

# Effect of Zeolite on the Properties of Natural Rubber Foams

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**Abstract-** In this research work Zeolite has been incorporated as filler with natural rubber latex (NRL) compounds to enhance the odour adsorption property of NRL foam products. Incorporation of Zeolite into NRL has not been reported in the literature. A methodology was developed to prepare stable colloidal dispersion of Zeolite and incorporate it into NRL compound without affecting the stability of the NRL compound and physical properties of final foam product. It was found that stable Zeolite dispersion with 32% Total Solid Content (TSC) can be prepared and 8% (on dry weight) optimum dosage of Zeolite can be incorporated into NRL compound considering the indentation hardness of foam product, sorption and flame retardant properties.

**Index Terms-** Flame retardant, Natural rubber foam, Sorption, Zeolite.

## I. INTRODUCTION

Latex foam rubber is a cellular rubber in which the cells are either all intercommunicating or partially intercommunicating and partly non intercommunicating[1]. The porous microcellular structure of latex foam provides the user in luxurious comfort, but has drawbacks such as it can adsorb dust, unpleasant odours and moisture.

Adsorption is a surface phenomenon that can be defined as the increase in concentration of a particular component on the surface or interface between two phases. Zeolite is a naturally occurring mineral, its porous structure enables to play a major role as an adsorbent and as a fire retardant in various fields.

Jha *et.al.*[2] successfully prepared activated carbon-zeolite composite from coal fly ash, which was proved to be having high capability of uptake of toxic metal ions such as  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . Mishra *et.al.*[3] also carried out a similar type of work. It is observed that 13X zeolite which derived from coal fly ash can be used as a better adsorbent for heavy metal sorption from acidic waste water in comparison to that of coal fly ash.

Wanget.*al.*[4] investigated the addition of 0.3 parts per hundred rubber (phr) of 4A zeolite into intumescent flame retardant filled natural rubber (NR) system and found that it could increase the limited oxygen index value and thermal stability. However, mass loss ratio, rate of heat release, carbon monoxide evolution and carbon dioxide ( $\text{CO}_2$ ) evolution, and improvement of fire retardant properties were decreased.

Demiret.*al.*[5] examined the thermal degradation and flammability of intumescent fire retardant polypropylene matrix consisting of ammonium polyphosphate (APP). APP was used as

an acid source and pentaerythritol (PER) as blowing agent and as a carbonization agent. Natural zeolite was used as a synergistic agent. A synergistic effect in flame retardancy was observed when natural zeolites were used in combination with APP and PER. Wang and Chen[6] observed the addition of microencapsulated intumescent flame retardant agent containing 4A zeolite into dry NR, resulted in an improvement in the physic-mechanical and flame retardant properties.

Activated carbon black has also been added to latex to enhance physical [7] and sorption [8] properties. But, one of the major drawbacks is the black colour. The main objective of this study was to introduce Zeolite as compounding ingredient into NR latex compound to enhance the sorption property of white NR latex foam products. In addition to sorption property, fire retardant property was also investigated.

## II. EXPERIMENTAL

### Preparation and Characterization of Zeolite Dispersion:

Low Ammonia latex (LA-TZ) was supplied by Lalan Group, Sri Lanka, zeolite and all the other standard chemicals were supplied by D. Samson Industries (DSI), Sri Lanka.

Moisture content of zeolite powder was measured using moisture balance (Citizen MB 200x). pH and average particle size of 1% zeolite solution were measured using pH meter and particle size analyzer (Light scattering-Fritsch Analysette 22 compact) respectively.

**Table 1. Formulation of Zeolite dispersion**

Ingredients	parts by weight
Zeolite	24.0
Tamol	0.5
Water ( $\text{H}_2\text{O}$ )	75.5

Zeolite dispersion, having 36% Total Solid Content (TSC), was prepared by mixing tamol with water first and followed by addition of zeolite. Finally it was mechanically agitated for 10 min.

**Table 2. The formulation of the LA-TZ latex foam compound**

Ingredient	Dry weight%
60 % LA-TZ latex	100.0
20% Potassium oleate	1.4
50 % Antioxidant (Nonax)	1.0
50% Sulphur	2.5

50 % Zinc diethyldithiocarbamate (ZDEC)	1.0
50% Zinc mercaptobenzothiozole (ZMBT)	1.0

Formulation of Zeolite dispersion is given in Table 1. Average particle size, % of particle size less than 10 µm and pH were measured for dispersion. TSC was measured as per ISO 124:1997(E) and viscosity was measured using Dial type Brookfield viscometer in accordance with ISO 1652:1985(E).

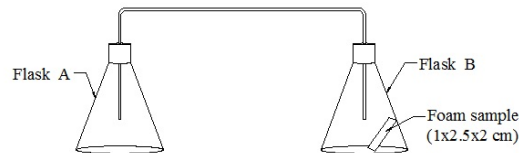
**Preparation of Zeolite incorporated natural rubber latex compound:** TSC, Mechanical Stability Time (MST) as per ISO35:1995 (E) and pH of LA-TZ latex were measured. Basic formulation of latex compound used for the study is given in Table 2. Zeolite dispersion was incorporated into latex compound and eleven different latex compounds were prepared by varying the percentage of zeolite on dry basis from 0% to 9%. Foaming ability of zeolite incorporated latex compound was measured using foam height and it was measured at 1 min time intervals up to 5 min and thereafter at 2.5 min intervals for a total time period of 10 min. Final compound height was taken into consideration when calculating the foam height.

**Preparation of Zeolite incorporated latex foam:** A 250 g of zeolite incorporated latex compound was matured for 8 h under room temperature and it was transferred into stainless steel bowl with the open beater. The latex compound was foamed at the highest speed of the beater until the batch volume turns to four times of the initial volume. Once the required volume was reached, the speed was reduced to medium and refined the foam for 2 min. ZnO (0.4phr) and DPG (1.0 phr ) dispersions were added gradually and mixed well at medium speed for 1 to 2 min. SSF (1.5phr) was added and further mixed for 1 min. The foam latex compound was poured into a pre-treated two pieces, 15 cm x10 cm x4.5 cm size mould with pins warmed to 35 °C. The lid was closed tightly and the foam was allowed to gel for 2 to 3 min and 20 min for subsequent curing. The cured latex foam block was stripped from the mould followed by washing and drying at room temperature.

**Physical Testing of Zeolite incorporated latex foam:** Indentation hardness of foam with different zeolite loading was measured as per SLS1334. Flame retardant property of zeolite incorporated foam was tested using the simple comparison method. In this method, foam strips having dimensions of 1 cm x1 cm x10 cm were prepared and mark at 5 cm (measured from one end of the strip) was drawn on each strip. The time to burn the foam strip from one end to the 5 cm mark was measured.

**Sorption Testing of Zeolite incorporated latex foam:** The apparatus for this test was set up according to the schematic diagram shown in Figure 1. Ammonia gas was synthesized by placing 5 ml of 25% ammonia (NH<sub>3</sub>) solution in flask A. It was kept in a water bath and according to the apparatus generated gas transferred into flask B where foam sample was kept. After 1 h

time period, remaining ammonia in the flask was titrated with 1M hydrochloric acid (HCl) in the presence of methyl orange as an indicator. Unabsorbed NH<sub>3</sub> in flask B was measured by adding distilled water and titrated with same titrant and indicator. Above procedure was carried out for a period of 3 h.



**Figure :1 Schematic diagram of sorption test apparatus**

The first reading was taken at the end of one hour and others were at 30 min intervals. NH<sub>3</sub> sorption percentage was calculated using the below formula.

$$\frac{B - A}{B} \times 100$$

Where A is remaining NH<sub>3</sub> moles in two flasks, B is the initial NH<sub>3</sub> moles taken.

Carbon dioxide (CO<sub>2</sub>) gas was prepared in flask A by mixing 0.5 g of calcium carbonate with 1M HCl. Let the sample to adsorb CO<sub>2</sub> and measured the sample weight after 1 h for a period of 2 h. The first reading was taken at the end of 1 h and others at 30 min intervals. CO<sub>2</sub> gas adsorption was calculated as follows,

Minimum CO<sub>2</sub> sorption %

$$\frac{(W_2 - W_1) - 0.09}{W_1} \times 100$$

Where W<sub>1</sub> is the initial weight of the sample and W<sub>2</sub> is the final weight of the sample. Since the water is released in synthesizing of CO<sub>2</sub>, the minimum adsorption is considered.

### III. RESULTS AND DISCUSSION

**Behavior of zeolite dispersions:** Moisture content of zeolite powder, pH and average particle size of 1% zeolite solution shown in Table 3. Properties of Zeolite dispersion with 36% TSC is given in Table 4. Its particle size and pH were in the acceptable range [1] as dispersion particle size should be below 5 µm and pH should be either neutral or basic in medium. According to the Table 5 addition of zeolite into latex solution did not disturb the colloidal stability of latex to an acceptable level, as its pH was in the base range

**Table 3. Properties of 1% (w/w) zeolite solution**

Property	Zeolite powder
Moisture content	3.0

pH	8.35
Average particle size (µm)	2.83

**Table 4. Properties of Zeolite dispersion with 36% TSC**

TSC %	36.1
pH	10.3
Avg. particle size (µ)	2.75
Max. particle size (µ)	5.13
Viscosity (cps)	7.0

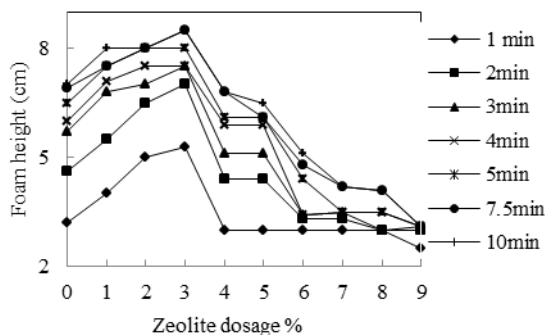
**Table 5: The stability of latex compound with 1% zeolite dispersion (36% TSC)**

Sample	pH of dispersion	pH of compounded latex	Coagulum content (g)
With zeolite	10.3	9.55	0.24
Control	-	9.65	0.00

**Stability of zeolite dispersion on latex foam:** Properties of LA-TZ latex is given in Table 6. Foam heights of latex compounds on partially foamed stage for different dosages of zeolite are given in Fig.2. Foaming ability increased up to 3% of zeolite dosage and it decreased again with increasing zeolite content. It can be seen that the excess of zeolite disturbed the foam structure. As zeolite consists with negatively charged surface, they may act as a foam stabilizer in to some extent and result increase in foam height. However, with the higher dosage of adsorbent, it only act as a foreign particle and disturb the compound foaming by adsorbing latex stabilizers. This can be clearly seen in compound prepared with 9% zeolite. It indicated that the addition of zeolite up to certain extent did not adversely affect the final foam structure of the product.

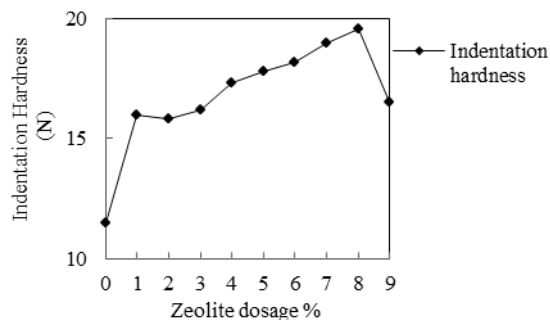
**Table 6: Properties of LA-TZ latex**

Total solid content (%)	Mechanical stability (sec)	pH
60.24	1281	9.85



**Fig.2. Foam heights of latex compounds at partially foamed stage for different dosages of zeolite**

**Physicochemical properties of latex foam compounds with zeolite:** Variation of Indentation hardness of zeolite incorporated latex foam with the zeolite dosage is given in Fig.3. Results showed that indentation hardness, increased up to 8% zeolite dosage in the foam. The hardness of latex foam was influenced by the geometry of the cores, spacing and configuration in relation to each other. It was shown that the indentation hardness, increased with the incorporation of adsorbent due to lack of free space in foam, which decrease the amount of air in the foam structure. However, beyond the above dosage the hardness decreased may be due to the phase separation which leads to a collapse in foam structure.

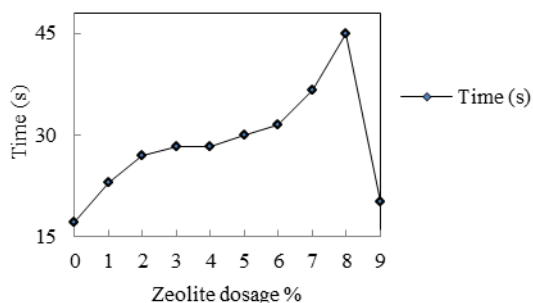


**Fig.3. Indentation hardness of latex compound with zeolite**

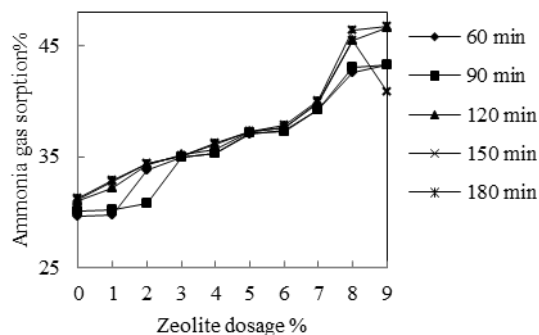
Results in Fig.4 showed that the flame retardant property improved with increased zeolite dosage in foam products. Previous works also proved that zeolite can be acted as a flame retarder [4- 6]. Zeolite is capable of adsorbing water and to make a bound water layer around them. When foam starts to burn these bound water adsorb the energy from the flame and evaporate the water. As a result of this endothermic reaction, it may prevent the flame propagation and protect the foam product, however the sample with 9% zeolite shows drop in flame retardant property. The reason may be due to the decrease of surface area of the Zeolite, due to the phase separation.

Sorption capacities for NH<sub>3</sub> and CO<sub>2</sub> for latex foam product with different zeolite dosages are shown in Fig.5 and 6 respectively. Results showed that zeolite incorporated NR latex foam had a higher sorption power for inorganic gases in comparison to normal NR latex foam. Zeolite pore diameters may suited to ammonia molecular diameter [9] hence ammonia gas molecule can be adsorbed easily and reached equilibrium within 60 min at low dosage level of Zeolite in foam. The shape selective properties of zeolite also facilitate the ammonia gas intake [10]. Ammonia molecules physically adsorbed on to the zeolite surface by weak Vander Waal forces and hydrogen bonds. Since ammonia molecule can donate electrons to Lewis acid sites of zeolite molecule (AlO<sup>+</sup>, Al(OH)<sub>2</sub><sup>+</sup>, AlO(OH), Si<sup>+</sup>) it could be chemisorbed the ammonia molecules [11].

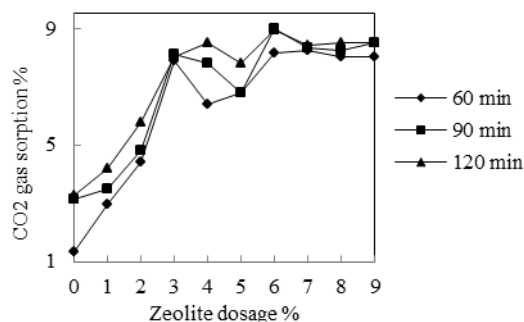
Adsorption of CO<sub>2</sub> into zeolite incorporated latex foam was less than ammonia. This may be due to chemical inert nature of CO<sub>2</sub> and it makes less chemical bonding with zeolite. However physisorption of CO<sub>2</sub> can occur on to zeolite [12].



**Fig.4. Flame retardant property of latex compound with zeolite**



**Fig.5. Ammonia gas sorption % of foam modified with zeolite**



**Fig.6. Carbon dioxide sorption % of foam modified with zeolite**

#### IV. CONCLUSIONS

The work and results reported in this paper suggests that zeolite dispersion can be successfully incorporated into natural rubber latex compound to enhance indentation hardness, fire retardant and sorption properties of latex foam products. Furthermore, the optimum level of Zeolite was identified as 8% considering the stability of latex compound and physiochemical properties of latex foam products.

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#### REFERENCES

- [1] D. C. Blackley, "Polymer Latices", in testing and applications, 2nd ed. Vol.3, Applied science publisher Ltd, London, 1997, pp.1 - 229.
- [2] V. K. Jha, M. Matsuda, and M. Miyake, "Sorption properties of the activated carbon-zeolite composite prepared from coal fly ash for Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>," J. Hazard. Mater., vol. 160, no. 1, pp. 148–153, Dec. 2008.
- [3] T. Mishra, S.K. Das, and B. Mahato, "Synthesis and Sorption Properties of 13X Zeolite Derived from Coal Fly Ash," J. Metall. Mater. Sci., Vol. 45, no. 4, pp.193-198, 2003.
- [4] J. Wang, K. Yang, and X. Zheng, "Studies on the effect of 4A zeolite on the properties of intumescent flame-retardant agent filled natural rubber composites," J. Polym. Res., vol. 16, no. 4, pp. 427–436, Jul. 2009.
- [5] H. Demir, E. Arkiş, D. Balköse, and S. Ülkü, "Synergistic effect of natural zeolites on flame retardant additives," Polym. Degrad. Stab., vol. 89, no. 3, pp. 478–483, Sep. 2005.
- [6] Jincheng Wang and Yuehui Chen, "Effect of Microencapsulation and 4A Zeolite on the Properties of Intumescent Flame-retardant Natural Rubber Composites," J. Fire Sci., vol. 26, no. 2, pp. 153–171, Mar. 2008.
- [7] J. Han, Y. Zhang, C. Wu, and Y. Ma, "Effect of Reynolds number on the dispersion of carbon black in natural rubber latex and filler-rubber interfacial interaction in high-speed jet flow field," Polym. Compos., vol. 34, no. 7, pp. 1071–1075, Jul. 2013.
- [8] A.R.M. Rajakaruna, "Incorporation of activated carbon Natural rubber latex foam for improvement in sorption property," M.Sc. dissertation, Dept. Chem. Eng, Moratuwa Univ, Sri Lanka, 2006.
- [9] Edith M. Flanigen, "Chap2 - Zeolite and Molecular Sieves: An Historical Perspective," in Surface Science and Catalyst, H. Van Bekkum, E.M. Flanigen, P.A. Jacobs & J.C. Eds. Elsevier, 2001, pp. 11-35.
- [10] Q. Huo, "Chapter 16 - Synthetic Chemistry of the Inorganic Ordered Porous Materials," in Modern Inorganic Synthetic Chemistry, R. Xu, W. Pang, and Q. Huo, Eds. Amsterdam: Elsevier, 2011, pp. 339–373.
- [11] L. Markovska, V. Meshko, V. Noveski and M. Marinkovski, "Solid Diffusion Control of The Adsorption of Basic Dyes onto Granular Activated Carbon and Natural Zeolite in Fixed Bed Columns," J. Serb. Chem. Soc. vol. 66, no 7, pp. 463-475, 2001
- [12] M. Elanany, M. Koyama, M. Kubo, E. Broclawik, and A. Miyamoto, "Periodic density functional investigation of Lewis acid sites in zeolites: relative strength order as revealed from NH<sub>3</sub> adsorption," Appl. Surf. Sci., vol. 246, no. 1-3, pp. 96–101, Jun. 2005.

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