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Synthesis of Limonia Acidissima (Wood Apple) Shell Micro and Nanoparticles via Top-Down Approach

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***Abstract*—**The need for completely/partially biodegradable composites has promoted the use of agricultural waste as probable alternates for synthetic fillers for polymer and metal as reinforcement. In this study, through a ball-milling approach, the degree of refinement of Limonia Acidissima shell was investigated. Using a disc grinder, the Limonia Acidissima shell was pulverized and refined under different milling durations (45 and 70 hours) using the top-down method. The morphology of micro and nanoparticles obtained from Limonia Acidissima shell was analyzed using a scanning electron microscope and Transmission electron microscope. The sizes of micro and nanoparticles were determined using particle size analyzer and image-J software. The different composition of shell powder was examined using Energy-dispersive spectroscopy and the crystallinity index of shell powder was determined using X-ray diffraction. Particle size analyzer shows that an average particle size of 284.8 ± 125.4 µm was obtained from the pulverizer and average particle size of 45 and 70 hours milled powder was 1.409 ± 1.011 µm and 60.23 ± 12.8 nm respectively. The crystallinity index of Unmilled, 45 and 70 hours milled powder was 41.74%, 40.61%, and 38.33% respectively.

Keywords- Limonia Acidissima; ball milling; micro, and nanoparticles

1. INTRODUCTION

The synthetic and glass fillers were the dominant reinforcement materials for polymer matrix composites (PMCs) and metal matrix composites (MMCs) over the years [1-3]. The different parameters like fibre wettability, fibre damage, huge production cost, and limited availability hinders the extensive usage of PMCs industrial applications [4-6]. Due to low cost, quality, environmental friendliness, renewability, material scientists and researchers have recently focused attention on natural fillers as an attractive alternative to synthetic fillers for reinforcement purposes [7]. Limonia Acidissima has been assessed as activated carbon using phosphoric acid (H3PO4) as the activating agent [8]. It has analyzed that the removal of Cr (VI) and fluoride by membrane capacitive deionization with nanoporous and microporous Limonia acidissima (wood apple) shell activated carbon electrode [9]. Moreover, the potential of Limonia acidissima shell particles as reinforcement in PMCs and MMCs is very limited in the available literature.

Proper and efficient use of agricultural waste would minimize the negative impacts of improper disposal such as air pollution caused by agricultural waste burning. This process results in the release of harmful gases that may cause breathing problems [10].

For the development of particulate composites, natural fillers have been used by many researchers [11-16]. The incorporation of nanoparticles along with microparticles in Vinylester composite enhances the wear behavior due to the synergistic effect [17]. The mechanical and wear properties improvement was observed due to the addition of particles/fibers to the polymers [18, 19]. In the preparation of Limonia Acidissima shell nanoparticles using ball milling the effect of ball-to-powder ratio and duration of milling were studied by Bello et al.,[20]. In the present work, an attempt has been made to prepare micro and nanoparticles by the top-down approach by varying milling duration (45 and 70 hours).

In the particulate composite, the strength of the composites mainly depends on many parameters like particle size, shape, filler loading, and wettability. The increase in the filler concentration in the particulate composite is directly proportional to the interplanar spacing of the fillers within the matrix. Consequently, in metallic composites the component packing densities increase and restrict the movement of dislocation within the matrix. Likewise, due to particle refinement, craze formation leading to shear yield in polymeric composites is decreased [21 - 23].

2. EXPERIMENTAL DETAILS

A. Material

Limonia Acidissima (Wood apple) belongs to the Rutaceae family, which is widely known as the ' Stone apple ' or ' Bael ' medicinal tree. Limonia Acidissima Fruit pictorial image is shown in Fig.1. It is an Indian indigenous fruit and found abundantly in the sub-Himalayan forests, Bengal, Central, and Southern India. Because of the high hardness and toughness, Limonia Acidissima shell seems to be a promising material for particulate composite among the various lignocellulosic fibers.

Figure 1. Limonia Acidissima Fruit

B. Methods of preparation of Limonia Acidissima shell particles

The Limonia Acidissima shell was used as fillers. Before using, it was washed several times in distilled water to remove the impurities and dried for 48 hours in a hot air oven at 110 °C to remove the excess water content and moisture. The dried shells were crushed into small pieces with the help of a hand hammer and subjected to disc grinder and pulverized into powder. The shell powder obtained from the pulverizer is sieved for 1 hour with the help of a sand siever(1-300µm). The powder which is retained in the pan (< 53µm) was used for the synthesis of nanoparticles.

The Ball milling of the powder is carried out for 45 and 70 hours duration with the help of planetary ball mill at 10:1 ball-to-powder ratio and 195 rpm using zirconia balls of the same size (5-60 mm). The analysis was done for each milled sample using Scanning electron microscope (SEM) and a Transmission electron microscope (TEM). Fig. 2 shows the whole Limonia Acidissima fruit, fruit with pulp broken and final shell after the removal of the pulp part. Further processing of shell into powder is shown in Fig.3.

Figure 2. Processing of Limonia Acidissima Shell

Figure 3. a) Micro Particles from the pulverizer, b) Nanoparticles from Ball milling.

3. RESULTS AND DISCUSSION

C. Scanning Electron Microscope(SEM) Micrographs

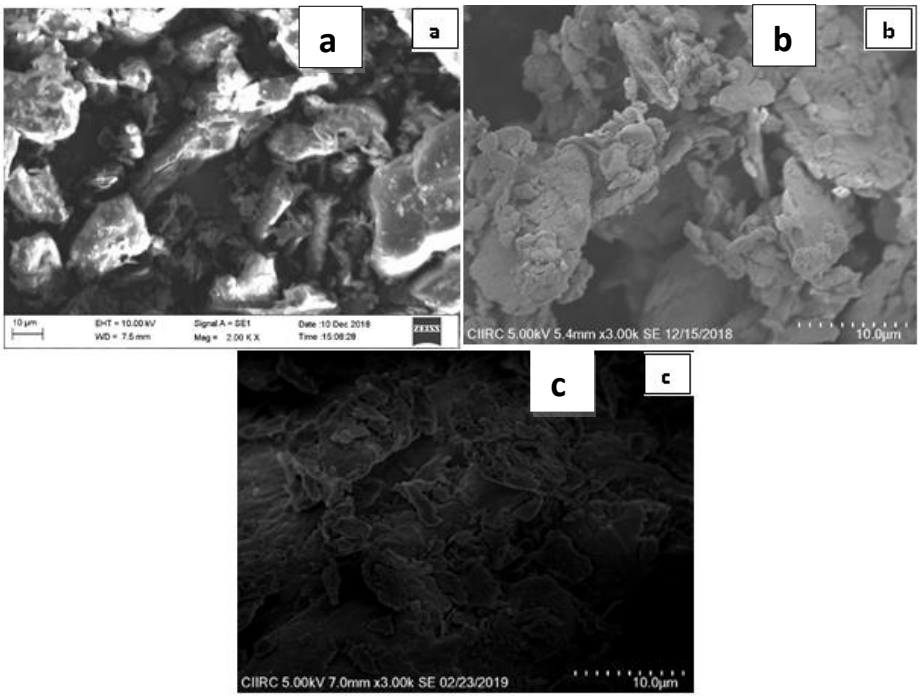

Figure 4. SEM micrograph of .a) Unmilled powder. b) Powder milled for 45 hours. c) Powder milled for 70 hour

The morphology of pulverized shell powder as shown in Fig. 4.a. indicates the random particle size and shape of the shell powder microstructure. The existence of irregular particle sizes and shape was due to the grinding for a short period. Fig. 4.b. shows the morphology of Powder milled for 45 hours in which the random particle size and shape of the powder were reduced and the majority of the particles obtained are in spherical shape. It is observed that there is a rise in particle agglomeration; this may be due to continuous fracturing and cold welding of powder particles from the shell. The cold welding of the fine particles can be attributed to the heat generated during the impact of the zirconia balls on the particles of the shell and the wall of the vial, which is sufficient to produce moisture that leads to cold welding. Fig. 4.c. shows the morphology of Powder milled for 70 hours. The microstructure present in the figure reveals the highest degree of fine particle agglomeration (nanoparticles) and less discrete fine particles. This can be due to an increase in impact time by the zirconia balls on the nanoparticles, as a higher degree of heat was produced leading to more humidity in the vial container resulting in cold welding of discrete fine particles on already agglomerated particles. This will not only create larger agglomerated particles but also resulted in less discreet fine particles. It can also be found that after milling for 70 hours; the smallest particle size was obtained compared with those milled at lesser hours. Using Image-J software, the particle sizes are measured. The average particle size of milled particles for 45 and 70 hours duration was 1.409 ± 1.011 µm and 60.23 ± 12.8 Nm respectively. From the result, it is evident that there has been a decrease in particle size as the milling period increases.

D. Energy Dispersive X-ray (EDX) spectrograph of wood apple shell powder

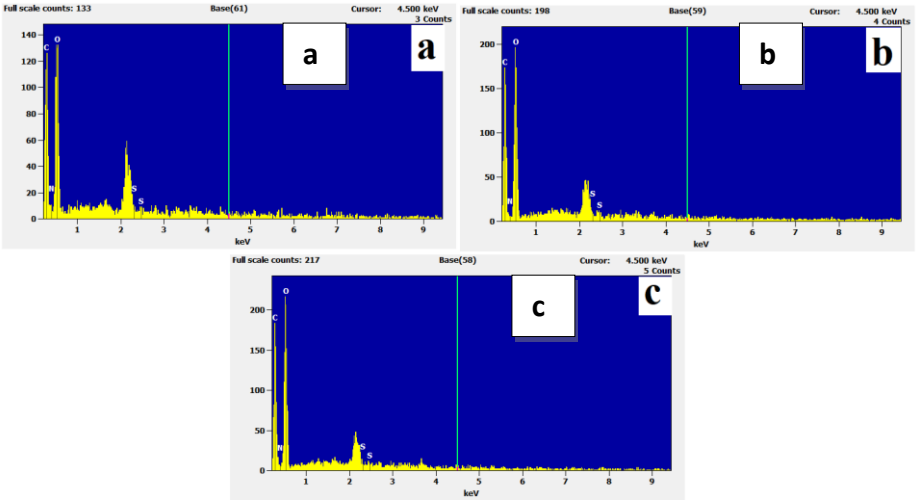

Figure 5. EDX of .a) Unmilled powder. b) Powder milled for 45 hours. C) Powder milled for 70 hours

Fig.5. a, b and, c shows the peaks of different elements that are present in the unmilled, milled shell particles for 45 and 70 hours. The weight % of different elements is shown in Table 1. The different elements which are present in the Unmilled powder, Powder milled for 45 and 70 hours are Carbon 27.55%, 26.97%, 26.55%, Nitrogen 3.98%, 3.05%, 3.35% and Oxygen 68.48%, 69.98%, 69.70%. Here the major constituent is oxygen and minor constituent is nitrogen, remaining peaks are impurities that are incorporated during the handling of samples.

TABLE I. QUANTITATIVE RESULTS FOR UNMILLED AND 45, 70 HOURS OF MILLED PARTICLES

Parameter	**Elements**			**Total**
	C	***N***	***O***	
Un milled	27.55	3.98	68.48	100
45 Hours Milled	26.97	3.05	69.98	100
70 Hours Milled	26.55	3.35	69.70	100

E. Particle size analysis of pulverized powder

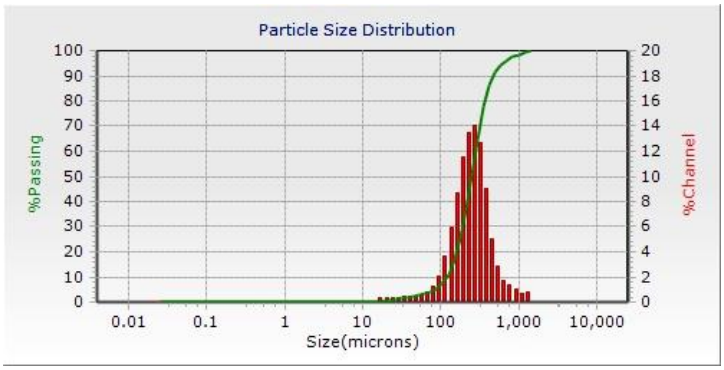

Figure 6. The particle size distribution of Unmilled powder

Fig. 6 displays the size distribution of Unmilled powder that are ranging from 20 to 1200 microns. It is observed from Fig. 6 that the particle size ranges from 200 µm to 700 µm are very broad. The average particle size was 284.8 ± 125.4 µm.

F. Transmission Electron Microscope(TEM) Micrograph of Nano shell powder

Fig. 7 shows a TEM micrograph of 70 hours of milled shell powder taken at 200 nm and 0.5 µm resolution. The image obtained from TEM has been more clearly showing the shape and size of the nanoparticles compared to the SEM image. It is clearly visible in the image that the particles were of spherical shape and the average particle size was 60.23 ± 12.8 nm. Few particles were agglomerated during processing for longer duration are observed in Fig 7b. In ball milling, contamination with surface and balls would cause more agglomeration in the processed samples.

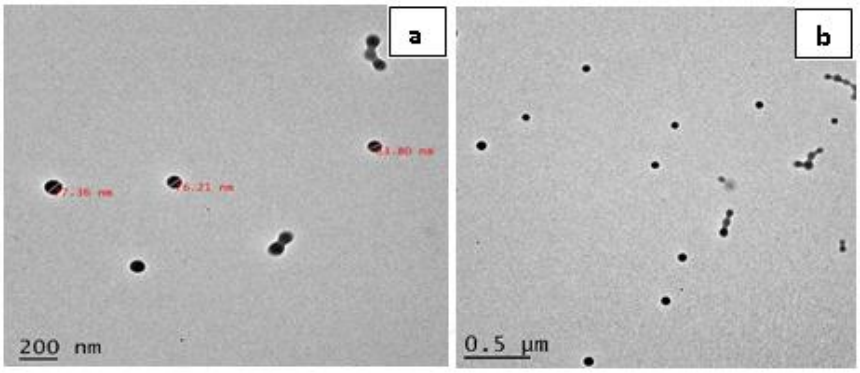

Figure 7. TEM image of shell powder milled for 70 hours. a) 200 nm, b) 0.5µm

G. X-ray diffraction(XRD)

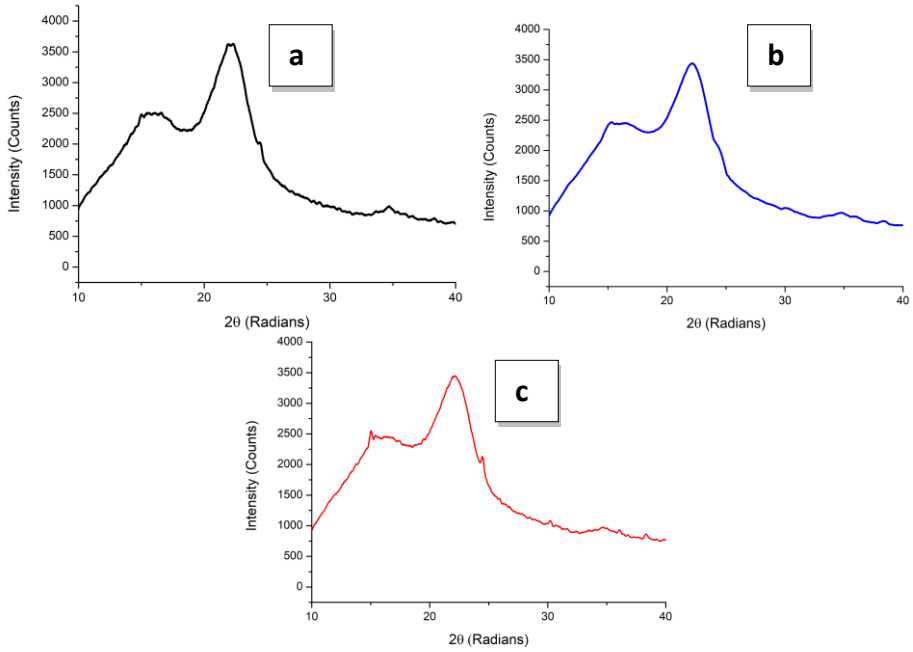

Figure 8. X-ray Diffractogram. a) Unmilled shell powder b) Shell powder milled for 45 hours c) Shell powder milled for 70 hours

Fig.8 shows a diffractogram of unmilled, 45 hours milled and 70 hours milled shell powder. It features two peaks, particularly well-defined for such a raw particle. The presence of these peaks of diffraction indicates the particle in semi-crystalline form. From the previous research work, it is shown that [24, 25], Cellulose I and cellulose IV, both of which have a monoclinic structure, can be ascribed to the two peaks at $2\theta = 16.3^{o}$ and $2\theta = 22.5^{o}$ [23, 24, 25]. Such two peaks are related respectively [20, 22, 21] to the crystallographic planes 200 and 1$\bar{1}$0. The crystallinity index (CI) is determined using the following relation:

$$CI = \frac{I_{22.5} - I_{18.5}}{I_{22.5}} \quad (1)$$

Where $I_{22.5}$ and $I_{18.5}$ are the diffracted intensities at $2\theta = 22.5^{o}$, $2\theta = 18.5^{o}$. $I_{22.5}$ is attributed to both crystalline and amorphous fraction whereas $I_{18.5}$ attributed to an amorphous fraction [26, 27]. The calculated CI of unmilled, 45 hours milled and 70 hours milled shell powder was 41.74%, 40.61%, and 38.33% respectively. The decrease in CI of 45 hours and 70 hours milled powder has been attributed to an increase in temperature during continuous milling of the powder for a long period.

4. CONCLUSION

The average size of the microparticles analyzed through particle size analyzer was 284.8 ± 125.4 μm and the SEM image depicts the existence of irregular particle sizes and shapes which can be attributed to grinding for a short period. The average size of the particles obtained after milling for 45 and 70 hours duration was 1.409 ± 1.011 μm and 60.23 ± 12.8 nm respectively. It shows that as the duration of milling increases the breaking tendency of the powder increases. The EDX analysis reveals that the milling duration does not affect much the chemical composition of the shell powder. The crystallinity index of the Unmilled powder and powder milled for 45, 70 hours was 41.74% and 40.61%, 38.33% respectively. Therefore, the synthesis of micro and nanoparticles from Limonia Acidissima shell powder indicates that proper charge ratio and sufficient ball milling duration are the significant factors.

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