Activated carbon from lignocellulose waste as filler in industrial rubber

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Petrol swelling behaviour of Chemically Activated Carbon based Nitrile Rubber Composite

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Abstract

In automobile sector, PVC/NBR blend is filled with carbon black to prepare fuel tube and hose pipe parts. Activated carbon is the carbon with altered surface properties. Acid treatment to generate activated carbon develops reaction sites over carbon surface that may increase compatibility of carbon with rubber. To study this, activated carbon is generated from different lignocellulosic materials *viz*: areca nut shell, coconut shell, and coconut leaves. The carbon is activated by H_3PO_4 as dehydrating agent in the ratio of 1:1 stoichimetrically. It is found that activated carbon is comparable with commercial carbon as filler with reference to petrol swelling test ASTM standard D-471-98 (€) results. Coconut shell based activated carbon filled NBR composite shows the least deviation in hardness. Areca nut shell based NBR composite shows the least density deviation. The composite prepared are of 20-PHR basis. The results obtained are tried to correlate with reference to proximate analysis.

Keywords: Lignocellulose, H3PO4,Activated carbon, NBR, Composites, D-471-98 (€)

1.0 Introduction

Lignocellulose refers to the specific structure of biomass. The main constituents of lignocellulosic biomass comprises lignin, hemicellulose and cellulose. This is a complex structure in which the cellulose is surrounded by a monolayer of hemicellulose and embedded in a matrix of hemicellulose and lignin. Esters and ethers are the integral parts of the lignocelluloses. Also, carbonyl groups are present over three of the carbohydrates, namely lignin, cellulose and hemicelluloses. This structure can be seen in the figure below.

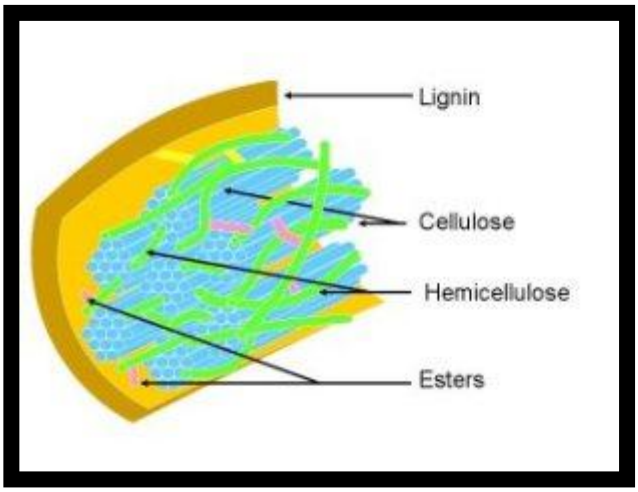


Fig 1: Structural representation of lignocellulose

Activated carbon is a versatile material with high porosity and surface area. The activation may be physical or chemical. Chemical activation reduces tar formation. Chemical activation is carried out with wood as the starting material. In the beginning, wood is impregnated with a concentrated solution of activating agents. It results in degradation of cellulosic material. Chemical-impregnated material is then pyrolysed between 400 and 600^0C in the absence of air. Pyrolysed product is cooled and washed to remove activating agent, which is recycled. On calcination, impregnated and chemically dehydrated raw material results in charring and aromatization, and creation of porous structure. Various types of activating agents are used. Some of them are: phosphoric acid, zinc chloride, H_2SO_4; K_2S, KSNS, alkali metal hydroxide, and carbonate and chlorides of $Ca+^2$; Mg^{+2} and Fe^{+3}. All activating agents are dehydrating agents which influence the pyrolytic decomposition and inhibit the formation of tar. They also decrease the formation of acetic acid, methanol etc. and enhance the yield of carbon.

Due to enhanced surface properties, it has become one of the technically important materials for selective separations commercially. Nevertheless, its application fields are restricted due to high cost.

This difficulty has led to search for the use of 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] and banana pith [10] etc. Biomass wastes are considered to be a very important feedstock because they are renewable sources. Activate carbon such produced can be used as effective adsorbent because of high adsorptive capacity. However, continuous production of activated carbon with reproducibility of characteristics is restricted by the seasonal availability of the starting materials.

To address this issue partly, we have tried coconut shell, areca nut shell and coconut leaves, which are available throughout the year irrespective of season, as starting materials for carbon preparation. Three of the starting materials are obtained from different parts of the plants. Accordingly they have got distinct lignocelluloses content than each other. Being in daily use in Indian continent as food ingredients and in some parts on auspicious occasions, the coconut shell is generated enormously. Areca nut is also chewed in Asian continent as mouth freshener and in India on auspicious occasions along with coconut.

Rubber industry is a huge consumer of carbon as reinforcing material. The filler, to impart certain properties to the rubber material such as colour, hardness and strength up to certain extent. However, so far there is no report for the use of activated carbon as filler material in rubber. For activation, the surface of carbon modifies to develop newer reactive cites inclusive of ester, ether and carboxylic.

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 (XNBR, Hot-Crosslinked NBR, HNBR) for more demanding service conditions.

The nitrile rubber, we have used for study, is Russian raw rubber normally used to blend with PVC for automobile applications. Nitrile rubber —(CH2-CH=CH-CH2)— is generally resistant to aliphatic hydrocarbons. It can be attacked by ozone, ketones, esters and aldehydes. Like carboxylated nitrile butadiene rubber (XNBR), the ester and ether linkages present on activated carbon may entangle with zinc during processing to furnish improved physical properties.

2.0 Materials and Methods

2.1 Selection of materials: By finding out the acid soluble and alkali soluble content of the different agricultural wastes, the coconut and the areca nut material were selected pertaining to the availability and the acid hydrolysable content.

Biomass waste such as coconut shell, areca nut shell and coconut leaves is used as the raw material for preparation of activated carbon. 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 110^0c. Biomass waste was finally crushed and sieved to 180 mesh size.

2.2 Methods –Experimental

2.2.1 Analysis of starting material

Cellulose content as acid hydrolysable using 73% H_2SO_4 solution and lignin content as alkali soluble using 17% NaOH solutions were found. The pre-weighed sample was first digested in acid at room temperature for 4hrs with constant stirring. Oven dried to constant weight to know the weight difference. The weight difference corresponds to the cellulose and hemicelluloses content. Later, the same sample was digested in NaOH solution at 80^0C for 2 hrs with constant stirring. The sample was oven dried till constant weight and weighed to know the lignin as alkali soluble content.

2.3 Preparation of Activated Carbon

A typical procedure to prepare activated carbon from lignocelluloses is as follow:

H_3PO_4 chemically pure quality [Merck and 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 1:3.

The impregnation was carried at ambient temperature for 24hr. After removal of residual water, the sample was kept in hot air oven at 110^0C till constant weight of the sample. A Weighed amount of oven dried impregnated samples was subjected for pyrolysis in muffle furnace maintained at 400^0C. The muffle furnace is purged with high purity nitrogen gas to avoid oxidation. Nitrogen flow was adjusted to 3ml/^{0}c at 400^0C. The activated carbon was subsequently removed from furnace and cooled to room temperature.

After activation, 3M hydrochloric acid used to remove the excess phosphoric acid from the activated carbon surface. The washed samples were dried at 110^0C for 6hr in oven and then ground to powder form carbon.

Following (figure:-1) are the photographs of the stainless steel container, carat (12 X 3.5 X 3.5 inch) fabricated to hold the container for pyrolysis of the acid impregnated lignocelluloses and (figure:-2) the pyrolysis set up.

Fig 2: Stainless steel container and carat

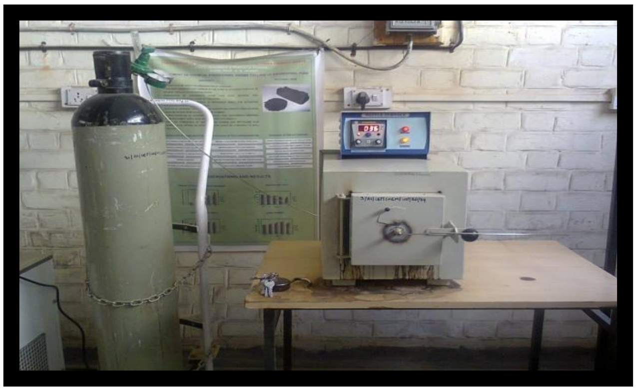


Fig 3: Experimental Set Up

2.4 Analysis of Activated carbon prepared from different lignocelluloses using H3PO4 as dehydrating agent:

2.4.1 Scanning Electron Microscope (SEM) Imaging

The prepared activated carbons were examined by Scanning Electron Microscope (SEM) Jeol Japan, JSM – 6390LV model having magnification ranging from 5X to 300000X with image mode secondary electron and back scattered image to analyze the surface of the adsorbents. Magnification used was 5X and 10X.

2.4.2 FTIR

Fourier Transform Infrared Spectroscopy, FTIR (IR Prestige-21, Shimadzu, Japan) was used to identify the different chemical functional groups present in the *chemically activated carbon* powder. FTIR analyses 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}. The mode of scanning was attenuated total reflection DSR.

2.5 Analysis of activated carbon:

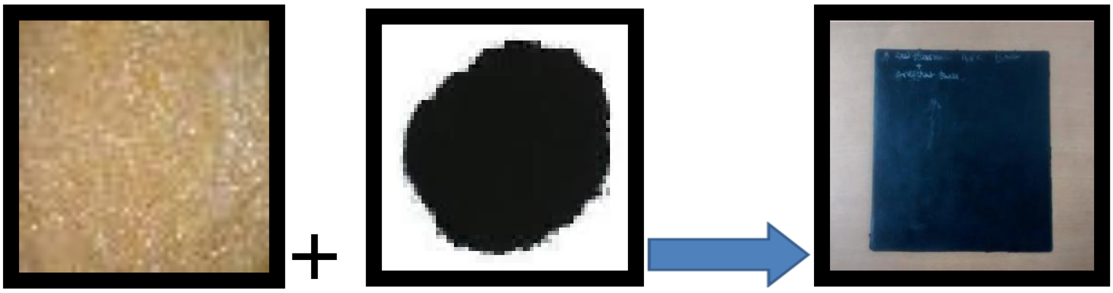
Proximate analysis activated carbon is followed by the standard methods set for coal. The analysis essentially involves the determination of ash, moisture, volatile matter (VM) and fixed carbon by difference using standard specified procedures [11-17].

The results are in percentage composition of 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 is 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 are detected by the thermal conductivity detector (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent compositions of elements in the sample.

2.6 Preparation of rubber composites:

The compounding of composites is done as reported in Table 1. Rubber chemical such as ZnO, Sulphur and Stearic acid were supplied by Sunrise Elastomers, Chakan MIDC, Mhalunge, Pune. The blending was carried out using two roll-mill at room temperature. The slabs of 10×10×0.5 cm were developed using compression moulding machine at 160^0C under pressure of 1Mpa for 12 minutes 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 for petrol swelling test and the hardness was referred to evaluate performance of composite.



Raw Rubber (NBR) **(Activated Carbon)** **NBR/Carbon composite**

Fig 4: Pictorial representation for composite preparation

Table 1: Formulation for composite preparation using different activated carbons

Arecanut Shell		**Coconut leaves**		**Coconut Shell**	
Material	PHR*	Material	PHR	Material	PHR
NBR	100	NBR	100	NBR	100
ZnO	5	ZnO	5	ZnO	5
Stearic Acid	1	Stearic Acid	1	Stearic Acid	1
Sulphur	1.5	Sulphur	1.5	Sulphur	1.5
MBT	1.5	MBT	1.5	MBT	1.5
Carbon	20	Carbon	20	Carbon	20

PHR* -Parts per hundred of rubber

2.7 Proposed reaction scheme:

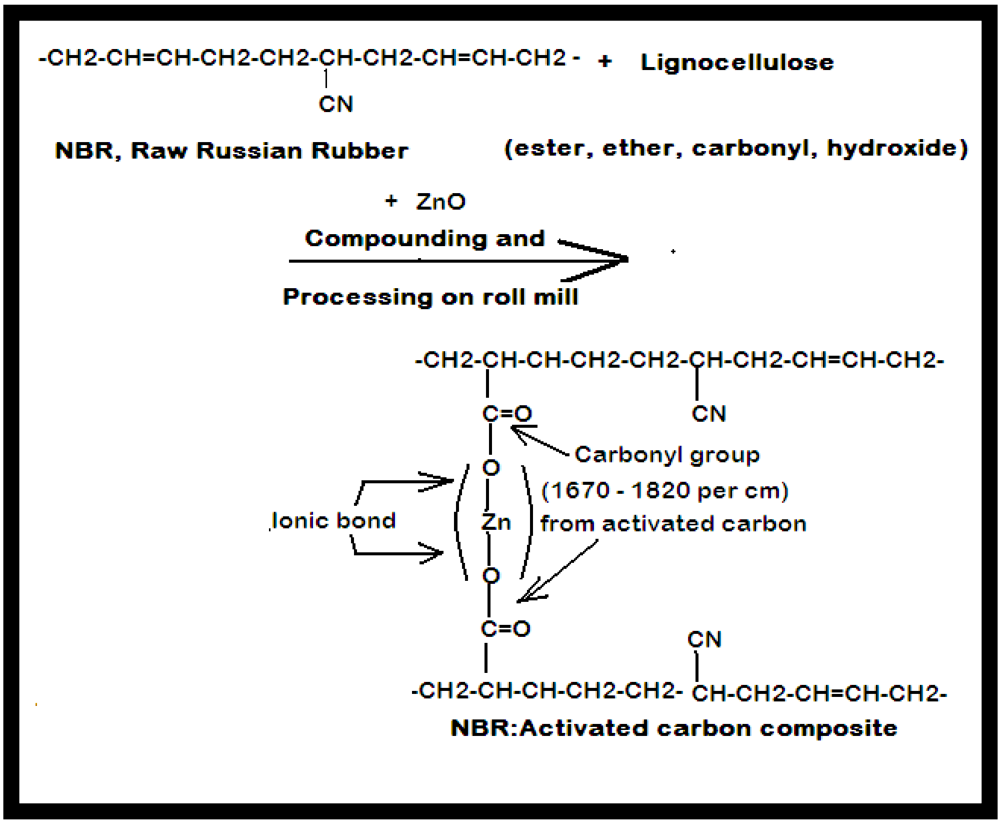


Fig 5: Proposed reaction scheme for composite preparation

The raw rubber having butadiene repeating units along with acrylonitrile part, will form ionic bond with carbonyl group as shown in figure from the activated carbon. The carbonyl group, is an integral part of every lignocellulose material, either cellulose, hemicellulose or lignin**.**

2.8 **Analysis of composites**:

In order to study the response of formed rubber composite using various filler materials, to the petrol for its application in automobile, the composite prepared was tested as per ASTM standard D-471-98 (€).

3.0 Results and Discussion:

3.1 Lignocellulose content of the starting material

From Table no. – 2, it is depicted that the acid hydrolysable is more in areca nut shell as compared to the other two materials. Three of the materials present three different classes of lignocellulosics. Coconut shell is the only woody material i.e. more complex and cross linked form of lignocelluloses. Areca nut shell is the material which has combination of fibrous and hard material. Whereas coconut leaves has on major watery content, comparatively simple form of polymer lignocelluloses.

Table 2: Lignin and cellulose content of the raw material

Sr. No.	Material	Cellulose % (as acid soluble)	Lignin % (as alkali soluble)	Weight of remainder
01	Coco nut shell	36%	16%	48%
02	Coco nut leaves	47%	40%	13%
03	Areca nut shell	58%	16%	26%

The same trend is observed in ultimate analysis results. The coconut shell has got all the values, for ultimate analysis in moderate range as compared to areca nut shell and coconut leaves except the % fix carbon content. Which is the highest i.e 81% followed by areca nut shell 75.9% and coconut leaves 75.3%. The % yield of carbonisation also follows the same trend as shown in above analysis.

3.2 Proximate and Ultimate analysis of activated carbons

Table 3 presents the values in the terms of activated carbon (wt %) dry basis.

Table 3: Proximate and Ultimate Analysis of activated carbons

Parameters	Activated carbon (wt%) dry basis		
	Areca nut Shell	Coconut leaves	Coconut Shell
Proximate Analysis			
Moisture	15.46	08.17	11.93
Ash	06.47	02.39	04.90
Fixed Carbon	75.90	75.38	81.44
Volatile Matter	06.47	14.06	04.99
Ultimate Analysis			
Carbon	54.86	23.56	57.62
Hydrogen	04.49	00.92	03.43
Nitogen	00.48	00.89	00.19

Sulphur	00.25	00.12	00.12

3.3 Scanning Electron Microscope (SEM) Anaysis

The prepared activated carbons were examined by Scanning Electron Microscope (SEM) to analyze the surface of the adsorbents. SEM micrographs of the chemically activated carbons by H_3PO_4 are presented in Figure 3.In all three cases, well-developed porous surface was observed at higher magnification. The pores observed from SEM images are having diameter in micrometer (µm) 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.

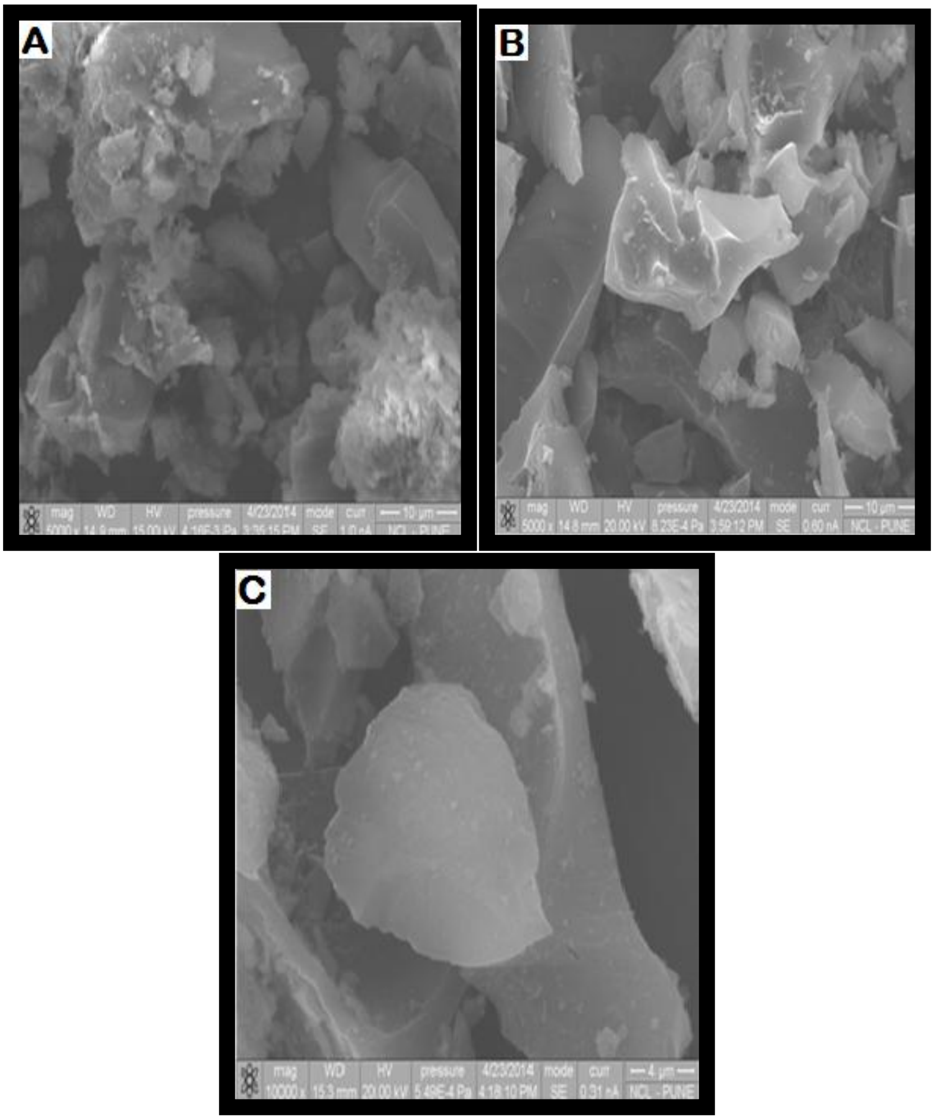


Fig 6: SEM images of chemically activated adsorbent, for 1:1 Acid: Adsorbent ratio.
(A) Coconut Leaves (B) Coconut shell (C) Areca nut Shell

3.4 FT-IR analysis

To investigate the functional groups of the activated carbon generated by chemical activation of three of the lignocelluloses, a FT-IR study was carried out and the spectra are shown in Figures 1, 2, 3. The three of the spectra shows prominent absorption peaks, in common, corresponding to carbonyl C=O stretching @ 1670 to 1820 cm-1, ether @ 1070 to 1150 cm-1 and ester @ 1000 to 1300 cm-1.

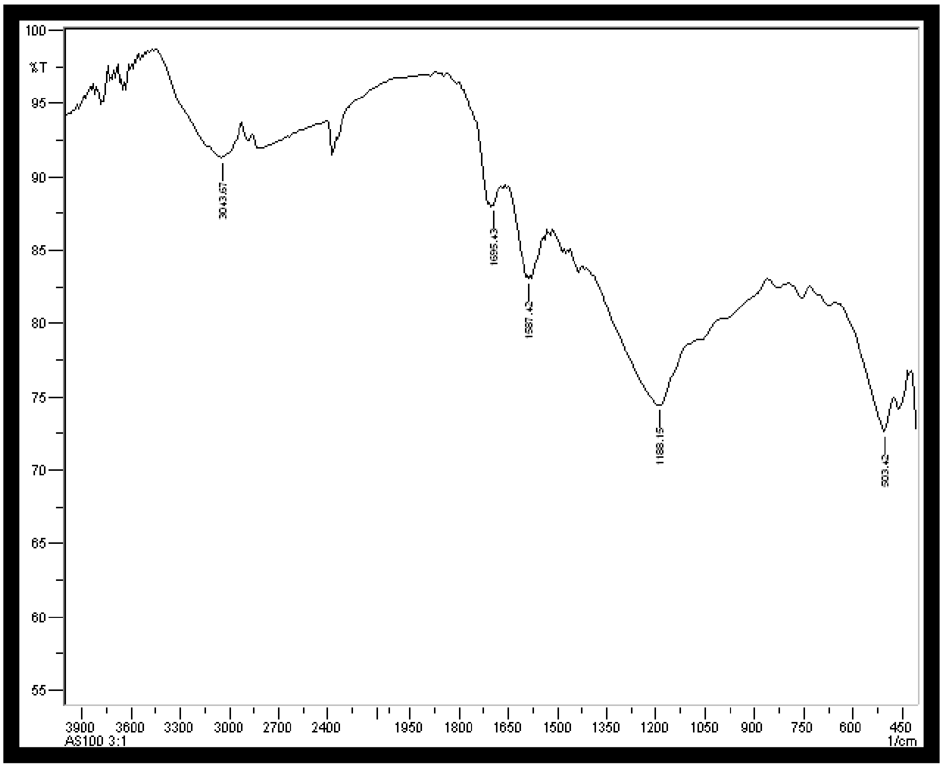


Fig 7: FTIR for activated carbon prepared from Areca nut shell

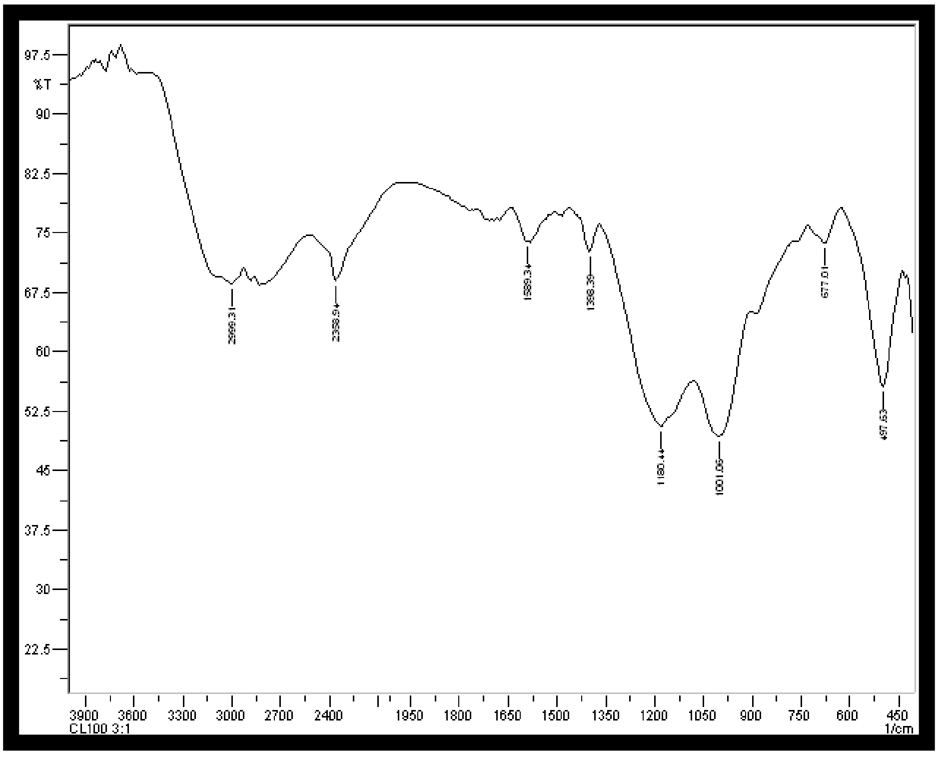


Fig 8: FTIR for activated carbon prepared from Coco nut leaves

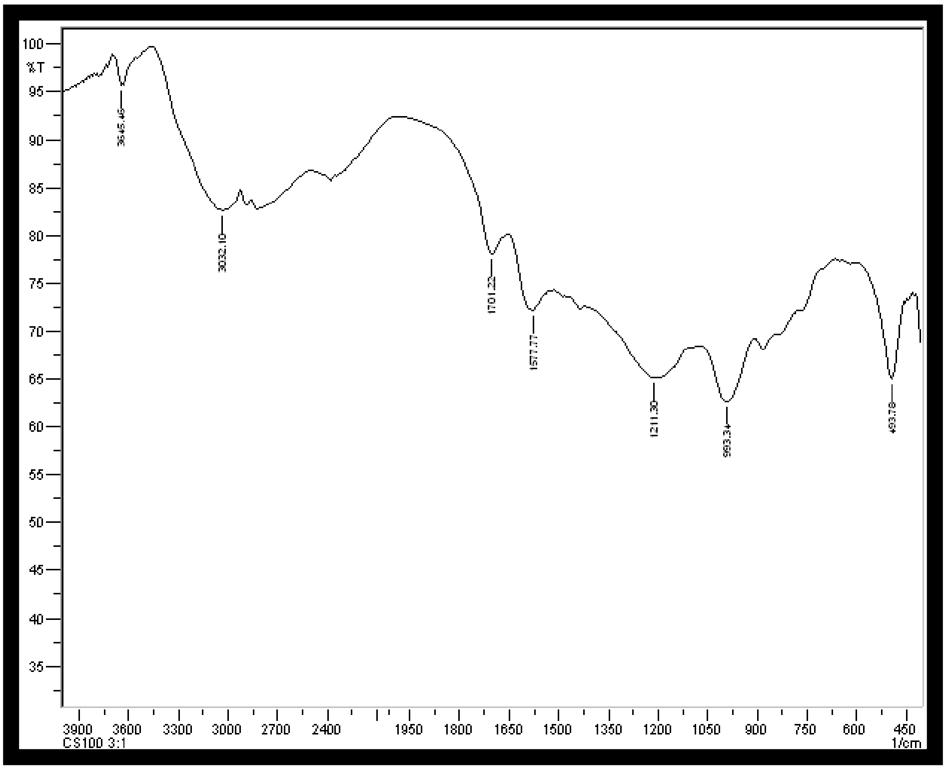


Fig 9: FTIR for activated carbon prepared from Coco nut shell

3.5 Rheology of rubber blend

To find out the processing condition the blends were tested rheological. Results are depicted in Table No. 5. Activated carbon give rise to reinforcing effect and therefore the aggregate is smallest form of a given activated carbon grade well dispersed in an elastomeric that will still keep all the reinforcing capabilities of a filler. Activated carbon aggregates contain internal voids which are capable of absorbing polymer.

More specifically NBR rubber composite filled by activated carbon from Coconut shell and Areca nut shell showed better tensile strength as compare to tensile strength of composite prepared from commercial carbon and NBR rubber.

Table 4: Rheological behaviour of the samples

Sr. No.	Material	TS 1	TS 2	TS 3
01	Coco nut shell	1.21	1.45	1.89
02	Coco nut leaves	0.36	0.45	0.50
03	Areca nut shell	1.00	1.22	1.50

Fig no 10: NBR- Arecanut Shell Composite

Fig no 11: NBR –Coconut Leaves Composite

Fig no 12: NBR -Coconut Shell Composite

3.6 Petrol Swelling Test (ASTM Standard no - D-471-98)

To assess the extent of swelling behaviour of composites, Petrol Swelling test ASTM Standard no - D-471-98 was carried. Following are the trends observed in the results. 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

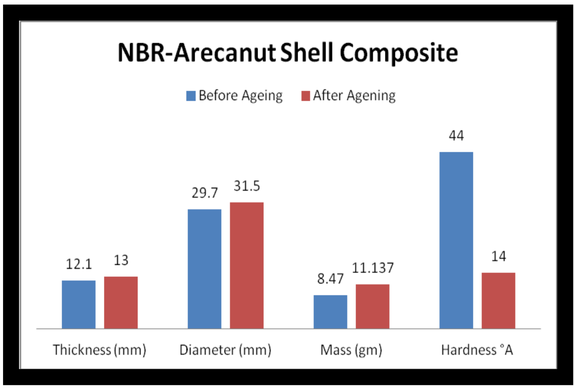


Fig. 13: Areca nut- NBR composite

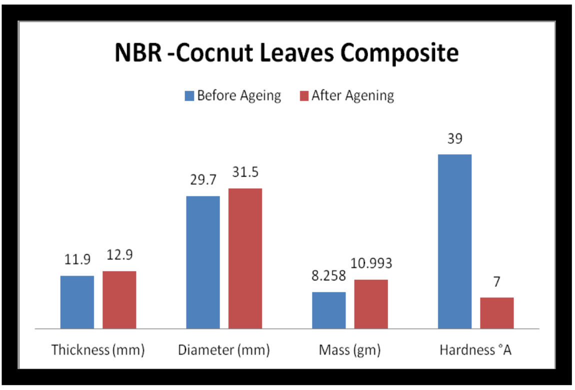
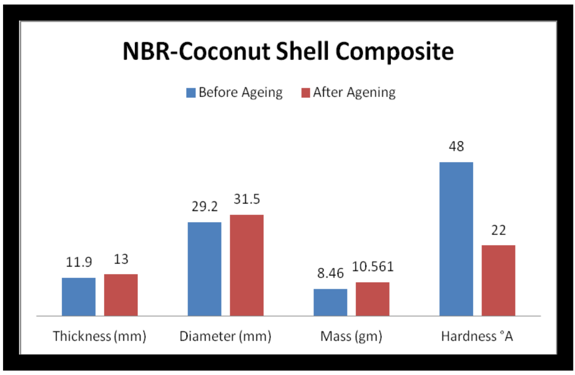


Fig. 14: Coconut leaves - NBR composite



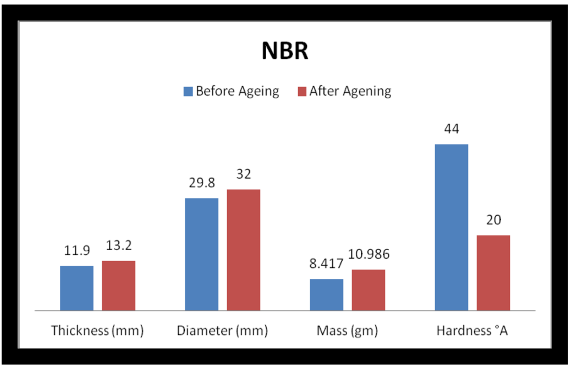


Fig. 15: Coconut shell- NBR composite

Fig. 16: NBR composite

deviation of density and hardness. From Fig. 3 – 6, it is clear that the coconut shell based activated carbon filled and areca nut shell based activated carbon filled rubber composites show less deviation for the petrol soaking. The coconut leaves based activated carbon filled rubber composite show maximum density deviation. This is because of the maximum portion of lignocelluloses in leaves is water soluble sugars.

Table 5: Effect of petrol swelling on NBR (raw) activated composites

Sr. No	Sample	% Deviation in density	% Deviation in hardness	Remark
01	NBR	87.18	54.16	This is matrix material
02	AS-NBR	11	82	This can be used for fuel tube application
03	CS-NBR	28.3	54	This can be used for hose pipe application
04	CL-NBR	61.9	68	Needs to be studied further

Fig.17: Buttons for petrol swelling

Thus material was found comparable with commercial carbon based composite. The fuel pipe or hose pipe application was aimed and the composite with commercial matrix were prepared. The coconut shell based composite deviate 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.

4 Future Scope:

The chemistry behind probable entanglement of activated carbon with NBR is to be studied further with the help of spectroscopy.

As the NBR (raw) based activated carbon composites were comparable to the commercial carbon based NBR (raw) composites, to find out the usability of activated carbons on industrial level, the activated carbons are proposed to use as filler from 20 to 70 phr in commercial blend Elastorene 673 EL (70/30 NBR: PVC, W/W) formulation.

5 Conclusion:

The results of this study showed 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 activated carbon has developed ether, ester and carbonyl groups over the surface for H_3PO_4 treatment. The reaction mechanism is proposed for the entanglement of activated carbon with rubber by the formation of ionic bond. It was found that the H_3PO_4 used for chemical activation has different impact on surface conversion of three different lignocelluloses pertaining to the lignin content of starting material. The coconut shell carbon and areca nut shell carbon were found comparable with commercial carbon in formation of rubber based composites for automobile applications.

6 Acknowledgement:

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