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Effect of nanoZnO over conventional ZnO on preservation of concentrated natural rubber latex

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Abstract

An attempt was made to replace conventional ZnO with nanoZnO in low ammonia, tetramethylthiuramdisulphide (TMTD)/Zinc oxide (ZnO) natural rubber latex preservative system (LATZ). Different percentages of TMTD and nanoZnO dispersions containing equal portions were prepared and used to preserve the latex. Centrifuged natural rubber latex (CNRL) thus prepared were tested for VFA (volatile fatty acid) number and MST (mechanical stability time) periodically over a period of 75 days. Mechanical properties of vulcanized latex thin films made out of CNRL preserved were measured. Development of VFA number in CNRL samples preserved with nanoZnO was lower than the sample prepared with the conventional ZnO (control). Both the VFA number results and surface plots of the matured CNRL samples showed that preservative action of the modified preservative system was mainly governed by the amount of nanoZnO in the system. MST values of CNRL preserved with nanoZnO substituted systems were significantly high when compared to the control. Tensile and tear properties of the vulcanized films prepared using CNRL preserved with nanoZnO were almost comparable with those of the vulcanized films prepared using control system. The statistical analysis indicated that CNRL preserved with modified preservative system of 10% and 15% of TMTD/nanoZnO could be stored up to 55 and 75 days respectively, without exceeding VFA value above 0.02.

Key words: centrifuged natural rubber latex, MST, nanoZnO, preservative system, TMTD, VFA

Introduction

Natural rubber latex (NRL), being a natural polymer obtained from *Hevea brasiliensis* possesses certain important unique characteristic properties owing to its high molecular weight polymer chains, and chemical structure of the polymer backbone. These characteristic features have enabled natural rubber to be among one of the highly consumed elastomers in the world with over 40,000 products (van Beilen and Poirier, 2007). However, the presence of non-rubber substances in latex, such as proteins and carbohydrates leads to spontaneous coagulation and putrefaction of field NRL, which is regarded as one of the major constraints in the NRL industry (Blackley, 1997).

In order to suppress the spontaneous coagulation and putrefaction and also to improve the stability of the latex for long term storage, field NRL need to be preserved. It is considered one of the most important steps in latex processing as it plays a vital role in keeping the properties of field NRL suitable for further processing. The effectiveness of a preservative system depends mainly on the ability to (a) suppress the activity and the growth of microorganisms, (b) enhance the colloidal stability of latex, and (c) deactivate trace metal~~s~~ ions (Blackley, 1997). In addition, a preservative system should be harmless, environmentally safe, odorless, commercially viable, low cost, and should not interfere with production processes.

The widely used preservative systems for CNRL include high ammonia (HA) latex preservation system and low-ammonia latex preservative system in tetramethylthiuramdisulphide (TMTD)/ Zinc oxide (ZnO). Ammonia, being a volatile and irritating substance, use of HA system has become a great challenge in NRL industry (Chaikumpollert, 2008). In LA system, ammonia is used as the primary preservative agent, while TMTD and ZnO are used as the secondary preservatives, thus called LATZ system (Nadarajah, 1979). For the industrial applications where HA system cannot be applied, LATZ is the commonly employed alternative preservative system used in the NRL industry. However, LATZ system is inherited with its own drawbacks; generation of carcinogenic nitrosamines during product manufacture and contamination of natural water resources (Lee, Chon and Kim, 2005; Miao *et al.*, 2010; Sheth and Desai, 2013; Rajput *et al.*, 2018).

As such, during past two decades, the researchers have carried out a considerable amount of research to find less risky, commercially viable alternative preservative system for field NRL and CNRL (Chaikumpollert, 2008; Loykulnant *et al.*, 2012; Wang *et al.*, 2015). However, to date, none of these studies have been able to come up with an industrially viable preservative system to replace the currently used LATZ preservative system. The recent advancement of nanomaterials, which involves the materials with the size of 100 nm or less in one or more dimensions (Espitia *et al.*, 2012), have shown their potential use in enhancing the antibacterial properties. Many researchers have studied the performance of inorganic nanomaterials, especially the nanoparticles of metal oxides, which are found to be effective and possess excellent antibacterial properties in comparison to their conventional micro and macro counterparts (Espitia *et al.*, 2012; Dizaj *et al.*, 2014). Among these metal oxides, nanoZnO has been widely studied in different preservative systems in a variety of applications owing to its enhanced antibacterial properties, low cost, excellent stability and less complex manufacturing processes (Wang *et al.*, 2003; Padmavathy and Vijayaraghavan, 2008; Dizaj *et al.*, 2014; Kołodziejczak-Radzimska and Jesionowski, 2014). It has been further shown that nanoZnO is more effective against certain bacteria when compared to some commonly used other metal oxide nanoparticles such as CuO, and Fe_2O_3 (Dizaj *et al.*, 2014). The ZnO is considered a comparatively less toxic material to human health as it is used as an additive in textile and rubber applications, which directly come in contact with human skin (Dizaj *et al.*, 2014). According to Dizaj *et al.*, the enhanced antibacterial activity of nanoZnO is attributed to its photocatalytic activity, high stability, and effectiveness against Gram-positive/Gram- negative bacteria, and their highly resistant pores. However, the same study reports that the antimicrobial activity of nanoZnO is largely depend on its particle size and concentration (Dizaj *et al.*, 2014).

Even though the antibacterial activity of nanoZnO has been widely reported, only a very few have reported about the antibacterial effect of nanoZnO in natural rubber. Rathnayake *et al.*, have recently shown that nanoZnO incorporated natural rubber latex foam possesses enhanced antimicrobial properties (Rathnayake *et al.*, 2014). A recent study carried out by Anand *et al.*, highlighted that pre-vulcanized latex films containing nanoZnO showed better antifungal properties when compared to latex films containing micro ZnO (Anand, Varghese and Kurian, 2015). Recently, Lv *et.al.*, reported that ZnO/ natural rubber nanocomposites have shown excellent antibacterial properties against *Escherichia coli* colonies (Lv *et al.*, 2014).

Despite having studied many novel preservative agents for NRL in recent years, none of the studies have focused on the use of nanoZnO as a preservative agent in LATZ system. The main objective of this study is therefore to reduce the amounts of secondary preservatives used in LATZ preservative system for CNRL. In this study, potential of nanoZnO and TMTD as secondary preservative system for CNRL at different loading is investigated. In addition, film properties of the CNRL preserved with nanoZnO and the CNRL preserved with conventional LATZ preservative system were compared.

Materials and Methods

Field latex with 30% (w/w) dry rubber content (DRC) was obtained from Dartonfield Estate of Rubber Research Institute of Sri Lanka. Industrial grade chemicals required for the preparation of centrifuged latex and vulcanized latex films, including ammonia, tetramethylthiuramdisulphide (TMTD), conventional zinc oxide (ZnO), lauric acid and phosphoric acid [for the preparation of di-ammonium hydrogen phosphate (DAHP)], nanoZnO (98.6% w/w), potassium hydroxide (KOH), sulphur, zinc diethyldithio carbamate (ZDEC), and phenolic -type antioxidant, were purchased from a general chemical supplier. All the analytical grade chemicals needed for latex testing were purchased from Sigma-Aldrich, GMBH, Germany.

Characterization of conventional ZnO and nanoZnO by using XRD, SEM and particle size distribution data

Bruker D8 Advance Eco X-ray powder diffractometer (XRD) with CuKα ($\lambda = 1.54060$ Å) radiation was employed to obtain X-ray diffraction patterns of ZnO samples in order to determine the purity of samples. The instrument was operated from 5-80° on 2θ scale at the scanning rate of 0.001θ/s.

The average crystallite size, L of both types of ZnO samples were calculated by Scherrer equation (Patterson, 1939; Monshi, Foroughi and Monshi, 2012),

$$L = \frac{K\lambda}{\beta \cos\theta} \qquad \text{Eq 01}$$

where, λ is the weighlength of X-ray in nanometer (nm), β is the peak width of the diffraction peak profile at half maximum height in radians, and K is a constant related to crystallite shape ($K = 0.9$).

The morphologies of conventional ZnO and nanoZnO powders were obtained by scanning electron microscope images by using a Zeiss Evo LS15 Scanning Electron Microscope (SEM) operated at the accelerating voltage of 5.0kV. Quorum SC7620 Mini Sputter Coater system was employed to apply a gold/palladium alloy coat on powder samples before performing the SEM analysis.

The particle size distributions of both powders were determined in Malvern NanoS 90 particle size analyzer by using polycarbonate cuvettes at 25 °C. The powder dispersions were made by using de-ionized water. Here, the refractive index and absorption of both conventional and nanoZnO were taken as 1.96 and 0.010, respectively.

Preparation of centrifuged natural rubber latex (CNRL) samples preserved with different preservative systems

CNRL samples were prepared using field latex preserved with different combinations of TMTD/ZnO along with 0.2% (w/w) ammonia as shown in Table 1. TMTD/ZnO dispersions were prepared by vigorous grinding of powder mixture at room temperature with the addition of water and dispersion agents in a ball mill for three days.

Table 1. *TMTD/ZnO compositions used*

Dispersion System	Chemical combination			
	TMTD % (w/w)	Conventional ZnO % (w/w)	Nano ZnO % (w/w)	Percentage of total dispersion of TMTD/ZnO (%)
Control	12.5	12.5	-	25
Nano-1	12.5	-	12.5	25
Nano-2	10.0	-	10.0	20
Nano-3	7.5	-	7.5	15
Nano-4	5.0	-	5.0	10
Nano-5	2.5	-	2.5	5

CNRL samples were prepared as mentioned elsewhere (Tillekeratne, Nugawela and Seneviratne, 2003). In brief, soon after collecting field latex, all the samples were first preserved with the addition of 0.2% (w/w) ammonia on latex using a 10% (w/w) ammonia solution. Then TMTD/ZnO dispersion systems were added as shown in Table 1. Here, if the strength of the dispersion is X, X% TMTD/ZnO is added at the rate of 1 L for 1000 L of field latex, so the final strength of TMTD/ZnO would be 0.00X% by weight on latex. Subsequently, 10% (w/w) ammoniumlaurate, 15% (w/w) DAHP were added and allowed to strand for 24 hours to settle magnesium ions in the latex. Then the sludge was removed and the latex samples were then centrifuged using a laboratory scale latex centrifuge machine with the rotational speed of 7000 to 10,000 rpm to obtain CNRL. After centrifugation process, 10% (w/w) ammonia solution and respective TMTD/ZnO dispersions were topped up assuming 50% of these chemicals were removed with skim latex during the process of centrifugation. In order to ensure the accuracy and precision of data, latex samples were prepared in triplicate. In this study, the control sample was prepared using 25% (w/w) TMTD and conventional ZnO dispersion as practiced by the CNRL manufacturers in the industry to meet the preservative strength of 0.025% on latex.

Characterization of CNRL samples

Raw rubber properties of CNRL including, total solid content (TSC), alkalinity and DRC of each sample were evaluated as per ISO 124, 125 and 126 standard test procedures, respectively**.**

Determination of VFA number

The VFA numbers of the CNRL samples preserved with different preservative combinations were determined according to ISO 506 after keeping the samples for 15, 35, 55 and 75 days subsequent to centrifugation process.

Determination of Mechanical Stability Time (MST)

Mechanical stability of CNRL samples were determined as per ISO 35, after 20 and 30 days from the date of centrifugation.

Preparation of compounded latex films and evaluation of properties

Each CNRL sample was compounded according to latex compounding formula shown in Table 2, and latex films casted on glass plates were oven dried at 70 °C for 24 hrs to obtain thin vulcanized latex films with ≤ 1 mm thickness.

Table 2. *Formulation of compounded latex films*

Ingredient	Dry parts per hundred rubber (phr)
60% CNRL	100.0
10% KOH	4.0
20% Potassium laureate	2.0
50% Sulphur	1.0
50% ZDEC	1.5
50% Phenolic type Antioxidant	2.0
50% ZnO	0.5

Determination of tensile and tear properties of compounded latex films

Tensile and tear tests were performed in a universal tensile machine (Model: Instron 3365) as per ISO 37 and 34. Tensile properties in terms of tensile strength, modulus at 100% elongation and 300% elongation, elongation at break were determined in all the samples using dumbbell-shaped films with a 5 kN load cell at a crosshead speed of 500 mm/min at ambient temperature (28 ^{0}C). Crescent-shaped films were obtained from compounded latex films by using a standard cutter and were used to measure tear strength at a crosshead speed of 500 mm/min.

Statistical analysis

Each system was prepared in triplicate. A statistical model was designed by reducing both TMTD and nanoZnO in equal amounts as mentioned in Table 1. Then the response-surface analysis was performed using MINITAB 17 by plotting ZnO and TMTD with respect to different levels of VFA number. Analysis of variance (ANOVA) was employed to analyze VFA number data of the six treatment levels (Control, Nano-1, Nano-2, Nano-3, Nano-4 and Nano-5) using SAS software. Mean separations were determined by Duncan's multiple range tests for the durations of 15, 35, 55, and 75 days at the alpha value of 0.05.

Results and Discussion

SEM analysis of conventional ZnO and nanoZnO powders

The SEM images of ZnO samples (Fig.1) show the morphological difference between nano and conventional ZnO particles. It could be seen in Fig.1a, that nanoZnO sample contains ZnO agglomerates, which are formed by the clusters of needle-like nano-rods. However, most of the conventional ZnO particles exist as agglomerates having particle size of more than 200 nm in all dimensions. Moreover, Fig.1c, which is a magnified part of Fig.1b, reveals the conventional ZnO particles are hexagonal-shaped crystals.

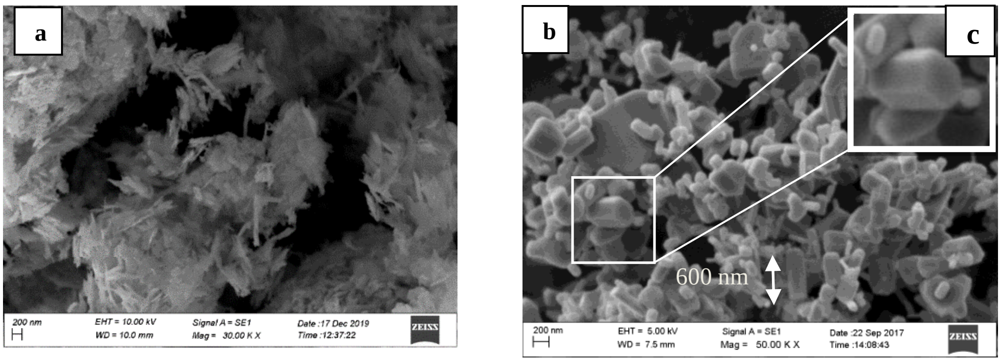

Fig. 1. SEM image analysis of **(a)** nanoZnO crystals, **(b)** conventional ZnO crystals, and **(c)** hexagonal-shaped ZnO crystal

XRD analysis conventional ZnO and nanoZnO powders

XRD is one of the most important and widely employed techniques in recent studies to determine the crystalline structure, purity and particle size of crystals especially when developing nanomaterials (Mantilaka *et al.*, 2014; Somarathna *et al.*, 2016). In our study, XRD patterns confirmed that the dominant crystalline phase is ZnO in both nano and conventional samples.

According to XRD pattern of nanoZnO (Fig. 2), the 2θ values of 31.7º, 34.4º, 36.2º, 47.5º, 56.6º, 62.8º, 66.4º and 69.0º confirm the presence of zincite as the crystalline form of nanoZnO (ICDD card No. 01-071-6424). The 2θ values of 31.7º, 34.4º, 36.2º, 47.5º, 56.6º, 62.9º, 68.0º and 69.1º indicate the presence of ZnO as the main crystalline substance (ICDD card No.1-082-3143) in conventional ZnO sample.

According to Scherrer equation, the average crystallite sizes of conventional ZnO and nanoZnO are 45.16 nm and 13.69 nm, respectively (Patterson, 1939; Monshi, Foroughi and Monshi, 2012). These results indicated that average crystallite size nanoZnO is smaller than that of conventional ZnO as seen on the SEM images.

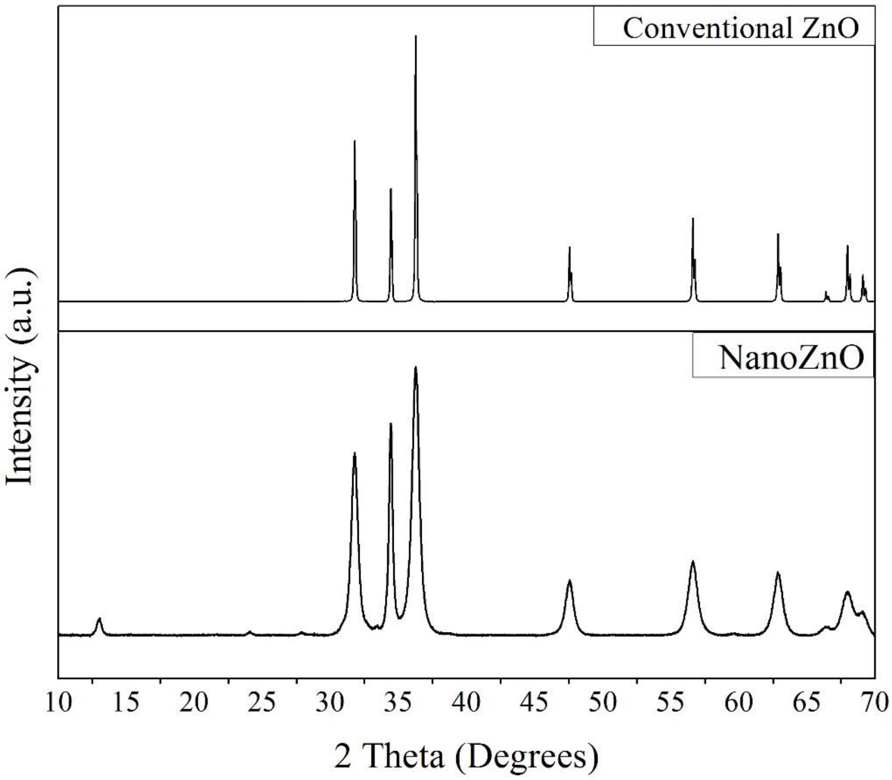

Fig. 2. XRD patterns of conventional ZnO and nanoZnO

Particle size distribution analysis of conventional ZnO and nanoZnO powders

The dynamic light scattering (DLS) technique is employed to obtain the particle size distribution data of two types of ZnO powders (Fig. 3). The DLS technique is widely employed to study average particle size and their agglomerations in colloidal systems (Fissan *et al.*, 2014). In our case, it is clear that the average particle distribution of conventional ZnO is broader than that of nanoZnO. This could be attributed by the presence of more particle agglomerations in conventional ZnO. It is noted that average particle size of nanoZnO is more than 200 nm, which may be due to the presence of crystal agglomerations as seen in SEM data. However, the narrow distribution of the particle sizes inferred that colloidal system of nanoZnO is more stable than that of conventional ZnO.

VFA number development in CNRL samples

The bacterial action on the carbohydrates present in latex mainly attributes to the formation of various volatile fatty acids. Volatile fatty acids formed in NRL is mainly composed of acetic acid, while formic and propionic acids also contribute to its composition as minor components (Pendle and Gorton, 1984; Blackley, 1997). VFA number is the key parameter that reflects the degree of bacterial action and hence the effectiveness of the preservation of CNRL. Therefore, lower the VFA number; better the state of preservation of latex.

According to VFA development results shown in Fig. 4, the preservation systems with nanoZnO yielded low levels of VFA development, when compared to that of the control sample. It was also revealed that the rate of VFA development increases with reduction of nanoZnO loading in the LATZ over the time period studied. The lowest VFA development was found in the Nano-1, which contains the highest dosage of TMTD/ nanoZnO, whereas the highest VFA number was observed in the sample, which contains the lowest amount of TMTD/nanoZnO over the entire period of the study.

Both Control and Nano-1 samples contain same quantities of TMTD (12.5 parts) along with 12.5 parts of conventional ZnO and nanoZnO, respectively. It is interesting to note that there is a significant difference between VFA developments in these two samples throughout the storage period studied. Replacement of conventional ZnO with nanoZnO in Nano-1 system has resulted in a significant reduction in VFA number suggesting that the latter has been the major contributor towards the enhancement of the antibacterial properties of CNRL.

It has been reported that the antimicrobial activity of nanoZnO is mainly attributed to its increased surface area/volume ratio (Zhang *et al.*, 2007; Jones *et al.*, 2008). This may be the reason for enhanced antibacterial properties of samples that contain nanoZnO compared to that of the control. Another reason for enhanced antimicrobial action might be the rod-shaped morphology of nanoZnO, which is more likely to achieve better dispersion in the aqueous phase than the bulky conventional ZnO.

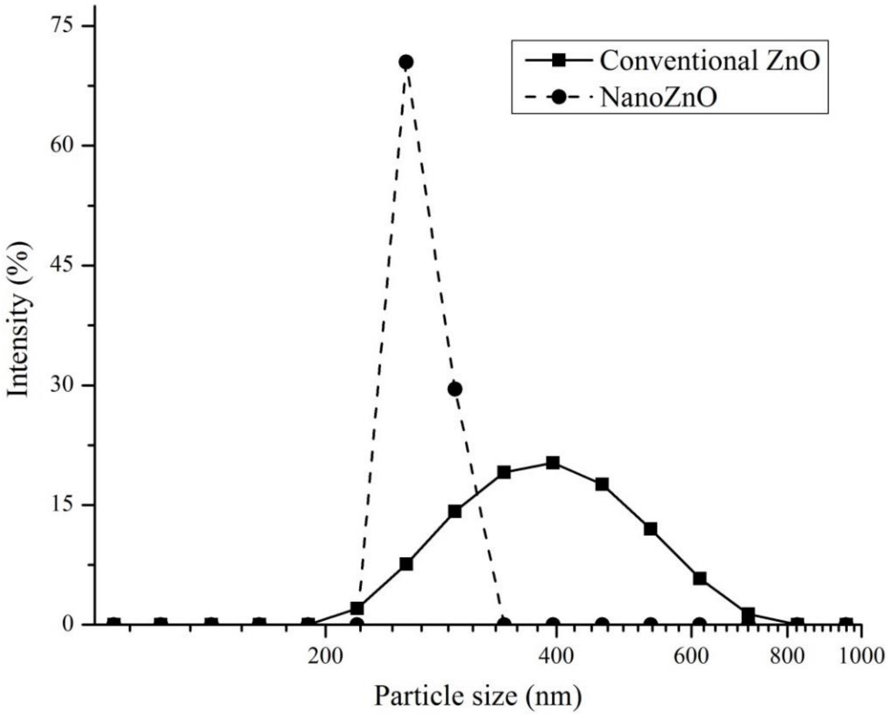

Fig. 3. Particle size distribution of conventional ZnO and nanoZnO by their intensities

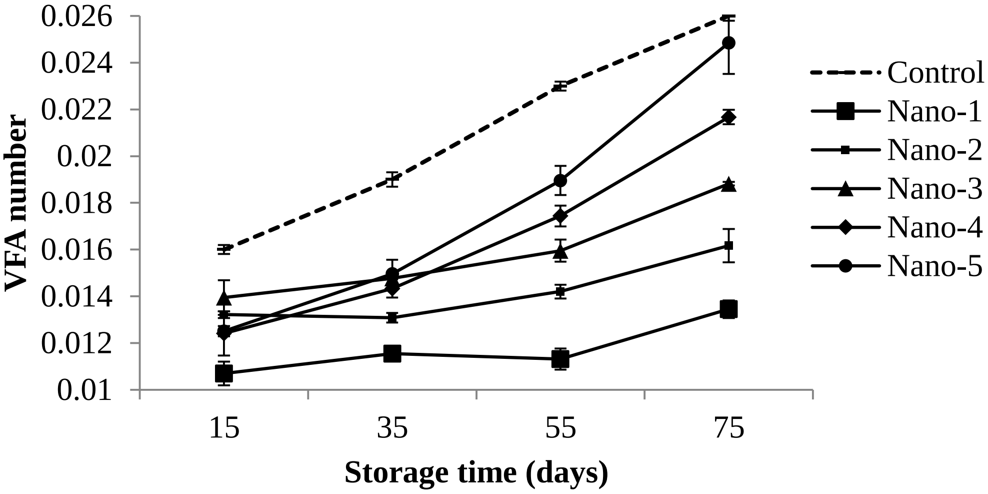

Fig. 4. Variation of VFA number of centrifuged latex samples with storage time

MST results in CNRL samples

MST is an important parameter of CNRL that measures the ability of latex to retain its colloidal stability against mechanical agitation during pumping, transportation, concentration, compounding, processing *etc*. As per the MST development illustrated in Fig. 5, all samples with nanoZnO/TMTD showed higher MST values than that of control sample after 20 days of storage time. It is further noted that MST of CNRL has shown a general trend of decreasing MST with the reduction of nanoZnO/TMTD with the exception of Nano-4 sample.

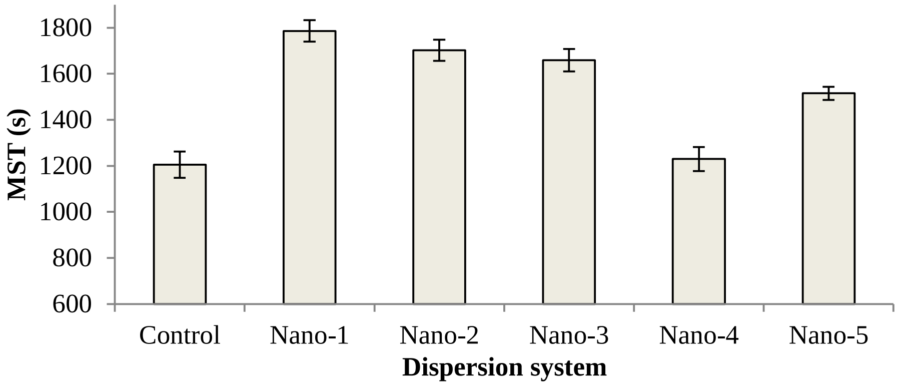

Fig. 5 Variation of MST after 20 days of storage time in CNRL samples

It is interesting to note that the MST of all the samples with nanoZnO registered significantly higher values compared to that of Control after 30 days (Table 3). A study conducted on the mechanical stability of natural rubber latex has suggested that the key factor that reduces the MST was the increase of ionic strength result in compressing the electrical double layer of the latex particles (Pendle and Gorton, 1984). Moreover, the same study proposed that the increase of VFA number may also be attributed due to the enhancement of ionic strength in the aqueous phase in latex. In our study, during first 35 days of centrifugation, the rate of VFA development in the systems with nanoZnO is very low resulting low rate of ionic strength development, thus maintaining the colloidal stability with time. Another recent study carried out on particle size and zeta potential of ZnO has shown that the alkaline pH with about 60-100 nm sized ZnO particles have negative zeta potential values (Marsalek, 2014). Similarly, the negative zeta potential values on nanoZnO may have reduced the ZnO thickening effect, thus enhancing the colloidal stability of latex resulting remarkably enhanced MST values in latex samples preserved with TMTD/nanoZnO.

Mechanical properties of vulcanized NR films

The suitability of CNRL samples for production of latex products are assessed by the mechanical properties of the vulcanized latex films made out of preserved latex films.

Table 3. *MST of CNRL samples after 20 and 30 days of centrifugation*

Sample name	MST (seconds)	
	After 20 days	**After 30 days**
Control	1205	1446
Nano-1	1786	> 1800
Nano-2	1702	> 1800
Nano-3	1659	> 1800
Nano-4	1230	> 1800
Nano-5	1515	> 1800

According to the results shown in Table 4, the properties including modulus at 300% elongation and elongation at break of Nano-1 to Nano-4 samples were almost comparable with those of control. It is further noted that the tensile strengths of Nano-1 to Nano-4 have slightly decreased with decreasing the loading of nanoZnO. This may be caused by the enhanced activity of nanoZnO as an activator in sulfur vulcanization, resulting more cross-links formation in rubber compounds with more nanoZnO (Sahoo *et al.*, 2007; Panampilly and Thomas, 2013). Further, modulus at 100% elongation values are also slightly higher in the samples preserved with nanoZnO when compared to control. At this strain, nanoZnO may have contributed to enhance the modulus by acting as filler in rubber compounds (Panampilly and Thomas, 2013), thus showing resistance to stretch.

Tear strengths, which depend on the crack propagation and the average molecular weight of the polymer, do not show any regular trend in all the samples (Sreeja and Kutty, 2000). In summary, the mechanical test results indicate that the nanoZnO quantities that we used in this study have very little effect on the molecular weight and cross linking densities of rubber vulcanizates. Therefore, it could be concluded that preservation of CNRL with nanoZnO does not adversely affect the final mechanical properties.

Statistical analysis of VFA number

A statistical model was developed to determine the best treatment levels to produce CNRL from nanoZnO based systems based on their VFA number variations. The surface plots revealed (Fig. 6) the effect of both TMTD and nanoZnO concentrations on VFA number after 15, 35, 55 and 75 days of centrifugation.

Table 4. *Mechanical properties of the vulcanized latex films*

Sample	Tensile strength (MPa)	100% modulus (MPa)	300% modulus (MPa)	Elongation at break (%)	Tear strength (MPa)
Control	20.22 ± 4.11	1.25±0.18	9.68±1.74	362.64±32.30	52.26±8.36
Nano-1	23.62 ± 1.96	1.59±0.11	7.00±2.60	402.71±29.99	46.48±4.19
Nano-2	21.77 ± 1.30	1.70±0.17	9.75±2.98	369.96±20.49	47.83±2.44
Nano-3	20.71 ± 2.55	1.55±0.25	8.90±2.67	372.75±25.17	53.18±5.20
Nano-4	19.48 ± 1.79	1.77±0.45	9.72±1.61	374.70±19.85	51.33±5.83
Nano-5*	-	-	-	-	-

*Mechanical properties of Nano-5 could not be determined due to the poor quality of the preserved latex

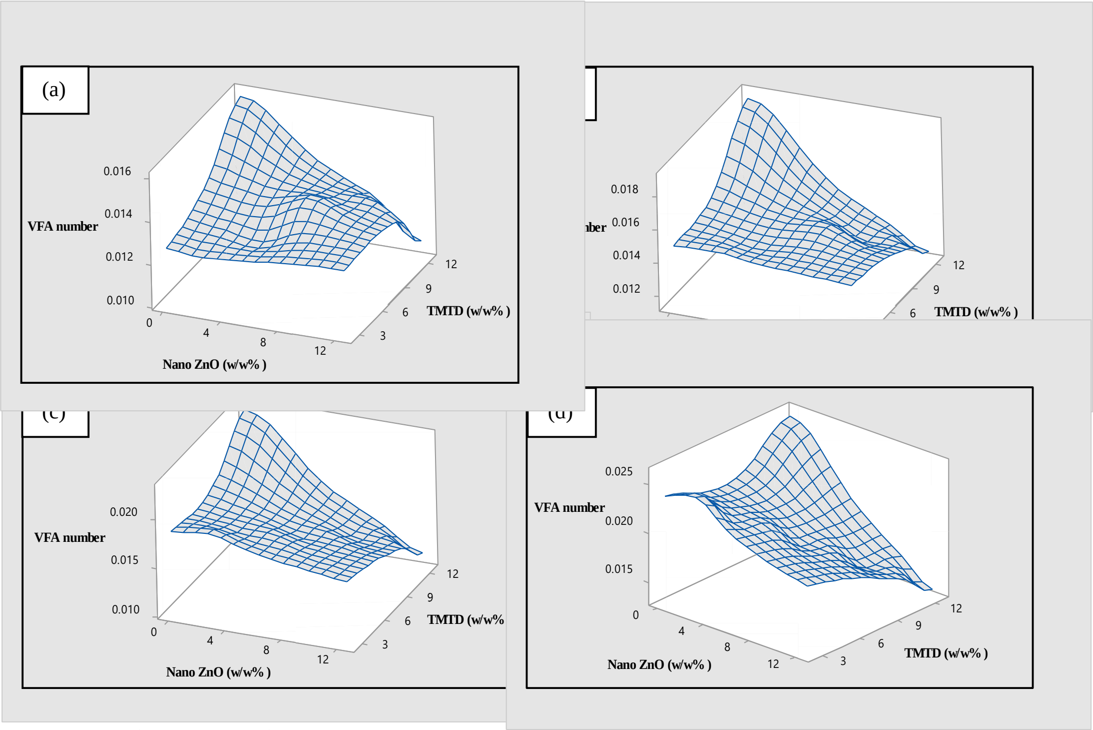

Fig. 6. Surface plots of VFA number variation with TMTD and nanoZnO after **a)** 15 days, **b)** 35 days, **c)** 55 days and **d)** 75 days of centrifugation

As per the surface plots, it is clearly seen that VFA levels are rapidly reduced with increasing both TMTD and nanoZnO amounts except in Fig. 6a. Further, VFA values are higher in the absence of nanoZnO in all the cases. The plots (a, b, c, and d) also reflect that the VFA number can be maintained less than 0.020 in the presence of only nanoZnO at 12.0 w/w %. Therefore, it could be inferred that the effect of nanoZnO is more significant than TMTD, when the preservation of CNRL is concerned.

The effects of ZnO/TMTD on VFA levels at each time interval (15, 35, 55 and 75 days) were compared using one-way ANOVA. Out of four time intervals, except for15-day time interval, the rest of the time periods showed significant differences among treatments at the probability level, $p < 0.05$.

Subsequently, the Duncan's multiple range test was employed to compare the means of VFA number values of systems at different time intervals with the exception of 15-day interval, as it was not significantly different at the probability level, $p= 0.05$. The test revealed that the Control has a higher mean VFA value when compared to mean VFA values of the rest of the systems at 35-day interval. At 55-day interval, mean VFA values of Control and Nano-5 systems were higher when compared to that of the other systems, among which, Nano-4 had the lowest amounts of ZnO and TMTD. In 75-day interval, mean VFA values of Control, Nano-5 and Nano-4 were higher than those in the rest of the systems, among which Nano-3 used the lowest amounts of ZnO and TMTD for the preservation. Therefore, based on this analysis, Nano-4 system might be optimum system to be used if the latex is stored up to 55 days, while Nano-3 can be recommended if the latex is stored up to 75 days until it reaches the production facility.

Conclusions

This study investigated the effect of nanoZnO as a component of a preservative system for CNRL along with TMTD and low ammonia. The characterization techniques including XRD confirmed both conventional ZnO and nanoZnO were in zincite crystalline form. The SEM data revealed that the nanoZnO crystals were in needle-like shape, while conventional ZnO were hexagonal-shaped crystals. VFA studies confirmed that nanoZnO has a significant contribution as a preservative for CNRL, when compared to conventional ZnO. This may be due to the higher surface area/volume ratio of nanoZnO resulting enhanced active surfaces against bacterial reactions. The rate of VFA development reduced with the increase of nanoZnO/TMTD concentration. Systems with nanoZnO had higher MST values than the control system, which may be due to combination of small particle size along with alkaline pH resulting negative zeta potential values in nanoZnO. Mechanical properties *i.e*. tensile and tear properties of vulcanized films prepared using CNRL preserved with conventional and modified preservative systems showed no significant difference. Therefore, it could be concluded that the effect of amounts of nanoZnO use in the experiment on mechanical properties of CNRL was insignificant. Surface plots indicated that nanoZnO was more effective than TMTD on preservation of CNRL. Thus, the use of TMTD could be reduced when nanoZnO is employed as the secondary preservative agent. Statistical analysis suggested that Nano-3 and Nano-4 systems could be employed, if the CNRL is stored up to 75 and 55 days, respectively. In summary, nanoZnO can be used as an effective preservative agent while lowering the usage of both toxic TMTD and ZnO for the preservation of low ammonia CNRL.

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