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Compatibility study of binary mixture for surface modifications of natural fibers using ultrasonic technique at different frequencies

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The ultrasonic wave can be used to study the compatibility between the solvent mixtures. The selective mixture of organic compounds minimizes the lignin present in the surface of the natural fibers by which the modified fibers may enable to be filler for making of composites. In present paper, date palm leave (DPL) has been chosen as natural fiber whose surface is modified with mixture of methanol and acetone. The ultrasonic velocities are determined in binary mixtures of acetone and methanol with different frequencies (1 MHz, 3 MHz and 5 MHz) at temperature of 303 K. The different acoustic parameters like acoustic impedance, bulk modulus, intermolecular free length and compressibility are computed from the ultrasonic velocities and densities. The variations of these parameters are discussed in terms of different intermolecular interactions present in the solvent mixture. The compatibility of solvent mixtures is determined from the nature of excess values of thermo dynamical acoustic parameters. The interactions of selected solvent mixture with surface of the fiber have been investigated by Fourier transform infrared (FTIR) spectroscopy and field emission scanning electron microscopy (FESEM).

Keywords: Date palm leave, Ultrasonic velocity, Acoustic parameters, FTIR, FESEM

1 Introduction

In recent years, industries are attempting to decrease the dependence on petroleum based fuels and products due to the increased environmental consciousness. This is leading to the need to investigate environmentally friendly, sustainable materials to replace the existing ones. The tremendous increase of production and use of plastics in every sector of our life lead to huge plastic wastes. Disposal problems, as well as strong regulations and criteria for cleaner and safer environment, have directed great part of the scientific research towards eco-composite materials. Among the different types of eco-composites those contain natural fibers and natural polymers have a key role. Since few years' polymeric biodegradable matrices have appeared as commercial products, however, their high price represents the main restriction to wide usage. Currently, the most viable way towards eco-friendly composites is the use of natural fibers as reinforcement. Natural fibers represent a traditional class of renewable materials which are experiencing a great revival. In the latest years, many researchers developed in the field of natural fiber reinforced plastics[1]. Due to their low density and their cellular structure, natural fiber posses very good acoustic and thermal insulation properties and demonstrate many advantageous properties over glass or rock wool fiber. Variation in thermal and acoustic properties with composition provides added information regarding the intermolecular interactions present in a system. The sign and magnitude of the nonlinear deviations from ideality as a function of composition and frequency may be ascribed to the presence of weak or strong type of interactions between unlike molecules. The excess acoustic parameters of binary mixtures have been satisfactorily used in explaining the extent of interactions between mixing components[2-4].

The most serious concern with natural fibers is their hydrophilic nature due to the presence of pendant hydroxyl and polar groups in various constituents, which can lead to poor adhesion between fibers and hydrophobic matrix polymers[5,6]. The hydrophilic nature of the fiber surface leads to high moisture up take for the natural fibers which can seriously lower the mechanical properties of the fibers. The natural fibers are inherently incompatible with nonpolar-hydrophobic thermoplastics, such as polyolefin. The chemical treatments can clean the fiber surface, modify the chemistry on the surface, lower the moisture up take and increase the surface roughness. The chemical analysis of natural fiber

clearly indicates that compositions of natural fiber are cellulose, lignin and hemicelloses[7]. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall, depolymerizes cellulose and exposes the short length crystallites. As the natural fibers bear hydroxyl groups from cellulose and lignin, they are amenable to chemical modification as in Fig. 1. The hydroxyl groups may be involved in the hydrogen bonding within the cellulose molecules thereby reducing the activity towards the matrix. Chemical modifications may activate these groups or can introduce new moieties that can effectively lead to chemical interlock with the matrix. The pretreatments of natural fibers with chemical mixture like acetone-methanol have achieved various levels of success for improving fiber strength, fiber fitness and fiber-matrix adhesion.

In earlier study[8], the mixture of organic liquids has been taken for surface modification of date palm leave which acts as a reinforcement agent with polyvinyl alcohol (PVA) bio composites. As a part of our on going research work, the present investigation deals with two important liquids namely acetone and methanol. Both the liquids under investigation are very useful chemicals and of industrial significance. The mixture of these liquids is used during the surface modification of date palm leave fibers in order to enable them for making of composites.

2 Materials and Methods

Date palm waste leaves were collected from agricultural farm areas and subjected to dry sun light in open place so as to bring down to lower moisture level to 10-20%. They were chopped to smaller length and further cut into required size approximately in a shredder machine and stored in suitable bags at dry place as in Fig. 2. The lignocelluloses fibers were obtained by cutting date palm tree leaves into small pieces of approximately 5 cm long10 mm wide. In the present study, the chemicals used are of analytical grade purified by standard procedure[9-12] and redistilled before use. Density was determined with a Pyknometer of 25 cm^3 capacity, calibrated with de-ionized double distilled water. Ultrasonic speed was measured by a single crystal variable path ultrasonic interferometer model MX-3, Mittal Enterprises New Delhi, India operating at different frequencies of 1 MHz, 3 MHz and 5 MHz.

The temperature stability is maintained within 0.1K by circulating thermo stated water around the interferometer cell that contains the liquid, with circulating pump. Binary mixtures of acetone were prepared with methanol with varying fraction of acetone. The fibers were then extracted for 24 h in a soxhlet reflux of binary mixture of acetone/methanol (75/25). Subsequently, the discoloured fibers were dried at room temperature. The used fibers are denoted as unmodified.

The FTIR spectra of the materials were recorded with the help of an Infrared Spectrophotometer (Perkin Elmer Paragon 500) in the range 400-4000 cm^{-1} using KBr pellet. The mixed powder was compressed to prepare the pellet of diameter 10 mm and thickness 0.25 mm. The surface morphology of the dried DPL was studied by Scanning Electron Microscopy (SEM) with the help of a Jeol Ltd., Japan model 5200 Scanning Electron Microscope with magnification of ×10,000. The samples were dried by low temperature vacuum drying method.

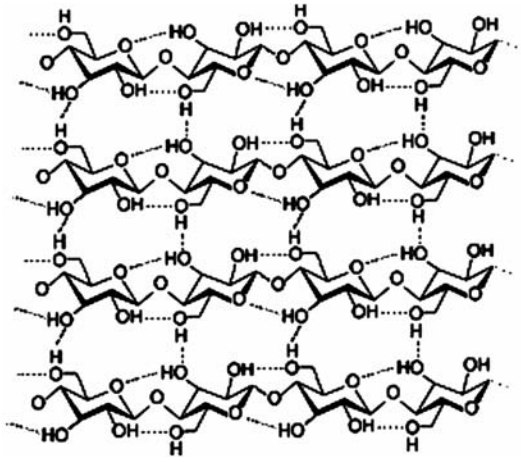

Fig. 1 — Strand of cellulose showing the hydrogen bonds (dashes) within and between cellulose molecules

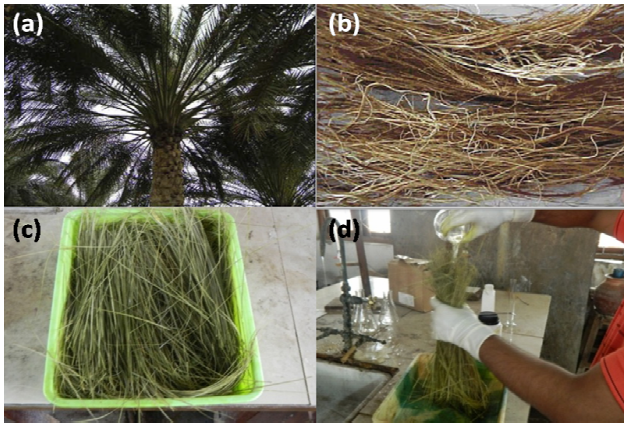

Fig. 2 — (a) Date palm tree, (b) Date palm tree fibers that surrounding the stems (c) Date palm leaves, (d) Soaked with the binary mixture of acetone-methanol

3 Theory

The experimental measured values of ultrasonic speed and computed values of density are used to compute acoustic parameters such as intermolecular free length (L_f), isentropic compressibility (β), acoustic impedance (Z) and bulk modulus (K) and their excess values. The above acoustic parameters are determined with the help of the following relationship [13].

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

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

Acoustic impedance, $Z = \rho C$ … (3)

Bulk modulus, $K = \rho C^2$ … (4)

and their excess values are calculated as :

$$Y^E = Y_{mix} - (X_A Y_A + X_B Y_B) \quad \ldots (5)$$

where X_A, X_B, Y_A, Y_B and Y_{mix} are mole fraction, isentropic compressibility, inter molecular free length,acoustic impedance bulk modulus of methanol, acetone and mixture, respectively. The constant k is temperature dependent which is given as $[93.875 + (0.375T)] \times 10^{-8}$ as per literature[14] and T being the absolute temperature.

4 Results and Discussion

The ultrasonic speed in methanol increases smoothly with mole fractions of acetone as shown in Fig. 3. Acetone contains carbonyl functional group, which is polar and hence, it can interact with methanol like polar molecules through dipole-dipole interaction. In pure acetone, there is dipole-dipole along with the dispersive interactions. As the concentration of acetone gradually increases the different type of interaction comes into existence due to tautomerisim. In acetone molecules, the hydrogen bonding comes into existence between the like molecules of aldol at –OH end. In addition with hydrogen bonding, keto and enol form of tautomerisim comes into existence with maximum percentage of keto which the dipole-dipole interaction takes vital role for increasing the ultrasonic speed in high concentration of acetone.As seen from the profile, the frequency has no significant contribution in variation of ultrasonic speed in the binary mixture though the frequency varies in the range 1-5 MHz. Similar results related to the inert effect of frequencies have been reported in earlier literature[15,16]. In these studies, variations of ultrasonic velocities have been investigated with variation of frequencies and it was reported that there was no substantial variation of ultrasonic velocities have been found by variation of frequencies.

Figure 4 shows the variation of β^E for binary mixture of acetone and methanol which is found to be negative over the entire composition range. The negative values of excess isentropic compressibility indicate that the liquid mixture is less compressible than the pure liquids forming the solution and molecules in the mixture are more tightly bound than in pure liquids. Thus, negative values of excess isentropic compressibility indicate strong specific interactions between component molecules and interstitial accommodation of smaller molecules in the void created by bigger molecules. The negative excess isentropic compressibility results reduction of volume of mixture favouring the fitting of component molecules into each other. Greater the negative value of β^E stronger is the attractive interaction between the component molecules such as hydrogen bonding; dipole-dipole interaction and other specific interactions between unlike molecules are operative in the system.

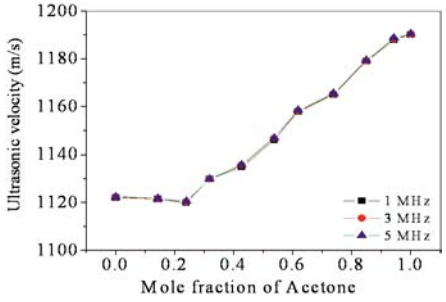

Fig. 3 — Variation of ultrasonic velocity in methanol with acetone

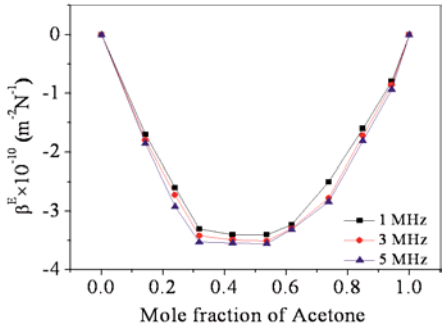

Fig. 4 — Variation of excess isentropic compressibility in methanol with acetone

This indicates that the interaction is stronger in acetone-methanol mixture. It supports the facts that acetone-methanol mixture is more compatible in bleaching of the surface of date palm leaves due to interaction between the composition of date palm leaves and chemical mixture. Again, the variation of frequency is also not given any significant result in excess values of isentropic compressibility except in equimolar region due to strong interaction there is slight separation in profiles.

The excess free length is negative over the entire range of composition investigated exhibiting a broad minimum around equimolar region of acetone and methanol as shown in Fig. 5. Considering the effect of frequency, it is observed that no significant results also obtained in this case like the above situations. The variation of excess free length further supports the variation of other excess parameters like excess acoustic impedance and excess bulk modulus of the mixtures. The excess acoustic impedance in the mixtures was found to be negative for the entire composition range of acetone.

From the Fig. 6, it is instructive that the variation of acoustic impedance is very smooth in acetone-methanol mixture. This is due to the fact that the occurrence of different intermolecular interactions like dipole-dipole interactions, dipole-induced dipole interactions, Vander Waals interactions is present in the liquid mixtures. The liquid mixture acetone-methanol has a clear minimum indicating that more structural changes takes place in this mole fraction of chemical mixture which may favours the interaction of the liquid mixture with the chemical composition of the date palm leaves. As the bulk modulus is the reciprocal of compressibility, so its variation is supported by variation of excess compressibility.

From the profiles for excess bulk modulus as shown in Fig. 7, it is informative that with decrease of volume of the mixture pressure increases. As a result of which the intermolecular interaction between the liquid molecules increases and the components of the mixture are tightly bound with each other and also with the chemical composition of the date palm leaves. This results in increase of surface roughness and interlocking in edges of the date palm leaves.

The main chemical compositions of date palm leaf fiber are cellulose (54.75%), hemicellulose (20%) and lignin (15.3%) along with other volatile substances. The FESEM micrographs of the cross-section of both untreated and treated date palm leaf have been given in Fig. 8(a and b). From Fig. 1(a), it is found that the

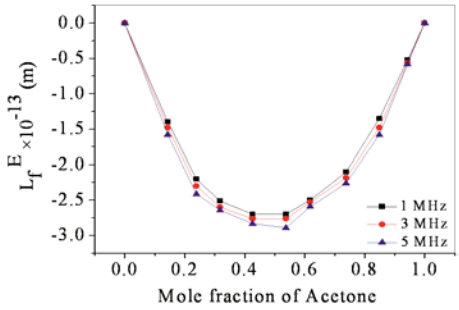

Fig. 5 — Variation of excess intermolecular free length in methanol with acetone

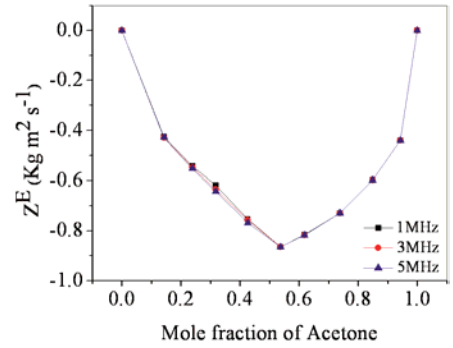

Fig. 6 — Variation of excess acoustic impedance in methanol with acetone

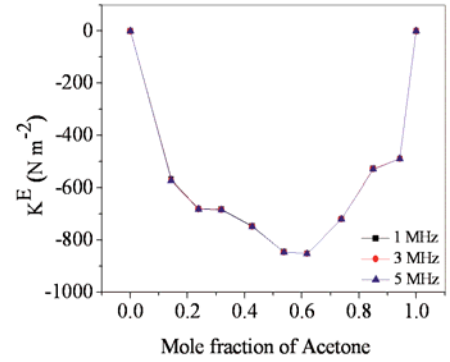

Fig. 7 — Variation of excess bulk modulus in methanol with acetone

cellular structures of the fiber are porous in nature. However, porous structures are found to be non-uniform with an average diameter of about 1 µm. in FESEM, it is noticed that, the fibers are found to be agglomerated locally. The FESEM of chemically treated fiber in Fig. 1(*b*) has compressed cellular structures with local porous spots. Further, the treated fiber shows uniform and compressed cellular structures. It is revealed that the treatment of acrylic acid has destroyed the pores of the date palm leaf fiber in order to reduce the void content. It may be

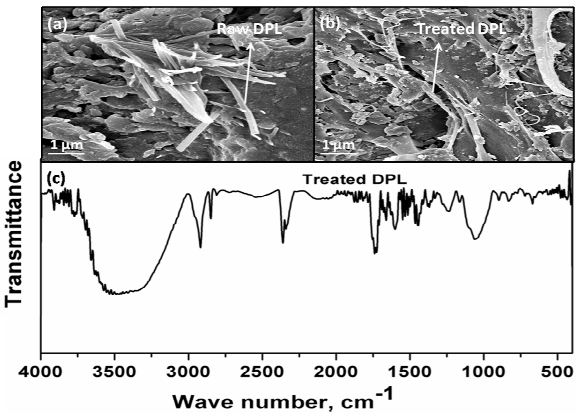

Fig. 8 — (a) FESEM of raw date palm leave (DPL) (b) surface modified chemically treated DPL (c) FTIR of chemically treated DPL

due to strong interaction of the functional group of the organic mixture with the hydroxyl group at the surface of the fiber. Hence, the hydrophilic nature of fiber changes to hydrophobic for better compatibility with polymer matrix during formation of composites. In Fig. 8(c), the FTIR of chemically treated DPL fiber is studied in order to support the interaction of functional groups of organic mixture with surface of the DPL fiber. The FTIR of treated DPL shows a broad peak at 3400 cm^{-1} due to the presence of (OH) bond present in the fiber. The sharp peak at 2900 cm^{-1} is due to the (CH) stretching. The peak at 1740 cm^{-1} in case of the DPL fiber may be due to >C=O stretching which evidence attachment of carbonyl group at fiber back bone (Fig. 8c).

5 Conclusions

The behaviour of different acoustic parameter clearly indicates that there is compatibility between the selected solvent mixtures of acetone and methanol. The compatibility is strongly dependent on different concentrations of binary mixture rather than frequency of ultrasonic waves. This compatibility leads to the presence of different intermolecular interactions like dispersions, H-bonding, dipole-dipole interaction and dipole-induced dipole interaction. Due to the presence of such fundamental interactions, the treatment of this mixture increases the surface roughness removing certain amount of lignin wax and oils covering the external surface of the date palm leaf cell wall. As a result, it is found that better mechanical interlocking takes place and increases the number of possible reaction sites which improves the fiber matrix adhesion, increases the strength of the composites, decreases its water absorption and improves its thermal stability of the composite.

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