ENHANCING RUBBER STOPPER PERFORMANCE: A COMPREHENSIVE ANALYSIS OF REINFORCEMENT WITH ALKALI TREATED ARECA NUT FIBER

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Abstract

The abundant availability of areca nut husks in Mone, Kyauk-kyi Township, Bago Region, as a byproduct from areca nut farming presents an opportunity for creating value-added materials of national significance. In this current research endeavor, the extracted fibers from these areca nut husks were subjected to a thorough washing followed by treatment them with a 5 % NaOH solution. Additionally, a portion of the resulting product underwent a separate treatment with permanganate to enhance the fiber's surface characteristics. The mechanical properties of the alkali-treated areca nut fiber-rubber composite, intended for use in stoppers, exhibited impressive values, including hardness (52.6 IRHD), specific gravity (0.98), tensile strength (6.8 MPa), elongation at break (737.3 %), and tear strength (23.8 kN/m). These properties outperformed those of rubber alone, which had a hardness of 30.0 IRHD and a specific gravity of 0.97. Detailed analyses, such as scanning electron microscopy (SEM) for assessing fiber dispersion in the composite, Fourier-transform infrared spectroscopy (FT IR) for confirming composite formation, and thermogravimetric-differential thermal analysis (TG-DTA) for evaluating thermal behavior, conducted on the stopper composites show favorable results. Furthermore, chemical resistance tests demonstrated the stopper's compatibility with various substances, including water, alcohol, concentrated hydrochloric acid (HCl), and moderately concentrated base solutions like 10 % NaOH and 10 % NH_4OH. These findings strongly suggest that areca nut fibers are suitable for reinforcing natural fiber-rubber composites. This study successfully transforms biowaste areca nut husks into a valuable material, specifically stoppers, through composite fabrication with natural rubber.

Keywords: Areca nut fiber-rubber composite, rubber, surface modification, mechanical properties

Introduction

Increasing environmental awareness to minimize the pollution and depletion of resources made researchers all over the world to develop composites using most environmental friendly agro-wastes (lignocellulosic materials) as reinforcing agent and thermoplastic polymers as a matrix (Kumar, 2008). The benefits offered by lignocellulosic materials include making the final product light, decreasing the wear of the machinery used, low cost, biodegradability and absence of residues or toxic byproducts. Composite is defined as the material consisting of binder which is a continuous phase and the fibrous filler as reinforcement which is the discontinuous phase (Sakshi *et al*., 2017).

This research highlights the use of areca nut fiber as new type filler in natural rubber composites. Areca nut fiber is a commercially available and cheap natural fiber; furthermore, it has high cellulose content. To use these lignocellulosic fibers in polymeric composites, removal of the lignin and other amorphous materials is necessary to allow a better separation of the fibrils (Ahmed *et al*., 2014). Alkali treatment procedure using a 5 % solution of sodium hydroxide was employed to remove these materials; further treatment with potassium permanganate solution or

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benzoyl chloride solution was also carried out as surface treatment of the fiber, to modify the interfacial adhesion between the fiber and rubber, which has profound influence on the mechanical properties of the composites (Li *et al*., 2007).

The applications of natural fiber-polymer composites are growing rapidly in numerous fields such as commercial, industrial, chemical and scientific applications. One of the most common applications of fiber-rubber stopper is the chemical ones. Some of the chemicals that are widely used in manufacturing are hazardous and can potentially cause grave bodily harm. Therefore, the containers holding these chemicals must be secure and tightly sealed, both for storing and handling them.

A laboratory stopper is mainly used in chemical laboratory in combination with flasks, test tube and also for fermentation in winery. Generally, in laboratory, the size of stopper can be varied up to approximately 16 sizes and each of it is specific to certain type of container. As the stopper is used in many experiments, some specific experiment requires a specific material. Most of the stoppers are oftentimes cylindrical with one tapered end. These parts have three distinct types:

1. The solid stopper: this rubber stopper is the most common one as it finds many applications in our everyday lives. Moreover, this rubber plug is also used in tube tube, wineries and breweries etc.
2. The one-hole stopper: this type of rubber part is very common in laboratories. The hole allows the scientists to insert thermometers and other devices in the container, without having to open it. This kind of rubber cork is manufactured in all of the sizes.

The aim of the present work is to fabricate the solid stopper and one-hole stopper for use in the chemistry laboratories and comparative study on the morphology and characterization of the rubber only and alkali treated areca nut fiber-rubber stopper.

Materials and Methods

Preparation of Areca Nut Fiber

The areca nut husks were collected from the local area, Mone, Kyauk-kyi Township, Bago Region.

The areca nut husks were taken directly from the areca nut fields containing a lot of dirt and dust. The dirt, dust, individual fiber and coarse fiber were removed by washing with distilled water. The selected areca fruit husks were soaked in distilled water for about five days. This process is called retting; allowing the fiber to be removed from the husk easily. Then areca nut fiber was manually separated from the husk. The resulting fiber was dried in the condition (temperature 30 ºC) for four days before the alkali treatment (Joseph *et al*., 1996). The dried fiber was designated as untreated fiber.

Alkali treatment

Areca nut fiber is amenable to chemical modification due to the presence of hydroxyl groups. One of the methods used commonly to treat the fiber is alkaline treatment method. Alkaline treatment or mercerization is used to modify the hydrogen bonding in the network structure, increasing the surface roughness of the fiber and exposing the microfibrils resulting in better mechanical interlocking.

The clean and dried areca nut fiber was soaked in a stainless-steel vessel containing 5 % NaOH at room temperature (30-32 ºC) for three hours (Sampathkumar *et al.*, 2014). The alkali treated fiber was immersed in the distilled water for 24 h in order to remove the residual NaOH. Final washing was done with distilled water containing a small amount of acetic acid for neutralization. Subsequently, the fiber was dewatered and dried under sun light for five days.

Preparation of Natural Rubber Composites Reinforced by Areca Nut Fiber

Natural rubber smoked sheets for the experiments were procured from Myanmar Gone Yee Rubber Plantation, Bago Region. The areca nut fiber-rubber composites were prepared and their mechanical characteristics were measured at Rubber Research and Development Centre in Yangon.

Natural rubber smoked sheet was first rolled for 5 min on a Two Roll Mill to break out the fibrous bond of rubber polymer chain. This step is called mastication. Then mercapto benzothiazole (MBT) was mixed on rolling. After 30 s, zinc oxide and stearic acid were added simultaneously and rolled for 2 min. And then petroleum oil was added and rolled for one minute. Sulphur was added and rolled about 3-4 min until thick sheet was obtained. Vulcanized rubber was obtained. Some vulcanized rubber was used for preparation of rubber stoppers, and the remaining vulcanized rubber was mixed with the alkali-treated fiber of 10 mm fiber length at the rate of 5 % fiber loading on roller. The fiber loadings were in weight based on 100 g of vulcanized rubber. Total mixing duration was 10 to 15 min. During mixing whenever the roller becomes hot, water was sprayed on the roller. The composite preparation obtained was allowed to age for 24 h.

Preparation of rubber and alkali treated areca nut fiber-rubber composite stoppers

The molded plates of the aged composite were compressed for shaping by Hand Press Machine. Firstly, the plates were hot pressed at 153-160 ˚C (solid stopper for 6 min and one-hole stopper for 8 min) under 1000 lb in^{-2} loading. (Figure 1 and 2)

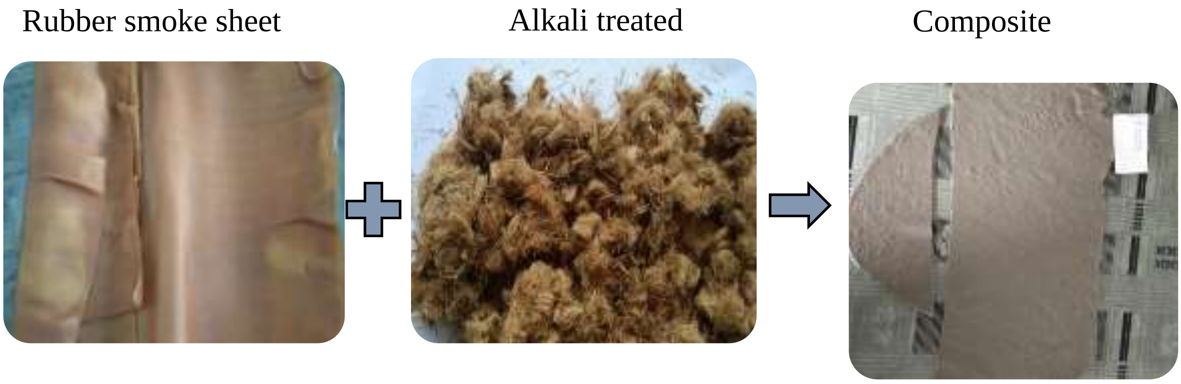


Figure 1. Preparation of alkali treated areca nut fiber-rubber composite for stopper

Figure 2. Making of alkali treated areca nut fiber-rubber stopper

Determination of Chemical Resistance for the Rubber and the Alkali Treated Areca Nut Fiber-Rubber Stoppers

Chemical resistance of areca nut fiber reinforced natural rubber hybrid composites was determined according to ASTM D 543-87 method (Mathew *et al*., 2006). The effect of some solvents, such as water, methanol and pet-ether, and some acids, such as conc. HCl, acetic acid and alkalies, such as 10 % NaOH and 10 % NH_4OH were studied on the hybrid composite (Jawaid *et al*., 2011). For chemical resistance tests, the three pre weighed samples (1.50 g) (with 35 mm length fiber x 25 mm dimension x 3 mm thick) were dipped in the respective chemical reagents at different intervals time for (24-96 h). They were then removed and dried by pressing them on both sides with a filter paper at room temperature. And then, the final weight of the samples and the percentage weight gain/loss were determined. The chemical test has been done for three samples in each case and the average value is reported (Rajulu *et al.*, 1998). The percentage chemical resistance was determined.

Comparative Study on the Surface Morphology of the Rubber and Alkali Treated Areca Nut Fiber-Rubber Stoppers

The difference in surface morphology between the rubber and the alkali-treated areca nut fiber-rubber stopper were studied using Evol 18 Zeiss scanning electron microscope (SEM) at Yadanabon University. The resulting SEM micrographs of the samples were recorded.

Comparative Study on Chemical Composition of the Rubber and Alkali Treated Areca Nut Fiber-Rubber Stopper

The changes of chemical constitution of the rubber-and the alkali treated areca nut fiber-rubber stopper were examined by infrared absorption spectra recorded on a Tracer 100 Shimadzu, Japan FT IR spectrometer at University of Yangon.

Comparative Study on the Thermal Properties of the Rubber and Alkali Treated Areca Nut Fiber-Rubber Stoppers

The difference in thermal properties between the rubber and the alkali treated areca nut fiber-rubber stoppers were studied using a TG-DTA instrument (Hi-TGA 2950 model) (Yadanabon University), at the temperature range, 0 ºC to 600 ºC under air.

Results and Discussion

Extraction of Areca Nut Fiber

After soaking and drying, 4.6 kg (2.8 viss) of fiber was extracted from 16.2 kg (10 viss) of raw areca husk. This is the mixture of coarse and fine fibers. (Figure 3)

Figure 3. Extracted areca nut fiber

Surface Modification of the Areca Nut Fiber

Alkali treatment

The extracted areca nut fiber was treated with 5 % NaOH solution. The resulting fiber have yellowish brown color. The colour of untreated fiber was paler than alkali treated areca nut fiber. (Figure 4)

Figure 4. Alkali treated areca nut fiber

Potassium permanganate treatment

After potassium permanganate treatment, as a result, areca fiber surface becomes darker, physically rough, bristly and this reduces hydrophilic nature of the areca fibers (Figure 5). This could improve chemical interlocking at the interface and provides better adhesion with the polymeric matrix.

Figure 5. Potassium permanganate treated areca nut fiber

Natural Rubber

Natural rubber used for the study was grade-1 (light colour) obtained from Myanmar Gone Yee Rubber Plantation, Bago Region. The results and specifications (reference with ISO) of the grade-1 rubber used at Rubber Research and Development Center in Yangon were summarized.

Table 1. Quality Specifications of the Grade-1 Natural Rubber

No.	Test	Results	Reference*
1	Plasticity number	32.50	ISO 2007 (30.0-32.5)
2	Plasticity retention index	85.00	ISO 2930 (71.05-85.00)
3	Volatile matter content (%)	0.27	ISO 248-1 (0.25-0.4)
4	Dirt content (%)	0.02	ISO 249 (0.01-0.04)
5	Ash content (%)	0.27	ISO 247 (0.25-0.5)
6	Nitrogen content (%)	0.45	ISO 1656 (0.23-0.7)
7	Mooney viscosity	63.00	ISO 289-1 (60.0-70.0)

*****International Standards Organization (ISO) for Rubber

Chemical Resistance of the Alkali Treated Areca Nut Fiber-Natural Rubber Composites

Chemical resistance tests were used to study the interfacial adhesion in areca nut fiber reinforced natural rubber composites. The presence of bonding agent increased the interfacial adhesion between the fiber and matrix. The composites containing bonding agents were less prone to solvent sorption. The chemical resistance of the prepared fiber-rubber composites was also investigated in various solvents such as water, methanol, pet-ether, various acids such as conc. HCl, acetic acid, and bases such as 10 % NaOH, 10 % NH_4OH. It was observed that the swelling behavior of rubber-alkali treated areca nut fiber composites in different solvents follows: pet-ether > methanol > water. Different acids it follows the trend: acetic acid > conc. HCl and then for the various alkalis it follows: 10 % NH_4OH > 10 % NaOH. The percent chemical resistance of the composite was found to be high. This is due to the increased hindrance exerted by the fibers at higher fiber loadings and also due to the good fiber-rubber interactions. Maximum absorption of solvent was observed with pet-ether, which may be due to the diffusion of hydrocarbons. The second highest absorption was observed with acetic acid; this may be due to acetylation of some hydroxyl groups of areca nut fiber.

The chemical resistance tests of these hybrid composites were performed in order to find out whether these composites can be used for making stoppers. The weight gains for fiber reinforced natural rubber composites with different chemicals are shown in Table 2 and Figure 6. From the results, it is clearly seen that for areca nut fiber-natural rubber composite in all cases a slight weight gain (swelling property) is observed after immersion, except for the large weight gains with petroleum ether and acetic acid. This indicates that the composites did not lose weight, and therefore it does not seem as any erosion occurred. The weight increase of the composites for aqueous solutions is a result of the hydrophilicity of the fiber. Based on the findings of this study, these rubber stoppers can effectively seal reagent bottles, flasks, test tubes, and other laboratory containers requiring chemical resistance.

Table 2. Chemical Resistance of Alkali Treated Areca Nut Fiber-Natural Rubber Composites

Dipping time (h)	Chemical resistance in various solvent (%)						
	Water	Methanol	Pet-ether	Conc. HCl	Acetic acid	10% NaOH	10% NH_4OH
24	0.67	1.33	62.67	0	8.00	1.33	1.33
48	2.00	2.00	75.33	0	11.33	1.33	3.33
72	2.00	2.00	82.00	0	16.67	1.33	3.33
96	2.00	2.00	62.00	0	17.33	1.33	4.67

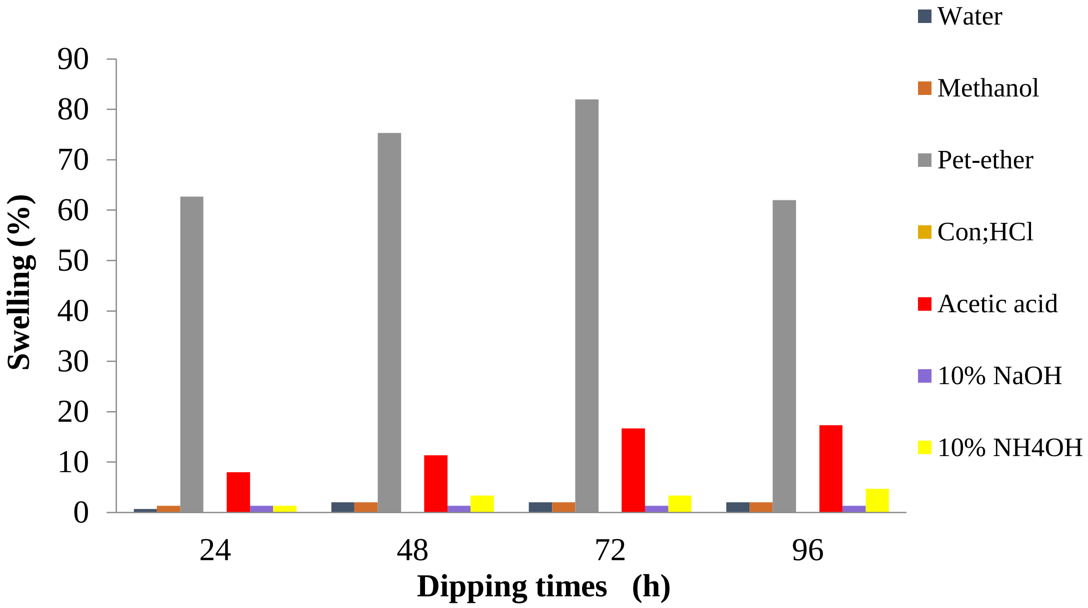


Figure 6. Swelling property of areca nut fiber-natural rubber composites towards the various solvents at different dipping time

Mechanical Properties of Rubber and Alkali Treated Areca Nut Fiber-Rubber Composite for Stopper

Based on the findings, it is evident that the composite, with alkali-treatment, featuring a 10 mm fiber length and a 5 % fiber loading, exhibited superior characteristics when compared to the rubber material. Notably, hardness and elongation at break were significantly enhanced in the composite, surpassing the performance of the rubber material (Table 3).

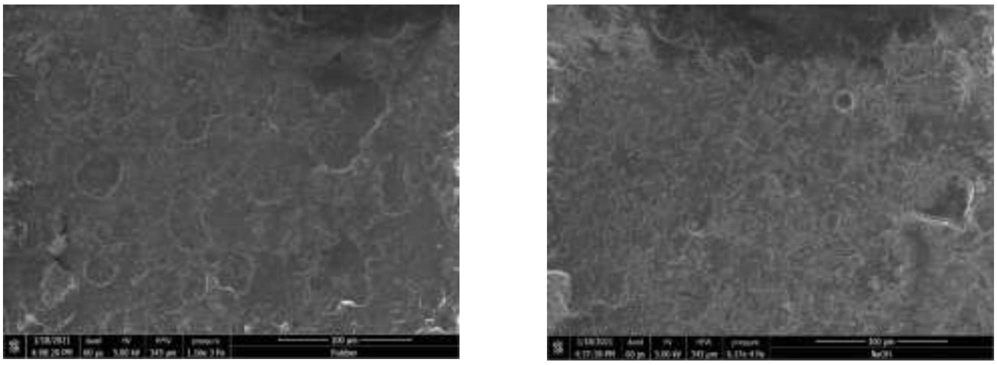
Although specific gravity and tear strength remained relatively consistent between the two materials, it is essential to emphasize that laboratory stoppers demand specific attributes. In this context, the desired attributes for laboratory stoppers include high values of hardness, specific gravity, and elongation at break. Consequently, the alkali-treated composite with a 10 mm fiber length and 5 % fiber loading emerges as the most suitable choice for fabricating laboratory stoppers based on these criteria.

Table 3. Physicomechanical Properties of Rubber and Alkali Treated Areca Nut Fiber-Rubber Composite Stoppers

Materials	Hardness (IRHD)	Specific gravity	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)
Alkali-treated	**52.6**	0.98	6.8	**737.3**	23.8
Rubber	30.0	0.97	10.6	680	24.1

Surface Morphology of Rubber and Alkali Treated Areca Nut Fiber-Rubber Stoppers

The better adhesion at the interface between the areca nut fiber surface and the rubber matrix resulted from good compatibility between the rubber-alkali treated fiber and rubber only. In this study, a good adhesion was obtained between alkali treated areca nut fiber and rubber matrix and fine dispersion of applied alkali treated areca nut fiber filler in rubber matrix was depicted in Figure 7 by SEM analysis.



(a) Rubber only material (b) Alkali treated fiber-rubber composite

Figure 7. SEM images of fracture surface of (a) rubber only material and (b) alkali treated areca nut fiber-rubber composite for stopper

Chemical Composition of Rubber Only and Alkali Treated Areca Nut Fiber-Rubber Stopper

In this study, comparison of the FT IR spectra before and after alkali-treated composite formation (Figure 8) shows notable changes of the absorption bands, namely shift to a higher frequency of the sp^2 C-H stretching band just above 3000 cm^{-1} in region (*i*), intensification of C-O stretching band in region (*iv*) which may indicate ether, more pronounced bands assignable to sp^2 C-H out-of-plane bending in the region (*v*), sharper bands in the region (*iii*), and also the change in shape of the bands in the region (*ii*) for C-H bending and C=C stretching. These changes are rubber only and the alkali-treated fiber, and thus evidences of the formation of a composite.

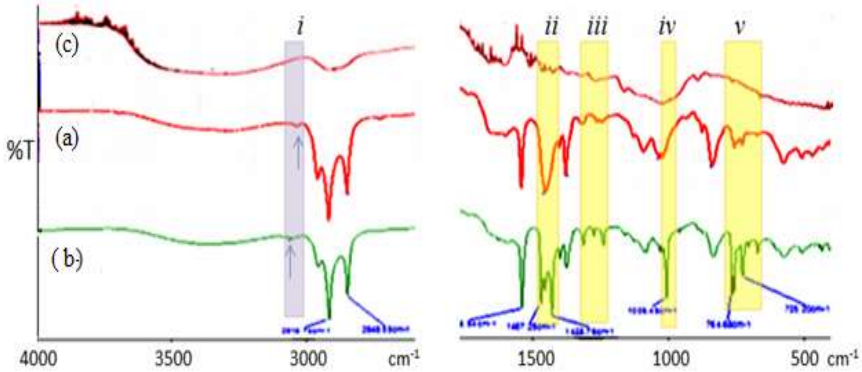
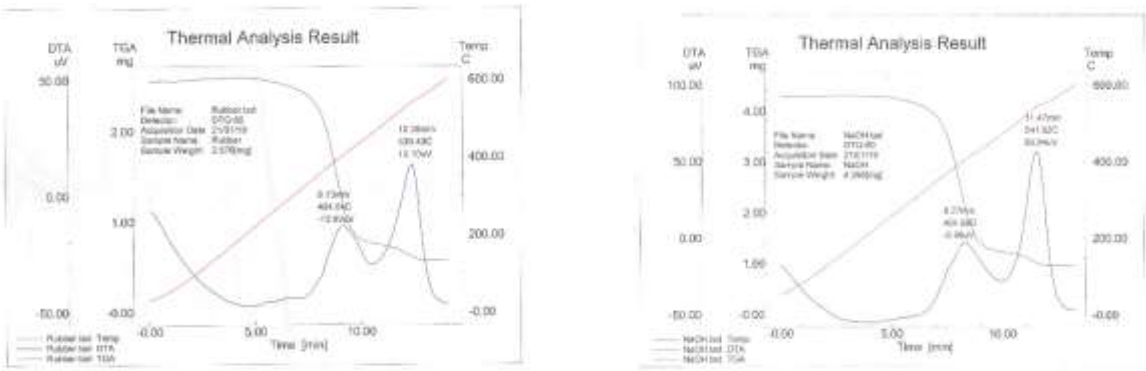


Figure 8. FT IR spectra showing (a) rubber (b) alkali treated areca nut fiber-rubber composite, and (c) alkali-treated areca nut fiber

Thermal Properties of Rubber and Alkali Treated Areca Nut Fiber-Rubber Stoppers

According to the results (Figure 9 and Table 4), the temperature of 363.35 ºC was observed as the onset temperature of thermal degradation for the rubber and the temperature of 365.49 ºC was observed as the onset temperature of thermal degradation for the alkali treated areca nut fiber-rubber sample. Thus, the alkali-treated areca nut fiber-natural rubber stopper showed higher onset temperature than rubber stopper, which supported the effectiveness of the alkali-treated fiber. It indicated that the thermal stability of the alkali-treated areca nut fiber-rubber stopper was higher than the rubber stopper.



(a) Rubber (b) Alkali treated fiber-rubber composite

Figure .9 TG-DTA thermograms of (a) rubber and (b) alkali treated areca nut fibre-rubber composite stoppers

Table 4. Initial Decomposition and Maximum Decomposition Temperatures of Rubber and Alkali Treated Areca Nut Fiber-Rubber Stoppers

Stoppers	Temperature range of initial decomposition (ºC)	Weight loss (%)	Temperature range of final decomposition (ºC)	Weight loss (%)
Rubber	363.35 - 421.57	34.41	450.91 - 569.43	65.10
Alkali treated fiber-rubber	365.49 - 427.27	34.45	453.37 - 571.92	65.21

Conclusion

In conclusion, this research has successfully addressed the primary objective of enhancing the performance of rubber stoppers through the reinforcement of natural rubber with areca nut husk fiber. The utilization of areca nut husk, an abundant and underutilized biowaste material from the areca nut industry, has not only contributed to environmental sustainability but has also led to the development of a composite material. The surface treatment of areca nut husk fiber, involving treatments with 5 % NaOH and potassium permanganate, was enhanced the fiber's surface properties. These treatments improved the adhesion between the fiber and the rubber matrix, ultimately leading to the creation of a composite material (alkali treated) suitable for producing rubber stoppers for reagent bottles.

The incorporation of alkali-treated areca nut fiber into the natural rubber matrix resulted in increased rigidity, making the composite an ideal choice for stopper applications. Scanning electron microscopy (SEM) analysis confirmed the strong adhesion between the fiber and rubber matrix, along with the even dispersion of the fiber within the composite-essential factors contributing to enhanced mechanical properties. Further characterizations through FT IR spectra, as suggested by changes in position, intensity, and shape of IR bands. The successful formation of areca nut husk fiber-natural rubber composites was suggested by FT IR, where band shifts, appearance of new bands and changes in the forms of bands were observed after the composite formation. TG-DTA studies provided compelling evidence and improved thermal stability. TG-DTA study also showed better thermal stability of the fiber by the treatments than rubber.

Moreover, the composite rubber stoppers exhibited robust resistance to various acids, bases, and organic solvents, highlighting their durability and suitability for laboratory use.

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