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Physical properties of natural rubber latex foams produced with processed mica waste powder and creamed natural rubber latex

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Abstract

Incorporation of finely powdered mica waste into natural rubber latex processed into foam rubber, consuming a minimum amount of energy could contribute to progress towards a greener environment. In this study, mica waste generated in the mining industry was finely powdered and incorporated into creamed natural rubber latex which is an alternative form of concentrated latex manufactured using a green process known as the creaming process. Finely powdered processed mica waste (PMW) was added as a filler into latex varying the loading from 0 to 10 pphr at 2 pphr intervals. The latex foam was then converted into a vulcanized natural rubber latex foam (NRLF). Effects of mica loading on certain properties of the foam rubber produced from creamed natural rubber latex were studied. It was found that the density and hardness of the mica powder incorporated foam rubber increased with increasing filler loading. Fourier transformed infrared spectroscopy (FTIR) studies confirmed that no structural changes occurred in natural rubber due to the addition of PMW. The overall results of the study showed the potential of utilization of mica waste and creamed natural rubber latex to manufacture greener natural rubber foam composites in cottage-level foam manufacturing industries.

Key words**:** creamed natural rubber latex, foam rubber, green foam composites, mica waste, physical properties

Introduction

The scientific community in the world has been paying higher attention to greener materials and processes due to the ever-increasing environmental issues faced by the entire world (Ciambelli *et al.,* 2020; Oksman *et al*., 2014; Yue *et al.,* 2020). Today, social and environmental impacts have become key parameters that influence consumer preferences for products and services. Simultaneously, international and local regulations enforced by authorities are encouraged by environmentally friendly industries (Zhang & Cao, 2020). Consequently, numerous studies have been conducted on energy-efficient recycled materials, biodegradable products, and even processing techniques to promote the sustainability of the products and services through the use of green materials and environmentally friendly material processing techniques.

Being one of the most widely used biodegradable and renewable industrial raw materials; natural rubber is continuously contributing towards a green environment for more than a century. In the face of growing interest in the green concept, studies on further improvement of green manufacturing of natural rubber products by the use of more energy-efficient manufacturing processes and utilizing industrial waste materials have become an emerging area in the natural rubber industry. In natural rubber latex-based industries, centrifuged latex is the widely used form of concentrated latex and is produced by a high-energy-consuming centrifuging process. Latex is also concentrated by the creaming process, where preserved latex is allowed to separate and creamed under gravitational force without using an electrical energy. Therefore, this creaming process could be considered a green manufacturing process and thus the resultant product, *i.e.* creamed latex is a greener product. However, there are quality variations between centrifuged latex and creamed latex. Creamed latex has smaller rubber particles with a wider particle size distribution, higher total solid content (TSC), dry rubber content (DRC), and viscosity than centrifuged latex (Suksup *et al*., 2017). These variations may influence the manufacturing process and performance of products produced from creamed latex. Suksup *et al.* have recently compared the behavior of unfilled foam rubber manufactured from centrifuged latex and creamed latex separately (Suksup *et al.*, 2017). It has been reported that creamed latex could also be successfully used to manufacture foam rubber (Suksup *et al.*, 2017).

In addition to the selection of creamed latex, the use of fillers derived from agricultural or industrial waste replacing synthetic commercial fillers could further improve the green nature of rubber products. Muniandy *et al.* applied rattan powder for the partial replacement of two commercial fillers namely carbon black and $CaCO_3$ in preparation for biocomposites based on natural rubber (Muniandy *et al.*, 2012). The results have shown the possibility of the generation of composites with some improved properties. Most of the work reported on green rubber composites consist of hybrid filler systems such as cocoa pod husks, rubber-seed shell powder, silica, and wood flour have shown similar trends (Okieimen & Imanah, 2006; Zhou *et al.*, 2015). Roy *et al*. have reviewed several research articles available in the literature on the use of natural fibers and particulate fillers derived from bio-based materials to prepare environment-friendly rubber composites (Roy *et al.*, 2020).

However, most of the work associated with fillers derived from waste materials including mica is based on the development of dry natural rubber composites. Compared to the number of studies carried out on such dry rubber composites, studies carried out on latex-based composites are limited. Our research group recently reported the incorporation of processed waste mica generated in the mica mining industry into centrifuged natural rubber latex to prepare mica-filled natural rubber latex foam composites (Dananjaya *et al.*, 2022). The study disclosed that the processed waste mica could be used as a promising filler for centrifuged natural rubber latex composites.

In this study, processed waste mica was incorporated into creamed natural rubber latex, which is considered a greener form of concentrated latex with some different latex properties compared to centrifuged latex. The objective of the study is to determine the effect of the use of creamed latex and processed mica waste for the manufacture of natural rubber latex foams with improved physical properties.

Materials and Methods

Natural rubber field latex (30% DRC) was provided by Rubber Research Institute, Ratmalana, Sri Lanka. Waste mica powder was obtained from a mica processing factory in Matale, Sri Lanka. Diammonium hydrogen phosphate (DAHP), sodium alginate (SA), and other industrial-grade compounding ingredients including, ammonia, potassium oleate soap, sodium laurate sulfate (SLS), poly(dicyclopentadiene-co-P-cresol)), sulfur, zinc oxide (ZnO), diphenylguanidine (DPG), sodium silico fluoride (SSF), zinc diethyldithio-carbamate (ZDEC) and zinc 2-mercaptobenzhiolate (ZMBT) were supplied by Richard Peiris Natural Foams Ltd. in Biyagama, Sri Lanka.

Preparation of creamed latex

20 L of field latex (NRL) was collected and preserved with ammonia 0.7% (w/w). For the removal of magnesium ions (Mg^{2+}) present, 36 mL of 10% (w/w) DAHP solution was added, mixed and the mixture was kept undisturbed for an hour. Then to stabilize the latex, 220 mL of 10% potassium oleate soap solution was added and mixed for 15 minutes. Then, 800 mL of 10% sodium alginate, the creaming agent, was added to the latex and mixed vigorously for another 15 minutes. Finally, the mixture was kept undisturbed for 14 days allowing for creaming.

Determination of properties of creamed natural rubber latex

Latex properties of creamed latex were evaluated following the standard test methods mentioned in Table 1.

Table 1. *Standard test methods for evaluation of properties/parameters*

Test	Test method
Dry rubber content (DRC)	ISO 126:2005
Total solid content (TSC)	ISO 124: 2014
Volatile fatty acid number (VFA)	ISO 506: 2020
Mechanical stability time (MST)	ISO 35: 2004 (En)
Alkalinity	ISO 125: 2020

Preparation of processed mica waste (PMW) dispersion

Finely powdered PMW with an average particle size of 19.62±12.52 µm used in this study was previously prepared and characterized (Dananjaya, *et al*., 2022b). In brief, PMW dispersions were made by ball milling 90 g of sieved mica waste along with 100 g of water and dispersion agents (5 g of dispersol LR and bentonite clay) for 7 days at 100 rpm. Composition analysis, average particle size distribution, and crystal morphology of PMW were determined by inductively coupled plasma–optical emission spectrometer (ICP-OES), particle size analyzer, and scanning electron microscopy (SEM). The characteriza-tion results were published in the previous studies conducted by the same research group (Dananjaya, *et al*., 2022a; Dananjaya, *et al*., 2022b).

Preparation of natural rubber latex foams (NRLFs)

Following the Dunlop process, NRLFs were manufactured using a latex compound prepared according to the formulation shown in Table 2. First, creamed latex was stirred under a continuous air flow for 15 minutes using a laboratory-scale mechanical agitator rotating at 50 rpm to remove the excess ammonia. Then, the mixture was stirred for 20 minutes after adding potassium oleate soap and sodium lauryl sulfate (SLS) into the latex using a magnetic stirrer. Subsequently, sulphur, ZMBT, ZDEC, antioxidants [poly (dicyclopentadiene-co-P-cresol)], and freshly prepared PMW filler dispersions were added into the latex mixture and mixed for another 20 minutes. After maturation for 8 hours at room temperature (28 ˚C), the latex compound was beaten using a hand mixer (Phillips HR-3740) until the volume reached approximately 3 times the initial volume (approximately within 3 minutes). After the required level of foaming was achieved, ZnO and the gelling agents (SSF and DPG) were added together into the mixture and mixed for another 30 seconds using a hand mixer (speed level 3) under the same conditions. Then the latex compound was immediately charged into an aluminum mold and placed in an oven operating at 100 ˚C for 2 hours to complete the vulcanization of the foam sample. Finally, the foam was washed thoroughly with pure water and squeezed well followed by drying in the oven at 70 ˚C for 8 hours. The same technique was used for the preparation of the control foam rubber sample without adding PMW.

Table 2. *Formulation and designation of filled natural rubber latex foams*

Ingredient	**Pphr**					
	R0	**R1**	**R2**	**R3**	**R4**	**R5**
Creamed Latex	100	100	100	100	100	100
50% Potassium oleate soap	6	6	6	6	6	6
50% SLS	0.25	0.25	0.25	0.25	0.25	0.25

Ingredient	Pphr					
	R0	**R1**	**R2**	**R3**	**R4**	**R5**
50% ZDEC	1.5	1.5	1.5	1.5	1.5	1.5
50% ZMBT	1.5	1.5	1.5	1.5	1.5	1.5
PMW	0	2	4	6	8	10
50% Sulphur	2.5	2.5	2.5	2.5	2.5	2.5
50% poly (dicyclopentadiene-co-P-cresol)	1.5	1.5	1.5	1.5	1.5	1.5
50% DPG	2	2	2	2	2	2
50% ZnO	6	6	6	6	6	6
12.5% SSF	7	7	7	7	7	7

Density

The density of NRLF samples (5×5×5 cm- l×w×t) was determined following the ASTM D1622-03. Equation 1 was used to calculate the density values.

$$\text{Density} = \frac{\text{M}}{(\text{l} \times \text{w} \times \text{t})} \quad (1)$$

Where, M, l, w, and t stands for mass, length, width, and thickness of the samples, respectively.

Hardness

According to ISO 3386 standard, the hardness of the foam rubber samples having the dimensions of 55 mm (length), 30 mm (width), and 25 mm (thickness) were measured using an Indentation Load Deflection machine (Model HD-F750, China).

Gelling time

The gelling time was taken as the time between the stopping of beating the latex compound and the time at which the latex compound became non-sticky (Dananjaya, *et al*., 2022b).

Fourier transform infrared spectroscopy (FTIR)

Fourier-transform infrared (FTIR) spectra of foam samples were recorded on an FTIR spectrophotometer (Perkin-Elmer Spectrum2, USA) using ATR (attenuated total reflectance) mode (Pike MIRacle single reflection ATR). All the spectra were obtained from 4000 to 400 cm^{-1} at the resolution of 4 cm^{-1} over 8 scans.

Results and Discussion

Latex properties of natural rubber creamed latex

Table 3 shows the characteristics of the creamed latex used in this study. It could be seen that creamed latex used has a dry rubber content (DRC) of 68.6% whereas centrifuged latex has a set value of much lower DRC based on the internationally accepted constant dry rubber content (60±0.02). One of the other major quality parameters is the percentage of the non-rubber present in creamed latex which is calculated as 1.2% and there was not much difference as far as that of the centrifuged latex is concerned.

Table 3. *Characteristics of creamed latex*

Parameter	Value
Total solid content % (w/w)	68.6
Dry rubber content % (w/w)	67.4
VFA number	0.1
Alkalinity % (w/w)	0.7
MST value (seconds)	800

The density of NRLF composites

Figure 1 depicts the density of the NRLF composites showing similar observations reported for NRLF composites filled with different fillers such as kenaf powder, chitin, and eggshell powder (Bashir *et al.*, 2017; Surya *et al.*, 2019; Zhang & Cao, 2020). The density increased in a narrow range from 0.31 to 0.41 g/cm^3 as filler is increased from 0 to 10 phr. PMW has a remarkably higher density (1.8 g cm^{-3}) when compared to the density of natural rubber (0.92 g cm^{-3}). Therefore, the incorporation of dense PMW into the lighter rubber phase increases the density of composites. As a result, the weight of the composite in a unit volume is increased. It should be noted that the hardness values of the composites do not follow the additive rule probably due to the unique porous structure of foam rubber. Even at a level of 10 phr, the density increased only by 25% of that in gum composite, suggesting its possibility to be used in light foam rubber products without having much effect on the weight of the products made out of PMW-filled foam composites. Further, this reduces the cost per unit volume increasing the economic viability of the product.

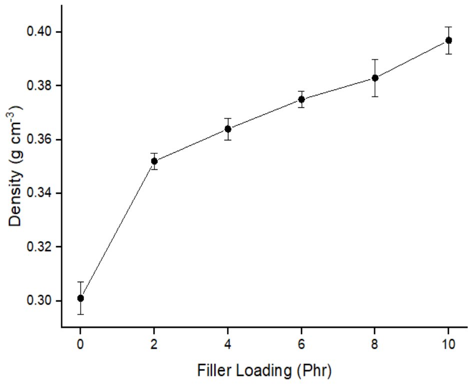

Fig. 1. The effect of PMW loading on the density of NRLFs

Hardness

Figure 2 represents the relation between the hardness of NRLF and mica loading. The hardness mainly denotes the ability of rubber to resist small indentation deformation caused by a hard object. As shown in Figure 2, a gradual improvement in hardness is observed with increasing PMW loading. This trend is also analogous to the general trend reported in the literature for the hardness of filled natural rubber composites (Ramasamy *et al*., 2012; Surya *et al.*, 2019). The hardness of the composites could be improved due to the incorporation of harder rigid filler into the rubber matrix. In addition, resistance exerted by filler particles on the mobilization of natural rubber macromolecules could also contribute to the increased hardness. (Bashir *et al.*, 2017).

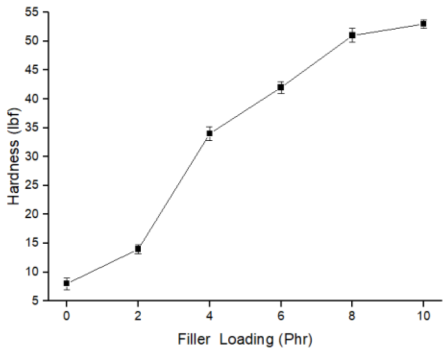

Fig. 2. The effect of PMW loading on the hardness of NRLFs

Gelling time

Gelling time of NRLF with varying PMW loading is illustrated in Figure 3. Gelling time is the period that has taken for the mixture in the liquid form to transform into a gel. Mica can establish physical interactions between the silicate groups in the mica and rubber matrix. Increasing density and the viscosity of the latex phase with the addition of fillers could facilitate the gelling process. The addition of inert foreign particles into latex could improve the nucleation ability of the macromolecules (Lin *et al.*, 2016). These factors may influence the reduction of gelling time with the incorporation of PMW. Short gelling time has a competitive advantage in industrial applications in terms of increased productivity.

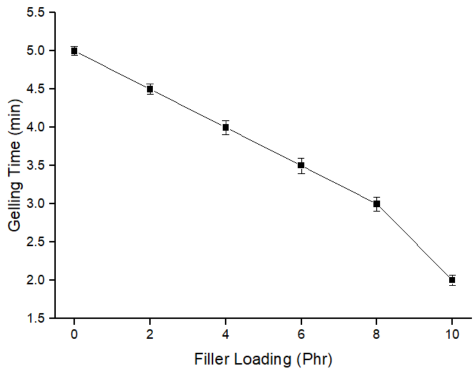

Fig. 3. The effect of PMW loading on gelling time of NRLFs

Fourier transform infrared spectroscopy (FTIR)

Figure 4 shows the composite spectrum of all the samples. Peaks that could be seen in the spectrum are listed in Table 4.The broad peak at 3380 cm^{-1} could be due to the presence of moisture and -OH groups presence in the waste mica. The peaks related to silica (995 cm^{-1}) have deepened with the increase in filler loading. The presence of characteristic peaks of natural rubber (834, 1375, 1452, and 1660 cm^{-1}) in all the samples confirmed that the bonds of natural rubber were not affected by the addition of waste mica.

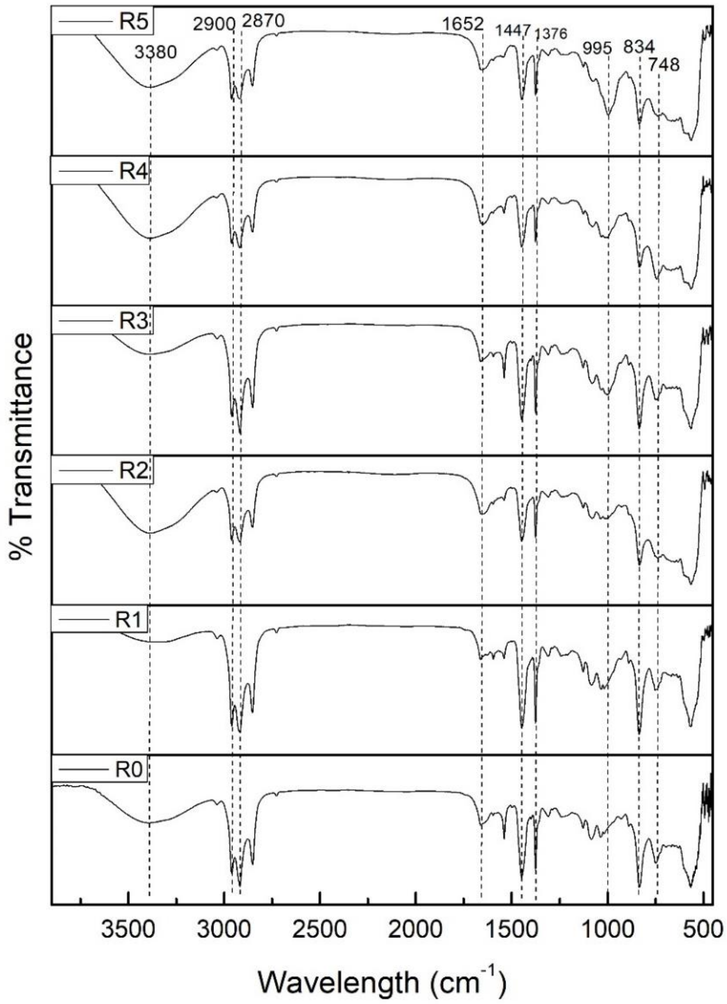

Fig. 4. FTIR spectra of PMW filled NRLF samples

Table 4. *FTIR data for PMW filled NRLF* (Beran, 2002; Suethao *et al*., 2021)

Frequency (cm^{-1})	Description
3380	-OH stretching vibration
2900	stretching vibration of the -C-H bonds in the methyl group of natural rubber
2870	Stretching vibration of -C-H bonds in methylene group
1652	stretching vibration of -C = C bonds natural rubber
1447	Bending vibration of -C-H bond

Frequency (cm^{-1})	Description
1376	Scissoring vibration of $–CH_3$ group
995	Si-O vibration
834	out-of-plane bending vibration of -C-H bonds

Conclusions

This study intended to determine the use of creamed natural rubber latex and processed waste mica for the manufacture of foam rubber with improved properties. The overall results showed that the density and hardness of the natural rubber latex foams could be improved while reducing the gelling time by the addition of processed mica waste powder. Further, FTIR results indicated that the bonds of natural rubber were not affected by the addition of processed mica waste powder. In conclusion, this study revealed that processed waste mica powder could be used to manufacture greener foam rubber products at the cottage level.

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