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Notes

Study of effect of ultrasonication on benzoylation of cellulose in synthesis of activated carbon for microwave absorbing material

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The efficiency of all microwave absorbing materials (MAM) /radar absorbing material (RAM) purely depends on their composition, particularly carbon and oxygen. Most of the biowaste being rich in cellulose contains carbon as the main component. The treatment of different biowaste like residues of agricultural products is a vital step before fabrication of biomaterial for different application. The present work describes the ultrasonic analysis of treatment of benzoyl chloride with aqueous cellulose. The variation of ultrasonic velocity and other acoustic parameters like compressibility and intermolecular free length with increasing concentration of benzoyl chloride suggests possible intermolecular interactions. The presences of such interactions have been well explained in terms of morphological changes in waste biomaterials like sugarcane bagasse. The presence of many reaction sites on the treated sugarcane bagasse increases its suitability for the synthesis of biomaterials. The SEM of treated sugarcane bagasse presents significant explanation for the absorption of incident microwave radiation on the prepared biomaterial.

Keywords: Biowaste, Sugarcane bagasse, Ultrasonic, Intermolecular interactions, Acoustic parameters, Microwave absorption

Natural fiber/bio wastes are the major component as reinforcement for any advance functional material like biocomposites. The composition of biowaste such as hemicellulose, cellulose, and lignin generally cover 20–40, 40–60 and 10–25 wt% for lignocellulose biomass respectively[1]. The elementary constituents such as carbon, oxygen and other inorganic material are the actual deciding factors for fabrication of biocomposites. The high percentage of carbon (44.44%) and oxygen (49.39%) in cellulose makes it possible for preparation of activated carbon after proper treatment and surface bleaching of the biomass .The high porosity structure, surface area and low cost of preparation of activated carbon makes it feasible for the fabrication of energy storage device like capacitors, microwave absorbing materials (MAM), stealth material for stealth technology and many more[2]. The poor moisture resistance and low mechanical properties of biocomposites limit its application to interior and non-supportive structures. In the composite material the interface between matrix and fibre has a significant contribution towards most of the characteristics of composites. The presence of hydrophilic hydroxyl groups at the surface of interface imposes number of problems in the designing of biocomposites. Again the presence of impurities like pectin and waxy substances, makes the functional group become unreactive. Thus, surface modification is an important step in the fabrication of biomaterial to activate the functional group so that the compositional elements like carbon and oxygen of the cellulosic part of the biowaste or natural fiber become more active. There are many methods and different chemicals are used for the surface modification of natural fibers/ biomaterials such as alkali treatment[3], silane treatment[4], peroxide treatment[4], permanganate treatment, isocyanate treatment[5] etc., for activating the functional group as well as to facilitate the fiber materials to become active for interaction with incident electromagnetic energy[6]. Though there are many bleaching agents for surface modification of bio residues but hit and trial methods for use of chemicals decrease the mechanical strength. 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 carry out a systematic study on chemicals by ultrasonic method. For an ultrasonic wave, high frequency can interact at molecular and sub-molecular region and the optimized amount of chemicals for the surface modification of bio materials and natural fibers, can therefore be estimated. The present paper describes the ultrasonic analysis on treatment of benzoyl chloride with aqueous cellulose. As an efficient bleaching agent benzoyl chloride can activate the functional group of the cellulose resulting in the hydrophobic nature of the fiber. The interactions of benzoyl chloride with the aqueous cellulose are discussed in terms of molecular interaction and then suitable modifications carried out on sugarcane

bagasse from which the biomaterial can be synthesized for different applications like microwave absorption and for energy storage devices.

Experimental

The cellulose and benzoyl chloride were used directly without further purification as obtained from NICE chemicals, India. The aqueous cellulose solution was prepared by sonication of powder cellulose followed by magnetic stirring in distilled water. The aqueous solutions with varied concentrations of cellulose are sonicated at frequency of 125 KHz for 15 min so that the solutions are well dispersed. The benzoyl chloride solutions of different weight percentage are added to obtain fixed weight percentage of aqueous cellulose. Similarly, by varying the concentration of aqueous cellulose solution four different samples were prepared. All the samples of different weight percentage are sonicated for better dispersion and kept in airtight glass stoppered containers. The ultrasonic velocities are measured in synthesized solutions using an ultrasonic interferometer working at 2 MHz (Model-M-81S). 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 g). During ultrasonic measurement the temperature of the sample contained within the cell was maintained constant within ±0.01 K by circulating water through a jacketed cell provided with a thermostatically regulated temperature controller. The different acoustic parameters are computed using standard formulas[7].

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

Intermolecular free length: $L_f = k\beta^{1/2}$ … (2)

where 'C' is the ultrasonic velocity, 'ρ' is the density of the solutions and 'k' is temperature dependent constant calculated by using the equation[8] [93.875 + (0.375T)]×10^{-8} with 'T' being the absolute temperature. The residues of sugarcane after the extraction of juice were collected and allowed to dry for 3–4 days in sunlight. The dried parts of sugarcane bagasse are cut in o small pieces with length 2–3 cm and thickness of 0.5 mm. The small pieces of sugarcane bagasse are kept in a beaker containing benzoyl chloride and placed in the sonicator for 15–20 min. After thoroughly washing with distilled water, the bagasse are dried at 50 °C for 12 h. This helps to eliminate the lignin and hemicelluloses residues which result in cellulose degradation[9]. Surface morphology are studied with HITACHI SU 3500 scanning electron microscope for both untreated and treated sugarcane bagasee from which the morphological change on the sugarcane bagasse can be studied for synthesis of biomaterial. The entire synthetic process and experimental methodology for biomaterial synthesis is represented step-wise in supplementary data, Fig. S1.

Results and discussion

The acoustic parameters β and L_f are computed from the measured data of ultrasonic velocity and density of the reaction mixture. The variation of ultrasonic velocity different samples with increasing concentration of benzoyl chloride is non linear as shown in Fig. 1 which clearly indicates the specific interactions like dipole-dipole and dipole induced dipole, between the composition of cellulose and benzoyl chloride in presence of ultrasonic wave.

The high frequency ultrasonic wave has very small wavelength nearly equal to the atomic dimension for which it can influence the atomic and subatomic part of the polymer cellulose. The initial increase of ultrasonic velocity at low concentration of benzoyl chloride indicates that the amount of aqueous cellulose and benzoyl chloride are well dispersed. But the decrease of ultrasonic velocity with increase of benzoyl chloride indicates that interaction of oxygen of cellulose and the chloride part of benzoyl chloride

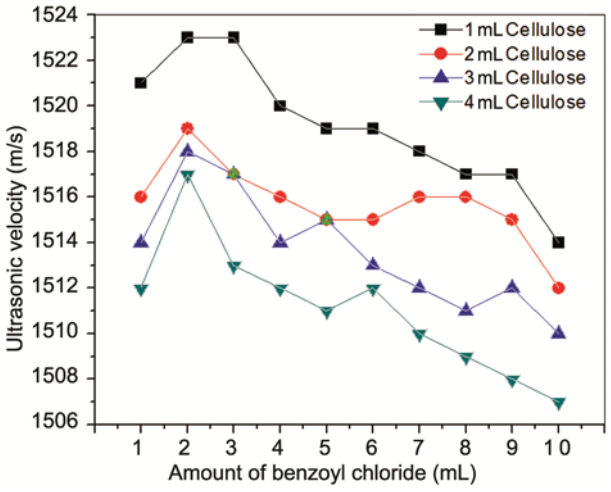
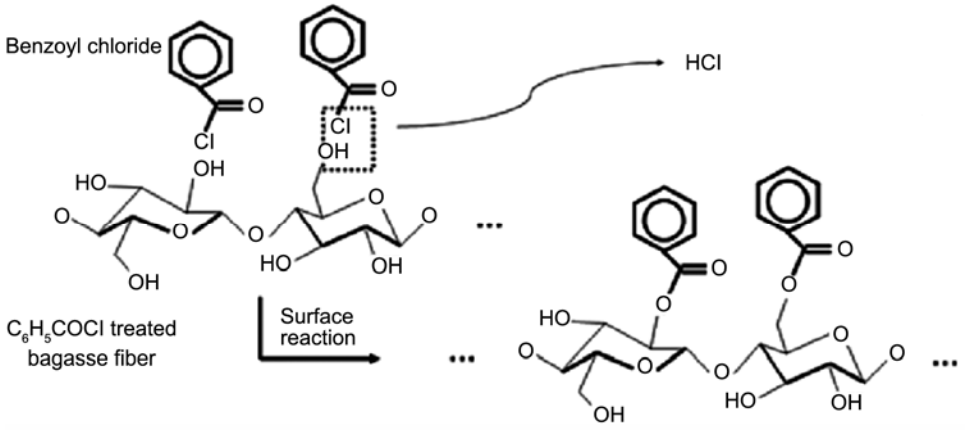


Fig. 1 — Variation of ultrasonic velocity in aqueous cellulose/ benzoyl chloride mixture.



Mechanism of interaction between benzoyl chloride and cellulose

Scheme 1

releases –OH group resulting in hydrophobic nature as shown in Scheme 1, in the interaction mechanism of modifier with cellulose.

Further, with the increase of concentration of cellulose, the ultrasonic velocity decreases due to increased networking structure of polymer cellulose. As aqueous cellulose solution is in ionic state, it has greater affinity to interact with benzoyl chloride which makes the aqueous cellulose solution an active medium for benzoyl chloride. As a result the ultrasonic velocity decreases suddenly with increase in the concentration of benzoyl chloride. The compressibility (β) increases with increase in the concentration of benzoyl chloride clearly indicates that there is breakage of bonding of cellulose water which decreases the number of water molecules. The decrease in β at higher concentration is due to the increase in electrostriction compression of benzoyl chloride around the molecules as shown in Fig. 2. The effect of ultrasonic wave is studied in terms of intermolecular free length (L_f) which is an important factor for the analysis of ultrasonic velocity in treated medium[10]. L_f is the average distance between the surfaces of the two molecules providing information on how much they compressed in order to interact by decreasing the gap between the two atoms as shown in Fig. 3 clearly supports the variation of compressibility as it is reciprocal of the ultrasonic velocity. The increase in L_f with concentration of aqueous cellulose indicates the significance of interactions between cellulose and benzoyl chloride and suggesting the structural change upon the addition of benzoyl chloride[11-12].

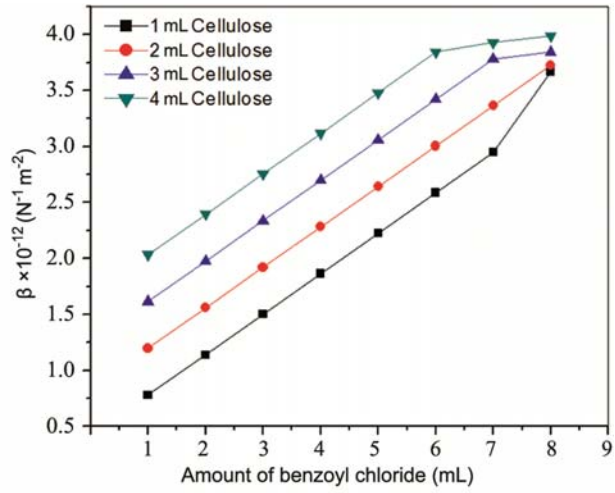


Fig. 2 — Variation of compressibility in aqueous cellulose/ benzoyl chloride mixture.

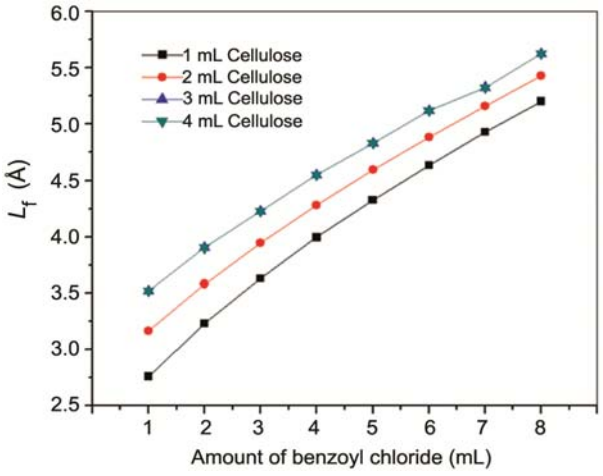


Fig. 3 — Variation of intermolecular free length in aqueous cellulose/ benzoyl chloride mixture.

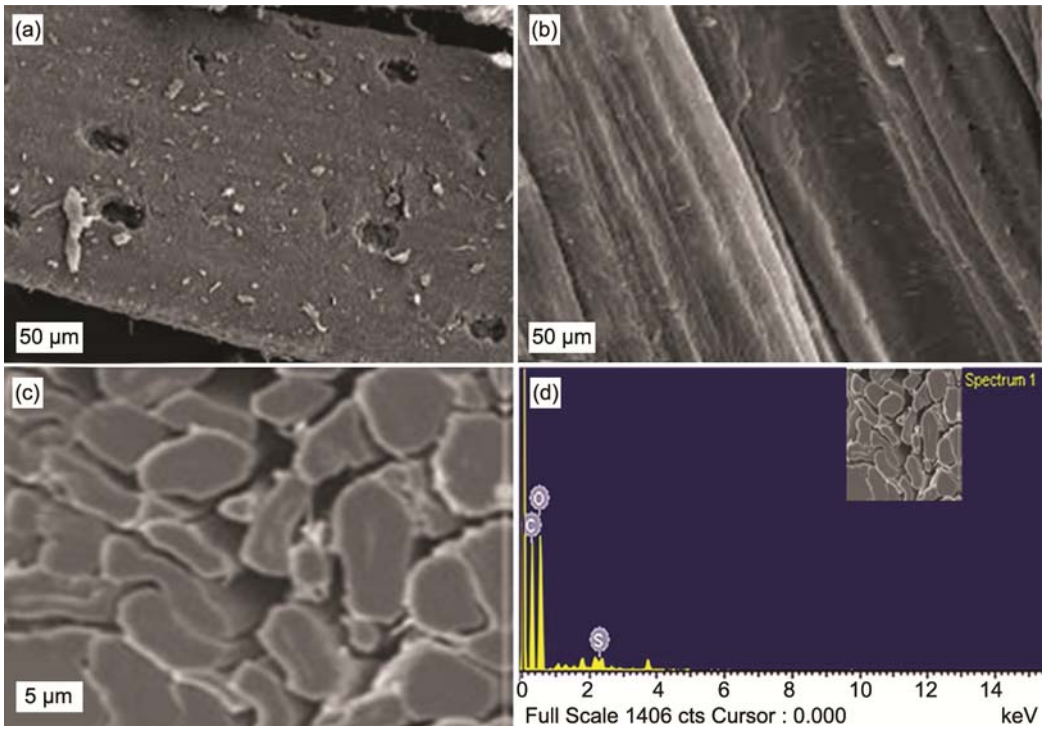


Fig. 4 — (a) SEM of untreated sugarcane bagasse, (b) SEM of treated sugarcane bagasse, (c) SEM of treated sugarcane bagasse at 5µm, and, (d) EDX of ultrasonically treated sugarcane bagasse in activated carbon.

The effect of ultrasonic treatment on sugarcane bagasse can be verified by SEM (Fig. 4a-c). The presence of a superficial layer with high percentage of extractives on the surface of fibers, disrupts the strength of reinforcement with matrix as shown in Fig. 4a. The treatment of benzoyl chloride solution on fiber surface presents morphological changes, indicated by the removal of extractives from the surface of sugarcane bagasse. This removal of extractives results in the exposure of fibrils by increasing the contact area (Fig. 4b). It is observed that the surface of sugarcane bagasse clearly forms a network structure after the treatment of benzoyl chloride (Fig. 4c). This suggests that when this treated fiber is mixed with resin material for fabrication of composite this surface structure will enhance the reduction of microwave intensity by completely absorbing the microwave. The interaction of microwave with the cellulosic part of sugarcane bagasse reinforced composite, increases the dielectric property and is responsible for storage of incident energy by creating number of dipoles in the composite material which is clearly observed from energy dispersive spectroscopy analysis at micro region of sugarcane bagasse as shown in Fig. 4d. The morphological studies of the composite reveal the abundance of carbon and oxygen in the synthesized material. The presence of components like carbon, oxygen and silica helps in the attenuation of electromagnetic wave due to their fundamental property.

In summary, the ultrasonic velocity data and computational acoustic parameters clearly signify the behavior of treated medium with the cellulosic part of sugarcane bagasse. The non linear variation of ultrasonic velocity and acoustic parameters indicate the significant intermolecular interactions such as dipole dipole, ion-solvent interactions. The formation of H-bond complex formation due to these interactions is the basis for the existence of heteromolecular interaction in the treated systems in the presence of ultrasonic wave. Thus ultrasonic wave can be considered as an efficient tool for surface bleaching and modification of natural fibers for the fabrication of composite material. Ultrasonication of biowastes with a suitable modifier provides necessary morphological changes on the fiber which enhances the interlocking resulting in reinforcement of the composite matrix. Thus, ultrasonic treatment can be suggested for efficient modification of surface of biowaste or natural fibers by optimum concentration of benzoyl chloride as

excessive use can destroy the organic component of fibers. This method may find use in the synthesis of biocomposites and the designing of different hybrid composites which have practical applications as dielectric materials for utility in energy storage devices and materials.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www. niscair.res.in / jinfo/ijca/IJCA_58A(05) 567-571_SupplData.pdf.

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