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Ultrasonic assisted synthesis of activated carbon for electromagnetic shielding material from rice husk fibre

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Synthesis of any biomaterials/biocomposites for different applications like in electromagnetic wave communication, radar, satellite system needs the processing of its raw material. The suitability of raw material is a challenging task for fabrication technology depending on its type of work performed and efficiency. The surface modification/surface bleaching is performed to facilitate the fillers and matrix for good interlocking between them for improvement in mechanical strength. The material used for microwave absorption or energy storage device in low observable technology (LOT) needs good mechanical strength. The present paper encloses the treatment of raw materials like rice husk with suitable blended chemicals maleic acid with different alcohols. The optimized blended chemicals are determined by computation of different acoustic parameters with the propagation of ultrasonic wave in low frequency range. The rice husk are treated with the optimized blended solution which results in increase of porosity of the material and hence for the fabrication of composites. The element dispersion study images of untreated and treated rice husk signify the suitability of the material for synthesis of microwave absorbing materials.

Keywords: Blended chemicals, Ultrasonic wave, Rice husk, Acoustic parameter, Microwave absorption

1 Introduction

Synthesis of materials possessing microwave properties has significant importance in recent days[1-3]. These microwave absorbing composites have wide applications such as improving antenna parameters, for reduction of radar cross sections, shielding from electromagnetic induction and compatibility of electromagnetic wave etc. for which a new technology developed called stealth technology and it involves design of special kinds of materials to be used as microwave absorbers in order to minimize the visibility of the target[4,5]. An ideal microwave absorbing material should possess strong absorption capability, wide bandwidth, light weight, mechanically strong, good thermal and oxidation stability[6]. Supporting to development of such material it is much more important for synthesis of microwave responding material from different carbonious material like waste of different agricultural products is now centre of attraction for material researcher. The compositional constituents of such agricultural waste are basically cellulose, hemicelluloses and lignin etc. The multicellular parts like cellulose, hemicelluloses which are basically enriched in carbon vary from 50-70 %. In the universe carbon is the fourth abdunt element and possesses the characteristics like inherent charge transport and achievable dimension with other compatible elements. Thus to utilize such carbon rich waste product is now a challenging issues, which are the potential alternative material for ceramic material[7,8]. Thus for activating such carbon component in those natural or agro waste, it is much necessary that the surface modification of such raw materials has significant effect. For optimization of fibre-matrix interfacial interaction in synthesis of composite material it is necessary to modify the surface of the raw materials by physical or chemical method. The modification has significant contribution for adhesion between the fibre and matrix. The hydrophilic nature of cellulose is inherently incompatible with hydrophobic polymer matrix which makes it necessary to introduce a coupling agent which can acts as bridge between fibre and matrix. As a result of which there is a good interfacial adhesion between fibre and matrix resulting better mechanical properties to composite material[9]. The present work provides a numerous discussion on surface treatment of rice husk in presence of maleic acid with different alcohols

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from which a optimized blend of maleic acid can be suggested for fabrication of composite material. Thus to optimize the use of chemicals for surface modification and to understand the basic mechanism of chemicals with cellulosic materials it is quite interesting to make a systematic study on chemicals by ultrasonic method. Being ultrasonic wave, high frequency can interact at molecular and sub molecular region and correctly estimate the optimized amount of chemicals for the surface modification of bio materials and natural fibres. As an efficient bleaching agent maleic acid with different alcohol can activate the functional group of the cellulose making hydrophobic nature of the fibre. The interactions of maleic acid with the cellulosic are discussed in terms of molecular interaction and then suitable blend are applied to rice husk in the present work. Rice husk consists of a large amount of carbon in the composition of the natural polymer-cellulose and lignin[10]. Besides carbon, these polymers contain sufficient amounts of hydrogen and oxygen which contribute to receiving activated carbon with the developed porous structure. This surface modified rice husk being rich in carbon, the biomaterial can be synthesized for different applications like microwave absorption and energy storage devices.

2 Materials and Methodology

In the present investigation all the liquids are of anal grade, manufactured by E-Merck Ltd (India), are redistilled and purified by the standard method under atmospheric pressure. The powder form of maleic acid have taken 0.01 gm of its molecular weight and dissolved in 20 ml water in a 100 ml conical flask. To make it more dissolve, the rest volume of the container filled with water. Binary mixtures of maleic acid with alcohol like metahanol, ethanol, propanol and butanol are prepared by mixing appropriate volume of the liquid components in the standard flasks with airtight caps and the mass measurements are performed on high precision balance with accuracy of +1 mg.The uncertainty in mole fraction is +0.001. Using the above pure and blended stock solutions of different blend solutions (0.1, 0.2, 0.3, 0.4 0.5, 0.6, 0.7, 0.8 and 0.9 (w/v) concentrations) were prepared. The ultrasonic velocities are measured in synthesized solutions using an ultrasonic interferometer working for different frequencies like 1 MHz-5 MHz. The velocity measurement was calibrated up to ± 0.01 m/s. The densities of pure liquids as well as the mixture were measured with pyknometer within ± 0.0001 kg/m^3. All the mass measurements were performed by a high precision electronic balance within (±0.001 gm). During ultrasonic measurement the temperature of the sample contained within the cell was maintained constant within ±0.01 K by circulating water with the help of a thermostatically regulated temperature water bath through the water jacketed cell. The different acoustic parameters are computed using standard formulas [11].

Isentropic compressibility: $$\beta = \frac{1}{\rho C^2} \quad \ldots (1)$$

Deviated isentropic compressibility:

$$\beta^E = \beta_{mix} - (X_A Y_A + X_B Y_B) \quad \ldots (2)$$

Where, "C" is the ultrasonic velocity, "ρ" is the density of the solutions, X_A, X_B are the mole fractions, Y_A ,Y_B and Y_{mix} represent the isentropic compressibility of maleic acid, alcohols and mixture, respectively. For synthesis of microwave shielding material from biomaterial, the residues of rice husk were collected after milling process from rice mill and allow to dry 3-4 days in sunlight. The dried parts of rice husk are kept in a beaker containing blended mixtures and allowed to place in the sonicator for 15-20 min. After through ringed with distilled water the rice husks are dried at 50 °C for 12 h. This helps to eliminate the lignin and hemicelluloses residues which results in cellulose degradation. For production of activated carbon firstly, the treated rice husks were grounded and sieved to fractions with average particle size of 150 μm. Secondly, the prepared husks were carbonized at 400 °C under nitrogen flow (300 mL min^{-1}) for 90 min. The resulting samples were impregnated with maleic acid blended ethanol and dried at 120 °C for 12 h. Finally, the activated product was grounded, neutralized by 0.1 M HCl solution and washed several times with hot distilled water to a constant pH (6.6–7.0). The washed activated carbon samples were dried under vacuum at 120 °C for 24 h and stored in desiccators.

3 Results and Discussion

3.1 Analysis of blended chemicals for surface modification

From the profiles it was observed that the ultrasonic velocity decreases with decrease of alcohol concentration up to 0.4 mole fraction of maleic acid blended solution and then again increases to a maximum value as compared to the ultrasonic velocity in pure alcohol region. With increase of

carbon chain the ultrasonic velocity also increases as evident from the Fig. 1. The non linear change in velocity with the mole fraction of maleic acid concentration is an indication of the existence of interaction between the components of the blended solution[12,13]. In the lower mole fraction of alcohol the number of dipolar molecules is high and so the expected interactions would be of much strength. The atoms of alcohols are having a characteristic carbonation. The stability of the charged system is increased by the dispersal of the charge.

Therefore, any factor that tends to spread out the positive charge of the electron-deficient carbon and distribute it over the rest of the ion must stabilize the carbonation. Thus, these carbonations will be stabilized by electron donating substituent and will be rendered less stable by electron withdrawing substituent. The alkyl group attached to the carbon atom bearing positive charge exerts an electron releasing inductive effect and thus reduces the positive charge of the carbon atom to which it is attached. In doing so the alkyl group itself becomes positive. Hence, weak interactions such as dispersive type or temporary dipoles may be expected between the molecules. In maleic acid rich regions the velocity increases due to high density value as the molecules are closely bound with each other. Again, with increase of frequency, the molecules may vibrate with high energy but due to weak dispersive force there is no more increase of ultrasonic velocity. The excess compressibility increases negatively with a clear minimum at 0.4 mole fraction of maleic acid blended alcohols as shown in Fig. 2.

The negative value of β^E suggests that the blended solution is more compressible due to strong inter-molecular interactions. This strong interaction may be due to contraction in volume of the interacting molecules of the blended solution. Contraction of volume due to dipole-induced dipole and dipole-dipole interaction leads to negative deviation in compressibility. The negative excess values have been due to the closely packed molecules which account for existence of strong molecular interaction. The sign of adiabatic compressibility (β^E) plays a vital role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole-dipole interactions and dipole-induced dipole interactions interstitial accommodation and orientation ordering leading to more compact structure making, which enhances excess adiabatic compressibility (β^E)

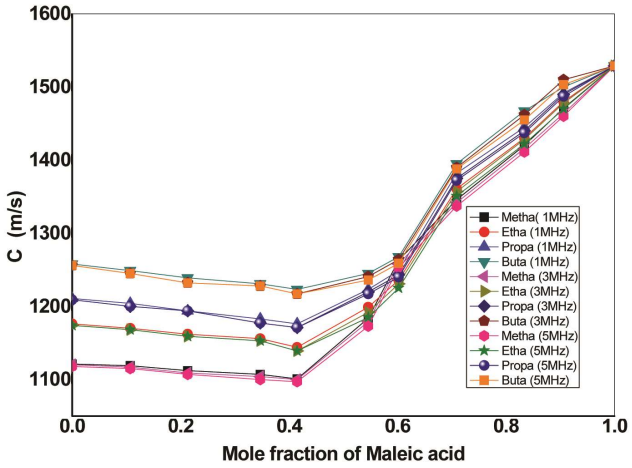

Fig. 1 – Variation of ultrasonic velocity.

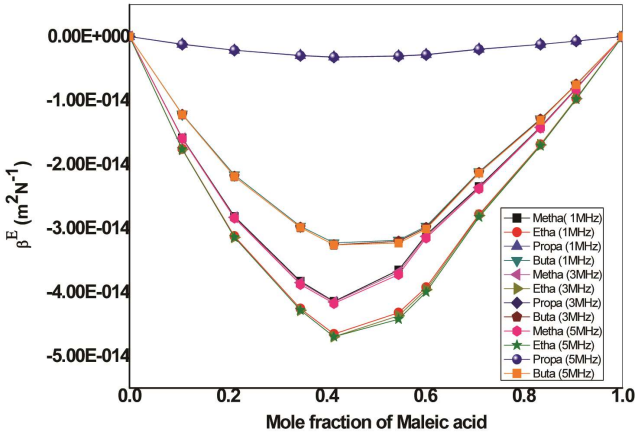

Fig. 2 – Variation of deviated compressibility.

to have negative values[14,15]. With increases of chain length the molecules of alcohols, inter-molecular free length increases leading to negative deviation in compressibility. The observed values of β^E imply that specific interactions dominate over the dispersive between the unlike molecules. The negative excess value of inter-molecular free length substantiates the above argument undoubtly and undeniably unveils the fact that the specific interactions are being operative between the molecules of blended solutions. When the blended chemicals are added proportionally to the weight of the rice husk and subjected to sonication for 15-20 min for well dispersion of chemicals in to surface of the rice husk then there is breakage of some H-bonding between the cellulose molecules internally as well as formation of new H-bonding takes place with intra cellulose molecules as shown in Fig. 3 making the surface of rice husk becomes rough due to hydrophobic nature[16,17].

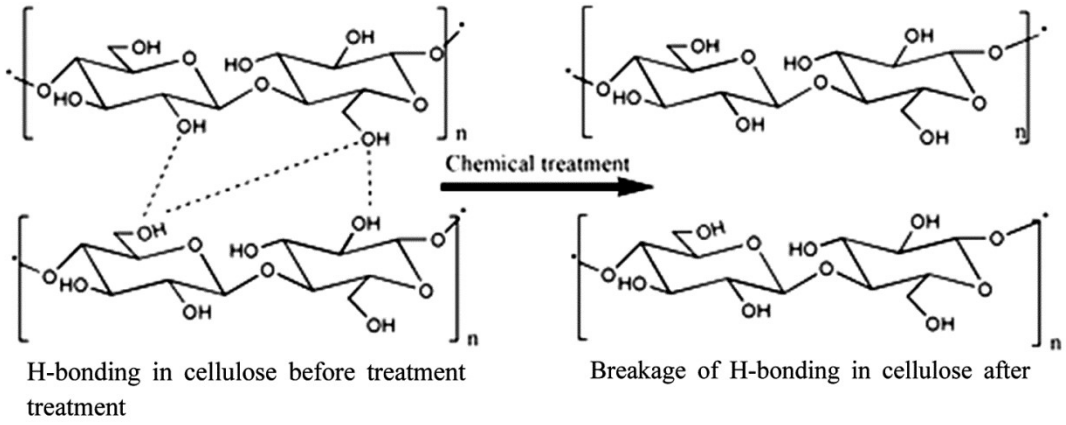

Fig. 3 – Mechanisms of rice husk structural changes during chemical treatment.

3.2 Effect of ultrasonication on rice husk bio waste

The effect of ultrasonic treatment of blended chemicals on rice husk can be well studied by morphology analysis and energy dispersive study (EDS) of rice husk. Surface morphology and energy dispersive study of untreated and treated rice husk are studied with HITACHI SU 3500 scanning electron microscope coupled with EDX spectrum analyzer from which the suitability of the rice husk can be studied for synthesis of biomaterial for fabrication of electromagnetic shielding material. Figure 4 shows the SEM of untreated rice husk having a smooth surface, which confirms the presence of wax and oil and some surface impurities. The removal of foreign material and other impurities makes the surface of rice husk become rough by detachment of moisture and the functional group are become more active as shown in Fig. 5. As a result the carbon and oxygen component of the cellulose, hemicelluloses are bonded with other atoms by formation of new H-bond as described in Fig. 3. This makes the rice husk surfaces becomes more porous which facilitates the absorption of any type high energy wave incident on it. As carbon is responsible for absorption and oxygen is responsible for making the material becomes lighter, the composite to be fabricated from it will be very light weight and high absorbing capacity. Maleic acid blended alcohol treatment reduces the lignin and hemicelluloses content in natural fibers, increases the surface area, allowing dissemination of water molecules to the inner layers, and breaks the bonds between lignin-carbohydrate and hemicelluloses[18]. In morphology properties, it can be seen that the effect of filler loading with the addition maleic acid blended alcohol in the treated sample. This is outstanding to the fact that maleic acid blended alcohol treatment

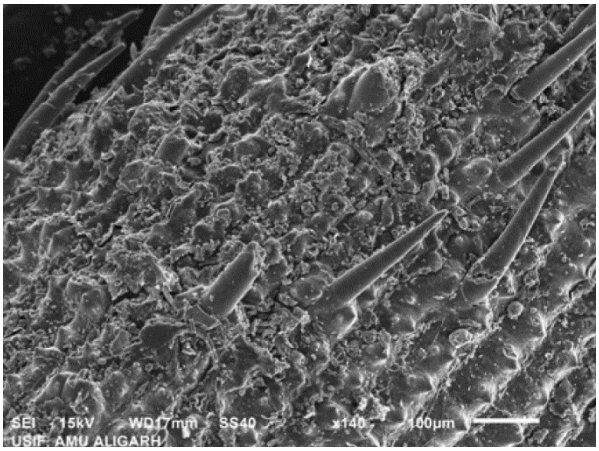

Fig. 4 – SEM of raw rice husk.

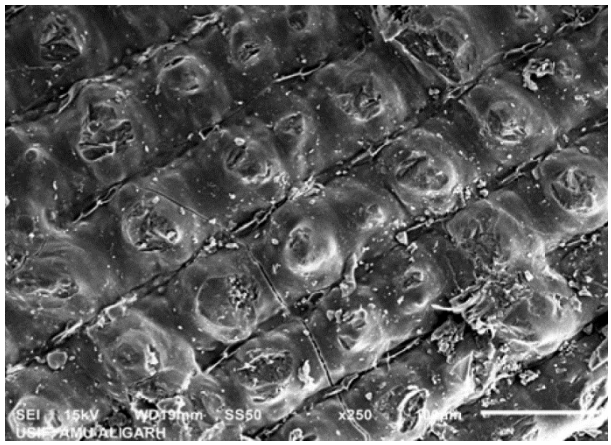

Fig. 5 – SEM of raw rice husk with blended chemicals.

improves the fiber surface bond uniqueness by removing hemicelluloses and producing rough surface. This topography offers better fiber matrix interface bond and an increase in mechanical properties[19,20].

The effect of the subsequent bleaching treatment with sonicator of frequency 125 kHz was evident from the comparison of SEM pictures in Fig. 5 and 6. From both the picture it is clearly observable that how high frequency ultrasonic wave is effective in modifying the surface with the ultrasonicated blended chemicals. Being, a high frequency wave it can well interact in to the atomic and subatomic region of cellulose of the rice husk fibre and able to eliminate the foreign particles and helps in breaking and formation of H-bond between the cellulose molecules. As a result the surface of rice husk fibre become rougher and enhances the formation of pore making the rice husk fibre become hydrophobic as shown in Fig. 6. It is observed that the rice husk fiber bundles were separated into individual fibres with decrease of thickness. The decreased thickness showed that after the potential chemical treatment all components bound to fibril structure were removed and thus individual fibres were separated. Figure 7 shows the scanning electron microscope (SEM) sample analysis of pure rice husk.

The size and morphological structure of fibres might be changed because of lignin and hemicelluloses removal from the rice husk as shown in Fig. 7. From the SEM picture it is oblivious that cellulosic materials are free from impurities and lingo cellulosic part of the raw rice husk. The EDS characterization of untreated rice husk fibre shows the presence of carbon, oxygen and silicon in different percentage as shown in Fig. 8 and the sonicated treated rice husk shows the presence of carbon and oxygen component in the resulting treated rice husk in Fig. 9 which confirms the importance of rice husk in fabricating carbonized material.

Scanning electron micrographs of activated carbon samples were shown in Fig. 10. It can be seen from the pictures that all the activated carbon samples exist in the form of spherical shaped particles which are aggregated together to form pieces with different sizes. All the activated carbon samples have porous structure with cracks and crevices[21,22]. This activated

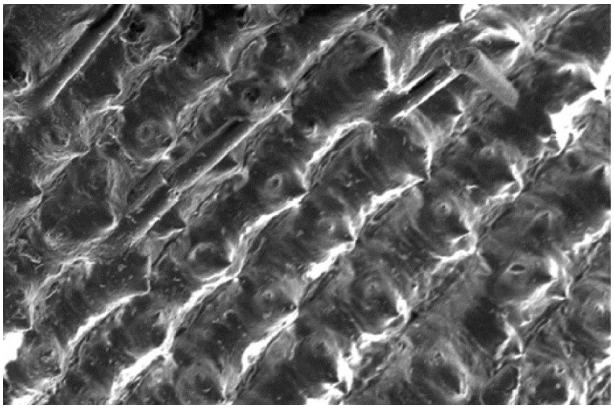

Fig. 6 – SEM of raw rice husk with ultrasonicated chemicals.

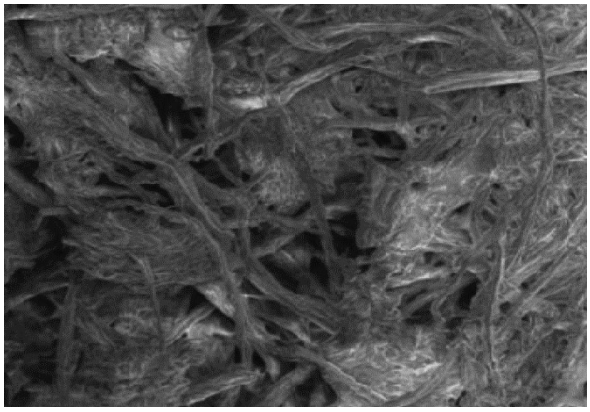

Fig. 7 – SEM of cellulose in treated blended rice husk.

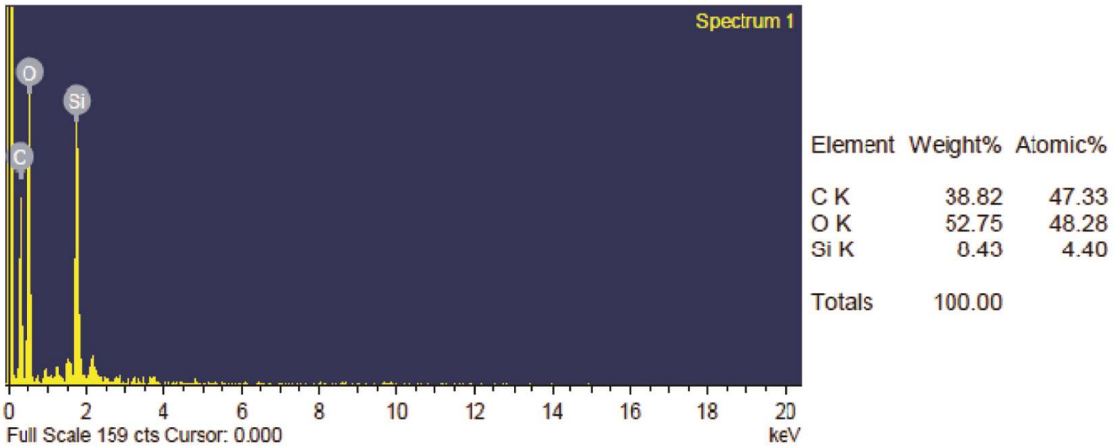

Fig. 8 – EDS of untreated rice husk.

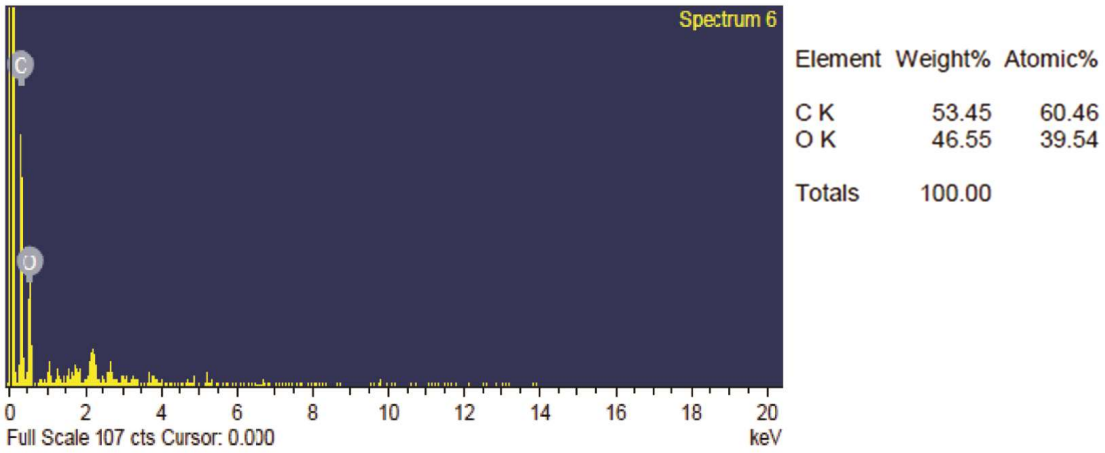

Fig. 9 – EDS of treated rice husk.

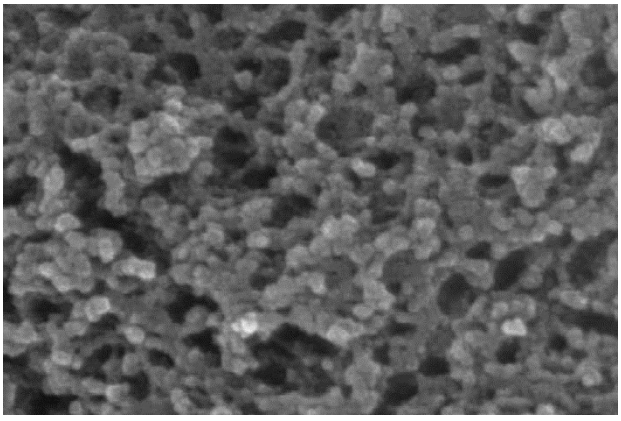

Fig. 10 – SEM pictures of activated carbon samples.

carbon samples are basic foundation material for fabrication of electromagnetic shielding material mixed with the proper matrix.

4 Conclusions

The ultrasonic velocity data and computational acoustic parameters clearly signify the behaviour of treated medium with the cellulosic part of rice husk. The non linear variation of ultrasonic velocity and compressibility indicates the significant intermolecular interactions such as dipole-dipole and ion-solvent interactions. The formations of H-bond complex formation due to these interactions are basic factors for the existence of hetero-molecular interaction in treated system in presence of ultrasonic wave. Thus ultrasonic wave can be considered as a sufficient tool for surface bleaching and modification of natural fibres for fabrication of composite material. Ultrasonication of bio waste with suitable modifier provides necessary morphological changes on the fibre which enhances the better interlocking in reinforcement and matrix of the composite. Thus, the ultrasonic treatment can be suggested for better modification of surface of bio waste or natural fibres by chemicals of optimum blend as excessive use can destroy the organic component of fibres. This method may find its application in synthesis of bio composites, designing of different hybrid composite which has large practical application as dielectric material for synthesis of microwave absorbing composite.

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