is constant, but applying the extension on the samples will causes the apparent cross link density to increase. In other words, since the composition is same in all nanocomposites, this increased cross link density correlates the boosted interactions between nanoparticles and polymeric chains (high-level contact area of nanoparticle with matrix) and also the decrement of free volume in the matrix is due to the orientation and the more compact arrangement of the chains. Therefore, It can be said that the cross link density would be higher for the extended nanocomposites. Using this idea to produce of NR nanocomposites without requiring a higher content of nanoparticles can boost solvent resistancy of NR.

Improving the solvent resistancy of these nanocomposites is due to the existence of hard filler phase and impermeable to the solvent molecules [27]. Also it is brought out by orientation of chains and nanolayers in the stretch direction and subsequently the reduction of free volume and development of interfacial area.

Dynamic-Mechanical Properties of NR Nanocomposites

Dynamic-Mechanical analysis is measure of material response under dynamic deformation. In other words this test is used to measure viscoelastic properties of materials in terms of temperature or frequency [28]. Changes in the storage modulus shown in terms of temperature for NR and their nanocomposites are presented in Fig. 7 and 8.

Increasing the nanofiller content, storage modulus in the glassy region (below the glass transition temperature) develops. Based on the presented curves, it can be seen that 5 phr nanoclay can dramatically develops storage modulus in the glassy, glass transition and rubbery regions. The developments of modulus are due to the decreased chain mobility in persence of hard nanofiller. When the rubber chains intercalated into gallery spacing, rubber confined within such space, so the effective volume fraction of filler is developed in the nanocomposite that this is a reason for the higher storage modulus in intercalated nanocomposite.

Applying extension on nanocomposites and the growth of extension ratio, the storage modulus in glassy region improves. Although surpassing the critical stretch ratio, the storage modulus is reduced for the nanocomposite with the extension ratio $\alpha=4$.

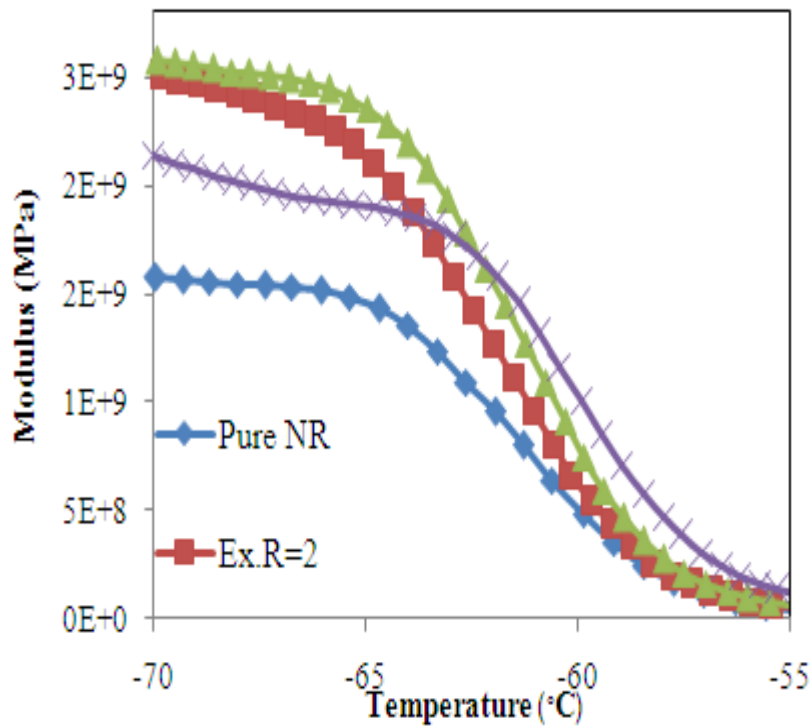


Fig. 7- Storage modulus of pure NR and extended NR nanocomposites in term of temperature.

Due to the hydrodynamic effects of filler in the glass transition region, the storage modulus of nanocomposite is more than pure NR. However, it should be noted that the difference in module in this region is less than the glassy region.

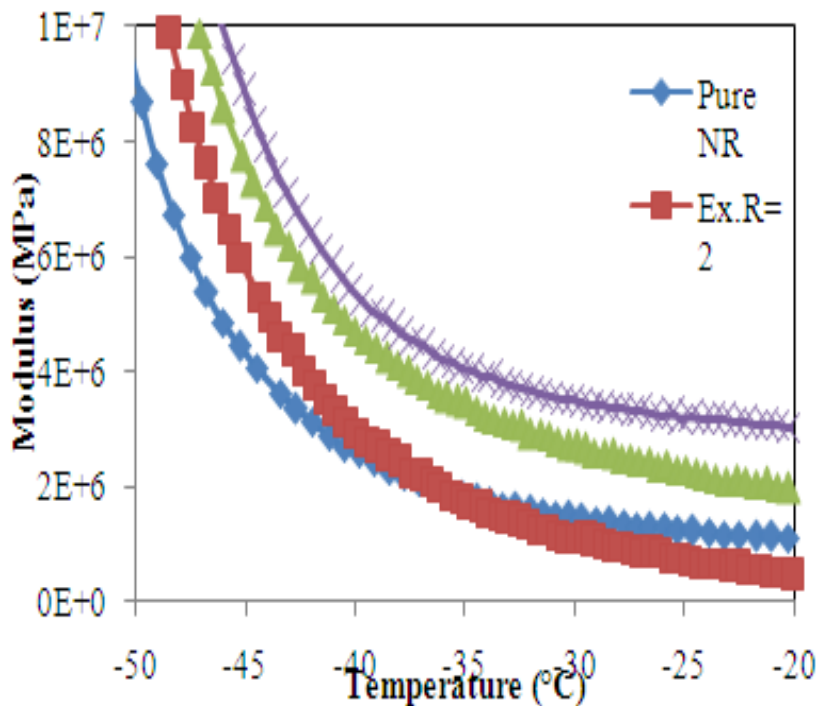


Fig. 8- Storage modulus of pure NR and extended NR nanocomposites in rubbery region.

Mechanical Loss Factor (Tan δ)

Important information can be obtained from plots mechanical loss factor in term of temperature (Tan δ-T) in the glass transition region. Another sign of the degree creating bond between the matrix and the filler can be

obtained from these curves [29]. In other words, a further hint of the degree of bonding between the matrix and the nanofiller can be derived from the $\text{Tan } \delta$ vs. temperature curves. According to the effect of filler, this parameter is considered as the ratio of fraction of the filler structure that breaks under dynamic strain to fraction that will remain unchanged [30]. The smaller peak for glass transition temperature shows the higher performance of filler.

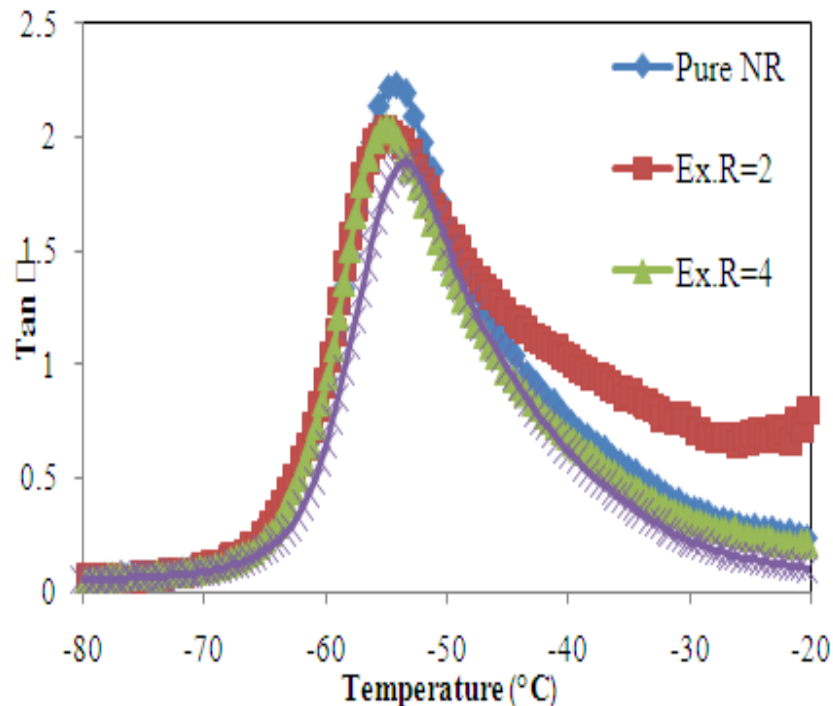


Fig. 9- Mechanical loss factor of pure NR, extended and ordinary NR nanocomposites in term of temperature.

Changes of the glass transition temperature caused by adding nanoclay and the loss factor ($\text{Tan } \delta$) of NR are illustrated in Fig. 9. The height of $\text{Tan } \delta$ peak declines after addition of nanoclay.

Reduction of $\text{Tan } \delta$ is due to decrement of deformable polymer content under oscillatory strain, that's a result of trapping a part of chains between the nanolayers and thus reduce the energy loss capability in the sample. Greater polymer - filler interaction improves the elasticity of nanocomposite, which can lead to a lower $\text{Tan } \delta$ peak height [31].

Throughout the temperature range, nanocomposite curve is lower than that of pure NR meaning that ordinary nanocomposite has lower loss energy capability than pure NR. Reduced chain mobility is caused by physical adsorption of chains on the surface of nanofiller, which reduce the height of transition temperature peak.

The decrease in the height of transition temperature peak as a result of adding of nanoclay has also been reported in many articles before [32-34]. The extended nanocomposites behave similarly as pure NR does in glassy region, based on the energy dissipation capability. In glass transition region, these nanocomposites have intermediate behavior of pure NR and ordinary NR nanocomposite.

Whereas in glassy region, the energy dissipation capability of ordinary nanocomposite is lower than the pure rubber due to lower segmental motion of chains. Nanoclay can greatly reduce the energy dissipation capability of chains throughout temperature region. This shows the limited mobility of chains, trapped between layers of nanoclay, as well as interfacial interactions.

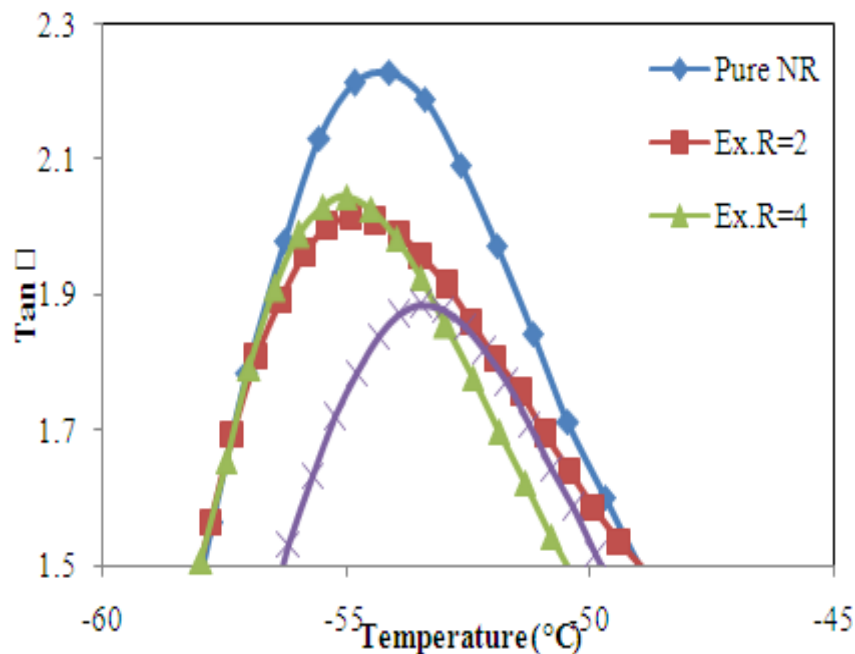


Fig. 10- Mechanical loss factor of pure NR, extended and ordinary NR nanocomposites in glass transition region.

As shown in Fig. 10, rising temperature and surpassing the glass transition region, extended nanocomposite would obtain more dissipation energy ability, with optimum extension ratio, than other nanocomposites and pure NR. This phenomenon can be regarded as positive and remarkable aspects of using this method in producing reinforced nanocomposites by nanoclay. In other words, nanocomposite obtains a very good energy dissipation capability. This shows the strong physical network in extended nanocomposite. Whereas after passing the glass transition temperature and reaching the rubbery region, the energy dissipation capability of nanocomposites is more than that of pure NR and this is due to the failure of physical network in the rubbery state. So we conclude that following idea can give a higher energy dissipation capacity to natural rubber, especially at above the glass transition temperature.

Field Emission Scanning Electron Microscopy

Investigation of filler dispersion in the matrix and the effect of nanoclay on the morphology were studied by the Field Emission Scanning Electron Microscope (FE-SEM). FE-SEM images of ordinary nanocomposite containing 5 phr nanoclay are shown in Fig. 11. Here, distribution of nanoparticles in micron range is illustrated. For ordinary nanocomposite, the nanoparticles have not been well dispersed in the matrix and can be seen filler agglomeration. Such dispersion of nanofiller would be inappropriate to achieve the desired mechanical properties.

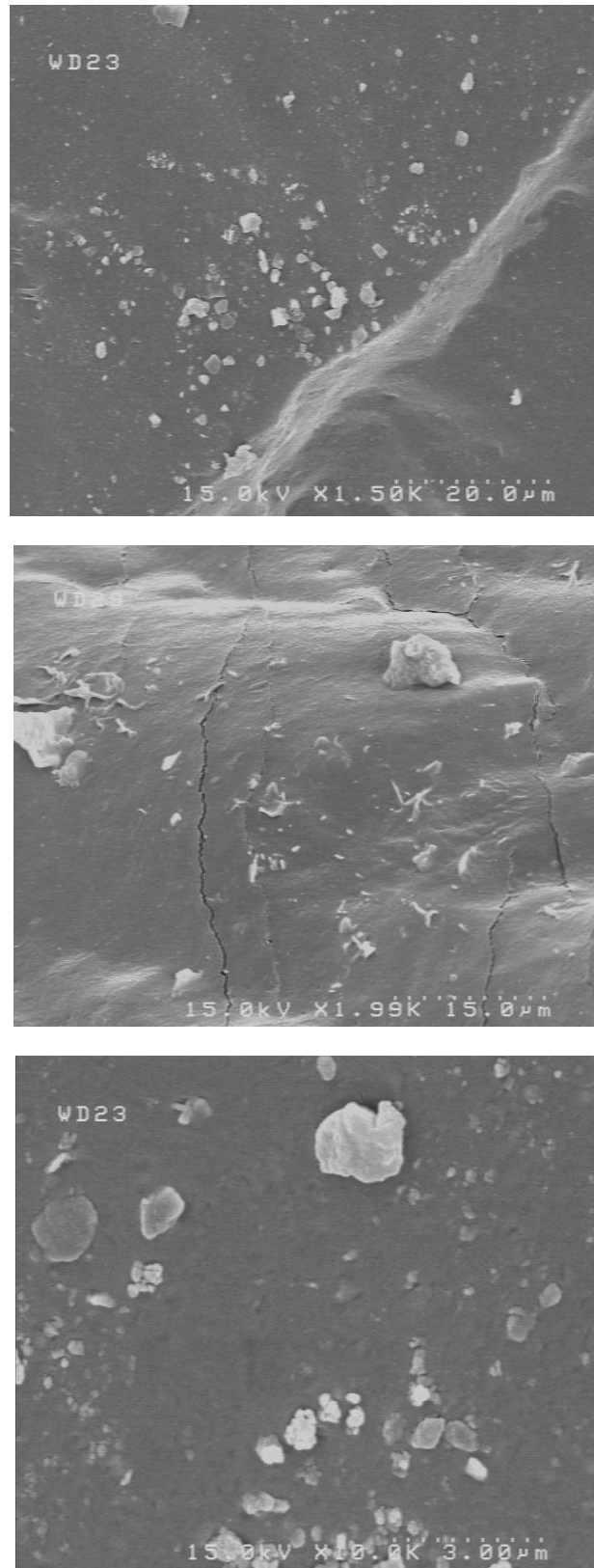


Fig. 11- FE-SEM micrograph of ordinary NR nanocomposite at various magnifications.

Fig. 12 shows that extension of samples under the curing process can improve the dispersion of nanoclay in NR matrix. There have been no agglomeration from nanoparticles and ideal morphology created for NR nanocomposite. Such dispersion of nanoclay in NR matrix reasons for the more desirable mechanical properties of extended nanocomposite rather than ordinary nanocomposite.

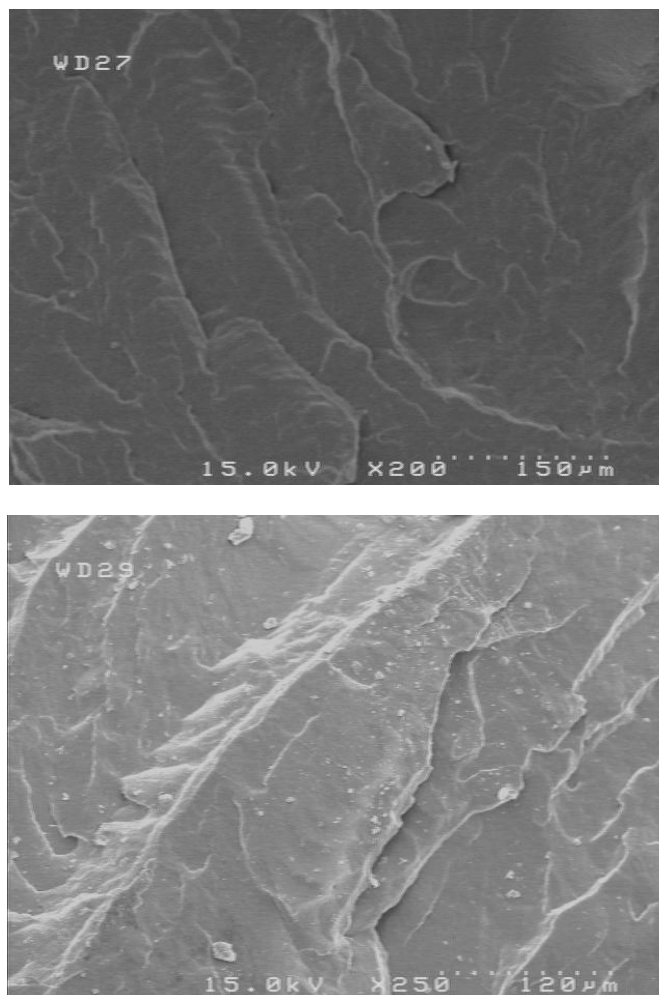


Fig. 12- FE-SEM micrograph of extended NR nanocomposite at various magnifications.

V. CONCLUSIONS

In this paper, two methods were used for the preparation of NR/nanoclay nanocomposites including ordinary method (single network NR nanocomposite) and extended NR nanocomposites. The effect of these two methods on the morphology, rheometry, and mechanical behaviors of natural rubber nanocomposites have been evaluated. The obtained results reveal that nanocomposites reinforced by extended structure have more adequate morphology, rheometry and mechanical behaviors as well as swelling resistance. It can be concluded that can be prepared nanocomposites with high strength and mechanical properties by using this method. Whereas the nanocomposites prepared by ordinary melt intercalation have lower strength. Incorporation of 5 phr nanoclay in NR and use of extension idea cause better dispersion and orientation of clay nanolayers. From curing study, faster scorch time, cure time and increase in maximum torque had been observed compared to pure NR. The effect of different extension ratios on dispersion of nanoclay layers in nanocomposites showed that the optimized value of extension ratio in extended NR nanocomposites was equal to 2.

VI. ACKNOWLEDGEMENT

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VII. REFERENCES

- [1] F. W. Barlow, Rubber Compounding Principles, Materials, and Techniques, New York: Marcel Dekker, Inc., 1988.

- [2] Lopez-Manchado M., Herrero B. and Arroyo M., Preparation and Characterization of Organoclay Nanocomposites Based on Natural Rubber, *Polym. Int.*, 52, 1070–1077, 2003.
- [3] Sun Y., Luo Y., Jia D., Preparation and Properties of Natural Rubber Nanocomposites with Solid-State Organomodified Montmorillonite, *J. Appl. Polym. Sci.*, 107, 2786–2792, 2008.
- [4] Wang S., Zhang Y., Peng Z., Zhang Y., Morphology and Thermal Stability of BR/Clay Composites Prepared by a New Method, *J. Appl. Polym. Sci.*, 99, 905–913, 2006.
- [5] Denardin E.L.J., Samios D., Janissek P.R., deSouza G.P., Thermal Degradation of Aged Chloroprene Rubber Studied by Thermogravimetric Analysis, *Rub. Chem. Technol.*, 74, 622–630, 2001.
- [6] Teh P. L., Mohd Ishak Z. A., Hashim A. S., Karger-Kocsis J., Ishiaku U. S., On the Potential of Organoclay with Respect to Conventional Fillers (Carbon Black, Silica) for Epoxidized Natural Rubber Compatibilized Natural Rubber Vulcanizates, *J. Appl. Polym. Sci.*, 94, 2438–2445, 2004.
- [7] Choudalakis S. and Gotsis A.D., Permeability of Polymer/Clay Nanocomposites: A Review, *Eur. Polym. J.*, 45, 967–984, 2009.
- [8] Zhang H., Wang Y., Wu Y., Zhang L., Yang J., Study on Flammability of montmorillonite/Styrene-Butadiene Rubber (SBR) Nanocomposites, *J. Appl. Polym. Sci.*, 97, 844–849, 2005.
- [9] Liu L., Jia D., Luo Y., Li B., Structure and Flammability Properties of NR-Organoclay Nanocomposites, *Polym. Compos.*, 30, 107–110, 2009.
- [10] R. Rajasekar, Kaushik Pal, Gert Heinrich, Amit Das, C.K. Das, Development of nitrile butadiene rubber–nanoclay composites with epoxidized natural rubber as compatibilizer, *Materials and Design*, 30, 3839–3845, 2009.
- [11] B. T. Poh, P. G. Lee, S. C. Chuah, Adhesion property of epoxidized natural rubber (ENR)-based adhesives containing calcium carbonate, *eXPRESS Polymer Letters*, Vol. 2, No.6, 398–403, 2008.
- [12] Varghese S., Karger-Kocsis J., Melt-Compounded Natural Rubber Nanocomposites with Pristine and Organophilic Layered Silicates of Natural and Synthetic Origin, *J. Appl. Polym. Sci.*, 91, 813–819, 2004.
- [13] Madhusoodanan K. N., Varghese S., Technological and Processing Properties of Natural Rubber Layered Silicate-Nanocomposites by Melt Intercalation Process, *J. Appl. Polym. Sci.*, 102, 2537–2543, 2006.
- [14] A. Jacob, P. Kurian, A. S. Aprem, Cure Characteristics and Mechanical Properties of Natural Rubber–Layered Clay Nanocomposites, *International Journal of Polymeric Materials*, 56, 593–604, 2007.
- [15] F. Avalos, J. C. Ortiz, R. Zitzumbo, M. A. L. Manchado, R. Verdejo, M. Arroyo, Effect of montmorillonite intercalant structure on the cure parameters of natural rubber, *European Polymer Journal*, 44, 3108–3115, 2008.
- [16] M. Arroyo, M. A. L. Manchado, B. Herrero, Organo-montmorillonite as substitute of carbon black in natural rubber compounds, *Polymer*, 44, 2447–2453, 2003.
- [17] Y. Zhang, W. Liu, W. Han, W. Guo, C. Wu, “Preparation and Properties of Novel Natural Rubber/Organo-Vermiculite Nanocomposites”, *Polym. Compos.*, 30, 38–42, 2009.
- [18] M. A. L. Manchado, B. Herrero and M. Arroyo, Organoclay–natural rubber nanocomposites synthesized by mechanical and solution mixing methods, *Polym. Int.*, 53, 1766–1772, 2004.
- [19] L. Qu, G. Huang, Z. Liu, P. Zhang, G. Weng, Y. Nie, Remarkable reinforcement of natural rubber by deformation-induced crystallization in the presence of organophilic montmorillonite, *Acta Materialia*, 57, 5053–5060, 2009.
- [20] S. Varghese, J. K. Kocsis, Melt-Compounded Natural Rubber Nanocomposites with Pristine and Organophilic Layered Silicates of Natural and Synthetic Origin, *J. Appl. Polym. Sci.*, 91, 813–819, 2004.
- [21] K. N. Madhusoodanan, S. Varghese, Technological and Processing Properties of Natural Rubber Layered Silicate-Nanocomposites by Melt Intercalation Process, *J. Appl. Polym. Sci.*, 102, 2537–2543, 2006.
- [22] Abi Santhosh Aprem, Kuruvilla Joseph, Sabu Thomas, Studies on Double Networks in Natural Rubber Vulcanizates, *J Appl Polym Sci* 91: 1068–1076, 2004.
- [23] Shinyoung Kaang and Changwoon Nah, Fatigue crack growth of double-networked natural rubber, *Polymer* Vol. 39 No. 11, 2209–2214, 1998.
- [24] J. Shah, Q. Yuan, R. D. K. Misra, Synthesis, Structure and Properties of a Novel Hybrid Bimodal Network Elastomer with Inorganic Cross-Links: The Case of Silicone–Nanocrystalline Titania, *Materials Science and Engineering A*, 523, 199–206, 2009.
- [25] L. H. Sperling, Introduction to Physical Polymer Science, 4th ed. Wiley: New York, 472–473, 2006.
- [26] Shinyoung Kaang, Donghwa Gong, Chang Nah, Some Physical Characteristics of Double-Networked Natural Rubber, *J Appl Polym Sci* 65: 917–924, 1997
- [27] H. Sadeghi Ghari and Z. Shakouri, Natural rubber hybrid nanocomposites reinforced with swelled organoclay and nano-calcium carbonate, *Rubber Chemistry and Technology*, Vol. 85, No. 1, (2012).
- [28] S. Pavlidou, C. D. Papaspyrides, A review on polymer–layered silicate nanocomposites, *Progress in Polymer Science*, 33, 1119–1198, 2008.

- [29] S. Varghese, J. Karger-Kocsis, K.G. Gatos, Melt compounded epoxidized natural rubber/layered silicate nanocomposites: structure-properties relationships, *Polymer* 44, 3977–3983, 2003.
- [30] Y. T. Vu, J. E. Mark, L. Pham, M. Engelhardt, Clay Nanolayer Reinforcement of cis-1,4-Polyisoprene and Epoxidized Natural Rubber, *J. Appl. Polym. Sci.*, 82, 1391–1403, 2001.
- [31] S. Praveen, P. K. Chattopadhyay, S. Jayendran, B. C. Chakraborty, S. Chattopadhyay, Effect of Rubber Matrix Type on the Morphology and Reinforcement Effects in Carbon Black-Nanoclay Hybrid Composites- A Comparative Assessment, *Polym. Compos.*, 31, 97–104, 2010.
- [32] S. Pradhan, F. R. Costa, U. Wagenknecht, D. Jehnichen, A. K. Bhowmick, G. Heinrich, Elastomer/LDH nanocomposites: Synthesis and studies on nanoparticle dispersion, mechanical properties and interfacial adhesion, *European Polymer Journal*, 44, 3122–3132, 2008.
- [33] R. Rajasekar, K. Pal, G. Heinrich, A. Das, C.K. Das, Development of nitrile butadiene rubber–nanoclay composites with epoxidized natural rubber as compatibilizer, *Materials and Design*, 30, 3839–3845, 2009.
- [34] P. Li, L. Wang, G. Song, L. Yin, F. Qi, L. Sun, Characterization of High-performance Exfoliated Natural Rubber/Organoclay Nanocomposites, *J. Appl. Polym. Sci.*, 109, 3831–3838, 2008.