SYNTHESIS OF BIOMASS WASTE DERIVED ACTIVATED CARBON-NBR COMPOSITES FOR AUTOMOBILE APPLICATION

*Abhijit Jadhav[1], Govindaraj Thangaraj Mohanraj[1, *], Ashok Gokarn[2],*
Suseeladevi Mayadevi[2]

Abstract. This paper reports on usability of activated carbon obtained from areca nut shell, coconut shell, and coconut leaves as a filler to prepare NBR based composite for automobile based application. The carbon was activated by phosphoric acid (H_3PO_4) as dehydrating agent. The stoichiometric ratio of biomass and phosphoric acid was found to be 3:1 for the batch size of 300 g. As compared to commercially available carbon filler, the activated carbon derived from biomass waste responded better to the petrol swelling test. Among three biomass waste sources, namely, areca nut shell, coconut shell, and coconut leaves, activated carbon derived from coconut shell was appeared to be the best for percent swelling and percent deviation in hardness. The results obtained are confirmed by proximate analysis.

Keywords: activated carbon, phosphoric acid, NBR, composites, hardness.

1. Introduction

In this paper activated carbon is prepared from coconut shell, areca nut shell, and coconut leaves, as these biomass wastes are abundantly available throughout the year irrespective of season. Three of the starting materials are obtained from different parts of the plants. Accordingly, they have distinct lignocelluloses content from each other. The coconut shell is used in Indian continent as food ingredient as well as on auspicious occasions. Areca nut is used on Asian continent as mouth freshener. In India Areca nut is served on auspicious occasions along with coconut. Even coconut leaves are abundantly available. This biomass waste is used as starting material for preparation of active carbon. Other cheap and efficient alternative materials such as rice husk [1], bamboo [2], sugarcane stalks [3], tamarind kernel powder [4], palm shell [5], babool wood [6], bagasse fly ash [7], ashoka leaf powder [8], coir pith [9], banana pith [10], *etc*. are also used.

Biomass wastes are considered to be a very important feedstock because they are renewable sources. This led to use coconut shell, areca nut shell and coconut leaves, which are available throughout the year irrespective of season as starting materials for carbon preparation.

Rubber industry is a huge consumer of carbon as reinforcing material. The filler imparts certain properties to the rubber material such as colour, hardness and strength up to certain extent. However, so far there is no report on the use of activated carbon as filler material in rubber. For activation, the surface of carbon modifies to develop newer reactive sites. The ratio of lignin to cellulose and the nature of starting material play certain role in the attribution of activity to the resultant carbon. For the treatment with alkali, the surface modification is limited. The acid treatment enhances porosity, and in turn increases the yield of activated carbon. Ours is the activated carbon prepared by acid treatment to the agricultural waste lignocelluloses materials. NBR is purposely selected because it is an oil-resistant synthetic rubber. Nitrile rubber is mostly used where high oil resistance is required, as in automotive seals, gaskets, or other items subjected to contact with hot oils. Another reason is that NBR is made in a hydrogenated version (abbreviated HNBR), that is highly resistant to thermal and oxidative deterioration and remains flexible at lower temperatures.

Polymer based composite materials have been used widely in home appliances, construction, automotive industry, packaging application, and aircraft engine blades due to their excellent specific mechanical and tribological properties for hundreds of years [11].

In the present work, we are reporting the use of biomass waste derived activated carbon as filler in rubber industry. The idea behind incorporation of this activated carbon is chemical reaction between nitrile rubber and the surface modified carbon imparted with ether and ester linkages on the surface.

[1] Department of Chemical Engineering, Birla Institute of Technology, Mesra 835215, Ranchi, India
[2] National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India
* *gtmohanraj@gmail.com*

In the present work, various properties of carbon composite prepared from coconut shell, coconut leaves and areca nut shell were compared with commercial carbon composite to check their applicability for commercial purpose in automobile industry.

2. Experimental

2.1. Materials

Biomass waste such as coconut shell, areca nut shell and coconut leaves is used as the raw material for preparation of activated carbon. By finding out the acid soluble and alkali soluble content of the different agricultural wastes, the coconut and the areca nut material were selected related to the availability and the acid hydrolysable content.

The biomass is first chopped into pieces of 2 cm wide and 5 cm long, then washed with distilled water to remove dust particles, and then dried at 383 K. Biomass waste was finally crushed and sieved to 180 mesh size.

NBR is a complex family of workhorse elastomers. The unique balance of oil, chemical, heat, and cold resistance allows it to work well in a wide variety of automotive and industrial applications. The family is well differentiated to include general purpose types for cost sensitive applications and specialty products (carboxylated nitrile butadiene rubber (XNBR), hot-crosslinked nitrile butydiene rubber (HNBR) for more demanding service conditions. Nitrile rubber is generally resistant to aliphatic hydrocarbons. The ester and ether linkages present on activated carbon may entangle with zinc during processing to furnish improved physical properties.

2.2. Preparation of Activated Carbon

Preparation of activated carbon is performed using batch size of 300 g of waste biomass. H_3PO_4 of chemically pure quality (Merck Co) was used as activating agent. A known mass of activated agent was mixed with distilled water and biomass waste was impregnated in acidic solution. The mass ratio of activating agent to dried material was 3:1. The impregnated sample was kept for 24 h. After 24 h the residual water was removed and the sample was kept in oven at 383 K. The weighed impregnated samples were kept in muffle furnace at 673 K. The muffle furnace was purged with high purity nitrogen gas to avoid oxidation. Activation was performed under anaerobic conditions. Thus nitrogen flow to muffle furnace was adjusted to 3ml/K at 673 K. The activated carbon was subsequently removed from furnace after 24 h and cooled to room temperature. After samples activation, 3M hydrochloric acid was used to remove the phosphoric acid compounds. The washed samples were dried at 383 K for 6 h in oven and then ground to form a porous carbon powder. The equipment was fabricated to hold the raw sample of 30×9×9 cm size as shown in Fig. 1.

2.3. Analysis of Starting Material

To find out the cellulose content as acid hydrolysable and lignin content as alkali soluble, 73% H_2SO_4 solution and 17% NaOH solutions were used. The pre-weighed sample was first digested in acid at room temperature for 4 hr with constant stirring and oven dried to constant weight to know the weight difference. The weight difference corresponds to the cellulose and hemicelluloses content. The same sample was digested in NaOH solution at 353 K for 2 h under constant stirring. The sample was oven dried till constant weight and weighed to find the lignin as alkali soluble content.

2.4. Analysis of Activated Carbon

2.4.1. SEM analysis

The prepared activated carbon was examined by JSM scanning electron microscope (Jeol, Japan). JSM is a 6390LV model having magnification ranging from 5× to 300000× with image mode secondary electron and back scattered image to analyze the surface of the adsorbents. Magnifications used were 5× and 10×.
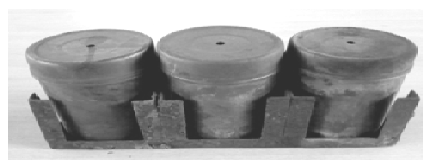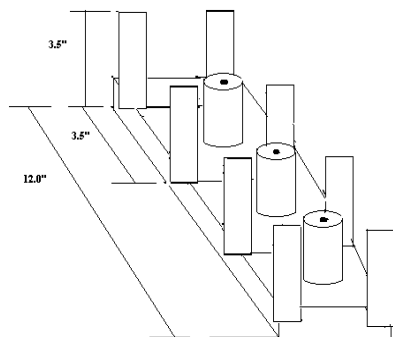

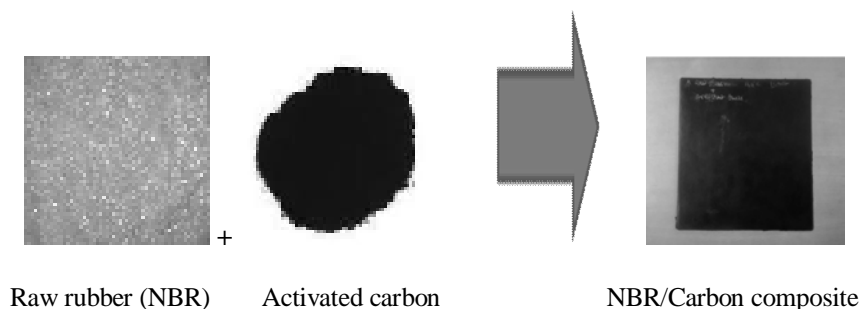**Fig. 1.** Fabricated equipment to hold the sample

Raw rubber (NBR)   Activated carbon   NBR/Carbon composite

Fig. 2. Pictorial representation for composite preparation

Table 1

Composition of materials for different biomass wastes

Areca nut shell	Coconut leaves	Coconut shell	Formulation
Material	Material	Material	PHR*
NBR	NBR	NBR	100
ZnO	ZnO	ZnO	5
Stearic acid	Stearic acid	Stearic acid	1
Sulphur	Sulphur	Sulphur	1.5
MBT	MBT	MBT	1.5
Carbon	Carbon	Carbon	20

Note: *PHR – parts per hundred of rubber

2.4.2. FTIR analysis

Fourier transform infrared spectroscopy (IR Prestige-21, Shimadzu, Japan) was used to identify the different chemical functional groups present in the chemically activated carbon powder. FTIR analyses were also used to determine the functional groups which are responsible for the entanglement of carbon with NBR. The analysis was carried out using KBr and the spectral range varying from 4000 to 400 cm^{-1}.

2.4.3. Analysis of activated carbon from biomass waste using phosphoric acid

Proximate analysis of activated carbon is followed by the standard methods for coal. The analysis essentially involves the determination of ash, moisture, volatile matter (VM), and fixed carbon by difference using standard specified procedures [11-17].

The results are in percentage composition (carbon, hydrogen, nitrogen, and sulphur). From these results the oxygen composition is determined by subtracting the sum of carbon, hydrogen, nitrogen, and sulphur compositions from 100.

The ultimate analysis was carried out in a CHNS analyzer. The sample was fed into the analyzer along with excess supply of oxygen. The reaction of oxygen with other elements (namely carbon, hydrogen, nitrogen, and sulphur, present in the sample, produces carbon dioxide, water, nitrogen dioxide, and sulphur dioxide, respectively. The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (TCD), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent composition of elements in the sample.

2.5. Preparation of Carbon Composite

The compounding of composites is done as reported in Table 1. ZnO, sulphur and stearic acid were supplied by Sunrise Elastomers, MIDC, Mhallunge, Pune. The representation of composite preparation is shown in Fig. 2. The blending was carried out using two roll-mills at room temperature. The slabs of 10×10×0.5 cm were developed using compression moulding machine at 433 K under the pressure of 1 MPa for 12 min with reference to the rheology results of the material.

The mechanical properties were tested using hardness tester supplied by Microvision Enterprises, Haryana. The composite prepared was subjected to petrol swelling test and the hardness was referred to evaluate performance of composite.

Stearic acid (SA) is used as a dispersing agent (Table 1). Contemporary science considers SA as an effective activator (along with ZnO) of non-saturated rubbers sulphur vulcanization. With regard to the mechanism of accelerated sulphur vulcanization, most of the presently proposed hypotheses suggest that under the process conditions a reaction occurs between SA and ZnO, which results in forming zinc stearate. SA salt participates in the formation of an activating complex with

the appropriated accelerator and sulphur which provokes the crosslinking of rubber macromolecules.

2.6. Petrol Swelling Behaviour of Rubber Composite

To study the response of formed rubber composite with various filler materials to the petrol for its application in automobile, the composite prepared was tested as per ASTM standard D-471-98.

2.7. Tensile Test of Rubber Composite

To study the tensile property of formed rubber composite using various filler materials, for its application in automobile, the composite prepared was tested as per ASTM standard D-412-98.

3. Results and Discussion

3.1. Lignin and Cellulose Content in the Starting Material

It is observed from Table 2 that the acid hydrolysable is more present in areca nut shell as compared to the other two materials. Three of the materials present three different classes of lignocelluloses. Coconut shell is the only woody material, *i.e.* more complex and crosslinked form of lignocelluloses. Areca nut shell is the material which has combination of fibrous and hard material, whereas coconut leaves have mainly watery content, a comparatively simple form of polymer lignocelluloses.

Here we propose the reaction scheme (Fig. 4).

Table 2

Lignin and cellulose content of the raw material

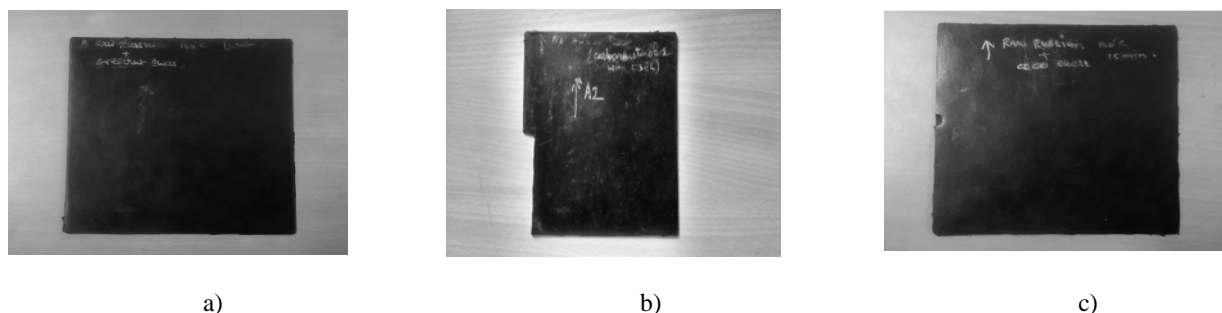| Material	Cellulose (as acid soluble), %	Lignin (as alkali soluble), %	Weight of remainder, %
Coconut shell	36	16	48
Coconut leaves	47	40	13
Areca nut shell	58	16	26

a)   b)   c)

Fig. 3. Composites NBR/areca nut shell (a); NBR/coconut leaves (b) and NBR/coconut shell (c)
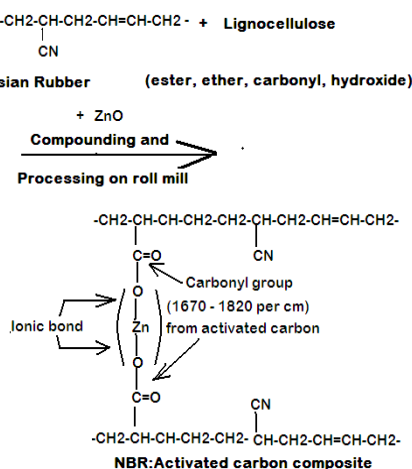

Fig. 4. Proposed reaction scheme for composite preparation

Proximate and ultimate analyses

Parameters	Lignocellulosic wastes dry basis, wt %		
	Areca nut shell	Coconut leaves	Coconut shell
Proximate analysis			
Moisture	15.46	8.167	11.93
Ash	6.473	2.39	4.90
Fixed Carbon	75.9	75.38	81.44
Volatile Matter	6.47	14.06	4.985
Ultimate analysis			
Carbon	54.86	23.56	57.62
Hydrogen	4.486	0.916	3.432
Nitrogen	0.475	0.889	0.191
Sulphur	0.251	0.115	0.119

The coconut shell values obtained by ultimate analysis are in moderate range as compared to areca nut shell and coconut leaves. The carbon content of coconut shell is 81 %, areca nut shell 75.9 % and coconut leaves 75.3 %.

The % yield of carbonisation also follows the same trend as shown in Table 2.

The photographs of the sheet prepared using areca nut shell (Fig. 3a), coconut leaves (Fig. 3b) and coconut shell (Fig. 3c) are presented below. The photographs show uniform curing of the composite material. The torque testing is followed using the part of blend from which the sheets are prepared. The raw rubber having butadiene repeating units along with acrylonitrile part, will form ionic bond with carbonyl group as shown in Fig. 4, from the activated carbon. The carbonyl group is an integral part of every lignocellulose material, either cellulose, hemicellulose, or lignin. Thus content of lignocellulose, cellulose, and hemicellulose is calculated.

3.2. Elemental Analysis

Table 3 presents the values in the terms of lignocellulosic wastes (wt %) dry basis.

One can see from the results of proximate analysis that moisture content and ash content in areca nut shell

was found to be higher than that in coconut leaves and coconut shell. Fixed carbon was higher and volatile matter was very lower in coconut shell in comparison with areca nut shell and coconut leaves. High moisture content provides the buckling of polymer chains by breaking hydrogen bonds resulting in the binding and bonding effect during processing.

According to ultimate analysis hydrogen and sulphur content is higher in areca nut shell in comparison with coconut shell and coconut leaves. Thus during processing with NBR rubber, high content of hydrogen and sulphur will lead to frictional loss.

3.3. SEM Analysis

The prepared activated carbons were examined by SEM to analyze the surface of the adsorbents. SEM micrographs of the chemically activated carbons by H_3PO_4 are presented in Fig. 5. In all three cases, well-developed porous surface was observed at higher magnification. The pores observed from SEM images are having diameter in micrometer range. These pores are considered as channels to the microporous network. From the figures below, it can be observed that all the adsorbents have rough texture with heterogeneous surface and a variety of randomly distributed pore size.
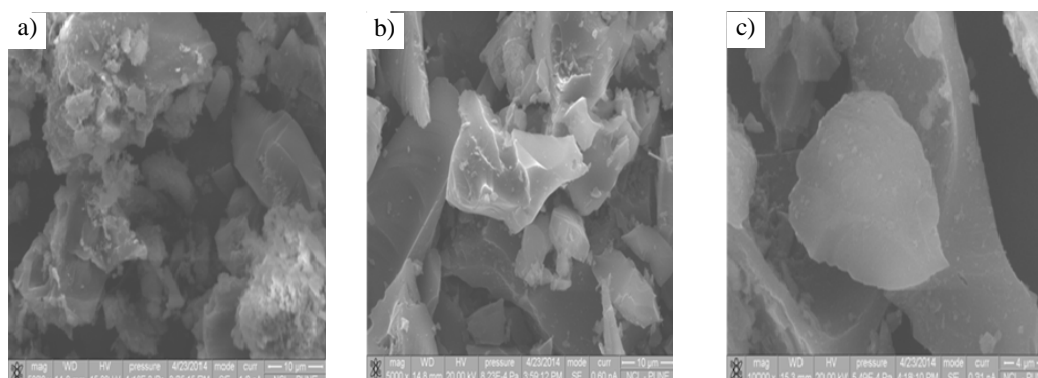
Fig. 5. SEM images of chemically activated adsorbent for 1:1 acid:adsorbent ratio: coconut leaves (a); coconut shell (b) and areca nut shell (c)

3.4 FTIR Analysis

To investigate the functional groups of the activated carbon generated by chemical activation of three of the lignocelluloses, FTIR study was carried out and the spectra are shown in Fig. 6. The spectra show prominent absorption peaks, in common, corresponding to carbonyl C=O stretching (1670–1820 cm^{-1}), ether (1070–1150 cm^{-1}) and ester (1000–1300 cm^{-1}). The major component for this type of materials is cellulose bound with lignin. Hemicellulose is also present over the material. Hydroxyl functional group undergoes esterification reaction in the presence of acids. Esters are generated over the material at the activation temperature of 673 K; otherwise the material contains prominent ether linkages.

3.5. Petrol Swelling Test (ASTM Standard D-471-98)

In order to assess the extent of swelling behaviour of composites, petrol swelling test ASTM standard D-471-98 was carried out. This test provided information on the interface strength, degree of dispersion of carbon and their alignment in the elastomeric matrix. Following results show the swelling index in terms of after ageing and before ageing. Petrol swelling test is also predicted in terms of deviation of density and hardness. It is observed from Fig. 7 that coconut shell based activated carbon and areca nut shell based activated carbon composites show less deviation for the petrol soaking. The coconut leaves based activated carbon composite show maximum density deviation. This is due to the maximum portion of lignocelluloses in leaves is water soluble sugars.

Active carbon NBR composite was found compatible with commercial carbon based composite (Table 4). The fuel pipe or hose pipe application was aimed and the composite with commercial matrix were prepared. The coconut shell based composite deviates the least, because of the complex nature of the lignocelluloses resulting into compact arrangement of the molecules during pyrolysis, whereas areca nut shell shows least deviation in density for petrol soaking but the maximum deviation in hardness. Such material may be used for fuel tube application. The coconut shell based rubber composite may be studied further for hose pipe application.

a)

b)

c)
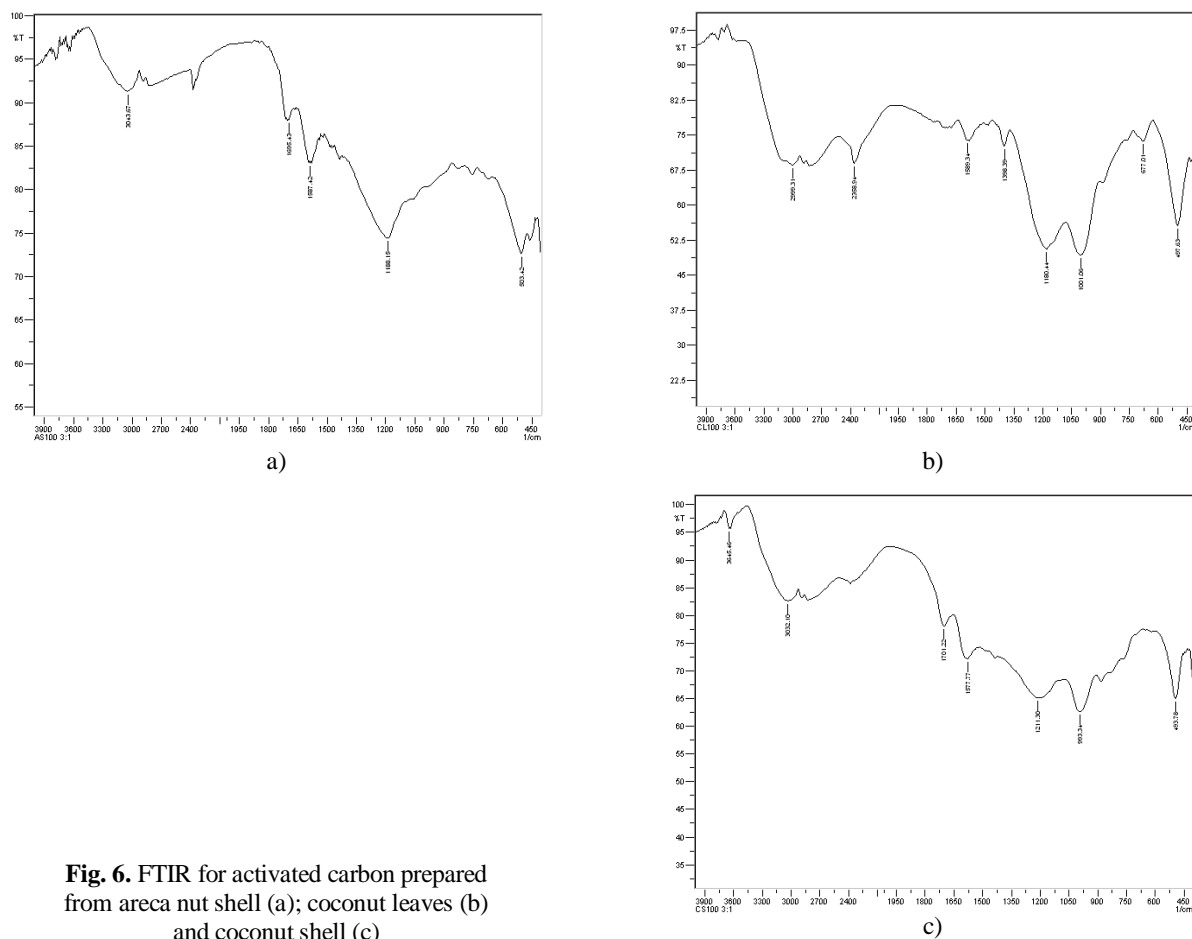
Fig. 6. FTIR for activated carbon prepared from areca nut shell (a); coconut leaves (b) and coconut shell (c)
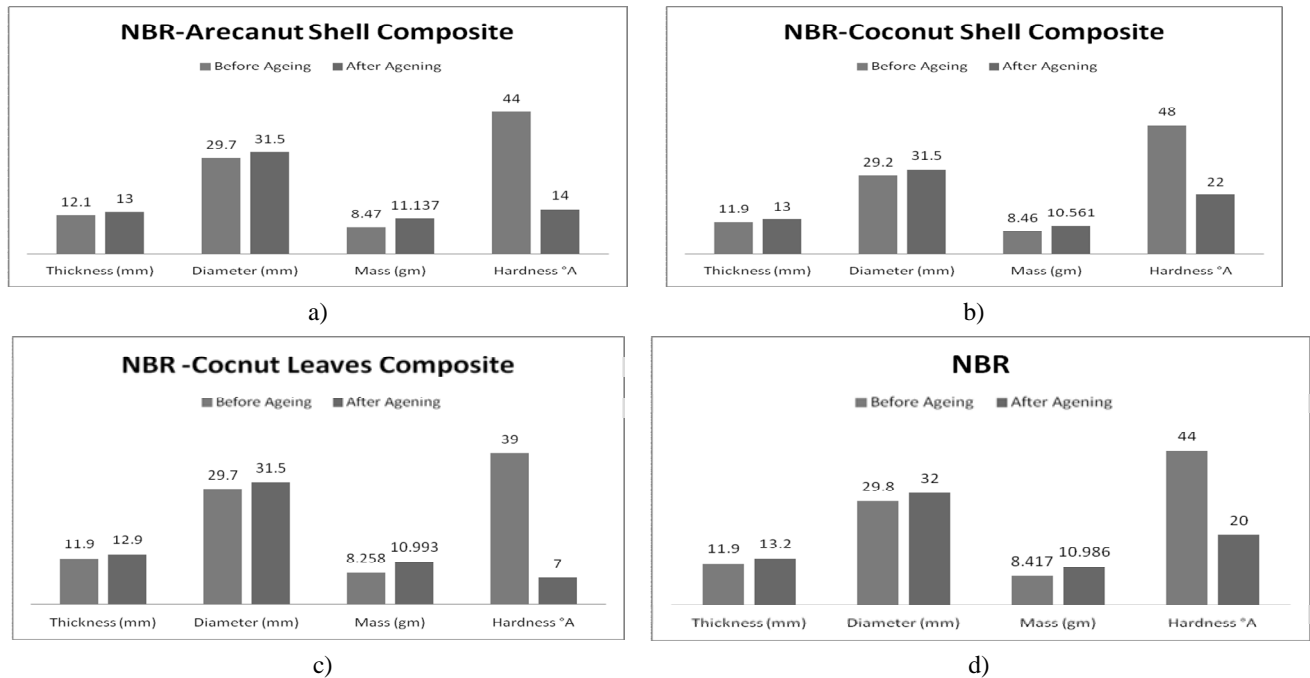
Fig. 7. Composites: NBR-areca nut shell (a); NBR-coconut shell (b);
NBR-coconut leaves (c) and pure NBR (d)

Table 4

**Effect of petrol swelling test hardness, tensile test for NBR, areca nut shell,
coconut shell and coconut leaves composite**

Sample	Deviation in density, %	Deviation in hardness, %	Remark
NBR	87.18	54.16	This is matrix material
AS-NBR	11	82	This can be used for fuel tube application
CS-NBR	28.3	54	This can be used for hose pipe application
CL-NBR	61.9	68	Needs to be studied further

Table 5

Rheological behaviour of the samples

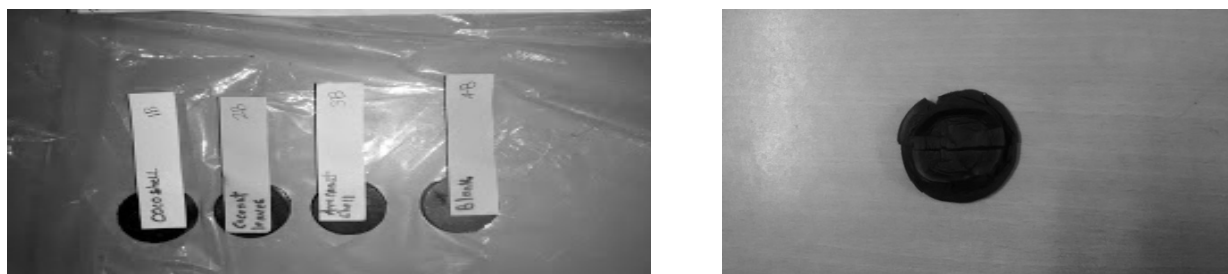| Material	TS 1	TS 2	TS 3
Coconut shell	1.21	1.39	1.93
Coconut leaves	0.35	0.41	0.51
Areca nut shell	1.07	1.22	1.52

Fig. 8. Active carbon-NBR buttons

3.6. Mechanical Properties of the Composites

The processing conditions for blends were tested rheologically. The results of the studies are presented in Table 5.

Activated carbon enhances the reinforcing effect. It means that active carbon is well dispersed because its aggregates contain internal voids capable of absorbing polymer.

More specifically NBR rubber composite from coconut shell and areca nut shell showed better tensile strength in comparison with tensile strength of composite prepared from commercial carbon and NBR rubber.

Mechanical properties of the rubber composites prepared from coconut shell and areca nut shell and activated by carbon were found to be the best at the lowest loading ratio of 20 phr. Coconut leaves exhibited very low values of mechanical properties as compared to the coconut shell and areca nut shell.

During preparation of rubber composite with commercial blend elastorene 673 EL (70/30 NBR: PVC, w/w) at loading ratio of 50 phr the composite is scorched. This is in agreement with the results reported earlier by Geyuo *et al.* [12] and Demrihan *et al*. [13]. Mechanical properties decrease drastically after 30 phr loading [12] but when the loading level reaches limit value the activated carbon does not act as reinforcing filler [13].

The photographs of the slab and button prepared for testing purpose are represented in Fig. 8.

4. Conclusions

Results and discussion show that coconut shell, coconut leaves and areca nut shell can be successfully converted into activated carbon by using H_3PO_4 as dehydrating agent. The coconut shell and areca nut shell activated carbon was found comparable with commercial carbon in formation of NBR composites for automobile applications because tensile strength and hardness shows least deviation with respect to commercial composite mechanical properties. Hence, activated carbon derived from areca nut, coconut, and coconut leaves can be used as filler in NBR for automobile application.

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СИНТЕЗ КОМПОЗИТІВ АКТИВОВАНИЙ ВУГЛЕЦЬ-БНК, ОДЕРЖАНИХ З ВІДХОДІВ БІОМАСИ, ДЛЯ АВТОМОБІЛЬНОЇ ПРОМИСЛОВОСТІ

Анотація. Показано придатність використання активованого вугілля, отриманого з шкарлупи горіхів пальми катеху, кокосової шкарлупи та листя кокосових горіхів, як наповнювача при приготуванні композитів на основі БНК для автомобільної промисловості. Проведено активацію вуглецю фосфатною кислотою (H₃PO₄) як дегідруючого агенту. Визначено, що стехіометричне співвідношення біомаси та фосфатної кислоти становить 3:1 для об'єму партії 300 г. У порівнянні з промисловим вуглецевим наповнювачем, активоване вугілля, отримане з відходів біомаси, краще витримує тест на набухання. Встановлено, що серед трьох протестованих зразків активізований вуглець, отриманий з кокосової шкарлупи, найкраще витримує тест на набухання та має найменше відсоткове відхилення в ступені твердості. Отримані результати узгоджуються з даними технічного аналізу.

Ключові слова: активований вуглець, фосфатна кислота, БНК, композити, твердість.