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REVIEW

Effect of Fiber Sizing on Mechanical Properties of Carbon Reinforced Composites: A Review

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ABSTRACT

Present study focuses on the carbon fiber sizing and their effect on overall mechanical properties of composites. Fiber sizing are one of the most important component in the manufacturing of composites. As the sizing are so much of importance in the manufacturing and development of composites which governs mechanical properties such as strength and stiffness. In this review some of the important articles are referred from the widely dispersed literature. This review covers the sizing effect, adhesion between fiber and matrix and characterization of composites.

1. Introduction

Carbon fibers are one of the most important choice for the industry in the area of fiber reinforced composites. The market of composite industry is expanding day by day because of the increased demand of the materials which have good strength to weight ratio. The production of carbon fiber has a very sophisticated procedure which has evolved in a very long span of approximately 60 years. The most critical component involved in the industry of carbon fibers is carbon fiber sizing or size. The sizing is a coupling agent coating which is coated over a carbon fiber to enhance the binding capacity of fiber to the resin. The term sizing is often used to get rid of confusion between size the coupling agent and the size relating dimension. It has been found in many studies that the unsized carbon fiber gives poor mechanical properties in comparison of sized carbon fibers. The carbon fiber sizing influence both long term and short term performance of the composites [1-4,22].

In recent years, Carbon fiber reinforced composites (CFRP) have been used for many offshore and marine applications. Composites are exposed to salt and high moisture conditions, hence sizing and interface play an important role. The performance of the composites in these critical environmental conditions have been a big issue. So it becomes important to make such fibers and fiber interphase which can work under intense weather conditions without or less degradation in the properties [5-6].

Commercially produced carbon fiber comes with a thin polymeric film which protects the fiber from damage due to friction between adjacent fibers during handling, transportation and textile processing and also provides good wettability during composite manufacturing. Sizing also acts as an adhesion promoter between the fiber surfaces to matrix. Recent work on the sizing has demonstrated that

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the polymeric sizing on carbon fiber reinforced composites can improve the durability and life span of composites.

2.1 Effect of Fiber Sizing on Carbon Fibers

The adhesion between the fibers and matrix is very important to have good mechanical properties as the fibers take maximum load and the load transfers from fiber to matrix through interphase, so it is very important to have a strong interphase. Different sizing chemicals are employed on the fibers to alter the surface morphology of the fibers. Different research works have been conducted in past to develop the sizing technology and to get compatible sizing chemicals for fibers and different polymer resins. The manufacturers keep the knowhow of sizing chemistry secret and researchers are trying to understand this technology and modify the sizing for the practical applications.

2.1.1 Carbon Fiber Sizing Technology

To develop a good sizing technology and to develop these apparatus have not been an easy task as sizing needs to be employed at the time of manufacturing of fiber itself. Broyles et al. [1] developed a sizing apparatus which could be used to coat carbon fibers with aqueous water-dispersible polymeric interfaces of poly vinyl pyrrolidone. A high level of fiber spreading achieved by controlling fiber tension and application of rollers.

2.1.2 Characterization of Carbon Fiber Reinforced Composites

It is very much needed to characterize the composites whenever there is a change in the morphology of fiber. Different techniques are employed to characterize the composites. Cho et al. [2] conducted dynamic mechanical analysis (DMA) on unidirectional and bidirectional woven carbon/ nylon 6 composites. The results of DMA and short beam shear tests indicate an enhancement in interfacial and inter laminar strength of woven composites. The authors also found that glass transition temperature (T_g) increased as the fiber matrix adhesion increased. Dilsiz and Wightman [3] compared the unsized fibers with Ultem polyamide and PU sized fibers. In the study it was evident that the sizing reduces the surface energy and acid-base sites. X-ray photoelectron spectroscopy (XPS) analysis showed that there is a decrease in hydroxyl groups on the carbon fiber surface. Single fiber fragmentation test showed the direct relation of surface energies to change the fiber matrix adhesion. Epoxy has also been used as a sizing agent. The effect of differ-

ent molecular weight sizing on the performance of carbon fiber was studied by Zhang et al. [4]. The sizing agent were epoxy 601, epoxy 6101 and epoxy 618 which are different in molecular weights. As the diameter of carbon fibers is in few microns so it is not feasible to study the surface of fiber from optical microscope for this purpose scanning electron microscopy (SEM) is a very important technique. Atomic Force Microscopy (AFM) and scanning electron microscopy (SEM) analysis showed that the sizing agent affects the surface topography. Interfacial shear strength (IFSS) results indicated that epoxy 6101 gave better results in comparison of other two. Yao et al. [5] compared of sizing effect on T700 grade carbon fiber on interfacial properties of carbon/epoxy and carbon/ bismaleimide (BMI) composites. Fourier-transform infrared spectroscopy (FTIR) analysis showed that the coupling agents are chemically reactive. Sizing react with bismaleimide and epoxy resin matrix. Micro droplet test indicated that desized fiber shows lower interfacial strength in epoxy resin than that of sized fibers, however, the trends in the case of BMI were reversed. This is also indicated by the chemical reactions, as the reaction between epoxy and sizing was sufficient in case of epoxy but partial reaction took place in case of BMI. Modification in surface roughness as well as chemical properties can be seen from the results of AFM and XPS analysis.

Some of the other techniques are also employed to modify the surface characteristics. Downey and Drzal [6] used the impact of UV-ozone on the fiber surface treatment with aromatic and aliphatic epoxy sizing. These sizing is used to enhance toughness of diglycidyl ether of bisphenol A (DGEBA)/ meta-phenylene diamine (mPDA) based carbon-epoxy composites without compromising static mechanical properties and glass transition temperature. The results showed significant increase in mode I fracture toughness as well as improved transverse flexural strength. Yuan et al. [7] modified the interface between carbon fiber and epoxy matrix. A modified polyacrylate sizing agent was applied on the fibers. The sized carbon fiber increase the wettability and decreased the surface roughness due to smooth sizing layer. Inter laminar shear strength increased by 14.2%. Liu et al. [8] synthesized a modified epoxy emulsifier (MEE) for preparing an aqueous epoxy sizing agent, the carbon fiber surface is evenly wrapped with tiny particles to increase the surface roughness. SEM, AFM and XPS analysis also showed the increase in activated carbon atoms on the surface of carbon fiber. The results of single fiber fragmentation test suggested inter facial shear strength increased by 70-76%. Han et al. [9] used polydopamine (PDA) as sizing on the carbon fiber surface. The authors observed that by implementing PDA as the sizing the behaviour of the crack

propagation becomes smooth whereas in the case of neat carbon fiber the curve is not uniform and it's like the teeth of a saw blade. They also reported that single fiber pull out test shows that the interface never failed in case of sized fiber the fracture took place in epoxy resin only. The SEM images of the neat and sized fiber also confirms that the surface of sized fiber is quite rough in comparison of neat fiber surface as shown in figure 1.
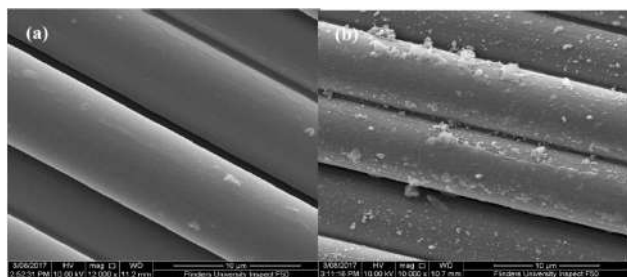

Figure 1. SEM image of (a) CF and (b) PDA-CF surface [9]

Sizing deposition ratio also affects the properties of composites. Stojcevski et al.[10] reported the effects of sizing deposition ratio on the properties of composites. The deposition ratio of unsized, 1:10, 1:15 and 1:20 parts of water and altering electrochemical oxidation with oxidation current 0 A, 2 A and 3.4 A on several fiber types. Two epoxy resin systems were used in the analysis and their effect on interfacial shear strength (IFSS) was studied. Epoxy RIMR935 with hardener RIMH 937 at 1:04 parts by weight ratio. Epoxy Bisphenol A diglycidyl ether (DGEBA) was mixed with 4,4′ Diaminodiphenylmethane (DDM) at a ratio of 1:0.3 by weight. Single fiber tensile test, fiber fragmentation test, AFM, contact angle and surface free energy were used to characterization of composite. The results showed that the unsized, unoxidized have least interfacial shear strength (IFSS).

Carbon nano tubes (CNT) have also been incorporated in sizing to enhance the adhesion between the fiber and the matrix. Zhang et al. [11] modified the carbon fiber surface by introducing carboxyl-functionalized carbon nanotubes (CNTs-COOH) and the amine-functionalized carbon nanotubes (CNTs-NH$_2$) in carbon reinforced composites. The results showed the betterment in the mechanical properties while CNTs-COOH, while CNTs-NH$_2$ gave adverse effects on mechanical properties as shown in figure 2. Yu et al. [12] studied the long term moisture effects on the interfacial shaer strength. Multi walled carbon nanotubes and silane coating was applied on the fibers. The increase in interfacial shear strength was 14.5% and 26.3% by using silane and CNT respectively. Also these strengths were maintained for 120 day immersion test in de-ionized water and simulated sea water.
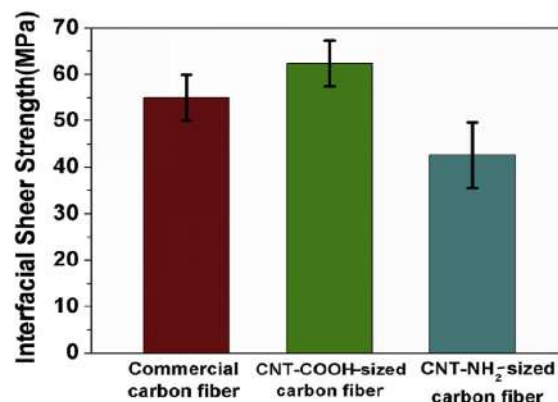

Fig. 5. Fragmentation tests for modified JH-T800 single-fiber composites.

Figure 2. Fragmentation test for modified carbon fiber [11]

The improvement in mechanical properties of carbon/epoxy composites by using hybrid **Poly Urethane (PU)/silane** coupling agent is studied by Mao et al. [13]. The silane coupling agent concentration affects the shear strength of composite and wettability of carbon fiber. If the sizing concentration was more than 3% the resin accumulated on the surface of fiber which reduced the mechanical properties again. Kobayashi et al. [14] studied the resin impregnation behaviour at different sizing content and found resin impregnation improved with decreasing sizing content. This impregnation causes larger permeability. Sizing agent on the fiber surface increased the resin flow among the fibers. It was also found that the sizing content which was optimized with epoxy does not provide good results with PA 6.

It becomes very important to analyse the surface of the carbon fiber while manufacturing a composite as the interfacial shear strength depends on the adhesion between the fiber and the matrix. Dilsiz and Wightman [15] did the surface analysis of sized and unsized fibers and found the thickness of poly(thioarylene phosphine oxide) (PTPO) thickness is greater than the thickness of poly(etherimide) (Ultem) sizing. The practical applications of carbon fiber and vinyl ester composites are restricted beacause of poor adhesion between the fiber and matrix which leads to lower IFSS. To resolve this issue N-(404-diaminodiphenyl methane)-2-hydroxypropyl methacrylate (DMHM) may be used as a sizing agent which can improve interfacial shear strength by covalently bonded carbon fiber and vinyl ester resin [16]. Zegaoui et al [17] incorporated various concentrations of silane treated carbon fiber in cynate ester/benzoxazine resin. 3-glycidyloxypropyltrimethoxysilane (GPTMS) was used as a sizing agent. FTIR studies showed that the treated carbon fiber had effectively reacted with the matrix, SEM micrographs confirmed the changes in the morphology of composites. At 20% treated carbon fiber filled composites had best mechanical properties. Ozkan et

al. [19] studies the effects of carbon fiber sizing on the short carbon fiber reinforced polycarbonate composites. Sizing materials were epoxy/phenoxy, phenoxy and polyimide. 1%, 2% and 3% by wt.% sizing is used on the carbon fiber, while the weight percentage of carbon fiber was kept constant at 30%. It was observed that tensile strength and modulus of sized carbon reinforced polycarbonate composites were higher than the unsized fibers. From the TGA analysis it was evident that the sizing material was stable at the time of composite processing.

2.1.3 Sizing on Recycled Fibers

The disposal of composites after the completion of life is a big issue in the application of composites. So composites can be collected after their lifetime and fibers can be extracted from these composites for recycling. Recycled fibers are available for free or at a very low cost. These fibers can be used in composites for secondary structural applications as the stiffness and the strength of composites decreases after the primary use. To again impart strength and stiffness to the fibers the coupling agents are applied on the fibers. The length of the recycled fibers is in millimeters so these fibers can be used a randomly oriented 2D mat or single direction aligned mat [19].

2.1.4 Effect of Sizing on Fatigue Properties

The study of the fatigue properties of a composite is very important. As in most of the applications the composites are not subjected to only static loading but also to dynamic loading which can be repeating in nature. So in these cases fatigue failure becomes predominant. In fatigue loading material fails well below its yield or ultimate strength so fatigue can be very detrimental to a structure. The fatigue limit is the value of stress which a sample can withstand for one million revolutions. The studies are conducted to find the fatigue life of composites. Broyles et al. [20] studied the effect of phenoxy polyhyrdroxyether (PKHW35) and poly vinyl pyrrolidone (PVP K17) as the sizing material in the composite of carbon fiber and vinyl ester. The stress levels of 75%, 65%, 55% and 45% were applied in compression to draw S-N diagram. From the studies it was concluded phenoxy sized composites gave about 60% increase in fatigue limit of the composites in comparison of unsized fiber while PVP gave an increase of just 20%. From this study is also concluded that sizing not only affects the static mechanical properties but also improve fatigue properties. Tsai et al. [21] incorporated silica nano particles (SNP) in the sizing HS-1 and Neoxil-965 as the emulsion of different weight percentages. The DCB specimen were used as the fatigue crack growth

test at room temperature. The displacement ratio used was 0.1 at a frequency of 10 Hz using a sinusoidal wave form. The sizing had no effect on the fatigue limit but the mode I fracture energy increased by 101%.

Table 1 consists of the list of common sizing chemical used for carbon fiber. GPTMS is also a very effective sizing chemical for glass fiber [22]. GPTMS can be used as a common fiber sizing for glass fiber and carbon fiber reinforced hybrid composites.

Table 1. Common Sizing chemicals used for carbon fibers

S.No.	Sizing	Ref.
1	Poly vinyl pyrrolidone	1,20
2	polyamide and PU	3,19
3	Epoxy	4,8
4	Polyacrylate	7
5	Polydopamine (PDA)	9
6	4,4′ Diaminodiphenylmethane (DDM)	10
7	Carbon Nanotubes	11
8	Poly(thioarylene phosphine oxide) (PTPO)	15
9	N-(404-diaminodiphenyl methane)-2-hydroxypropyl methacrylate (DMHM)	16
10	3- glycidyloxypropyltrimethoxysilane (GPTMS)	17
11	Phenoxy polyhyrdroxyether	20
12	HS-1 and Neoxil-965	21

3. Conclusion

The current study shows the different compounds used as sizing on carbon fiber. The methods to characterize the interface also discussed. The primary function of fiber sizing is to enhance the adhesion between the fiber and the matrix material and to protect fibers from the neighbouring fibers. Sizing also affects the glass transition temperature and morphology of fiber surface. The discussed methodology can be used for recycled composites and the recycled fibers can be used in the secondary structural applications.

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ARTICLE

Synthesis and Characterization of 4,4′-Dibromoazobenzene

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ARTICLE INFO	ABSTRACT
	Azobenzene molecules show excellent application potential in many fields due to their photoisomerization properties. Azobenzene molecules will gradually change from trans-structure to cis-structure under the irradiation of UV. In this paper, we have synthesized 4,4'-dibromoazobenzene molecules and characterized their photoisomerization properties. We found that with the extension of UV time, the trans absorption peak at 343 nm decreased significantly, while the cis absorption peak at 435 nm showed an upward trend. Furthermore, photoisomerization of azobenzene is not a first-order reaction.

1. Introduction

Azobenzene molecules and their derivatives refer to aromatic compounds containing a functional structure of -N=N- in the molecule. In 1858, Johann [1] discovered a diazotization reaction that could be used to synthesize azobenzene compounds. Under the specific wavelength of light radiation, azobenzene molecules will have obvious photochromism. This phenomenon is because azobenzene molecules have two geometric isomers. They can be converted to each other under the stimulation of a specific wavelength of light. This phenomenon is called photoisomerism. Azobenzene molecules can undergo trans to cis conversion under the irradiation of ultraviolet light, and cis to trans conversion can be achieved under the irradiation or heating of visible light (Figure 1).
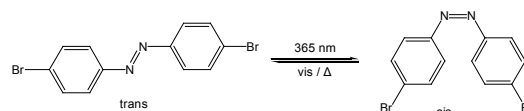
Figure 1. Photoisomerization of azobenzene

The classic methods for preparing azobenzene are azo coupling reaction, Mills reaction, and Wallach reaction. The azo coupling reaction is a nucleophilic reaction with short reaction time and high yield [2]. Primary aromatic amines initially diazotized at low temperatures before reacting with electron-rich phenol. Diazonium salts are weak electron systems and are prone to reactions in electron-rich systems [3]. This reaction needs to be performed in an acidic environment [4]. The reaction of aromatic nitroso derivatives and aniline in glacial acetic acid is the Mills reaction [5]. Aromatic nitroso derivatives can be prepared from aromatic methyl hydroxylamine by t-butyl hypochlorite oxidation. This oxidation reaction needs

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to be carried out in a dilute solution at -78 ℃ to prevent excessive oxidation. For the Wallach reaction, there is an explanation of the reaction mechanism. Azobenzene oxide is first protonated, dehydrated, and isomerized, and then attacked by nucleophiles. After rearrangement, azobenzene products are obtained[6]. In this paper, 4,4'-dibromoazobenzene is prepared from 4-bromoaniline by the method of primary oxidizing amines to azo by $KMnO_4$ supported on Fe(Ⅱ)SO_4 (Figure 2) benzene. The trans to cis conversion was achieved under UV light at 365 nm.
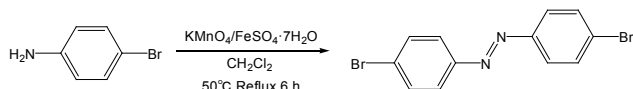

Figure 2. Synthesis of 4,4'-dibromoazobenzene

2. Experiment

Synthesis of 4,4'-dibromoazobenzene

Pour equal amounts of $KMnO_4$ (5 g) and $FeSO_4 • 7H_2O$ (5 g) in a mortar and lightly grind (to prevent oxidation of ferrous ions) to obtain the oxidant. 4-Bromoaniline (1.75 g, 1 mmol) was placed in a 250 mL round bottom flask, dissolved in dichloromethane, and a homogeneous mixture of oxidant (10.0 g) was added thereto. The mixture was refluxed for 6 h. The reaction mixture was cooled to room temperature and filtered through celite. The residue was washed with CH_2Cl_2 (3 x 15 ml) and ether (3 x 15 ml). The resulting solution was dried over anhydrous sodium sulfate. The solvent was removed and purified by column chromatography (basic alumina, 200-300 mesh, n-hexane: ethyl acetate = 4: 1). Vacuum drying box at 60 ℃ for 6h. An orange-red solid was obtained (87% yield). ^{1} H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 8.68 Hz, 4H , H^2), 7.66 (d, J = 8.68 Hz, 4H, H^1).

UV irradiation experiment

Use a volumetric flask to accurately configure 4, 4'-dibromoazobenzene with a concentration of 3×10^{-5} mol / L ethyl acetate solution. Add 1 ml of the ethyl acetate solution in 1.5 ml centrifuge tubes. The tubes were irradiated with 450 nm LED blue light for 30 min in order to convert all cis-azobenzene molecules into trans. The tubes were irradiated with a 365 nm UV lamp in a dark box, and a solution was taken every 1 minute for UV-vis spectrophotometry.

3. Results and discussion

The ^{1}H NMR (Figure 3) of the product showed that the ratio of the integrated values of 1 and 2 was 0.99: 1. This result is consistent with the theoretical value. Therefore, 4, 4'-dibromoazobenzene can be prepared by the method of

oxidizing primary amine to azo by $KMnO_4$ supported on Fe (II) SO_4.
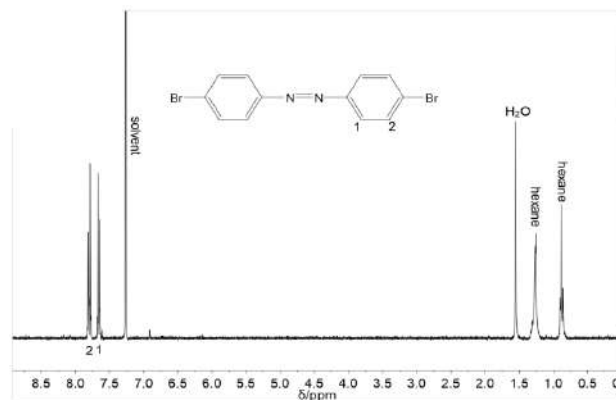
Figure 3. ^{1}H NMR spectrum of 4, 4'-dibromoazobenzene （CDCl3， 300 MHz， 298 K）

Figure 4 shows the UV-vis absorption spectrum of 4,4'-dibromoazobenzene. From the image, we found that with the increase of the 365 nm UV lamp irradiation time, the absorption peak at 343 nm gradually decreased, while the absorption peak at 435 nm showed an upward trend.
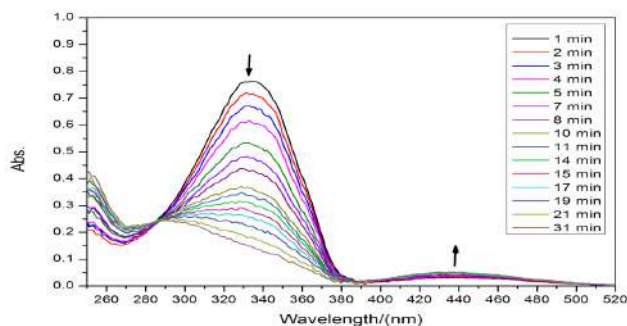
Figure 4. UV-vis absorption spectrum of 4,4'-dibromoazobenzene

Under UV radiation at 365 nm, 4,4'-dibromoazobenzene will undergo a π-π * transition, and its structure will change from trans to cis. The absorption at the wavelength of 343 nm corresponds to the trans structure, and the absorption at the wavelength of 435 nm corresponds to the cis structure. The formula for the first-order reaction is as follows:

$$\ln(c_0) - \ln(c_1) = Kt \qquad (1)$$

Then through Lambert-Beer law $A = \varepsilon bc$ （2).

Where c is the solution concentration, K is the reaction rate constant, ε is the molar absorbance, and b is the cuvette thickness [7]. Wherein the molar absorbance, cuvette thickness, and reaction rate constant are all quantitative,

and we can derive that:

$$\ln(A_0) - \ln(A_1) = Kt \qquad (3)$$

Substitute Figure 4 data into the formula and find that the value of K is constant. This result indicates that the reaction is a first-order reaction.

4. Conclusion

In this paper, we successfully synthesized 4,4'-dibromoazobenzene molecules via $KMnO_4$ and Fe（Ⅱ）$SO_4 \cdot 7H_2O$ and characterized their photoisomerization properties. We found that with the extension of UV light irradiation time, the trans absorption peak at 343 nm decreased significantly, while the cis absorption peak at 435 nm showed an upward trend. The photoisomerization of azobenzene is not a first-order reaction.

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REVIEW

Cashew Nut Shell Liquid (CNSL) Based Bio-Derived Resin And Composites for Advanced Structural, Automotive, Electronic Packaging and Medical applications- A Review

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ARTICLE INFO	ABSTRACT
	As India is a world class producer of sugarcane, sugar beet, other tubers like potato and vegetables with starch, cashew and badam, castor oil and soybean, the quantum of bio resins and bio plastics that can be produced from these conventional, organic and genetically modified plants is immense. As on date, advanced and state of the art plastics and composites are being used in many applications as there is no incentive for farmers to produce plants and vegetables for the plastics and resins market exclusively. The use of advanced composites in varied applications escalates costs and shifts the material consumption that would deplete the natural resources, through excessive usage at one end and lack of demand for natural resources at the other end as bio derived composites become under-utilized. This review paper attempts to project the actual possibilities of the bio resin and bio plastic market in this country and provides the knowhow for the production of bio-phenolic cashew nut shell resin which are more than a substitute for the synthetically produced epoxies. Their true potentialities in composites product applications involving structural, thermal, electronic, pharmaceutical and petroleum engineering markets is discussed in this paper. A novel working model with an economically feasible option is also provided for those concerned about their safe disposal, recycling, reuse and conversion into useable fuel with virtually no impact to the environment. Cashew Nut Shell Liquid (CNSL) is an abundant natural source for synthesizing phenolic compounds. The excellent monomer, Cardanol is isolated from CNSL for polymer production. These are polymerized with aldehydes and acids at a particular mole fraction in the presence of catalysts like alkalis to convert into rigid resins. Differential Scanning Calorimetric (DSC) and Thermo Gravimetric Analysis (TGA) were studied for the thermal characterization of the synthesized CNSL Resins. Characterization of the synthesized resins was also carried out with respect to the evaluated mechanical properties such as hardness, strength, elastic modulus and fracture toughness. The synthesized CNSL resins yielded many interesting compositions with varied properties increasing the possibilities of various resin formulations which could be used for composites applications in vibrational damping. The electronic packaging applications of nano-composites with high dielectric strength produced with the CNSL matrix are also highlighted.

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1. Introduction

India is a world class producer of sugarcane, sugar beet, other tubers like potato and vegetables with starch, cashew and badam, castor oil and soybean, the quantum of bio resins and bio plastics that can be produced from these conventional, organic and genetically modified plants is large. The byproduct of cashew industry, CNSL is unique resource of unsaturated long chain phenolic resin [1]. India produces about 25 000 tons of cashew and 2500 tons of CNSL per annum. Most of the CNSL oil is consumed internally for furnace oil, paints, pharma, cosmetics, resins and adhesives, and less than about 20 % is exported. The cashew liquid Cardanol is a laminating resin, used in paints, coats, bonding resins and varnishes [2]. CNSL and cashew friction dust are used in brake linings, pads, faces, discs and shoes. CNSL comes with asbestos or non asbestos containing brake applications. The natural meta substituted alkyl phenol can be produce a series of phenolic resins by catalyzed aldehydes or acids. Many have and characterized the polymerization of cardanol[3]. Some investigators have synthesized CNSL based phenol-formaldehydes and studied their properties like thermal stability and compared them with standard phenol formaldehydes [4]. The thermal characterization and physical properties of CNSL were also studied. Tejas S Gandhi et. al . characterized the Mannich base with Cardanol at a low viscosity and concluded that it can used as a polyol for synthesis of rigid polyurethanes [5]. At VIT, a better variety of CNSL matrix materials for composite applications have been synthesized [6,7,8]. Novel mechanical properties were obtained and the thermal characterization of different combinations of CNSL were done. This review paper attempts to project the actual possibilities of the bio resin and bio plastic market in India [9] and provides the knowhow for production of CNSL resins that are known to be termite resistant and hygrothermally more stable than some of the epoxies as cardanol is hydrophobic.

The byproduct of cashew industry, CNSL is a unique resource for unsaturated long chain phenolic distillates, mainly cardanol [1]. The natural Meta substituted alkyl phenol is polymerized to yield varieties of phenolic resins by catalyzed aldehydes or acids . Due to the phenolic structure of cardanol it can be polymerized and suitably modified for applications [2]. Menon et al studied and characterized the polymerization of cardanol [3]. Papadopoulou et al synthesized CNSL phenol-formaldehyde and studied properties and thermal stability comparing with standard phenol formaldehyde [4]. In industry, resins derived from CNSL are widely employed as friction materials, laminates, adhesives, surface coatings, flame retardants, anti-corrosive paints and medicinal drugs etc. [1] . One of the main requirements of fiber-reinforced composite materials to be successfully used in practice are their static and dynamic mechanical performance . This review paper focuses on the evaluation of thermal, static, vibrational and electronic properties of naturally derived composite materials with CNSL as the matrix and nano fillers or glass fibres as the reinforcements. Some of the reported findings form first of their kind in the documented literature.

The mechanical properties of glass fabric used in the layup of the composite are, Elasticity modulus = 35 GPa, Shear modulus = 14 GPa , Density = 2.52 g/cm^3, Poisson's ratio 0.25. The mechanical properties of CNSL matrix used are, elastic modulus= 1.5 GPa, Density = 0.95 to 1.00 g/cm^3, Poisson's ratio= 0.35.

2. Experimental Details

The CNSL made available from Cuddalore (In Tamilnadu which is a cashewnut farming area) is preheated with toluene at 70^{0}C for about an hour and then cured with formaldehyde and alkali at 120^{0}C for two hours or with any of the acids like HNO_3 or H_2SO_4 at 180^{0}C for two hours and then cooled in the oven [7,8]. The DSC (Differential Scanning Calorimetry) and TGA (Thermal Gravimetric Analysis) analysis were carried out in milligram sized cured samples from room temperature to about 700^{0}C at a heating rate of 10^{0}c/min to obtain information on the thermal stability, glass transition temperature and weight loss versus temperature [7,8].

The hardness experiments for polymers are normally carried out with Durometers that are of type Shore A for soft plastics and Shore D for hard plastics. The hardness of the material is read off from the display on a scale of 100 [7,8]. Tensile and Single Edge Notch (SEN) test specimens were prepared from the laminate, as per requirements for the tensile test and the Mode I fracture toughness test, respectively [10-14] .Tests carried out on an electronic Tensometer give the data of load applied and the displacement in the specimen when tested in the opening mode . Tensile specimens are loaded until the failure of the specimen, whereas the SEN specimens are loaded until the pre- crack starts propagating consistently.

Impact modal analysis is one experimental modal analysis technique that is widely used. The vibrational response of the structure to the impact excitation is analysed and measured through the signal analyser and transformed into frequency response function using FFT technique. The measurement of the frequency response function is the heart of modal analysis and the FRFs are used to ex-

tract the frequency modal parameters such as natural frequency and mode shape. The experimental setup is shown in Figure 1.
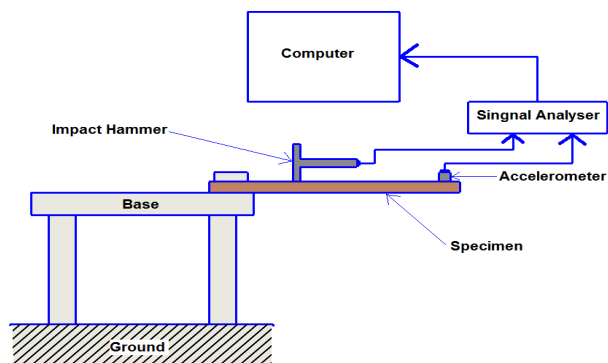

Figure 1. Block diagram of impact hammer modal analysis fixture

The vibrational properties like natural frequencies and damping percentage are extracted from the experimental modal analysis. The prepared composite is first cut into pieces to make specimens for impact hammer modal analysis. The dimensions of the specimens are 250 mm along the length and 25mm along the width at a 3 mm thickness. To carry out the modal analysis 5 such specimens are prepared [15-18].

The experimental modal analysis of the specimen is carried out in a fixed- free cantilever condition which is fixed to a trestle. A three dimensional accelerometer (KISTLER 8778A500) is glued to the specimen which sends the vibrational response to the connected signal analyser (DEWE 501). Impact hammer (DYTRAN 1051V) is used for the excitation of the specimen in selected locations due to which the specimen vibrates. The vibrational response sent by the accelerometer is amplified by the signal analyser and forwarded to the computer for the post processing. Post processing of the vibrational response is carried out by the software (RT Pro Photon) to plot FFT (force frequency time) and FRF (force response function) . The vibrational properties such as first three natural frequencies, damping percentage, etc. of the corresponding modes were extracted [15-18]. The accelerometer is fixed at the edge of the specimen and excitation is given on the top surface of the cantilever specimen. Excitation is given on the specimen by increasing the distance from the accelerometer till the support is reached, to attain vibrational responses for different modes. The results from tests were plotted.

Electronic packaging applications are decided by high dielectric permittivity and thermal conductivity and very low electrical conductivity of the non-hermetic polymeric package composition. Tan δ and the dielectric permittivity

or constant were measured versus frequency using a N4L impedance analyser.

3. Results and Discussion

The Differential Scanning Calorimetry (DSC) curves present the endothermic and exothermic processes. The DSC endothermic peaks near 250^0C correspond to the mass loss observed in Thermal Gravimetric Analysis (TGA) curves . Glass transition causes endothermic shifts in the initial baseline because of the samples' increased heat capacity. Exothermic peaks are observed around 400 to 430 ^{0}C temperature for all the six samples which is related to the thermal decomposition and degradation of the resin. Normally DSC peaks are directly related to enthalpy changes in samples. The Parameters studied with the aid of TGA instrument are, a) CNSL decomposition, b) Peak Temperature (T_{max}) for significant degradation and, c) Residual mass at 850 ^{0}C.These parameters give information on the thermal stability of CNSL resin. The glass transition temperature for the CNSL resins is around 38^0C as evaluated from the DSC plots.

DSC for the samples and the curves of TGA analysis reveal that the CNSL resin decomposition is in three steps. In the first step from 0-300 ^{0}C mass loss up to 5 % was observed in the first 4 samples where as in sample 5 and 6 it is maximum i.e. about 10%. This may be due to the moisture removal retained in CNSL. In the second step gradual weight loss occurs in the temperature range 300-450 ^{0}C which may be due to degradation of the side chain and small fragments like CH_3 and OH radicals. CNSL is thermally stable up to 450^0C. However, in the third and last stage of thermal degradation, a weight loss of around 70% can be observed. This may be due to de-polymerization and degradation of the CNSL matrix. The cured CNSL samples can be safely used up to 250 degree Celsius .

The different combinations of CNSL resin exhibit different physical properties. Samples which are formaldehyde cured, exhibit the highest hardness values in both shore A and D Durometers. The Shore A hardness was about 95 and shore D, about 48. Increasing the percentage of sodium hydroxide catalyst from 5 wt % to 15 wt % causes a decrease in the hardness of the cured CNSL resin down to 85 and 43 in the respective scales. HNO_3 cured samples were foamy, soft and flexible possessing the lowest hardness values in the range of 25 to 30 in shore A scales. Shore D measurements were not possible due to the foamy porous nature of these samples. The H_2SO_4 cured samples exhibited considerable hardness, almost equal to that of the formaldehyde plus alkali cured

samples [7,8]. Depending on the hardness, strength, stiffness or toughness requirements, these resins or sponges may be chosen for composites applications.

The tensile strength of the composite is observed to be lower than that of a glass fabric/ epoxy composite laminate with the same volume fraction of resin. The specimens show moderate interfacial strength between the resin and the fibre. To increase the interfacial strength, different ways of alkali and acid curing could be attempted. The toughness properties are good but slightly lower than that of glass/epoxy or metal modified glass /epoxy composites whose fracture toughness and the strain energy release rate values lie in the region of 20 -40 MPa $\sqrt{m}$ and 2-8 KJ/m^2, respectively . A higher volume fraction of glass fabric is also expected to ensure higher fracture toughness values [14]. Efforts are on to improve the mechanical properties of CNSL composites through chemistry and fabrication techniques.

Our earlier work gives a detailed discussion of the dynamic testing of glass fabric/ CNSL matrix composites using an impulse hammer technique. Vibrational properties like natural frequencies, Q factors and damping percentages of the glass fabric/ CNSL matrix composite were recorded and analyzed for the first time and reported. The CNSL resin is found to be a good damping material. The composite's dynamic characteristics were compared with those of glass/ epoxy and carbon/epoxy specimens. From the vibration response plots the vibration properties are given below. The 1st natural frequency for the CNSL Glass fabric/ epoxy composite was around 10 Hz, the corresponding Q factor was very low at about 1.6 and damping at about 28 %. The facts establish a better damping than glass /epoxy specimens. Thus, the CNSL composites exhibit a higher damping under vibrations than other synthetic epoxy based composites [15-18]. The CNSL resin can also be used as an effective electronic IC or system packaging material. The existing epoxy-phenolic composites are costlier, toxic and derived from synthetic resources. Hence, they are environmentally toxic and difficult to dispose. A novel nano-composite was derived from an environment friendly cashew nut shell liquid by curing it with thermally conducting and electrically insulating fillers and formaldehyde. It is also relatively cheaper. Heat generated during operation was dissipated off effectively. The application's functional areas include good thermal conductivity at a low electrical conductivity like Use in electronic packaging materials, encapsulants and sealants for electronic devices and components that require high heat dissipation of the heat generated and a low electrical conductivity with a high dielectric breakdown strength . The nano-composite was made from bio resources making

it eco-friendly. Figure 2 shows a CNSL nano-composite disc cured for dielectric measurements [19].

Figure 2. CNSL Resin matrix disc cured for Dielectric permittivity measurements

One of the foremost applications of these bio plastic and bio resin composites in their recyclability and ease of disposal through conversion of the bio-plastics in to useable fuel by de-polymerization with the aid of a catalyst and condensing the pyrolysed gas in to fuel oil .

Figure 3. Waste bio-plastics to fuel production through de-polymerization

Bio-plastic waste can be pyrolysed and bio plastic petrol, diesel kerosene and wax can be derived from de-polymerisation through a catalyst chamber using Ammonium Sulphate as the catalyst. The condensed vapours can be collected based on their boiling points as shown in Figure 3 which describes the apparatus that was designed and developed by us to achieve these goals successfully [20].

The cashew nut shell liquid based extracts have also been successfully synthesized into medicinal drugs for treating fever, inflammation and analgesic symptoms as the phenolic Cardol derivatives from the CNSL liquid are known to possess pharmaceutical qualities. Their potential in treating and curing corona virus related infection can be explored.

4. Conclusions

In this investigation, we found that the CNSL resin can be cured with formaldehyde and acid curing. From the results of DSC and TGA, it is observed that the CNSL resins show good thermal stability up to 450^0C. The glass transition temperature for the CNSL resins is around 38^0C. The alkali catalyzed resins were found to be harder than the acid catalyzed resins. Thus, the thermal and physical properties were studied and reported. The tensile properties, fracture toughness in mode 1 and its strain energy release rate were evaluated for a CNSL/ glass fabric composite and reported. They were found to be comparable but lower than glass/ epoxy composites. The vibration properties such as natural frequencies, Q factors and damping percentages of a CNSL based glass fabric composite show only up to 3 modes. The CNSL composite is a high damping material wherein the natural frequencies are low and the Q factor is lower than that of glass/epoxy for the same volume fractions. The damping percentage is also higher. The electronic applications of these bio synthesized materials and their nano-composites in packaging is proven due to the possibilities of high thermal conductivities, low electrical conductivity, very high dielectric constants and low costs. A method for safe disposal of these plastics and their composites after use with significant returns in the production of useable fuel through reverse polymerization and recyclability has been demonstrated with success.

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ARTICLE

Investigation of the Mechanical Properties of Flexible Polyether Foam Filled with Eggshell and Groundnut Husk Powder

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ARTICLE INFO	ABSTRACT

The study investigated the effect of eggshell and groundnut husk as fillers on flexible polyether foam. The fillers with the particle sizes of 50μm each were mixed in the ratio of 50:50. Diverse percentages of the two combined fillers ranging from 10%, 20%, 30%, 40% and 50% were incorporated into the polyether recipes in the appropriate foam formulations and foam samples were produced. The unfilled foam (0%filler) served as the standard control sample. The physico-mechanical test carried out on the foam showed increase in the properties such as density, compression set test, indentation hardness test, tensile strength test and decrease for elongation at break test as compared to the unfilled foam. The scanning electron microscopy result showed the cell sizes became smaller and concentrated with an irregular shape as the filler load increased, thereby making it denser and thicker. Eggshell and groundnut husk fillers may be used in the making of flexible polyether foam since these materials are organic in natures. They can improve the mechanical properties and biodegradability of polyurethane product. The utilization of these fillers in polymer composites productin will help in sanitizing the environment by reducing landfills and producing eco-friendly waste and also it influences cost positively.

1. Introduction

Polyurethanes are polymers that consist of units joined by urethane links [1]. Flexible polyurethane (PU) foams are main products from urethane materials. They are obtained by polymerizing multifunctional isocyanates and polyol. Flexible polyurethane foams can be in the applications of the following; as cushion materials for automotive seat, mattress, refrigerators, insulations furniture, and in packaging [2]. Flexible polyurethane material has become such an extensively used material because of its exceptional light weight, vigor to weight ratio performance and principally, is the amount of comfort, safety and value not matched by other sole materials [3]. This usefulness prompts the increase in the prices of polyurethane products consistently over the years which in turn necessitated the incorporation of variety of fillers into foam samples.

Also, the costs of flexible polyurethane foams are

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becoming progressively high due to the elevated price of raw materials [4]. Flexible polyether foams are classified as low density, medium density and high density [5]. The worth of foam depends mostly on its density. Consequently, for the high price of raw material, it is important to source for cheaper, easily accessible and eco-friendly material that can be used as filler. Fillers are used in plastic and rubber industries as finely divided solid materials which are incorporated into the liquid, semi-liquid or solid composition to transform the physical properties of the composition and to lessen cost. Primarily, fillers are used to lower end products, thus, they are called extenders. Along with over twenty most key fillers, calcite ($CaCO_3$) holds the largest market volume and is chiefly used in plastic sectors. Other fillers include dolomite ($CaMg (CO_3)_2$), kaolin and talc [6].

In recent times, there is growing efforts to expand novel classes of bio-inspired composite materials. The major benefit of these types of materials is that they are environmentally friendly and do not add to the depletion of energy resources because they are derivatives of renewable resources [7].

However, earlier studies have shown that chicken eggshell (ES) is an agricultural by-product that has been listed globally as one of the most awful environmental problems. This eggshell contains about 95 % calcium carbonate in the form of calcite and 5 % organic materials such as type X collagen, sulphated polysaccharides, and other proteins, which makes it a rich source $CaCO_3$ as well as being environment friendly, biodegradable, available and low dense. This uniqueness succeeds eggshell as a superior entrant for bulk quantity, economical, lightweight and low load-bearing composite uses, such as the automotive industry, trucks, homes, offices, and factories. Even though, there have been numerous attempts to exploit eggshell components for diverse applications, its chemical composition and accessibility makes eggshell a prospective resource of filler in polymer composites [8].

Thus the aim of this study is to harness the potentials of these mixed organic waste materials as fillers incorporated into flexible polyether foam.

2. Experimental

2.1 Materials and Chemicals

The foam chemicals; toluene diisocyanate, TDI, polyol, silicon oil, stannous octate and amine used for the production of the foam samples were obtained from Vita Foam Nig. Plc. Ikeja, Lagos State, Nigeria; while the fillers; egg shells and groundnut husks were sourced from Chrunches and Eke- Awka market respectively all in Awka, Anambra State, Nigeria.

2.2 Preparation of the Fillers

The egg shells were washed carefully and sun desiccated. They were then pulverized into fine powder, using an electric grinding appliance. Further sieving was done to obtain a fine smooth powder with a mesh of 50µm and then stored in polyethylene bag.

The groundnut husks were hand-picked, washed, sun dried and milled into fine powder using an electric grinding appliance. Further sieving was done to obtain a fine smooth powder with a mesh of 50µm and then stored in polyethylene bag. The egg shells and groundnut husks powders were mixed homogeneously in the ratio of 50:50 and stored in a polyethylene bag.

2.3 Preparation of Flexible Polyether Foam

The polyol, toluene diisocyanate and fillers with particle size of 50µm were precisely weighed into different beakers using triple beam weighing balance. The supplementary raw materials required in minute quantities were measured using syringes. Polyol and the mixed fillers were poured in a plastic container, and the blend was stimulated very well until total homogenization was achieved. About 500g of polyol was poured into an empty clean jug while 50g of the mixed fillers (groundnut husk and eggshell mixture) was added to the polyol and stirred vigorously. 28g of distilled water and 2g of amine was added while mixing. 5g of the silicon oil and 1g of stannous octate was also added to the jug while stirring. Lastly (325g) of TDI was poured into the jug and the mixture was stirred until it was fully homogenised. The whole mixture was then smartly poured into a prepared metal mould. This procedure was repeated 2, 3, 4 and 5. Sample zero (X_0) has no addition of fillers (eggshell and groundnut husk). The measurements of these recipes were based on parts per hundreds of polyol [9].

A stopwatch was used to monitor the rise time of each foam sample, and foam sample was allowed to cure for 24 hours. Then, the cured foam blocks were cut to standard sample sizes for analysis. Thereafter, the foam samples produced were subjected to mechanical properties test.

Table 1 shows the foam formulation with its recipes and appropriate quantities.

Table 1. Foam formulation

Raw materials	Pph	X_o (g)	X_1 (g)	X_2 (g)	X_3 (g)	X_4 (g)	X_5 (g)
Polyol	100	500	500	500	500	500	500
TDI	58.99	325	325	325	325	325	325
Water	4.36	28	28	28	28	28	28
Amine	0.422	2	2	2	2	2	2
Silicon oil	0.822	5	5	5	5	5	5
Tin	0.139	1	1	1	1	1	1
Filler load		00	50	100	150	200	250

Note: Pph = Part per hundred; X=sample; g=grams; X_0 = 0% filler; X_1 = 10%; X_2 = 20%; X_3 = 30%; X_4 = 40% and X_5 = 50%

3. Results and Discussion

The results of the physico-mechanical properties of the produced foam samples were discussed. The unit mesh size of filler has a dominating impact on all the properties.

3.1 Creaming Time

This is the first incident measured and occurs usually a short time after incorporation when the mixed liquid turned cloudy in appearance and liquid starts to rise from its initial stable stage. The cream time was observed to be higher than that of the unfilled foam. As soon as the generation of carbon (iv) oxide starts, the creaming time is dependent upon the quantity of amine used. High amount of amine starts the cream time.

3.2 Rising Time

This occurs when the reacted foam has reached its biggest level or utmost height. At this stage, the foam increase has taken place such as cell structures are foamed, gas reaction accompanied by generation of carbon (iv) oxide takes place and exploration of auxiliary blowing agent is present in formulation.

3.3 Curing Time

This also occurs when the foam is completely risen, the foam is firstly soft gelatinous mass and the phase between the accomplishment of full rise and whole solidification of the produced foam is the curing time. This is basically the moment main cross linking occurs. The results of creaming, rising and curing times recorded during the production of flexible polyether foam are as shown below.
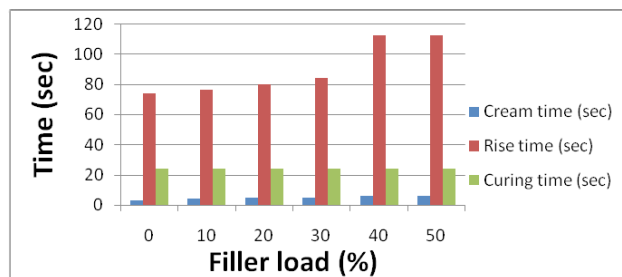

Figure 1. The effects of the mixed fillers on creaming time, rising time and curing time of filled flexible polyether foam

The filler was observed to increase the creaming and rising time as shown in Figure 1. This means the filler increased the reaction time, giving room for complete nucleation of the foam recipes.
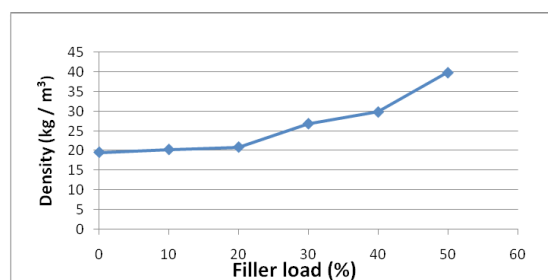
3.4 Density

Figure 2. Result of filler load on density of the produced foam samples

From the result above, it is seen that the density of the polyether foam was improved by the filler load. As the filler load increased, the density also increased from 10%, 20%, 30%, 40% and 50% filler loads as shown above in Figure 2. A formulation of 22kg/m³ density was used to prepare the entire laboratory mixing and it was discovered that the densities increased as the quantity of fillers (egg shell and groundnut husk) were increased and this could be due to the better mechanical properties exhibited by the fillers. Hence, the increase in the density can be said to be due to the filler particles filling the voids in the flexible polyether foam structure which tend to compact the materials thereby reducing the foam porosity and make it denser. As the filler content increased, the hardness f the foam samples also increased. It would not simply collapse or descend after weight is positioned on it. In other words, the produced foam samples will be durable and not sink nor collapse when sat upon. Hence, additives and fillers are used to increase foam density and it is the ability of the foam to provide support. This is in accordance with other related researches [10-12].
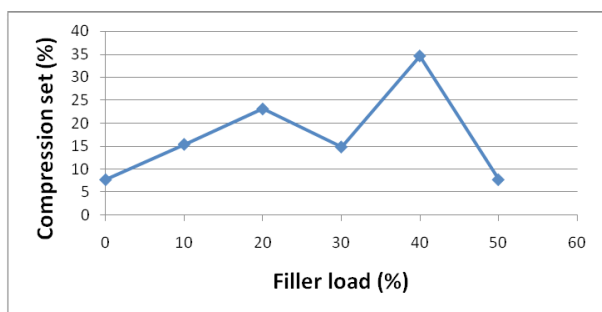
3.5 Compression

Figure 3. Result of filler load on the compression set of the produced foam samples

The compression set result as shown in Figure 3 was seen to increase as the filler load increased. This implies that the foam sample would easily regain its original height after a bulky mass is lifted from the foam. This is one of the qualities of superior and resilient foams. This could be accredited to the enhanced mechanical properties exhibited by the fillers.

The filler increased the compression set test by almost 100% except at 50% filler load which had the same value with the unfilled foam. This enhanced compression set could be due to the reinforcing nature of the mixed filler, thereby improving the mechanical property of the foam sample. So the optimum filler load for the compression set is at 40% and adding more filler could affect the property of the foam. This is in agreement with the results obtained by some other authors [4,13,14].

3.6 Tensile Strength

This is one of the most important mechanical tests for any polymeric material. It shows the stress-strain curve in tension.
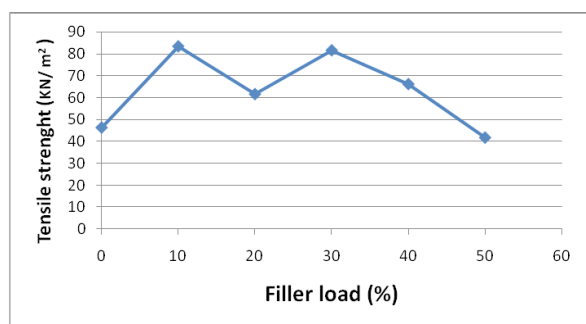

Figure 4. Result of filler load on the tensile strength of the produced foam samples

It is seen from Figure 4, that the result of the tensile strength of the produced foam samples improved as the filler load increased but a sharp decrease was observed at 50% filler content with the value 41.8 %.. This increment could

be attributed to cellulosic nature of the groundnut husk and reinforcing nature of the eggshell. These combined together improved the tensile strength of the foam samples. The foam samples tend to be strong. This is in accordance with the result of some order related works [14,15].
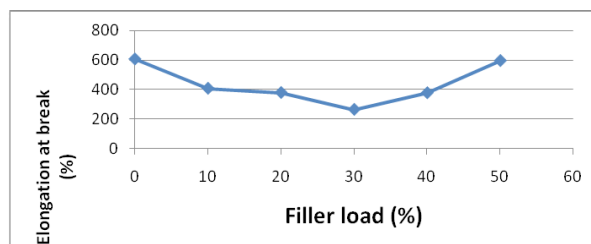
3.7 %Elongation at Break

Figure 5. Result of filler load on the %elongation at break of the produced foam samples

The result of the filler on the %elongation at break of the flexible polyether foam is as shown in Figure 5. It is experimental that elongation slightly decreased as the filler load increased. This decrease was lower than that of the unfilled foam (0% filler load) with the highest value (609.0%). 50% filler load experienced a greater value for elongation at break (598.2%) than other samples with value of 409.0%, 380.6%, 265.3% and 378.7%. This could be as a consequence of its greater tendency to extend with a smaller filler ratio than a higher ratio. That shows the flexibility of the produced foam samples, that is its ability to return to its original shape after bending or folding, which is part of a good quality of foam. This is in agreement with the results of some other researchers in the past [14,16].
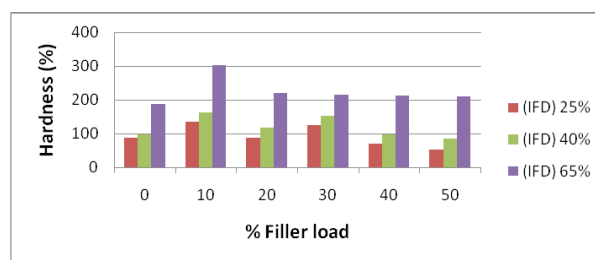
3.8 Hardness

Figure 6. Result of filler load on the hardness (IFD) of the produced foam samples

The stability of polyurethane foam is considered as a physical property called indentation force deflection (IFD). The boost in the filler load was observed to have a positive effect on the produced foam samples by its increase on the hardness properties of the foam samples as shown in Figure 6. This implies that the filler will have a hard result on the

foam and will bear a lot of heaviness over an extended period of time without failing immediately. The crystalline nature of the egg shell and cellulosic nature of the groundnut husk have been proved to be very tough and resilient. The hardness of foam is seen by its ability to withstand heavy weights without collapsing. And this was exhibited by these fillers, so the produced foam samples could carry heavy loads. This result is in agreement with other related works [13,14].
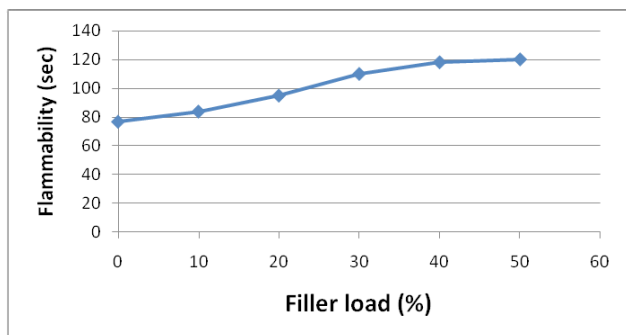
3.9 Flammability

Figure 7. Result of filler load on the flammability property of the filled polyether foam

From Figure 7, the flame duration time are 77sec, 84sec, 95sec, 110sec, 118sec and 120sec for 0%, 10%, 20%, 30%, 40% and 50% filler loads respectively. This simply shows that the filler increased the flame duration of the foam sample. This may be due to the interaction between the fillers and foam matrix phase which fills up the pores in the foam making it harder for the flame to go off if it ignites. This could also be attributed to the fact that one of the filler (groundnut husk) is flammable and that the filled foam constitutes more residues after ignition. So, it is advised that local materials that can reduce the flammability or act as flame retardant should be incorporated into the foam in order to reduce its flammability.

4. Results of the Surface Morphology of the Filled Polyether Foam via the Scanning Electron Microscope
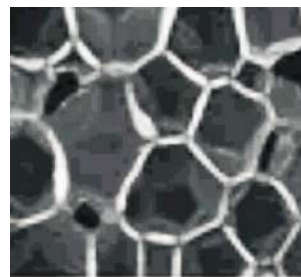

Figure 8a. 0% Filler

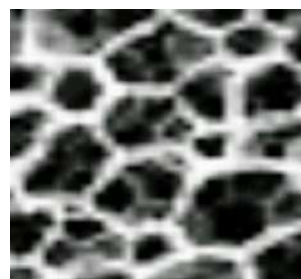**Figure 8b.** 10% Filler

Figure 8c. 20% Filler
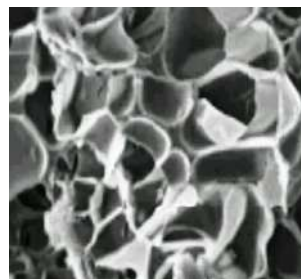

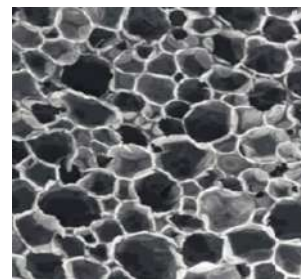**Figure 8d.** 30% Filler

Figure 8e. 40% Filler

Figure 8f. 50% Filler

Figure 8. Effects of the filler load on the surface morphology (SEM micrographs) of the filled polyether foam

The result obtained from the SEM analysis of the flex-

ible polyether foam produced showed that the control experiment (0% filler load) displayed a cell morphology that basically appeared to be hexagonal or heptagonal in shape, with thicker strut on the walls. The produced foam has many pores/voids which makes it flexible polyether foam.

The increased mechanical properties exhibited by the foam sample can be explained by the surface morphology result. It could be seen that as the filler loads increased, the sizes of the pores were reducing as shown in the micrographs Figures 8b-f. As the filler was observed to compact and distort the cell walls of the polyurethane foam, thereby making the foam denser, thicker and harder. Hence, the SEM results could be used to deduce the improved mechanical properties of the filled flexible polyether foams.

5. Conclusions

This study has shown that the incorporation of mixed organic fillers (eggshell and groundnut shell) in foam formulation has impacted good qualities on the produced flexible polyether foam samples. This was due to the strengthening nature of the fillers and small mesh size of the mixed fillers; that created a good surface area for the filler-polymer matrix interaction thereby enhancing the foam's mechanical properties. The increase in quantity of fillers resulted in the progressive increase in density, hardness indentation and compression thus affecting cost positively. The use of organic fillers will have a positive impact on the environment. It brings to rest the challenges of waste disposal by polyurethane foam manufacturing company due to its biodegradable property. The optimum mechanical property was achieved at 40% filler load.

Hence, foams produced with these fillers are strong, dense, flexible and can return to its original size and shape after being bent or folded. Foam manufacturers are encouraged to harness these organic waste materials in their production of foams due to their availability, cost effectiveness, processability, economic and environmental impacts; as they can replace conventional materials like calcium trioxocarbonate (iv) in foam production.

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