Effect of Micro and Nano Zinc Oxide on the Properties of Pre-vulcanized Natural Rubber Latex Films

Anand K[a], Siby Varghese[a] and Thomas Kurian[b]

[a]Technical Consultancy Division, Rubber Research Institute of India, Rubber Board, Kottayam 686 009, Kerala, India

[b]Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682 022, Kerala, India

Received: 29 April 2014, Accepted: 11 August 2014

SUMMARY

Zinc oxide (ZnO) nanoparticles were synthesized through a solution free mechano-chemical route and their effects on pre-vulcanized natural rubber latex properties were investigated. Effect of nano ZnO loading on swelling, antimicrobial, mechanical and ageing properties of pre-vulcanized latex vulcanizates were examined and compared with conventional micro ZnO filled vulcanizates. In comparison with micro filled system, nano filled system exhibits better performance in all respects. The ageing resistance of nano ZnO incorporated latex films was found to be high.

Keywords: Elastomers; Antimicrobial activity; Swelling; Mechanical properties; Ageing

INTRODUCTION

Pre-vulcanized natural rubber latex (PVL) is a convenient raw material for the manufacture of several latex products. Drying of PVL produces a crosslinked film that does not require further vulcanization. Crosslinking reaction in latex takes place over a range of conditions such as temperatures ranging from 20° to 90°C for appropriate periods [1]. The crosslinking of rubber in latex can be effected by the reaction with sulphur [2], sulphur donors [3], peroxides [4] or by γ-radiation [5]. The attractive feature of PVL is that it requires shorter drying time and high product clarity. Pre-vulcanization of latex enables the

---

Correspondence to: Siby Varghese (E mail: sibyvarghese100@yahoo.com)

removal of sedimentable impurities and unreacted ingredients which may cause blooming. The consistency of the properties of PVL products is excellent and they show minimum allergenic reactions.

Zinc oxide is an essential additive both in dry rubber and latex based formulations. Sulphur pre-vulcanized natural rubber latex is prepared by allowing rubber molecules to react with sulphur under the influence of one or more accelerator and zinc oxide. Being an activator of vulcanization, ZnO enhances the crosslinking efficiency in latex products. An important function of ZnO is to regenerate the accelerator as the vulcanization reaction proceeds.

It has been reported that the addition of ZnO reduces the latex stability and film clarity when used above 0.2 phr [6]. Moreover, ZnO is classified as a hazardous chemical and the excess release of which is highly toxic to aquatic species. For humans the recommended intake should not exceed 12-15 mg/day. Around 100000 tonnes of ZnO and other zinc containing chemicals are consumed by rubber industry in European Union (EU) alone. Global consumption will be much higher. To reduce the use of zinc in rubber products, “Eco Zinc” concept has been set up by EU. With increase in concern about the excess release of zinc to environment, rubber products manufacturers are looking for process/chemicals which can minimize the concentration of ZnO in their products.

The requirement of ZnO in latex based formulations could be considerably reduced by using nano-dispersions of ZnO [7]. By reducing the particle size of ZnO, the vulcanization time could be reduced and the mechanical properties could be improved. The smaller the particle, higher the surface to volume ratio and are expected to be more active.

Use of nano ZnO as cure activator in natural rubber is studied [8]. Addition of nano ZnO decreases the cure time (t_{90}) and increases the cure rate index as compared with 5 phr micro ZnO. The optimum dosage of nano ZnO as a cure activator in NR vulcanization was found to be 0.5 phr. Thomas et al. synthesized novel accelerators *N*- benzylimine aminothioformamide (BIAT)-capped- stearic acid- coated nano ZnO (ZOBS), BIAT- capped ZnO (ZOB) and stearic acid-coated nano zinc phosphate (ZPS), to investigate their effects in NR vulcanization [9]. They found that BIAT- capped- stearic acid- coated nano ZnO (ZOBS) exhibit superior curing and improved physico-mechanical properties compared with the reference mixture containing uncapped ZnO. NR/ZnO nanocomposites were prepared by blending NR latex with aqueous suspension of ZnO nanoparticles [10]. They exhibit excellent antibacterial characteristics and improved mechanical property when the dosage ZnO is <4 wt%. Rathnayake et al. reported that the antibacterial activity of natural rubber latex foam can be improved by the addition of ZnO nanoparticles [11].

The objective of the present paper is to study the performance of synthesized nano-ZnO on the properties of pre-vulcanised natural rubber latex and to compare them with control vulcanizate containing micro-ZnO. Effect of reducing the concentration of nano ZnO on the mechanical properties of the vulcanizate is evaluated. The antifungal activity of pre-vulcanized natural rubber latex films containing micro and nano ZnO is also studied.

MATERIALS AND METHODS

Centrifuged high ammonia latex (BIS 5430-1981) (**Table 1**) collected from Central Experimental Station of Rubber Research Institute of India, Kottayam was used for pre-vulcanization. The other compounding ingredients used were of commercial grade. Nano-ZnO was synthesized by mechano-chemical method using zinc acetate dihydrate, sodium hydroxide and CTAB [12]. Nano-ZnO was used as 5% dispersion. All other vulcanizing agents used were 50% dispersions prepared by conventional ball-milling method.

Table 1. Properties of centrifuged latex used for pre-vulcanization

Property	Value	Requirement (BIS 5430-1981)	Test method
Dry rubber content (%)	60.5	60 min.	IS 3708 (part 1) 1985
Non rubber solids (%)	1.6	2 max.	IS 9316 (part 4) 1988
Ammonia content (%)	0.9	0.6 min.	IS 3708 (part 4) 1985
*VFA number	0.035	0.15 max.	IS 3708 (part7) 1986
**MST (s)	980	475 min.	IS 3708 (part 6) 1985

**Volatile fatty acid number*
***Mechanical stability time*

Formulations of the compounding ingredients are given in **Table 2**. Pre-vulcanization was carried out at 70°C for 3 h. Films were cast with pre-vulcanized latex (designated as A, B, C and D, based on the amount of ZnO: *A- 0.5 phr micro ZnO; B- 0.5 phr nano ZnO; C- 0.1 phr nano ZnO; D- 0.05 phr nano ZnO).* The stability and physical properties of latex vulcanizates containing micro and nano-ZnO dispersions are given in **Table 3**.

Viscosity measurements were performed at 25°C (ASTM D 2526-269) using a Brookfield viscometer (Brookfield Laboratories, Stoughton-USA). Zwick universal testing machine, model 1474 was used to measure the physical properties and the tests were carried out as per ASTM D 412. Mettler Toledo AG digital pH meter (Switzerland) was used to record the pH of latex samples.

Table 2. Formulation (dry weight) for the preparation of pre-vulcanized natural rubber latex

Ingredients		Formulations (Dry weight)		
	A	B	C	D
60% Centrifuged latex (HA type#)	100	100	100	100
10% Potassium hydroxide solution	0.20	0.20	0.20	0.20
20% Potassium laurate solution	0.24	0.24	0.24	0.24
50% Sulphur dispersion	1.5	1.5	1.5	1.5
50% ZDC* dispersion	1.0	1.0	1.0	1.0
50% Micro-ZnO dispersion	0.5	-	-	-
5% Nano-ZnO dispersion	-	0.5	0.1	0.05
# *High ammonia latex* **Zinc-diethyldithiocarbamate*				

Table 3. Physical properties of pre-vulcanized latex films containing micro and nano ZnO

Formulations	Chloroform number	Viscosity (cPs)	pH	Elongation at break (%)	100% modulus (MPa)	500% modulus (MPa)
A	2	418	10.42	1005	0.81	3.45
B	3	500	10.48	940	0.95	3.51
C	2	130	10.49	1277	0.78	1.89
D	2	65	10.42	1460	0.72	1.64

The extent of vulcanization was assessed from chloroform number. A portion of latex sample was mixed with equal volume of chloroform and after 2 minutes the coagulum was examined and graded.

The volume fraction of rubber (V_r) was determined by equilibrium swelling in toluene at 30°C following the method suggested by Ellis and Welding [13] and crosslink density was determined using Florey-Rehner equation [14]. Volume fraction and crosslink density of PVL vulcanizates containing micro and nano-ZnO are shown in **Table 4**.

For antifungal activity studies, 3 replicates from each vulcanizate (A, B, C and D) were cut into same dimension and inoculated with a common contaminant fungi of rubber sheets belonging to *Trichoderma* sp. and *Aspergillus* sp. under room temperature in moist atmosphere. The period of observation was confined to about two months. After 2 months the samples were tested for any fungal and bacterial growth in PDA (Potato-Dextrose Agar) and NA (Nutrient Agar) respectively.

Table 4. Volume fraction of rubber and crosslink density of pre-vulcanized latex films containing micro and nano-ZnO

Sample type	Volume fraction of rubber (V_r)	Crosslink density x 10^{-5} (mol/cm^3)
A	1.0477	12.3196
B	1.0685	14.1252
C	1.0524	12.1484
D	1.0512	10.7797

Ageing studies were performed in air oven at 100°C for 22 h and physical properties of the aged samples were estimated.

RESULTS AND DISCUSSION

Figure 1 shows the swelling characteristics of vulcanizates in toluene at 25°C. From the graph it is clear that PVL vulcanizates with 0.5 phr nano-ZnO offers better resistance to swelling in toluene. This shows that there are restrictions for the solvent to penetrate through the matrix. Latex vulcanized with 0.05 phr nano-ZnO shows maximum swelling due to lower crosslink density as shown

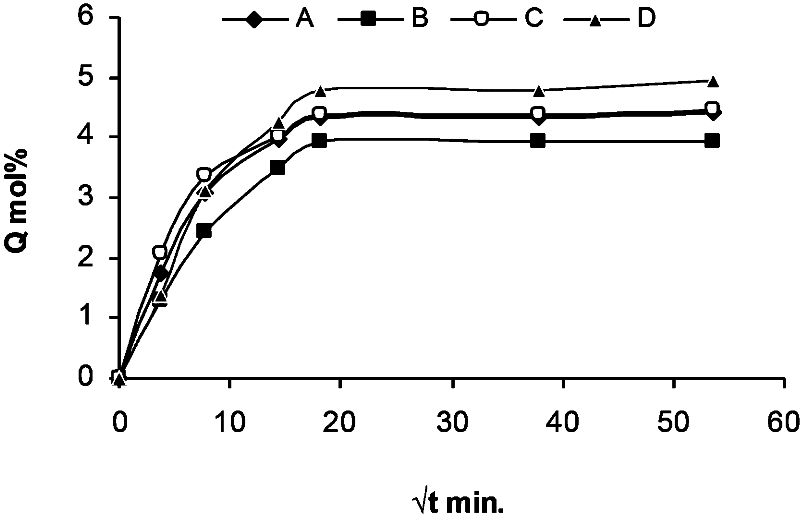

Figure 1. Swelling behaviour of pre-vulcanized latex films with micro and nano-ZnO vulcanized for 3 h

in **Table 4**. An interesting observation is that the crosslink density is almost same for PVL films containing 0.1 phr nano-ZnO (sample C) and 0.5 phr micro-ZnO (sample A), which indicates that nano-ZnO even at low loading can impart better solvent resistance.

Antimicrobial activity of PVL films against the fungi *Trichoderma sp*. and *Aspergillus sp*. are shown in the **Table 5**. The bits of the film from all the four treatments (A, B, C and D) did not show any fungal growth up to 6 weeks. *Trichoderma sp*. and *Aspergillus sp*. isolated from the contaminated bits did not grow in any of the bits up to the period under observation. After 6 weeks visible growth was observed in A, C and D. In sample D, after 2 weeks, all the replicates showed visible growth with the inoculated fungi *Aspergillus sp.* and *Trichoderma sp.* None of the replicates of sample B showed visible fungal infection. This shows that the nano ZnO can impart better anti fungal activity in pre-vulcanised latex films as compared to an equal dosage of the micro ZnO. However, when these samples were tested in PDA and NA after 2 months, fungal and bacterial growth was observed in all these samples. Photographs of the contaminated vulcanized films after 2 months are shown in **Figure 2**.

Table 5. Antimicrobial properties of micro and nano ZnO incorporated pre-vulcanized NR latex films

Sample	Up to 6 weeks	After 6 weeks	After 2 months	
	Fungi	Fungi	Fungi	Bacteria
A	-	+	+	+
B	-	-	+	+
C	-	+	+	+
D	-	+	+	+

The stress-strain curves of vulcanizates are shown in **Figure 3**. Strain induced crystallization at large elongations (>300% strain) plays a major role in the mechanical properties of natural rubber [15]. Presence of nano-ZnO at higher dosage (0.5 phr) in the latex based vulcanizate gives high initial modulus, indicating high reinforcement. As the concentration of nano ZnO increases, the stress-strain curve is shifted towards high stress values indicating high level of crosslinks in nano-ZnO incorporated vulcanizates. As elongation increases to >400%, strain amplification (strain induced crystallization) come into play and increases proportionally with elongation. Strain induced crystallization of natural rubber is affected by filler content [16]. At high strains, the strain amplification along with effect of immobilized rubber gives 30-90 fold rise in the effective volume fraction and which in turn affect modulus [15].

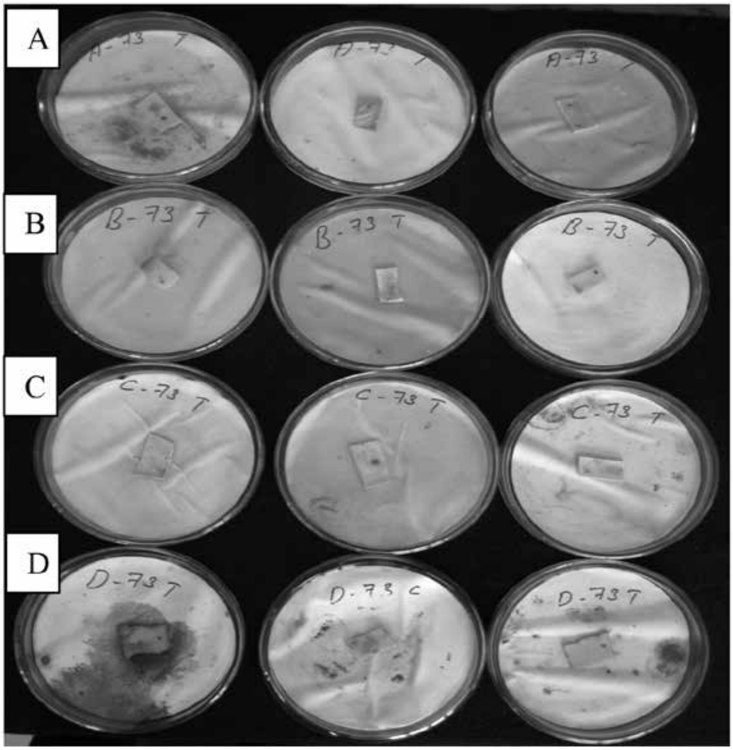

Figure 2. *Photographs showing anti-fungal activity of ZnO in pre-vulcanized NR latex films with three replicates against fungi* ***Aspergillus sp.***

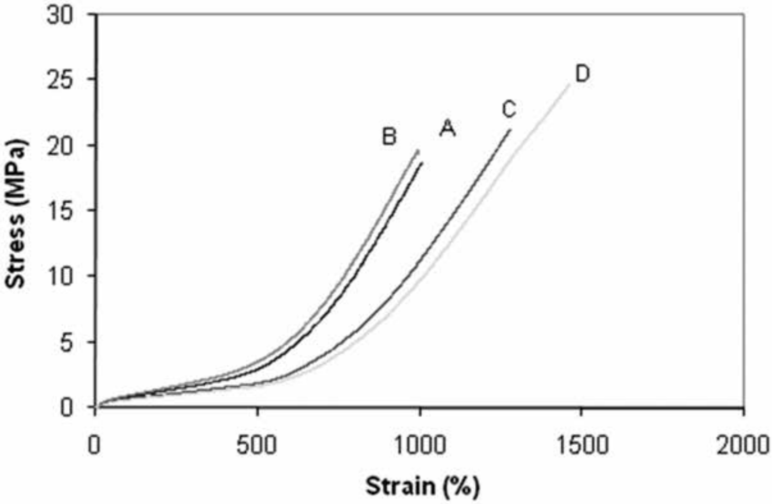

Figure 3*. Stress strain behaviour of pre-vulcanized natural rubber latex films containing micro and nano ZnO*

The tensile strength of micro and nano particulate filled composites depends on the effectiveness of stress transfer between matrix and fillers [17]. **Figure 4** shows the effect of micro and nano-ZnO at various amounts (0.5 phr, 0.1 phr and 0.05 phr) on tensile strength of pre-vulcanized NR latex films. From the graph it is obvious that nano-ZnO filled PVL films exhibited higher tensile strength than conventional ZnO incorporated films. By reducing the amount of nano ZnO from 0.5 phr to 0.05 phr, tensile strength increases. This is due to higher reinforcement offered by nano-ZnO. Latex pre-vulcanized with 0.5 phr nano-ZnO, resulted in lower tensile strength. The decrease in tensile strength at higher nano-ZnO loading is due to particle-particle aggregation, resulting poor interaction with rubber matrix. However, this drop in tensile strength is still on par with the tensile strength offered by conventional ZnO. The crosslink density of 0.5 phr nano ZnO incorporated latex vulcanizate was found to be high. The formation of too many crosslinks affects the degree of crystallinity of rubber during stretching [18]. The tensile strength of pre-vulcanized films is governed not only by introducing crosslinks but also the ability of particles to coalesce among themselves. When the film is prepared from highly crosslinked latex, coalescence of rubber particles become more and more difficult, resulting in lower tensile strength [19]. The agglomeration of ZnO nanoparticles at higher levels also leads to lower tensile properties [20].

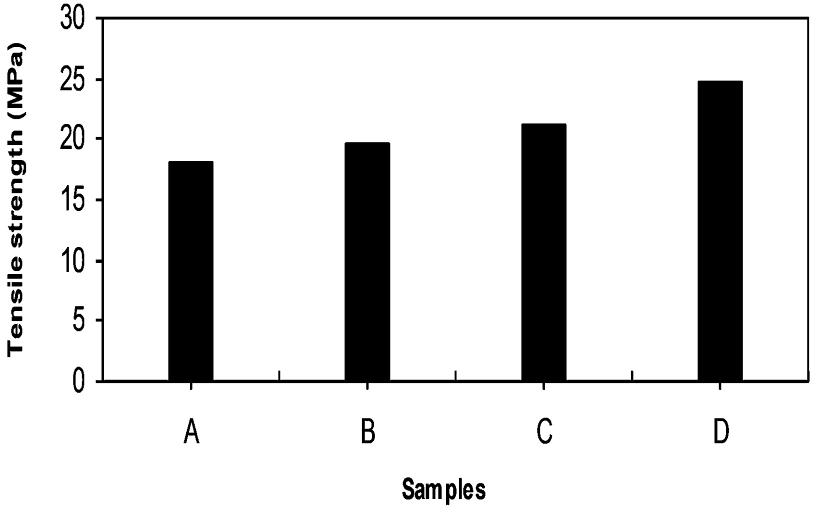

Figure 4. Tensile strength of pre-vulcanized natural rubber latex films containing micro and nano ZnO

Modulus is the ratio of stress to strain in the linear region of stress-strain curve. It is a bulk property and depends primarily on the geometry, particle size distribution and concentration of filler [21]. Other parameters attributed to an increase in modulus are the aspect ratio of the filler and the orientation of fillers. **Figure 5** displays the modulus of PVL films containing conventional micro-ZnO and nano-ZnO at 700% elongation. The modulus value decreased on decreasing the concentration of nano-ZnO. The modulus of elongation of the sample containing 0.5 phr nano-ZnO was 8.04 MPa whereas modulus of the vulcanizate containing the same loading of micro-ZnO was 7.63 MPa. From this it is clear that nano-ZnO exhibits good reinforcibility with the polymer matrix. Further the particle size of nano-ZnO is ~ 55 nm so that the aspect ratio is high and the reinforcement provided by them will be higher.

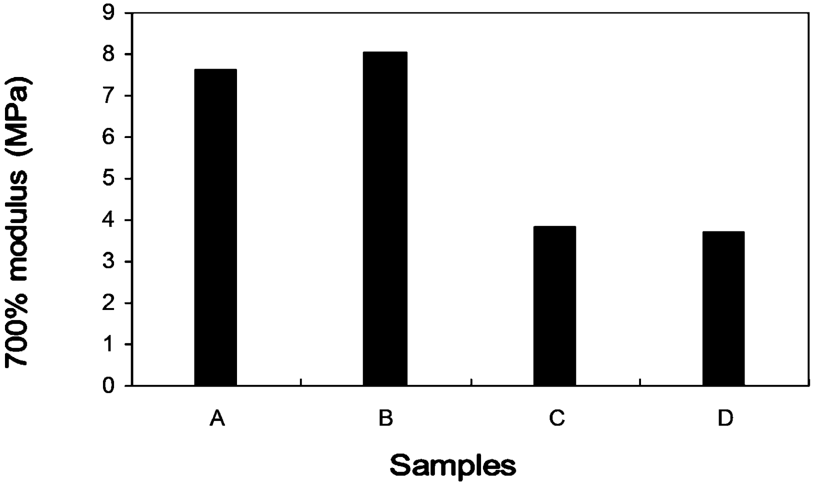

Figure 5. *Modulus at 700% elongation of pre-vulcanized natural rubber latex films containing micro and nano ZnO*

The effect of ageing at 100°C for 22 h on tensile strength and modulus of pre-vulcanized films containing micro and nano-ZnO are shown in **Table 6**. It was observed that ageing resistance was improved significantly by adding nano-ZnO. It has been found that, after ageing, the tensile strength of the vulcanizate incorporated with 0.5 phr nano-ZnO was 5.07 MPa whereas the corresponding value for micro-ZnO filled films were 3.50 MPa only. This shows that addition of nano-ZnO offers better retention in tensile strength after ageing compared to the conventional micro ZnO. But, by reducing the concentration of nano ZnO, tensile strength decreases.

Table 6. Effect of micro and nano ZnO on mechanical properties of pre-vulcanized natural rubber latex films after ageing at 100°C for 22 hours

Sample	Tensile strength (Before ageing) MPa	Tensile strength (After ageing) MPa	% retention in tensile strength MPa	100% modulus MPa	500% modulus MPa	700% modulus MPa
A	19.85	3.50	17.64	0.29	1.00	2.11
B	19.37	5.07	26.18	0.36	1.06	2.25
C	21.24	4.58	21.57	0.3	1.03	2.15
D	24.68	3.60	14.59	0.25	0.87	1.98

Elongation at break (EB) indicates the maximum extension of samples under tension. Elongation at break for PVL films containing micro and nano-ZnO before and after ageing is shown in **Figure 6**. The EB depends on polymer-filler interaction. By reducing the amount of nano-ZnO from 0.5 phr to 0.05 phr the elongation at break increased. This increase in elongation at break is due to homogeneous and uniform distribution of nano-ZnO in the rubber matrix and better interaction of nano-ZnO with the matrix at lower doses. The reduction in elongation at break in higher nano-ZnO loading is apparently due to the increase in modulus as stiffer materials are not expected to elongate as much as soft materials. However, the vulcanizates containing higher amounts of

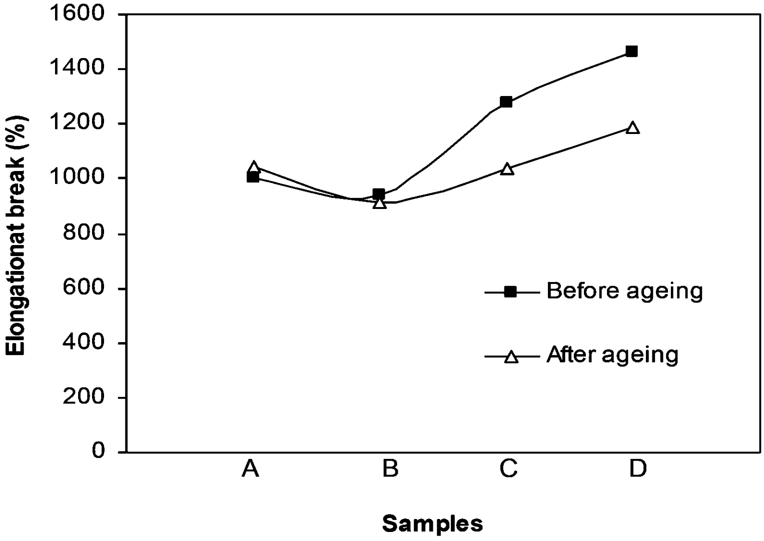

Figure 6. *Elongation at break of micro and nano ZnO filled pre-vulcanized NR latex films before and after ageing*

ZnO (micro and nano - 0.5 phr each) showed lower reduction in elongation at break after ageing as compared to the vulcanizates containing lower dosages of ZnO.

CONCLUSIONS

- The better solvent resistance (in toluene) was shown by pre-vulcanized natural rubber latex films containing 0.5 phr nano-ZnO. Also, the swelling behaviour of pre-vulcanized films containing 0.1 phr nano-ZnO and 0.5 phr conventional micro ZnO are the same.
- Nano ZnO imparts better antifungal activity in pre-vulcanised latex films as compared to an equal dosage of the micro ZnO.
- The tensile strength and elongation at break of the pre-vulcanized latex films increases with decreasing the concentration of nano ZnO indicating better reinforcement of nanoparticles with rubber matrix. At higher dosage (0.5 phr nanoloading), agglomeration among the high surface area ZnO nano particles causes reduction in tensile strength and elongation at break.
- Modulus of latex films increases by increasing nano ZnO addition.
- Compared with micro ZnO, incorporation of nano-ZnO results in better retention of mechanical properties after ageing.

ACKNOWLEDGEMENTS

The first author acknowledges Rubber Research Institute of India (Rubber Board), Kottayam, India for the financial assistance in the form of RRII fellowship.

REFERENCES

1. Gazeley K.F., Gorton A.D.T. and Pendle, T.D., Natural Rubber Science and Technology (Ed. A.D Roberts); Oxford University Press: Oxford, United Kingdom, (1988) Chap 3. 85.
2. Sasidharan K.K., Rani Joseph., Shiny Palaty., Gopalakrishnan K.S., Rajammal G. and Viswanatha Pillai., *J. Appl. Polym. Sci.*, **97** (2005) 1804-1811.
3. Philpott M. W., *J. Rubb. Res. Inst. Malayasia.,* **22** (1969) 441-449.
4. US Patent 2802891 A.

5. Zakir Hossain K.M., Sarwaruddin Chowdhury A.M., Haque M.E., Dafader N.C. and Akhtar F., *Polym. Plast. Technol. Engg.* **49** (2010) 136-140.

6. Pendle T.D., Latex Technology educational symposium (18) (1987) 131st meeting Rubber division ACS Canada **1987**.

7. Chapman A. and Johnson T., *Kautschuk Gummi Kunststoffe* **58** (2005) 358-361.

8. Bindu P. and Thomas S., *Polym. Engg. & Sci.* **53** (2013) 1337-1346.

9. Thomas S.P., Mathew E.J. and Marykutty C.V., *J. Appl. Polym. Sci.* **124** (2012) 3099- 3107.

10. Ming-Zhe Lv, Lei Fang, Pu-wang Li and Chun-Liang Yang *Adv. Mater. Res.* **936** (2014) 394-399.

11. Rathnayake W.G.I.U., Ismail H., Baharin A., Bandara I.M.C.C.D. and Rajapakse S., *J. Appl. Polym. Sci.* **131** (2014) 1-8.

12. Anand K., Varghese S. and Kurian T., *Inter.J. Theo. and Appl. Sci.* **6** (2014) 87-93.

13. Ellis B. and Welding G.N., *Rubb. Chem. Technol*. **37** (1964) 571-575.

14. Mathew A.P., Packiriswamy S., Kumaran M. and Thomas S., *Polymer* **36** (1995) 4935-4942.

15. Ozbas B., Toki S., Hsiao B. S., Chu B., Register R. A., Aksai I.A., Prud'homme R.K. and Adamson D.H., *J of Polym. Sci. PART B: Polym. Phys*. **50** (2012) 718-723.

16. Gent A.N., Kawahara S. and Zhao J., *Rubb. Chem. Technol*. **71** (1998) 668-678.

17. Fu S.Y., Feng X.Q., Lauke B. and Mai Y.W., *Composites: PART B*. **39** (2008) 933-961.

18. Roslim R. and Amir Hashim M.Y., *J. Rubb. Res*. **13** (2010) 125-138.

19. Claramma N.M. and Mathew N.M., *J. Appl. Polym. Sci*. **65** (1997) 1913-1920.

20. Altan M., Yildirim H. and Uysal A., *The Online J of Sci. and Tech*. **1** (2011), 25-30.

21. Ochigbo S.S. and Luyt A.S., *Intl. J of Composite Mater*. **1** (2011) 7-13.