

Nano ZnO · Latex compounding · Thermal ageing · Leaching · Tear strength

Zinc oxide (ZnO) plays a major role in the accelerated sulphur vulcanization process. Nano ZnO at different levels were incorporated into natural rubber latex (NR) and the properties of the resulting vulcanizates were compared with conventional micro ZnO incorporated into films. The latex compounds (containing micro and nano ZnO) were cast into sheets and cured. The antifungal activities of nano ZnO incorporated into dry films were evaluated. Mechanical properties such as tensile strength, elongation at break, modulus and tear strength were measured and compared with dry vulcanizates containing micro ZnO. Effect of ageing and leaching on the properties of the dry films were also evaluated. The reinforcing effect of nano ZnO was observed from the mechanical property measurements.

Einfluss von nanopartikulären Zinkoxid auf die Eigenschaften von durch Latex-Compounding hergestellten Naturkautschukvulkanisaten

Nano-ZnO · Latex Compounding · Thermische Alterung · Rissbeständigkeit

Zinkoxid (ZnO) spielt in der beschleunigten Schwefelvulkanisation eine große Rolle. Nano-ZnO wurde mit verschiedenen Konzentrationen in Naturkautschuklatex (NR) eingearbeitet und die Eigenschaften der resultierenden Vulkanisate mit denen von Filmen verglichen, in die konventionelles Mikro-ZnO eingearbeitet worden war. Die Latex-Compounds mit Mikro- und Nano-ZnO wurden in Streifen zerlegt und vulkanisiert. Die antifungielle Aktivität von in Filme eingearbeiteten Nano-ZnO wurden untersucht. Die mechanischen Eigenschaften wie Zugfestigkeit, Reißdehnung, Modul und Rissbeständigkeit wurden ermittelt und mit denen von getrockneten und Mikro-ZnO enthaltenden Filmen verglichen. Der Einfluss von Alterung und Auslaugen auf die Eigenschaften der Filme sowie der Verstärkungseffekt von Nano-ZnO wurde betrachtet.

Figures and Tables:
By a kind approval of the authors

Effect of nanoparticulate Zinc Oxide on the Properties of natural Rubber Vulcanizates produced by Latex Compounding

Introduction

Latex compounding involves the process of mixing of natural rubber latex (NR) with vulcanizing ingredients i.e. sulphur, activator, accelerator, stabilizer, filler, special additives etc. Each ingredient has a specific function either in processing, vulcanization or end use of the products. Therefore getting a finished product with specific properties, it is desirable to add necessary ingredients to the latex. Earlier period onwards it has been observed that, for curing unsaturated rubber, metal oxides can be used. Metal oxides improve the efficiency of sulphur-based cure systems. The most useful metal oxide used in this regard is zinc oxide (ZnO). ZnO acts as an activator for rubber crosslinking by sulphur or sulphur donors [1, 2]. It increases the amount of bound sulphur and the efficiency of the vulcanization [3] and reduces the vulcanization time. Besides its effect on the curing process, ZnO also contributes beneficial effects on the physical properties of rubber too [4]. However, the exact role of ZnO as an activator is highly dependent on the type of accelerator present in the vulcanization system. Besides NR, ZnO is also used as a good crosslinking agent in carboxylic rubbers [5, 6], neoprene rubber [7] and elastomers containing halogen groups [8]. Global production of zinc oxide is about 10^5 tonnes per year, and rubber industry alone utilizes a major portion of it for the manufacturing of different rubber products. Despite the beneficial role of ZnO in the mechanism sulphur vulcanization, there are issues associated with them when they are released to the environment. Zinc is considered as a heavy metal and European Union classified ZnO as hazardous chemical to the environment. The release of which adversely affect the eco-system especially to the aquatic organisms. Therefore, Government Organizations and Environmental Protection Agencies proclaimed that its application in rubber technology should be reduced and controlled [9]. Various efforts have been taken

to reduce the zinc levels in rubber compounds [10–13].

Release of zinc into the environment from rubber occurs at various ways such as during production, during disposal and recycling of rubber products and during service conditions, e.g. through wear of tires etc. Therefore decreasing the ZnO level in rubber products is important and safer in environmental as well as economic point of view. Experiments including use of various metal oxides, nano-ZnO, zinc complexes and clay loaded with zinc ions has been prepared and is mixed to evaluate its effectiveness as activator for sulphur vulcanization [14–17]. For reducing zinc levels, studies on the use of alternative zinc carboxylates, [10, 18] activators based on other metal centres, [19] were carried out by the researchers.

To minimize the usage of ZnO without compromising the technological properties of the vulcanizates, nano concept has come in to existence. In order to reduce the amount as well as to improve the efficiency of ZnO in latex/rubber compounds, the activity of ZnO should be increased. By using highly active ZnO, its surface area increases and Zn^{2+} ions at the surface of the crystals also increases, which results in a higher reactivity [20]. The increased surface area of the particle favors better contact between crosslinking agents and elastomer chains and improves the ultimate properties of the vulcanizates. Uses of nanoparticulate

Authors

**K. Anand, Siby Varghese,
Thomas Kurian, Kerala, India**

Corresponding author:
Siby Varghese
Technical Consultancy Division,
Rubber Research Institute of India
(RRII), Kottayam 686 009, Kerala,
India
siby@rubberboard.org.in

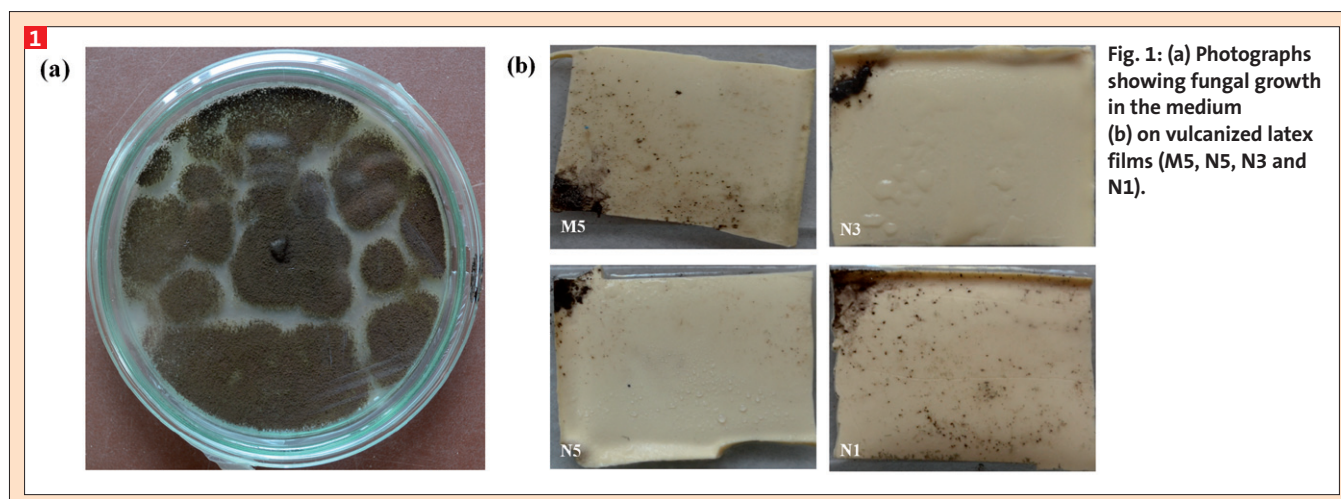


Fig. 1: (a) Photographs showing fungal growth in the medium (b) on vulcanized latex films (M5, N5, N3 and N1).

ZnO in natural rubber [21, 22] and as filler in elastomers [23] were studied in detail.

In the field of rubber science and technology, now researchers are focusing on using nano-ZnO as a substitute of micro-ZnO in the sulphur vulcanization process [24-27]. It has been reported that the equivalent replacement of conventional ZnO (Red Seal) by nano-ZnO leads to an improvement in the properties of the rubber compound, especially the abrasion resistance, H-pullout force, and tear strength [28]. Although alternative metal oxides as activators for sulphur vulcanization have been studied thoroughly, none of them find suitable to replace ZnO without significantly affecting processing as well as performance characteristics of rubber compounds. As far as activity of ZnO is concerned, the dispersion of ZnO particles in the elastomer matrix is of great importance. Therefore, effective control of the performance of ZnO as an activator with respect to processing and final properties of rubbers is a challenging task.

In this study, NR latex compounds were prepared by adding ZnO nanodispersions at different levels and the technological properties of the resulting latex vulcanizates were examined. The efficiency of nano ZnO against fungal attack on latex films were also evaluated and compared with conventional ZnO incorporated films.

Experimental

Materials

Centrifuged natural rubber latex (60% dry rubber content) was collected from Central Experimental Station of Rubber Research Institute of India (RRII), Kotta-

1 Formulation of latex compound

Ingredients	Dry (phr)			
	M5	N5	N3	N1
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	0.10	0.10	0.10	0.10
50% Sulphur dispersion	1.5	1.5	1.5	1.5
50% ZDC* dispersion	1.0	1.0	1.0	1.0
50% TDQ** dispersion	0.4	0.4	0.4	0.4
50% ZnO [#] dispersion (Micro)	0.5	-	-	-
50% Nano-ZnO dispersion	-	0.5	0.3	0.1

[§] High ammonia type

* Zinc-diethyldithiocarbamate

** 2,2,4-trimethyl-1,2-dihydroquinoline

Zinc oxide

yam, India. Nano-ZnO dispersion (50% concentration) with an average particle size of 35 nm was procured from Sigma Aldrich (product of Buhler, Inc). Commercial rubber grade ZnO (White Seal) having particle size of few micrometer used as control and 50% aqueous dispersions of other compounding ingredients were prepared by ball milling.

Methods

Preparation of latex compound and its vulcanizates

The ingredients used for compound formulation are given in Table 1. Before compounding, the total solid content of latex has been reduced to 55%. ZnO samples were designated as M5, N5, N3 and N1. The letters 'M' and 'N' refers to micro and nano-ZnO. The number followed by the letter indicates 0.5, 0.5, 0.3 and 0.1 phr ZnO respectively.

The latex compound was matured for 1 h and films were cast on side raised glass plates having dimensions 13cm x 10cm x 2mm and left at room tempera-

ture for a day. The films were dried in hot air circulated oven at 60°C for 2h and have been allowed to go to 90°C and kept at this temperature for 1h to obtain vulcanized films.

Antimicrobial activity of latex films

Isolation of contaminated fungi and its efficiency evaluation

A bit of contaminated film was placed over a PDA plate and incubated. After 7 days of incubation, the fungal contaminant from the bit was isolated and purified. The growth of fungus in the medium is shown in Figure 1(a). To confirm the efficiency of the isolated fungi, a bit of which is placed over fresh rubber film and incubated for 1 week under moisture condition.

Testing of the latex films for fungal growth

A bit of latex film from each treatment was placed over a petri plate and the fungal contaminant (a loopful of spores) was inoculated on one side of each sam-

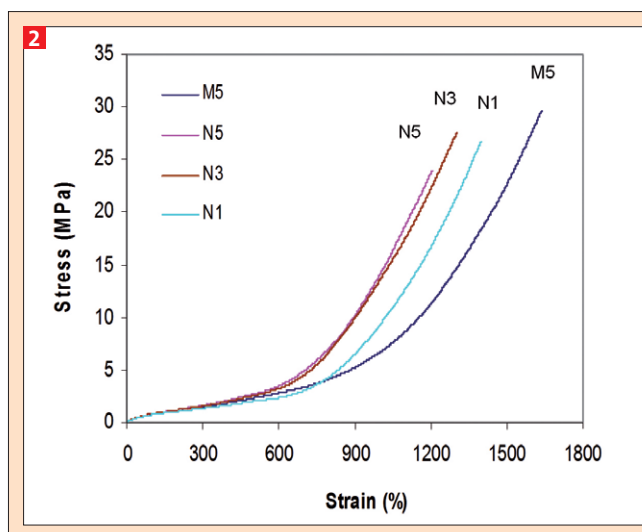


Fig. 2: Stress-strain behaviour of latex films containing different doses of ZnO.

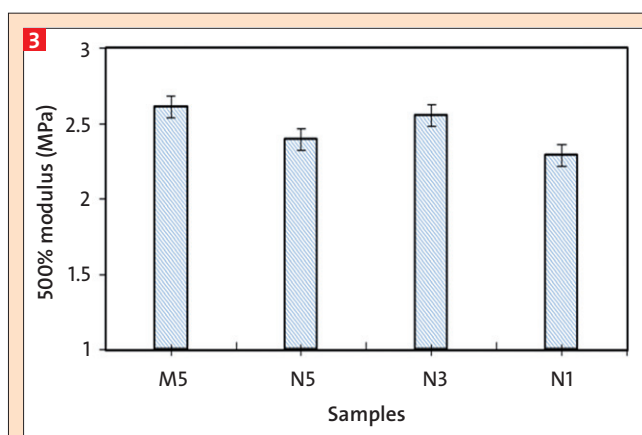


Fig. 3: Modulus at 500% elongation of latex films vs. ZnO content.

2 Antimicrobial activity of latex films

Sample	Fungal growth (in %)		
	After 5 days	After 10 days	After 15 days
M5	25	50	75
N5	0	25	50
N3	0	0	0
N1	50	75	100

the magnitude of surface coverage was 25% and 50% respectively (Table 2). After 5 days, no fungal growth was observed on specimens N5 and N3. However, after 10 days fungal growth was observed with the specimen N5. After 15 days of incubation, the specimens M5, N5 and N1 were found to be susceptible for fungal growth whereas no fungal growth was seen on N3. Thus, the addition of 0.3 phr nano ZnO resulted in better protection of latex film against the fungal growth. Maximum fungal growth was observed in the specimen N1, after 15 days of storage.

Mechanical properties

The stress-strain curves of compounded NR latex films with various ZnO contents are shown in Figure 2. The strain induced crystallization is accelerated by adding nano-ZnO, as it is evident from a sharp increase in stress after 500% elongation. At the breaking point the curves come closer except the compound with micro-ZnO. In the lower strain region modulus is low and it increases with increase in strain. At higher strain (>700%), the stress increases sharply due to crystallization phenomena. In the case of micro-ZnO loaded specimens, increase in stress happens only at higher strains whereas for nano-ZnO incorporated compounds, a sharp rise in stress were seen at lower strains. This accounts better onset crystallization for nano-ZnO induced compounds than specimens with conventional ZnO. Effects of functionalized graphene sheets (FGSs) on strain-induced crystallization of NR are investigated [29]. The authors reported that, the onset of crystallization occurs at significantly lower strains for FGS-filled NR samples compared with carbon black filled NR, even at low loadings. Effect of micro and nano-ZnO on 500% modulus of compounded NR latex films is represented in Figure 3. At equal amount of ZnO (0.5 phr level), a slight decrease in modulus is observed for vulcanized films containing nano-ZnO than conventional ZnO. Modulus is a bulk property. Particle

ple bit. Moisture was provided on alternate days and the observations (fungal growth) of the bits were taken in five days of interval.

The mechanical properties of vulcanized latex films at different ZnO loadings were tested using dumbbell shaped specimens on ZWICK Universal Testing Machine (Model 1474) as per ASTM D-412. Also, mechanical properties of leached and aged samples were conducted using the above manner. Tear strength of samples were carried out according to ASTM D-624 using an unnicked 90° angle test piece at a cross head speed of 500 mm/min. All mechanical tests were carried out at 27°C.

Leaching of latex films were carried out in distilled water. The latex films were kept in distilled water for about 6h and dried in hot-air oven to remove water and measured the mechanical properties.

Ageing studies of latex films were conducted by keeping the samples in hot-air oven at 70°C for 7 days and measured the mechanical properties.

Swelling studies

Circular samples having a diameter of 2cm were cut from the vulcanized film using a standard die. Initial weights of the samples were noted. The films were immersed in toluene and were taken at various intervals of time and weighed again after removing the solvent from the surface of the samples using blotting paper. This procedure continued until no more solvent uptake by the polymer was noted. The amount of solvent absorbed at various time intervals were measured and graphs were plotted.

Results and discussion

Antimicrobial activity studies

The result of antimicrobial activity of latex films were shown in Table 2. The growth as well as the extent of surface coverage by the fungus were given in percentage. Photographs of the fungus inoculated latex film bits and their growth are shown in Figure 1(b). It can be seen that within 5 days, the bits M5 and N1 was covered by inoculated fungi and

agglomeration dominates as particle size reduces and this is more significant at higher nanoparticle loading. Thus, lower modulus resulting by 0.5phr loading of nano-ZnO is mainly because of non-uniform distribution in the latex polymer in the form of clusters. However, 0.3phr nano-ZnO yielded competent modulus of 2.55MPa to the latex vulcanizates which comparable to 2.61MPa given by latex films consisting 0.5phr conventional ZnO.

Swelling behavior

Figure 4 shows the swelling behavior (solvent resistant capacity) of latex vulcanizates containing micro and nano-ZnO. The solvent uptake was found to be lower for films containing 0.3 phr nano-ZnO. Compared with micro-ZnO, a slightly higher solvent uptake was observed for 0.5 phr nano-ZnO filled films. This might be due to improper distribution of ZnO. Nano-ZnO owing to its higher surface activity may undergo agglomeration immediately after their addition in to latex. This can cause the formation of weak/improper networks and open new pathways for the solvent to enter in to the polymer matrix. Therefore, it has been observed that 0.3phr nano-ZnO is optimum for latex films with good solvent resistance capacity.

Effect of ageing

Figure 5 shows the variation in tensile strength of latex films containing micro and nano-ZnO before and after ageing. Tensile strength of a composite material purely depends on effectiveness of stress transfer between polymer matrix and filler [30]. Geometry of the filler, particle size distribution of filler, filler concentration and polymer-filler interaction controls the tensile strength of the material. Polymer matrix-nanoparticle interface controls stress transfer and is very important for the improvement of tensile strength [31]. Before ageing, 0.5phr nano-ZnO filled latex compound showed a slightly lower tensile strength compared to the other one having the same dosage of micro ZnO. This is attributed to poor dispersion of nano-ZnO in the latex matrix. Nanodispersions at higher loading can cause agglomeration between particles and may not be distributed uniformly with in the polymer matrix that leads to the formation of defects. This creates chance of discontinuity at polymer-filler interface. Thus, poorly bonded particles are inefficient to transfer stress

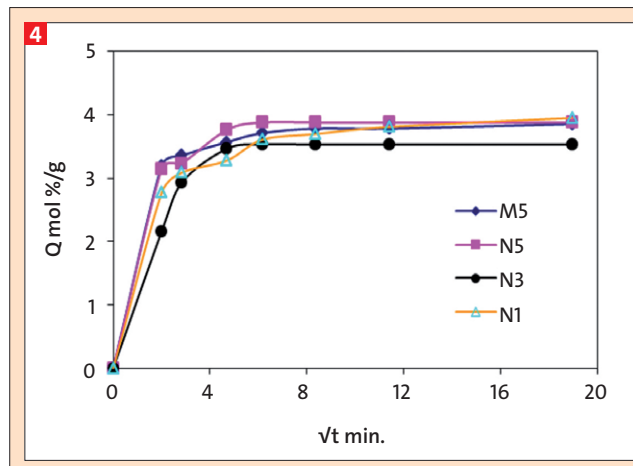


Fig. 4: Swelling behaviour of latex films containing different doses of ZnO (Q- Mole per cent uptake per 100 g of the sample)

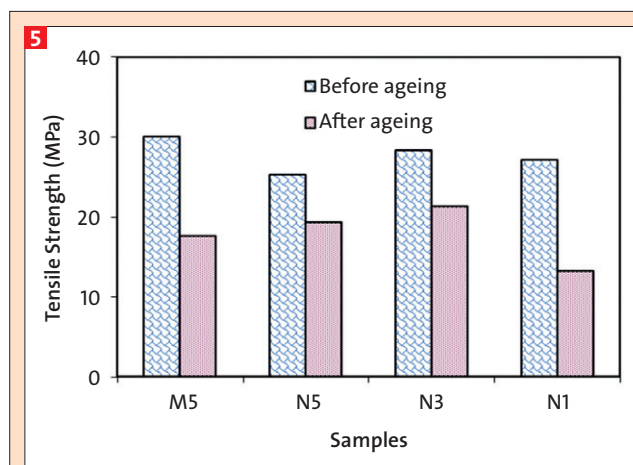


Fig. 5: Tensile strength of latex films vs. ZnO content before and after ageing.

and yields composites with lower strength. At the same time, 0.3 and 0.1phr nano-ZnO provides a higher strength to the compounded latex films and are comparable with micro-ZnO filled one at a higher loading of 0.5phr. Significant improvement in ageing resistance was achieved by using nano-ZnO in latex compounding (at levels >0.1phr). At nanometer level, ZnO offers better thermal stability to the vulcanizates [10]. However, all the systems exhibited lower tensile strength after ageing at 70°C for 7 days. After ageing, there will be change in crosslink density, crosslink type (poly, di and monosulphide) and main chain modification. Crosslink reformation into a stable network inhibited the ability of natural rubber to strain-induced crystallization at longer durations of ageing. Effect of micro and nano-ZnO on elongation at break of latex compounds before and after ageing is represented in Figure 6. Elongation at break denotes the maximum extension experienced by the sample under tension. The elongation at break also depends on filler-polymer interaction. After ageing, the percent re-

tention in elongation at break values of M5, N5, N3 and N1 are 69%, 90%, 83% and 74% respectively.

The effect of ageing on the variation in tear strength of latex vulcanizates containing micro and nano-ZnO are depicted in Figure 7. It can be seen that addition of nano-ZnO improved the tear strength of the films. The increase in tear resistance with ZnO loading is due to the increased ability of the elastomer to dissipate strain energy near the tip of growing cracks. Improvement in tear strength at lower nano-ZnO- loading (0.3 phr) is attributed to uniform distribution of ZnO nanoparticles in the polymer matrix. Moreover, the higher surface area of ZnO nanoparticles also offers improved interfacial properties and better rubber-filler interaction than conventional ZnO.

Effect of Leaching

Leaching is a common procedure for the manufacture of latex products especially dipped articles. Leaching is considered as an important process because; it can reduce water soluble latex proteins which are identified as root cause for latex al-

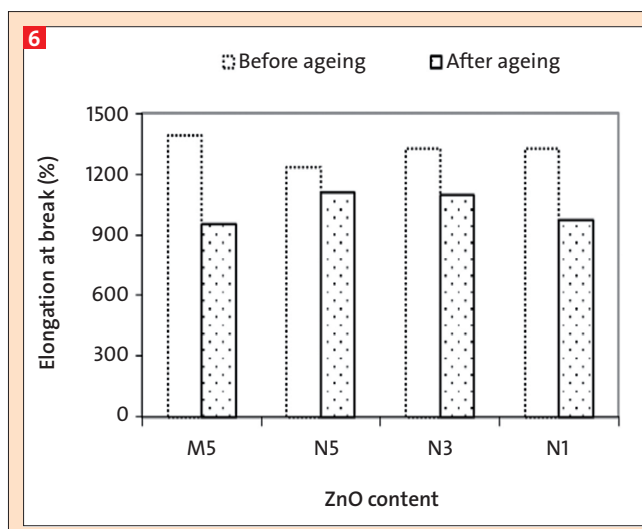


Fig 6: Elongation at break of latex films vs. ZnO content before and after ageing.

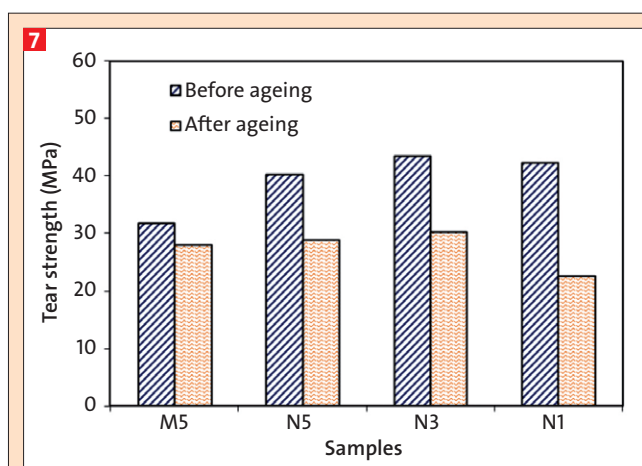


Fig. 7: Tear strength of latex films vs. ZnO content before and after ageing.

lery [32]. Leaching also improves the tensile strength and modulus of cast NR latex films [33]. It has been reported that under high humidity conditions, pre-vulcanized NR latex films showed increased modulus after leaching [34].

Figure 8 shows variation of 100% modulus before and after leaching for latex vulcanizates containing micro and nano

ZnO. It can be seen that an increase in modulus is observed for all the systems after leaching. The increase in modulus after leaching is expected to be due to the removal of greater amount of hydrophilic non-rubbers. The non-rubber constituents hinder the particle-particle cohesion by making a physical barrier between them. Leaching effectively removes

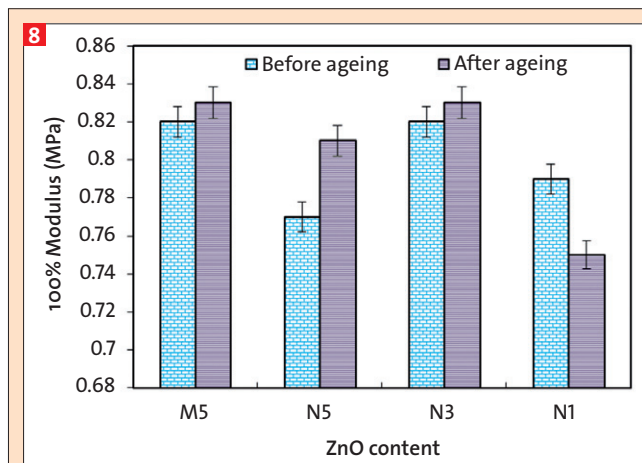


Fig. 8: Modulus at 100% elongation of latex films vs. ZnO content before and after leaching.

this physical barrier and enables better modulus. It has been reported elsewhere [34] that highly vulcanized latex has more added non-rubbers. The decrease in modulus after leaching for latex films containing 0.1phr nano-ZnO might be due to excess water absorption by the film. Increase in moisture content leads to an increase in size of the flaws and causes early tensile failure [35].

Effect of addition of micro and nano-ZnO on tear strength of compounded latex vulcanizates before and after leaching is represented in Figure 9. Improvement in tear strength can be attributed to the improved interaction between ZnO nanoparticles and latex particles. At similar loading (0.5phr), the higher surface area of nano-ZnO and their distribution also contributes enhanced tear strength. All the samples exhibited slightly higher tear strength after leaching. Nano-ZnO at 0.5phr loading exhibited the highest tear strength of 49 kN/m after leaching. This is expected to be due to the removal of non-rubber constituents, promoting better particle to particle cohesion.

Conclusions

Latex vulcanizates incorporated with nano ZnO exhibited improved modulus and tear strength. The antimicrobial activity of nano ZnO incorporated latex film was also found to be good. Thermal stability of nano ZnO incorporated vulcanizates were found to be superior, which was revealed from ageing studies. Agglomeration of ZnO in NR caused by high particle-particle interaction would be severe and the modulus was affected by adding 0.5 phr nano ZnO. Leaching resulted improved modulus to the latex films. In short, compared with NR compounded with micro ZnO, NR vulcanizates containing nano ZnO exhibit excellent mechanical properties and antifungal activity where the optimal dosage of nano ZnO is 0.3phr. Adding excess amount of high surface area ZnO dispersions not only diminishes the technological properties but also have a detrimental effect on latex stability too.

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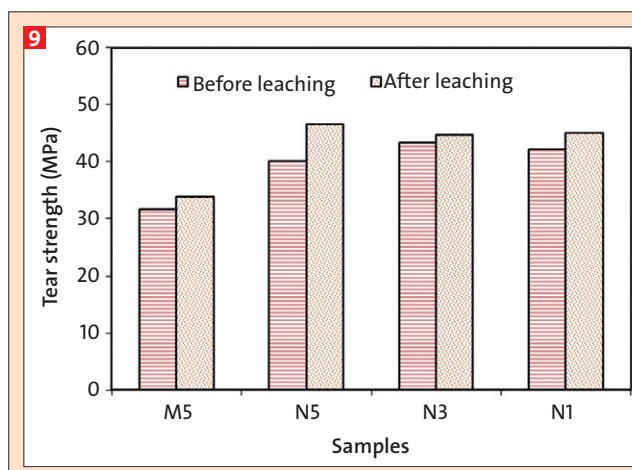


Fig. 9: Tear strength of latex films vs. ZnO content before and after leaching.