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Ultrasound-assisted surface modification of cellulose isolated from rice husk to impart hydrophobicity

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Abstract
The present work evaluated the surface modification of cellulose by methyl methacrylate using ultrasound assisted graft copolymerization method to reduce the hydrophilicity of cellulose fiber. Potassium per sulfate was used as initiator. Cellulose was extracted from rice husk using alkali-chlorination method and grafting of cellulose was done using two concentrations of MMA (2.5 and 3.5 × 10^{-1} mol L^{-1}), three reaction temperature (60, 70, 80 °C) and three ultra-sonication time (20, 30, 40 min). Effect of these on grafting efficiency was evaluated. Results indicated that the grafting efficiency was varied from 30.34% to 86.65%. The structural analysis of rice husk, raw and grafted cellulose was done by scanning electron microscopy (SEM) and revealed that alkali chlorination method successfully removed non cellulosic fibers and other impurities from rice husk and grafted cellulose had rough surface than un-grafted cellulose. The swelling% was decreased up to 30.6% which makes it more compatible to use as filler in hydrophobic polymers.

Keywords: Surface modification, graft copolymerization, cellulose, hydrophilicity, grafting efficiency

Introduction
Increasing environmental consciousness requires the development of less harmful substances to our atmosphere and taking benefits of the natural environment around us. Due to increasing population, pressure has been placed on natural resources – water, forest and land as well as the environment, challenging the sustainable development. In an attempt to compromise the sustainable development rules and polymer technology, it is important to integrate eco-friendly materials and limit the lethal chemical compounds labored in polymer processing. Therefore, searching for some natural alternatives seems to be a great option and it is widely being developed. There is a growing urgency to convert agricultural byproducts and surpluses of the crops into new, profitable products [1]. This type of biomass is the most abundantly available biopolymer in nature. The worldwide production of lignocellulosic biomass is estimated to be about 146 billion tons per annum [2]. Rice Husk is considered as agricultural waste abundantly available throughout the world. Rice husk consists of organic components, i.e., 35% cellulose, 25% hemicellulose, 18% lignin and15–17% silica [3-4]. Rice husk is considered as a waste from rice milling rice husk thus, it is mainly used as the raw material for animal bedding, absorbent, building material, and seed growing [5]. It has the potential to be used as a filler in the manufacturing of lignocellulosic fiber reinforced polymer matrix composite, because it is capable of reducing the density of the furnishing products, and requires less processing energy, Due to its low commercial value and high availability, it can be used as filler in bio-composite materials. Also, it can be considered as a most available source of cellulose
Cellulose is the most promising natural biopolymer available on earth, having environment-friendly nature and attractive properties such as renewability, remarkable thermal and mechanical properties, economical, easy modification, and biodegradation [6-7]. Natural fibers or plant fibers are hydrophilic due to attraction or interaction between the hydroxyl groups of fiber components and water molecules. Plant fibers often result in poor compatibility with hydrophobic polymer matrices due to their hydrophilic nature. The combination between the rice husk fiber and biodegradable polymer matrix may always be incompatible due to their opposing nature, which leads to poor interfacial adhesion [8]. Poor bonding between the cellulose fiber and the polymer matrix results in poor mechanical properties, and a higher rate of moisture absorption. The potential scope of cellulose is limited because of its insoluble nature to common solvents. As a consequence, it requires surface modification to improve its functional properties as well as to make it more hydrophobic so that its compatibility would be

improved with hydrophobic matrix. Various surface modification methods of natural cellulosic fiber have been adopted to improve the fiber-matrix adhesion, such as the addition of silane coupling agent, alkaline treatment, plasma treatment of the bio-filler surface, and grafting polymer matrix with a functional group. Amid the various modification methods of cellulosic fiber, Graft copolymerization is a promising method to impart functional groups to polymer backbone or modify the cellulose's physicochemical properties. Radical polymerization is a useful method for the polymerization of a wide variety of vinyl monomers and can be plagued by a lack of control over the mechanism; radical polymerizations have many different reactions occurring simultaneously namely initiation, propagation, and termination by coupling, disproportionate or chain transfer. Ultrasound waves of frequencies greater than 20 kHz have been described as a convenient and "green" way to promote chemical operations and organic transformations [9]. Compared with the conventional emulsion polymerization process, ultrasound induced polymerization has several advantages: lower reaction temperatures and short time, faster polymerization rate and good yield. Under low-frequency ultrasound, it has often been observed that the addition of a radical initiator is essential for polymerization**.** Ultrasound has been applied as a supplementary source of energy to enhance radical polymerizations initiated by typical thermally-activated radical sources such as potassium persulfate, peroxides, or azocompounds [10]. The physical effects associated with acoustic cavitation provide very efficient mixing and strong dispersion of the components making up the liquid mixture. The effects of ultrasound in the polymer synthesis include generation of free radicals, activation of free radical initiators, degradation of polymers to produce macroradicals and dispersion of monomer to form heterogeneous particles [11]. Grafting percentage and grafting efficiency are two important indicators of grafting polymerization [12]. Cellulose can be successfully synthesized by the application of ultrasound energy and chemical initiation under mild aqueous conditions. Heat and ultrasound, both affects the efficiency of grafting. The present work has been focused on the extraction of cellulose from rice husk and then surface modification of rice husk cellulose by ultrasound- assisted graft copolymerization method to impart new functional properties.

Materials and Methods

Rice husk was collected from Madan milling, Kichha. India. Standard chemicals *viz*. Sodium hydroxide, acetic acid, sodium chlorite, methyl methacrylate, potassium per sulfate for cellulose extraction and surface modification of rice husk.

Extraction of Cellulose from Rice husk

For extraction of cellulose extractives, hemicellulose and lignin was removed. The rice husk sample was thoroughly washed with tap water, following by washing with distilled water and then drying in tray dryer at 80 °C for overnight and then grounded, screened using 250 μm aperture sieve. Cellulose was extracted from rice husk by chlorination and alkaline method. The screened rice husk (5 g) was dewaxed to remove extractives wax, pectin, and other impurities) by refluxing them using Soxhlet apparatus with toluene and ethanol (2:1) for 6 h. After that, it was oven-dried at 55°C for 24 h. Extractive free sample was delignified with 3% sodium chlorite solution adjusted to pH 4-4.2 in hot water bath at 85 °C for 1.5 hours. After chlorine treatment, sample was washed with distilled water and dried at 85 °C to obtain holocellulose. The total process was repeated twice for better removal of lignin. The holocellulose was treated with 10% sodium hydroxide solution at 55 °C for 90 minutes, filtered and washed with distilled water. Finally, extracted cellulose was dried in hot air oven at 85 °C. Hydrogen peroxide bleaching was carried out to convert dull white microcrystalline cellulose into milky white colour. Finally, extracted cellulose was dried in hot air oven at 40 °C until constant weight.

Modification of cellulose

Modification of cellulose by ultrasound assisted graft copolymerization was initiated by immersing 0.5 g cellulose in 50 ml distilled water. Subsequently, predetermined amount of monomer was added into it. Known amount of initiator (potassium persulfate) were then added into the solution The grafting reaction was carried out under ultrasonic irradiation at 20 kHz with an output power of 250 W. After certain time, reaction was stopped by quenching cold water. Resulting product was extracted with acetone for 4 h to remove homopolymer formed during reaction. After washing the copolymer with ethanol and water three times, final product was filtered and dried in an oven at 50 °C until constant weight (Fig. 1). The grafting efficiency was calculated according to reported elsewhere [9].

$$\text{Grafting Efficiency (\%)} = \frac{\text{wt.of grafted cellulose} - \text{wt.of cellulose}}{\text{Wt.of celluloe} + \text{Wt.of MMA monomer}} \times 100 \quad (1)$$

Swelling (%)

Swelling in water was calculated by formula reported earlier [13-14]. The grafted cellulose was immersed in water for 24 h. Swelling (%) was calculated from following formula:

$$\text{Swelling (\%)} = \frac{\text{Final wt.} - \text{initial wt.}}{\text{initial wt.}} \times 100 \quad (2)$$

Results and Discussion

The present work aims the extraction of cellulose from rice husk as fig 2 shows the images of untreated rice husk powder and treated rice husk cellulose and modified cellulose. The extracted cellulose powder is completely white in color which is a clear indication of removal of lignin, hemicellulose, waxes and other impurities during chemical treatment. The modification of extracted cellulose was done by graft copolymerization method using methyl methacrylate as monomer and potassium per sulfate as initiator. C_2, C_3 and C_6 hydroxyl and C-H groups are active for grafting of MMA chains. The effect of monomer concentration and reaction temperature is investigated. The structure of rice husk powder, extracted cellulose powder and modified cellulose powder was also investigated through SEM and will be discussed further.

Effect of Monomer concentration, reaction temperature and ultra-sonication time on grafting efficiency

The grafting efficiency of ultrasound assisted graft copolymerization for different experimental conditions is shown in table 1. As shown in fig 3, the grafting efficiency for 2.5×10^{-1} mol L^{-1} monomer concentration was varied from 30.34% to 68.25%. However, at monomer concentration of 3.5×10^{-1} mol L^{-}, the grafting efficiency was varied from 46.79% to 86.79% (fig 4). The increase in grafting efficiency at higher monomer concentration can be explained by the phenomena that more number of free radicals are available to reach polymeric backbone for participating in grafting reaction, which increase the grafting efficiency [15]. Thakur *et al.*, 2014 [13] also reported the increase in the percentage grafting onto Grewia optiva fibers with increasing the monomer concentration. It can be seen from the figure that different temperature and different ultra-sonication time had the significant effect on grafting efficiency. As it can be seen from the figure that after 70 °C, grafting efficiency was declined at different utrasonication time. The increase in grafting efficiency with increased temperature could be due to the enhanced chemical energy in molecules which results in formation of free radicals, causes fastest diffusion of monomer onto cellulose backbone [16]. The decline in grafting efficiency after 70 °C may be due to the availability of more radicals to form homopolymers which restricts the grafting [17]. The effect of ultrasound energy and heat was also significant and same was reported by Sanaeishoar *et al.*, 2018 [9] where for same conditions grafting efficiency was increased by 22% in presence of heat and ultrasound energy. Ultrasound energy generates the free radicals and assists the creation of homogeneous conditions [18]. The reaction temperature had profound effect on grafting efficiency as it was increased with increasing temperature from 60 °C to 70 °C for MMA concentration of 2.5 and 3.5 × 10^{-1} mol L^{-1}. At 80 °C the effect of temperature was not prominent. The same results have been reported by Chu *et al.*, 2015 [11]. where the graft ratio and graft efficiency of the reaction with ultrasound showed a little decline when the temperature was increased to 80 °C. When temperature was increased, the grafting efficiency increased due to that reactant molecules possess higher activation energy at higher temperature. The ultrasonic wave passed easily through the reactant. With the vibration of ultrasound the efficient collisions of the reactants increased drastically. At 80 °C, the decline in grafting efficiency might be due to the reason that at high temperature, initiator (KPS) decompose quickly and more collision occur between two radicals, brought the formation of homopolymer which consequently results in radical termination.

Swelling (%)

To improve the polymer compatibility of cellulose, less hydrophilic character of cellulose is necessary. Therefore, we investigated the swelling property. As show in fig. 5 that swelling (%) was decreased from 150% to 30.6% when grafting efficiency increased from 0 to 55%, indicating the hydrophilic character of cellulose to hydrophobic. Above 50% grafting efficiency no further change in swelling was observed. Therefore, this grafting efficiency is sufficient to improve the compatibility of cellulose with hydrophobic polymers.

Scanning electron microscopy

The structural change during cellulose extraction of rice husk was investigated through SEM. It is clearly shown from fig. 6(a) that untreated rice husk fiber has rough surface, which is due to the hemicellulose and lignin complex structure that binds the fiber components [19] Whereas, Fig 6 (b) shows the clean and fibrillated structure due to successful defragmentation of long fiber into small individual fibers, which shows better removal of non-cellulosic fibers and other impurities. The effect of the chemical treatment for removal of lignin, hemicellulose and other impurities is evident from the comparison of fig.6 (a) and (b) which is also seen in fig 2 (a) and (b). The SEM image of modified (grafted) cellulose is depicted in fig. 6 (C). It is quite clear from the image that grafted cellulose has rough surface than un grafted cellulose and has reduced inner fiber surface due to more polymeric chains attached onto cellulose backbone.

Table 1: Grafting efficiency at different experimental conditions

Monomer concentration	Temperature (°C)	Time (min)		
		20	30	40
2.5	60	30.34	45.45	61.76
	70	40.44	58.34	68.25
	80	38.54	55.69	65.5
3.5	60	46.79	70.16	71.43
	70	65.79	76.65	86.79
	80	64.21	74.88	85.65

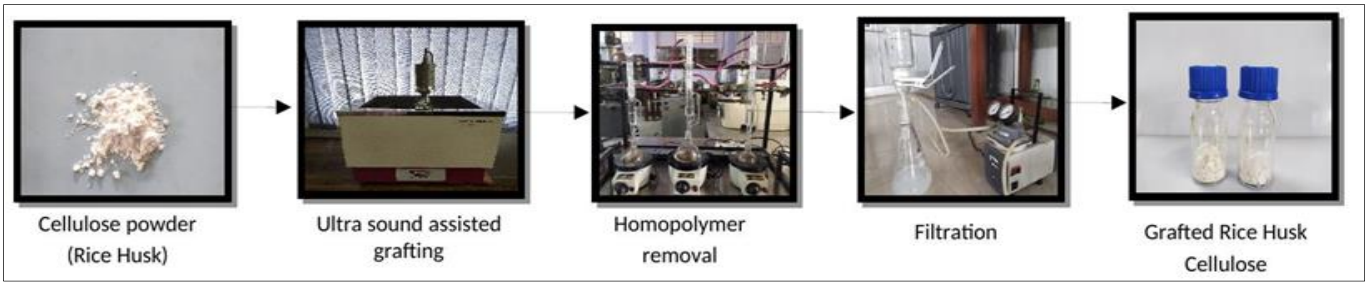


Fig 1: Schematic diagram of ultrasound assisted graft copolymerization

(a) (b)

Fig 2: (a) Untreated rice husk powder (b) extracted cellulose powder

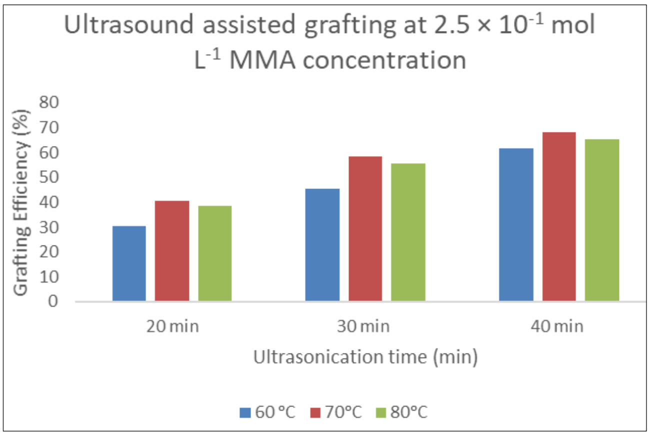


Fig 3: Ultrasound assisted grafting at 2.5 × 10^{-1} mol L^{-1} MMA concentration

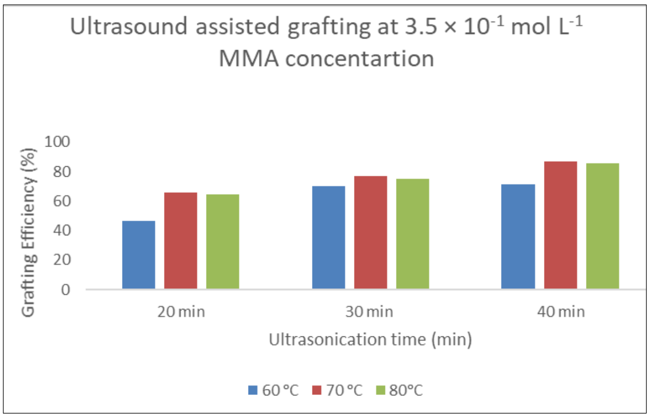


Fig 4: Ultrasound assisted grafting at 3.5 × 10^{-1} mol L^{-1} MMA concentration

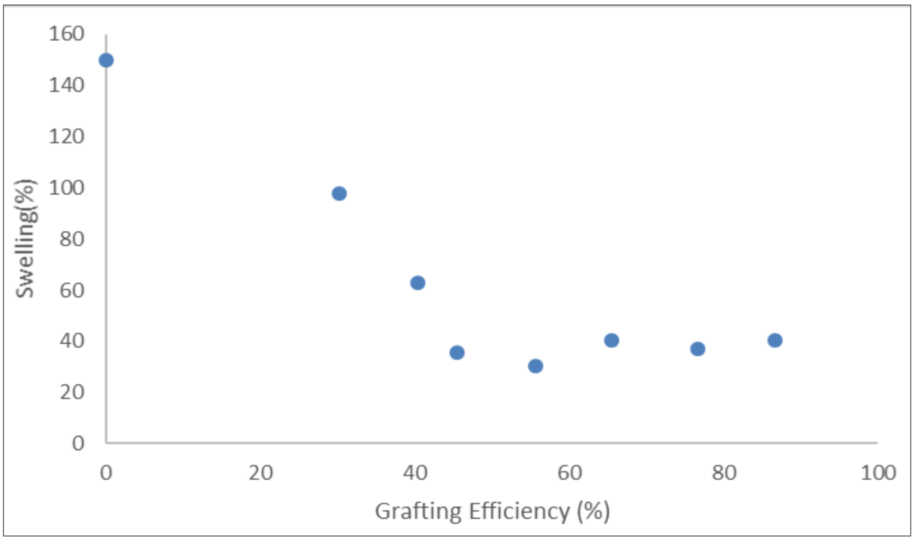
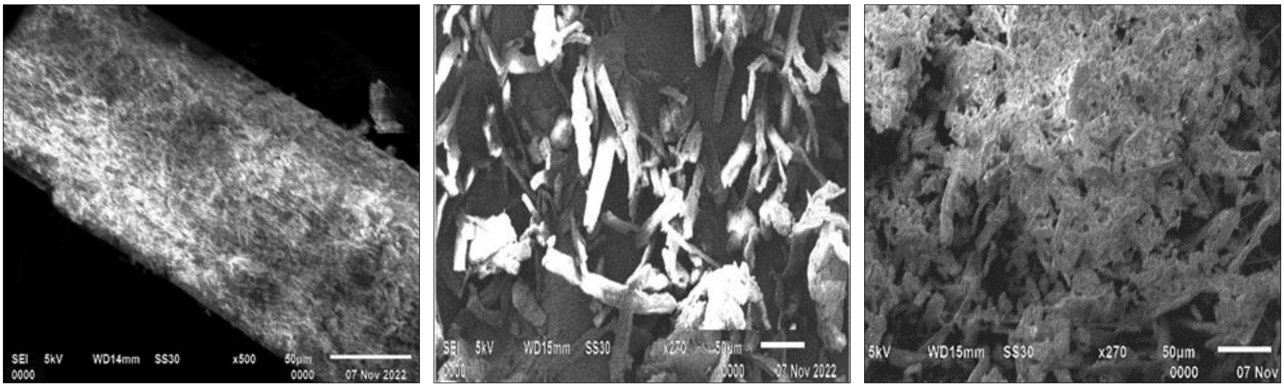


Fig 5: Swelling in water as function of grafting efficiency of MMA grafted cellulose



(a) (b) (c)

Fig 6(a): Untreated rice husk powder (b) Extracted cellulose powder (c) Modified (grafted) cellulose

Conclusion

In the present study, cellulose powder was synthesized from rice husk as raw material using alkali and bleaching method. The SEM images showed structural changes in untreated rice husk powder and rice husk cellulose. The extracted cellulose was successfully modified by graft copolymerization of MMA as evident from SEM images. The grafting efficiency for all the experimental conditions was varied from 30.34 to 86.79%. The modified cellulose offers variety of functional groups to cellulosic backbone which consequently can enhance the compatibility of cellulose with hydrophobic polymers. Due to aforementioned reasons grafted/ modified cellulose could be used as potential reinforcement for development of bio composites with improved physiochemical properties.

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