



INVESTIGATION OF ABRASION AND MORPHOLOGY OF RUBBER/NANO TITANIUM OXIDE NANOCOMPOSITES

Alireza Yekrangi¹, Mohammad Afrasiabi², Ameneh Langari³ and M. K. Hafshejani⁴

¹Ramsar Branch, Islamic Azad University, Ramsar, Iran

²Materials Department, University of Sistan and Baluchestan, Iran

³Bojnurd University of Medical Sciences, Bojnurd, Iran

⁴Shahrekord University of Medical Sciences, Shahrekord, Iran

E-Mail: maryam.keivani@yahoo.com

ABSTRACT

Rubber/Titanium oxide nanocomposites might be considered as potential materials in medical and industrial applications due to the flexibility of the polymer and antibacterial properties of nanometric additive. In this research paper, the morphology and physical properties of nanocomposites based on Styrene Butadiene rubber have been investigated in the presence of nano titanium oxide additive. The nanocomposites have been prepared by mechanical blending using two roll mills. Nano Titanium oxide particles have been added to Styrene Butadiene rubber and the abrasion and thermal properties have been surveyed. Optical microscopic observation and scanning electron microscopic pictures have been used to investigate the morphology of nanocomposites based on rubber. Abrasion test results showed that the nano Titanium oxide particles could enhance the abrasion resistance of Styrene Butadiene rubber matrix due to appropriate properties of nano Titanium oxide particles.

Keywords: styrene butadiene rubber, titanium oxide, abrasion, morphology.

INTRODUCTION

Polymer materials could be used in various fields especially as the matrix in reinforced composite materials (Razavi hesabi *et al.*, 2011, Abadyan *et al.*, 2009a, 2009b, 2010, 2012a, 2012b). One of these fields is composite materials. The commercial importance of polymers has been driving intense applications in the form of composites in various fields. In these materials, based on the size of additives, there are some categories of these composites. If the size of additives to the polymeric based composites is less than 100 nm, this category of composites named nanocomposites. Nanocomposites based on polymeric materials have been attracted in recent years (Salehi Vaziri *et al.*, 2011a and 2011b; Pandey *et al.*, 2005; Huang *et al.*, 2003; Giannelis, 1998). Nanostructured materials gained great importance in the past decade on account of their wide range of potential applications in many areas. Polymer nanocomposites represent an alternative to macroscopically filled polymers. Because of their nanometer size of particles, the nanocomposites exhibit markedly improved properties when compared with the pure polymers or conventional composites (Koo *et al.*, 2002; Jordan *et al.*, 2005). These include increased modulus and strength, decreased gas permeability, increased solvent and heat resistance (Munusamy *et al.*, 2009; Tai *et al.*, 2008). In addition to their potential applications, polymer based nanocomposites are also unique model systems to study the structure and dynamics of polymers in confined environments (Lai *et al.*, 2008; Zhao *et al.*, 2008; Liu and Zhao, 2008).

Combination of rubber with other polymeric and non-polymeric materials is one of the subjects that attracted in recent years. In literature, the two parts matrix composing thermoplastic or thermoset have been used. Rubber and resin combination matrix is prepared in some

works for their expletive properties. Bonnia and his coworkers prepared the Natural rubber / polyester nanocomposites with nanoclay (Bonnia *et al.*, 2012). In the other work, Boukerrou and his coworkers worked on the rubbery epoxy resin with organoclay (Boukerrou *et al.*, 2007). They reported morphological, mechanical and viscoelastic properties of this ternary nanocomposite and showed that the good dispersion of nanoclay in the rubbery epoxy resin matrix. Moreover improvement of mechanical properties with addition of nanoclay has been reported. Zhao and coworkers investigated on the hindered phenol and acrylonitrile butadiene rubber compounds (Zhao *et al.*, 2007). They reported that this combination could be used as a high performance damping material. Rubber materials are attracted for elastic properties and resin materials show good thermal and mechanical properties. Yu and coworkers prepared the nanorubber particles for improving the wear properties of epoxy resin (Yu *et al.*, 2008). They mixed ingredients by mechanical mixing and reported the sliding wear properties by block-on-wheel friction and wear tester. They reported that the specific wear rate of epoxy have been decreased with addition of nanorubber particles.

In this work, we investigated on the abrasion properties of two parts matrix nanocomposites composed of styrene butadiene rubber (SBR) in the presence of nano Titanium oxide. In the literature investigation on the wear properties of other types of polymeric matrix have been confined. But in our work, the influence of nano particles of nano Titanium oxide have been investigated on the behavior of Styrene Butadiene rubber compounds. For more investigation on the wear properties of these samples, the optical microscopic images and the scanning electron microscopic pictures have been used.



EXPERIMENTS

Materials

The Styrene Butadiene Rubber (SBR) has been used as main part of polymeric matrix of the nanocomposite samples. The Styrene Butadiene rubber with 1502 code was produced by Jilin Rubber Co. Ltd. China. Styrene content is 22.5% and Rubber Mooney viscosity ML (1+4)100°C. The resin is cured by HMTA (Hexamethylenetetramine). Sulfur, ZnO, stearic acid and N-cyclohexyl-2-benzothiazyl sulphenamide (CBS) is composing the curing system. Sulfur and Zinc Oxide is the main part of curing system. Two other parts are comprised stearic acid as activator and CBS as accelerator. The curing system was prepared by local company.

The Nano Additive (NA) is nano Titanium oxide that is used as reinforcement in rubber matrix. Nano titanium oxide is obtained from Sigma-Aldrich with particle diameter of less than 25 nm.

Sample preparation

Sample preparation was done by two roll mills method. In the first stage, styrene butadiene rubber passes through two roll mills for some minutes which named mastication. Mastication process is diminishing the viscosity of rubbers like styrene butadiene rubber which caused better condition for dispersion of particles. The mastication stage has been last for 5 about minutes.

After that, nano titanium oxide powders were gradually incorporated to SBR compound. Then curing system well mixed with each other except sulfur and added to SBR paste. Sulfur is added to paste as the last ingredient for inhibiting the occurrence sooner cross linking reaction.

After finishing the incorporation stage, the paste is passed through the two roll mills for better distribution of nano particles in styrene butadiene rubber matrix. The resultant sample was prepared for curing stage. The paste was cured for 40 minutes at 140°C. After curing, compounds were post cured for about 4 hours. The formulation of compounds is shown in Table-1 based on one hundred parts of SBR.

Table-1. Formulation of compounds based on phr of SBR.

Sample code	SBR	NA	Sulfur	ZnO	Stearic acid	CBS
SR	100	0	2	4	2	1
SR-0.5A	100	0.5	2	4	2	1
SR-1A	100	1	2	4	2	1
SR-1.5A	100	1.5	2	4	2	1

Characterization

Abrasion test

In the characterization section, abrasion test and microscopic observations have been used. The abrasion test was done with the DIN abrader according to DIN 53516. The cylindrical sample, 16 mm in diameter and 10 mm in height, was contacted with the abrasive surface of a rotating drum under 1 N load. The direction of abrasion changed continuously through the rotation of the specimen on its own axis while it underwent abrasion. After finishing abrasion path, sample was weighted by 0.001 balance tools. The abrasion was defined as a volumetric loss of a cylindrical sample.

Optical microscopy

For better understanding the results of abrasion test, Optical observations have been used. The optical microscope that used is Olympus bx51m which product by Japan. The microscope is connected to computer for saving the pictures.

Scanning electron microscope

Moreover, scanning electron microscope or SEM pictures were captured from abraded surfaces. Field emission SEM is used that captured better pictures from

abraded surface. SEM tool that used is TESCAN MIRA LM by USA. The picture was photograph at 15 KV.

RESULTS AND DISCUSSIONS

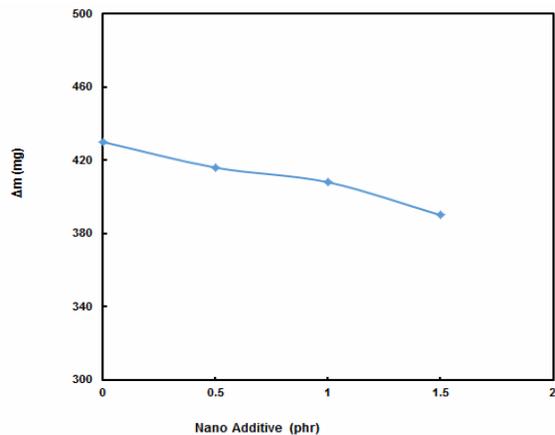
In Table-2, abrasion test results of SBR/NA nanocomposites have been shown. Moreover the results are illustrated in Figure-1. The densities of compounds have been measured by weighting of samples in air and in water. The density is defined by difference of weight in air and water divided to weight in air of samples. As it could be seen, with addition of nano titanium oxide to styrene butadiene rubber compounds, the sample densities have been increased. With addition of 1.5 phr of nano titanium oxide particles to Styrene Butadiene rubber compounds, about four percent increase in density has been shown compare to Styrene Butadiene rubber base sample (SR). This addition in density is due to nano titanium oxide particles' densities which is greater than density of both Styrene Butadiene rubber.

Abrasion results show that the abrasion content of Styrene Butadiene rubber base sample (SR) is about 430 mg which is equivalent to 413 mm³. This content of abrasion of base sample is lower than styrene butadiene rubber sample abrasion which reported in the literature (Gopi *et al.*, 2011). Moreover, with addition of nano titanium oxide particles, abrasion content of compound has been decreased. As it could be seen in Table-2, with

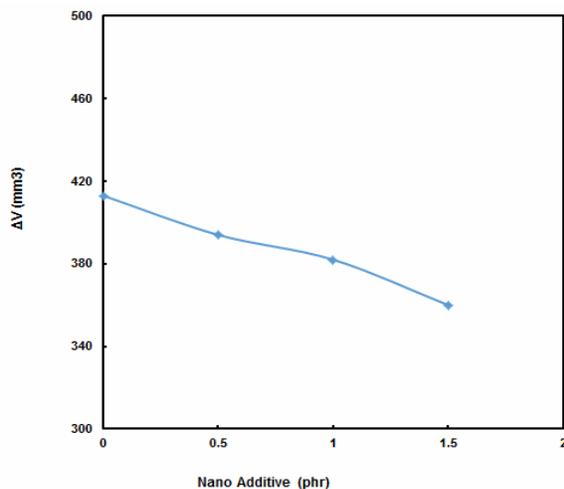


addition of just 0.5 phr nano titanium oxide to Styrene Butadiene rubber compound, the abrasion content decreases from 413 mm³ to 394 mm³. Most decrease in abrasion content could be seen in SR-1.5A. In this sample decrease in abrasion content is about 13% comparing to base sample SR. This decrease in abrasion with presence of nano titanium oxide may be due to good interaction between nano titanium oxide and the matrix of nanocomposites.

Nano titanium oxide as stiff particles caused better physical and mechanical properties of Styrene Butadiene rubber. This improvement could cause good homogeneity of rubber / resin matrix and leads to small debris in abrasion surface. Moreover, the nano particles of titanium oxide have better abrasion resistance compare to Styrene Butadiene rubber. As a consequence, with addition of nano titanium oxide to Styrene Butadiene rubber, enhancement in abrasion resistance has been occurred.



(a)



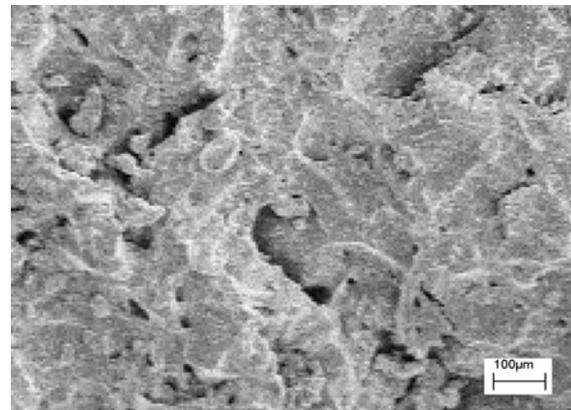
(b)

Figure-1. Variation of (a) mass and (b) volume loss as the additive content.

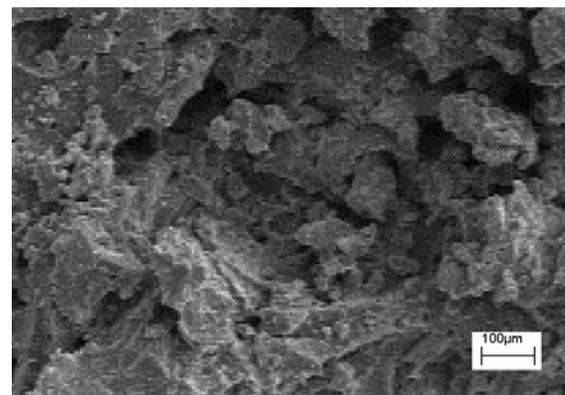
Table-2. Characteristics of SBR/NA nanocomposites.

sample	Δm (mg)	ρ (g/cm ³)	Δv (mm ³)
SR	430	1.041	413
SR-0.5A	416	1.055	394
SR-1A	408	1.068	382
SR-1.5A	390	1.082	360

For more observation of abrasion properties of Styrene Butadiene rubber with presence of nano titanium oxide, scanning electron microscopic picture have been captured from abraded surfaces. In Figure-2, the SEM image of abraded surface of base sample (SR) and SR-1.5A compound which has 1.5 phr nano titanium oxide has been observed. As it could be seen in Figure-2, there are more cavities on the abrasion surface of base sample in comparison with SR-1.5A compounds. Moreover the rougher surface could be seen in abraded surface of Styrene Butadiene rubber base sample.



(a)



(b)

Figure-2. SEM image from abraded surface of base sample a) SR and b) SR-1.5A.

This microscopic observation is in agreement with the abrasion test results in Table-2 and Figure-1. These deeper cavities could lead to generate more debris



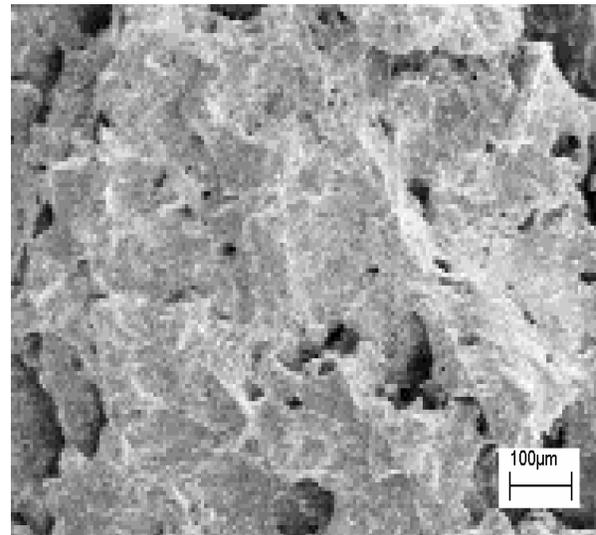
in abraded surface. Please note that the more and rough debris in abraded surface could act as an abrasive particle and caused more content of abrasion of samples. In base sample of Styrene Butadiene rubber deeper hole exist in abrasion surface. It may concluded that nano titanium oxide particles could properly interact with polymeric matrix and lead to softer abrasion surface that based sample.

In Figure-3, scanning electron microscope picture from the abraded surface of base sample Styrene Butadiene rubber and SR-0.5A nanocomposite sample (with 0.5 phr nano titanium oxide) have been shown. As it could be seen in Figure-2, more holes or cavities is observable in abraded surface of base sample (SR). But in SR-0.5A sample, presence of nano titanium oxide may lead to better surface for abrasion. Softer with proper homogeneity could be seen in abraded surface of SR-0.5A. This phenomenon could attribute to existence of nano titanium oxide in Styrene Butadiene rubber nanocomposites. Although in SR-0.5A nanocomposite sample there is some debris in abraded surface which is shown in Figure-2. This may be due to lower content of nano titanium oxide in this sample compare to SR-1A and SR-1.5A nanocomposite samples. With increase in nano titanium oxide particle content to Styrene Butadiene rubber, the size of debris was small as is shown in Figure-1.

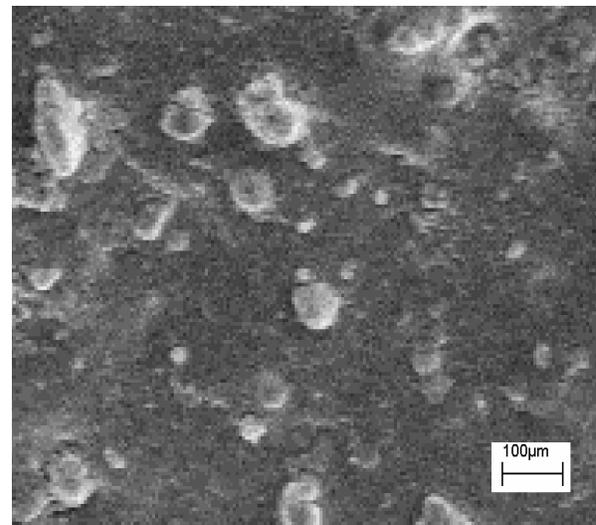
Beside the SEM image from abraded surface of nanocomposites, the optical microscopic pictures have been captured from abrasion surface of Styrene Butadiene rubber / nano Titanium oxide nanocomposites. In Figure-4, optical graph from abraded surface of base sample Styrene Butadiene rubber Compound (SR) and SR-1.5A compound which has 1.5 phr nano Titanium oxide has been brought. Similar to what observed in SEM image, there is signs of rough surface on the abrasion surface of Styrene Butadiene rubber base sample. Meanwhile, in abraded surface of SR-1.5A nanocomposite sample, the abraded surface is softer that the abraded surface of base sample. It supports the abrasion results of these nanocomposites. Moreover, the debris in abraded surface of base sample is rougher and bigger that debris in abraded surface of SR-1.5A nanocomposite sample. This rough debris could act as abrasive particles at surface and increase abrasion content.

For more comparison of abrasion behavior between SBR / NA nanocomposite samples, optical micrograph of abraded surfaces of SR-0.5A and SR-1A nanocomposite samples have been shown in Figure-5. Abrasion surface of SR-0.5A nanocomposite sample with lowest content of nano titanium oxide shows bigger debris compared to SR-1A nanocomposite sample. Abrasion content of SR-0.5A and SR-1A nanocomposite samples is about 394 mm^3 and 382 mm^3 respectively. Abrasion content of SR-1A is about 4% lower that abrasion content of SR-0.5A compound. But with addition of nano titanium oxide additive to the SBR compounds, the abrasion content has been decreased to 360 mm^3 .

As it could be seen in Figure-5, abrasion surface of SR-0.5A and SR-1A nanocomposite samples is to some extent similar. But comparison between these abraded surfaces with abraded surface of SR-1.5A sample (Figure-3b) shows that smoother surface of SR-1.5A compare to SR-0.5A and SR-1A. These optical observations from abrasion surfaces confirm the abrasion test results.

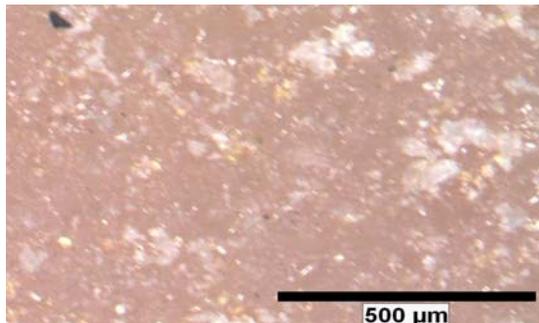


(a)

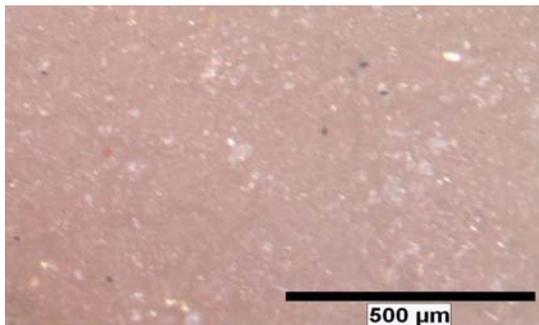


(b)

Figure-3. SEM image from abraded surface of base sample a) SR and b) SR-0.5A.

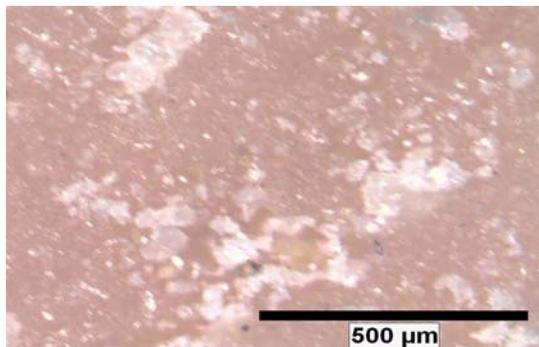


(a)

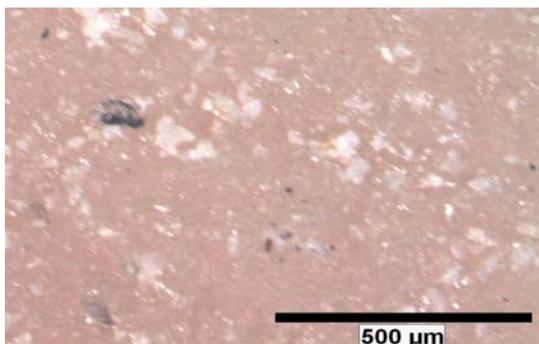


(b)

Figure-4. Optical microscopic pictures from abraded surface of base sample a) SR and b) SR-1.5A.



(a)



(b)

Figure-5. Optical microscopic pictures from abraded surface of SR samples with a) 0.5 phr and b) 1 phr nano titanium oxide.

CONCLUSIONS

Styrene Butadiene rubber compounds with and without nano titanium oxides particles have been prepared successfully. For preparation of rubber / resin based nanocomposites, mechanical blending using two roll mills method has been selected. For abrasion results DIN abrader machine have been used. Abrasion results showed that the volumetric mass loss content of Styrene Butadiene rubber sample is about 413 mm^3 . This abrasion content is higher than abrasion content of Styrene Butadiene rubber base compound. It showed that an increase of abrasion content of Styrene Butadiene rubber samples. Moreover, with addition of nano titanium oxide to Styrene Butadiene rubber sample, abrasion content of samples decreased. The lowest abrasion content was observed in SR-1.5A compound with 1.5 phr nano titanium oxide. It may be due to good influence of nano titanium oxide on the mechanical and physical properties of Styrene Butadiene rubber. SEM and optical graph observations is in accordance with abrasion results. Optical microscopic and SEM pictures showed that with addition of nano titanium oxide to base sample, more soft particles or smaller debris observed in the abraded surface. This microscopic picture emphasized abrasion results.

ACKNOWLEDGEMENT

Islamic Azad University is acknowledged for the support of this investigation.

REFERENCES

- Z. Razavi Hesabi, A. Koochi, Y. Tadi Beni and M. Abadyan. 2011. Modeling fatigue behavior of quasi-isotropic laminates. *Procedia Engineering*. 10: 3772-3776.
- M. Abadyana, V. Khademi, R. Bagheri, H. Haddadpour, M.A. Kouchakzadeh and M. Farsadi. 2009a. Use of Rubber Modification Technique to Improve Fracture-Resistance of Hoop Wound Composites. *Materials and Design*. 30: 1976-1984.
- M Abadyan, R Bagheri, H Haddadpour and P Motamedi. 2009b. Investigation of the fracture resistance in hoop wound composites modified with two different reactive oligomers. *Materials and Design*. 30(8): 3048-3055.
- M. Abadyan, V. Khademi, R Bagheri, P Motamedi, ma. Kouchakzadeh and H Haddadpour. 2010 Loading rate-induced transition in toughening mechanism of rubber-modified epoxy. *Journal of Macromolecular Science Part B*. 49: 602-614.
- Abadyan M, Bagheri R and Kouchakzadeh MA. 2012 (a). Study of fracture toughness of a hybrid rubber modified epoxy: Part I. Synergistic toughening. *Applied Polymer science*. 125: 2467-2475.
- Abadyan M, Bagheri R and Kouchakzadeh MA. 2012 (b). Study of fracture toughness of a hybrid rubber modified



- epoxy: Part II. Effect of loading rate. Accepted for publish in Applied Polymer science. 125: 2476-2483.
- Abadyan M. 2011. Exploring the tensile strain energy absorption of hybrid modified epoxies containing soft particles. *Materials and Design*. 32: 2900-2908.
- Salehi Vaziri H, Abadyan M, Nouri M, Amiri Omaraei I, Sadredini Z and Ebrahimmia M. 2011a. Investigation of the fracture mechanism and mechanical properties of polystyrene/silica nanocomposite in various silica contents. *J. Mater Sci*. 46: 5628-38.
- Salehi Vaziri H, Amiri Omaraei I, Abadyan M, Mortezaei M and Yousefi N. 2011b. Thermophysical and rheological behavior of polystyrene/silica nanocomposites: Investigation of nanoparticle content. *Mater Design*. 32: 4537-42.
- Pandey J. K., Reddy K. R., Kumar A. P. and Singh R.P. 2005. An Overview on the Degradability of Polymer Nano - composites. *Polymer Degradation and Stability*. 88(2): 234-250.
- Huang Z., M., Zhang Y.Z., Kotaki M. and Ramakrishna S. 2003. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology*. 63: 2223-2253.
- Giannelis E. P. 1998. Polymer-layered silicate nanocomposites: synthesis, properties and applications. *Applied Organometallic Chemistry*. 12: 675-680.
- Koo C.M, Ham H. T., Choi M. H., Kim S. O. and Chung I. J. 2002. Characteristics of polyvinylpyrrolidone-layered silicate nanocomposites prepared by attrition ball milling. *Polymer*. 44(3): 681-689.
- Jordan J., Jacob K. I., Tannenbaum R., Sharaf M. A and Jasiuk I. 2005. Experimental trends in polymer nanocomposites-a review. *Materials Science and Engineering: A*. 393(1-2): 1-11.
- Munusamy Y., Ismail H., Mariatti M. and Ratnam C.T. 2009. Effect of electron beam irradiation on the properties of ethylene-(vinyl acetate) copolymer/natural rubber/organo clay nanocomposites. *Journal of Vinyl and Additive Technology*. 15(1): 39-46.
- Tai Y., Miaoa J., Qian J., Xia R. and Zhang Y. 2008. An effective way to stabilize silicon nitride nanoparticles dispersed in rubber matrix by a one-step process. *Materials Chemistry and Physics*. 112(2): 659-667.
- Lai S.M., Chen W. C. and Chen C. M. 2008. Preparation, structure, and properties of styrene-ethylene-butylene-styrene block copolymer/clay nanocomposites: Part II fracture behaviors. *European Polymer Journal*. 44(11): 3535-3547.
- Zhao S., Schadler L. S., Duncan R., Hillborg H. and Auletta T. 2008. Mechanisms leading to improved mechanical performance in nanoscale alumina filled epoxy. *Composites Science and Technology*. 68(14): 2965-2975.
- Liu X. and Zhao S. 2008. Study on structure and properties of SSBR/SiO₂ co-coagulated rubber and SSBR filled with nanosilica composites. *Journal of Applied Polymer Science*. 109(6): 3900-3907.
- Bonnia N. N., Ahmad S. H., Surip S. N., Nurul S.S., Azlina H.N. and Anuar H. 2012. Mechanical properties and environmental stress cracking resistance of rubber toughened polyester/clay composite. *Advanced Materials Research*. 576: 318-321.
- Boukerrou A., Duchet J., Fellahi S., Kaci M. and Sautereau H. 2007. Morphology and mechanical and viscoelastic properties of rubbery epoxy/organo clay montmorillonite nanocomposites. *Journal of Applied Polymer Science*. 103(6): 3547-3552.
- Zhao X.Y., Xiang P., Tian M., Fong H., Jin R., and Zhang L. Q. 2007. Nitrile butadiene rubber/hindered phenol nanocomposites with improved strength and high damping performance. *Polymer*. 48(20): 6056-6063.
- Yu S., Hu H., Ma J. and Yin J. 2008. Tribological properties of epoxy/rubber nanocomposites. *Tribology International*. 41(12): 1205-1211.
- Gopi J. A., Patel S. K., Chandra A. K. and Tripathy D. K. 2011. SBR-clay-carbon black hybrid nanocomposites for tire tread application. *Journal of Polymer Research*. 18: 1625-1634.
- Gu Z., Song G., Liu W., Li P., Gao L., Li H. and Hu X. 2009. Preparation and properties of styrene butadiene rubber/natural rubber/organo-bentonite nanocomposites prepared from latex dispersions. *Applied Clay Science*. 46: 241-244.
- Wang Q., Wang F. and Cheng K. 2009. Effect of crosslink density on some properties of electron beam-irradiated styrene-butadiene rubber. *Radiation Physics and Chemistry*. 78: 1001-1005.