

A study of the mechanical, thermal and morphological properties of microcrystalline cellulose particles prepared from cotton slivers using different acid concentrations

Kunal Das · Dipa Ray · N. R. Bandyopadhyay ·
Tony Ghosh · Amar K. Mohanty ·
Manjusri Misra

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Abstract Microcrystalline cellulose (MCC) particles are mostly prepared by acid hydrolysis of various agro sources. Acid hydrolysis is usually carried out with high concentration (64 wt%) of sulfuric acid. Here, an attempt has been made to optimize lower acid concentrations which can effectively produce MCC particles. In this work, different concentrations of sulfuric acid (20, 30, 35, 40, 47 and 64 wt%) have been used to prepare MCC particles, which have been characterized by XRD, particle size analysis, scanning electron microscopy, transmission electron microscopy, nanoindentation and thermogravimetric

analysis. MCC prepared with 35 and 47% sulfuric acid (MCC 35 and MCC 47) had finest particle size and fibrils were produced in the range of 15–25 nm. MCC 20 showed wide particle size distribution, indicating low breakdown of the cellulose chains. *The energy absorption behavior and mechanical properties of the MCC pellets were determined by nanoindentation test for the first time.* MCC 35 pellets exhibited lowest modulus and hardness.

Keywords Microcrystalline cellulose · Acid hydrolysis · X-ray analysis · Thermogravimetric analysis · Transmission electron microscope

K. Das · N. R. Bandyopadhyay
School of Materials Science and Engineering,
Bengal Engineering and Science University, Shibpur,
Howrah 711103, India

D. Ray (✉) · T. Ghosh
Department of Polymer Science & Technology,
University College of Science and Technology,
University of Calcutta, 92 A.P. C Road, Kolkata 700009,
India
e-mail: roy.dipa@gmail.com

A. K. Mohanty
Department of Plant Agriculture & School of
Engineering, Crop Science Building, University of
Guelph, Guelph, ON N1G 2W1, Canada

M. Misra
School of Engineering and the Department of Plant
Agriculture, Thornbrough Building, University of Guelph,
Guelph, ON N1G 2W1, Canada

Introduction

Microcrystalline cellulose represents a novel form of commercial cellulose and exists as a fine, white, odorless, crystalline powder. Because of its unique physical characteristics, MC cellulose has been used for many years in different industries like cosmetics, plastics, food, pharmaceuticals etc. But recently, environmental concerns have prompted the material scientists to explore MC cellulose as green filler in developing environment-friendly polymer composites.

In cellulose, which is built up of $\beta(1 \rightarrow 4)$ -linked D-glucose units, juxtaposition of several extended

cellulose chains permits extensive intra- and inter-chain hydrogen bonding and cellulose occurs as whisker like microfibrils in plants. In presence of strong acid and mechanical force, native cellulose breaks down into micro- or nanocrystalline cellulose particles (whiskers) with almost no weight loss. Due to its high aspect ratio and a high Young's modulus, these cellulose crystallites can be effectively used for preparation of high performance composite materials. This reinforcing capability results from the intrinsic chemical nature of cellulose and from its hierarchical structure.

Many researchers have reported on the preparation and characterization of MC cellulose particles prepared from various cellulosic sources (Chakraborty et al. 2005; Lu et al. 2006; Mathew and Dufresne 2002; Shlieout et al. 2002; Tang et al. 1996). Tang et al. (1996) evaluated the changes in the microcrystalline cellulose particles prepared from different sources like viscose staple, bagasse, ramie and cotton by dilute acid hydrolysis. They reported the changes in crystallinity, size of crystallites, grain size distribution and morphological features of the MCC particles. They concluded that recrystallization in some of the defective crystallites and degradation in the disordered areas of cellulose occurred simultaneously in the preliminary hydrolysis process during the production of MCC. Shlieout et al. (2002) investigated the powder and mechanical properties of MCC with different degrees of polymerization (DOP). They prepared MCC by acid hydrolysis of cellulose pulp with dilute hydrochloric acid and established a correlation between DOP and compactability and compressibility of the MCC particles. They concluded that crystallinity did not have a primary influence on the mechanical properties of the produced MCC tablets. Lu et al. (2006) prepared cellulose nanocrystals from ramie fibers by acid hydrolysis with 64% sulfuric acid. They ultimately prepared biocomposites with these nanocrystals as potential reinforcement and investigated those biocomposite films for various properties. Chakraborty et al. (2005) produced cellulose micro fibers by cryocrushing. A wide range of micro fibers were generated (0.1–1 μm). The high aspect ratio was the key tool for potential application of these micro fibers. Choi and Simonsen (2006) prepared cellulose nanocrystals from cotton with 65% sulfuric acid followed by neutralization and sonication. Chakraborty et al. (2007) prepared microfibrils (MF) from wood, <1 μm

in diameter, by combination of high shear and high impact and isolated by filtration through a mesh size of 60. Bhatnagar and Sain (2005) prepared MCC by acid hydrolysis after pretreatment of fiber with alkali. Angle's and Dufresne (2000), generated cellulose microcrystals or whiskers from tunicate (sea animal) using sulfuric acid (55 wt%). The mantle of tunicate is formed of cellulosic microfibrils (tunicin), which are very well organized and therefore highly crystalline. Mathew and Dufresne (2002) used sulfuric acid (55 wt%) to prepare cellulose whiskers from tunicate and used them as reinforcement in sorbitol plasticized starch film. Lu et al. (2005) investigated starch films reinforced with cellulose micro crystal prepared from cottonseed linters with 64% sulfuric acid. Habibi and Dufresne (2008) prepared highly filled bionanocomposites from functionalized polysaccharide nanocrystals. They used sulfuric acid (65 wt%) at 55 °C for 30 min to prepare the nanocrystals from ramie fiber. Bondeson et al. (2006) isolated nanocrystals from microcrystalline cellulose by acid hydrolysis with 63.5% sulfuric acid. They obtained nanocrystals/nanowhiskers with a length between 200 and 400 nm and a width <10 nm in 2 h. Cao et al. (2008) did acid hydrolysis (64% sulfuric acid) of flax fibers to prepare cellulose nanocrystals in the range 100–500 nm and used them as reinforcement to develop starch nanocomposites. Paul et al. (2008) prepared banana fibrils by steam explosion method and did their solvatochromic and electrokinetic studies. Apart from preparing cellulose nanofibrils, cellulose nanofiber network structure, cellulose nanopaper structures of high toughness are also being reported by some researchers (Henriksson et al. 2008; Iwamoto et al. 2008), which are opening new avenues for their diversified and environment-friendly applications.

Thus, preparation of MC cellulose from natural resources can be an effective means of producing biocomposites in an economic way. Although acid hydrolysis has been practiced for many years by many researchers, but in most of the works, the concentration of sulfuric acid is kept in the range 63–72 wt% (Chakraborty et al. 2005; Choi and Simonsen 2006; Lu et al. 2005; Habibi and Dufresne 2008; Cao et al. 2008). If this acid concentration can be reduced to a lower level, this will have both economic as well as an environmental benefit.

The present work investigates the possibility of preparing MCC particles with sulfuric acid of lower

concentrations and an attempt has been made to establish a structure-property correlation. To prepare the MCC particles, different concentrations of sulfuric acid were used for hydrolysis of cotton keeping other parameters like mechanical treatment, time, temperature, etc., constant. The MCC particles thus produced were subjected to X-ray diffraction study. The morphology of the particles was observed under scanning electron microscope and the size of the individual particle generated was measured with Transmission electron microscope. The particle size distribution was examined with the help of particle size analyser. Nanoindentation was carried out on MCC pellets to investigate their mechanical properties. The thermal degradation behavior of the particles was also examined with thermogravimetric analyser.

Experimental

Materials

Cotton slivers, collected from Hada Textile Mill, South Bishnupur, Kolkata, India, were used for preparing the microcrystalline cellulose (MCC) particles. Different % concentration of sulfuric acid (Merck) was used to prepare the MC cellulose particles.

Preparation of MCC

Microcrystalline cellulose (MCC) particles were prepared by acid-catalyzed hydrolysis of cotton slivers by a method similar to that used by some researchers (Dong et al. 1996). Acid solutions of concentration 64, 47, 40, 35, 30 and 20% sulfuric acid were used. Briefly, the calculated amount of cotton slivers were mixed with measured amount of sulfuric acid (with different % concentration) and vigorously stirred at 45 °C for 1½ h. A dispersion of cellulose micro crystallites resulted. After sonication, the suspension was neutralized with 0.5 N NaOH solution and then centrifuged and washed with distilled water.

Test methods

X-ray diffraction studies of the MCC samples were carried out by high resolution X-ray Diffractometer

(X'Pert PRO) Model RIGAKU MINISLEX with a scanning rate of 2 °C/min with CuK α radiation operating at 45 KV and 40 mA. Thermogravimetric analysis of the MCC samples was done with TGA-Model Pyris Diamond TGA/DTA (Perkin Elmer) with a heating rate 5 °C/min in nitrogen environment. The surface morphology of the MCC particles was investigated under SEM (Leica S 440) using a coating of Au–Pd alloy. TEM analysis was done with TEM, Technai Spirit Electron Microscope (SEI).

The bulk and tapping densities of the prepared MCC particles were determined as per the method mentioned by El-Sakhawy and Hassan (2007), in their work. For this test, an appropriate amount of the sample was poured in a 50 ml tarred graduated cylinder. The cylinder was lightly tapped twice to collect all powder sticking on the wall of the cylinder. The volume was then read directly from the cylinder and used to calculate the bulk density according to the relationship: mass/volume. For tapping density, the cylinder was tapped until there was no change in volume. The volume of the sample was then read and used in the calculation of tapping density. Particle size distribution was measured with Mastersizer 2000, Malvern Instruments Ltd, Malvern, UK MCC pellets were prepared for nanoindentation test. To make the pellets, a measured amount of MCC powder was compacted in a metal mold in a compression molding machine. The quantity of MCC powder and the pressure were kept constant in all the samples. Nanoindentation was carried out in NHTX-S/N: 0055-0109 CSM Instrument.

Results and discussion

Acid hydrolysis of cellulose causes bond cleavage, i.e., hydrolytic cleavage of glycosidic bonds between two anhydroglucose units. This action is counteracted by rearrangement of the tangling chain ends, which is favoured by release of internal strain. Thus the amorphous portion gets dissolved by the acid hydrolysis, leaving behind the crystalline regions. Acid hydrolysis followed by mechanical treatment results in disintegration of the cellulose structure into microcrystalline cellulose particles. In our study, MCC particles were prepared by 64, 47, 40, 35, 30 and 20% sulfuric acid solution, keeping other processing parameters constant. The particles

generated were dried to powder form and subjected to XRD study. The XRD graphs are shown in Fig. 1a, b. The crystallite size was calculated by using the Scherrer equation:

$$L_{h,k,l} = K\lambda/\beta \cos \theta \quad (1)$$

where, $K = 0.94$ (Revol et al. 1987). The microstrains were also calculated as per the formula:

$$\varepsilon = \beta \cos \theta/4 \quad (2)$$

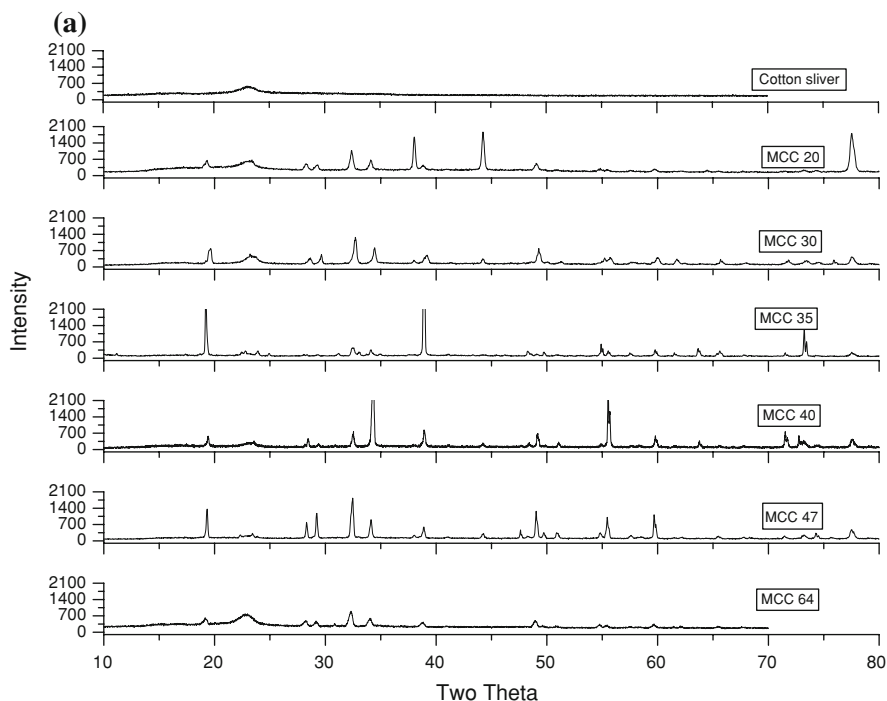
where β is the full width at half maximum of [101] peak. The crystallite sizes and the microstrains of the MCC samples are given in Table 1. The crystallite size was found to be lowest in MCC 64 and the microstrain developed was also lowest.

The particle size analysis of the dried powder samples was carried out to determine the particle size distribution in the samples. The particle size and particle size distribution depend on the structure of the source sample, acid concentration, temperature, time, procedure of hydrolysis and the mechanical treatment. The particle size distribution of the MCC particles is shown in Fig. 2. It was evident from Fig. 2 that MCC 47 and MCC 35 had very fine particles in the range 1–5 μm , which was not observed in other MCC samples. Apart from that,

MCC 47 had almost all the particles distributed within 1–100 μm , the highest vol% (6%) being at 22 μm . MCC 35 showed an almost similar type of distribution, with the peak (6 vol%) being at 30 μm . Along with that, MCC 35 also had larger sized particles in the range of 150–410 μm . MCC 64, MCC 40, MCC 30 and MCC 20 samples showed the major particle size distribution between 10 and 120 μm , the peak being within 30–34 μm . They all showed a second distribution range within 130–420 μm , where the peak was at 250 μm . In case of MCC 20, a broad hump was observed in the range 550–1,900 μm , indicating lower breakdown of cellulose chains. MCC 64 also showed a small fraction of particles in the high range. Thus, it was clearly evident that the breakdown of the cellulose chains and their re-entanglement and agglomeration were significantly dependent on the acid concentration used.

The MCC particles were investigated under SEM to determine their size, shape, nature of breakdown and surface morphology. The particle shapes were not isometric, but resembled the morphology of the source cotton. The MCC particles were observed to be flat, with a convoluted, ribbon like structure. The SEM micrographs of the MCC particles have been shown in Fig. 3a–f. Figure 3a (MCC 20) showed long

Fig. 1 XRD graph of the MCC samples **a** $2\theta = 10^\circ\text{--}80^\circ$, **b** $2\theta = 14^\circ\text{--}26^\circ$



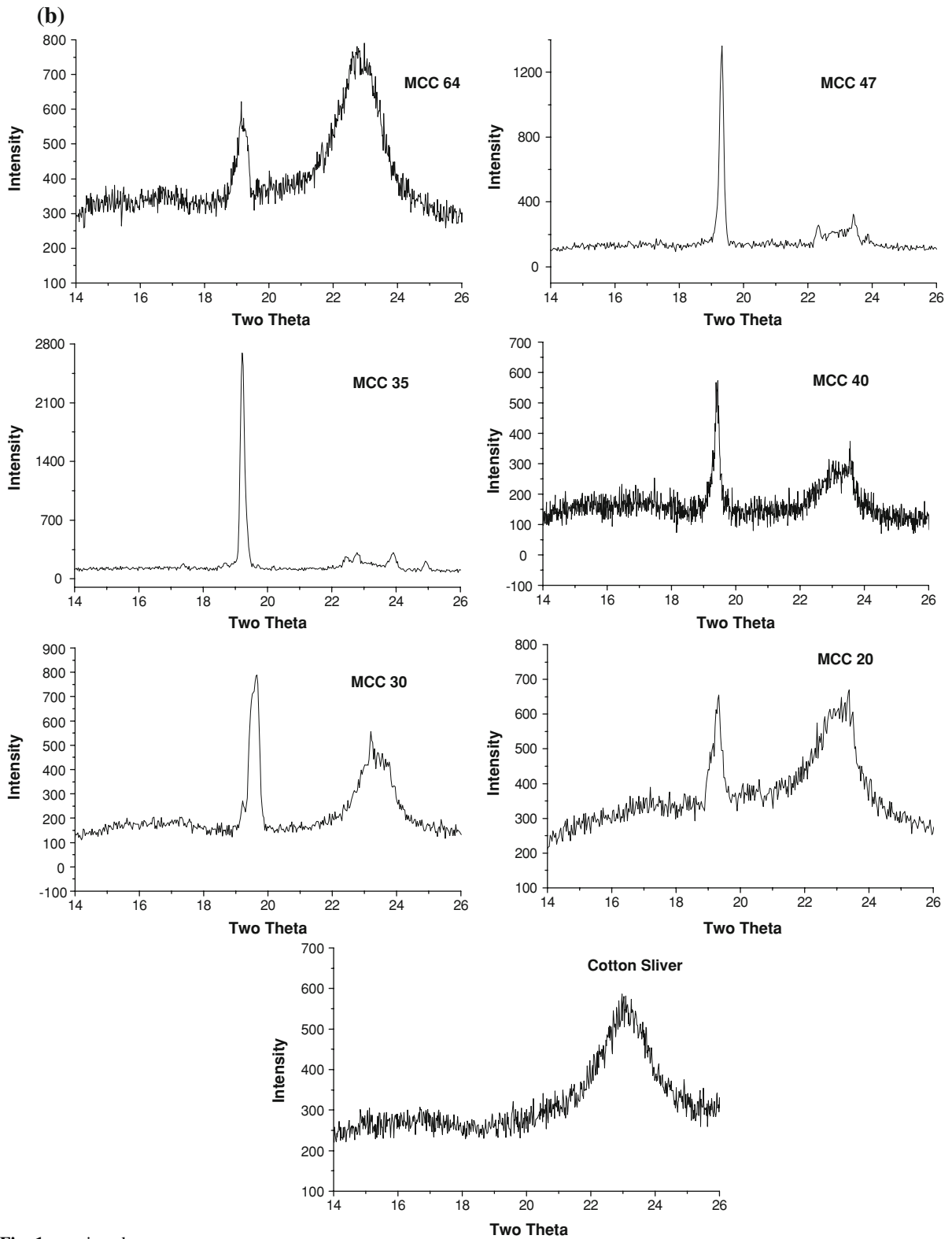
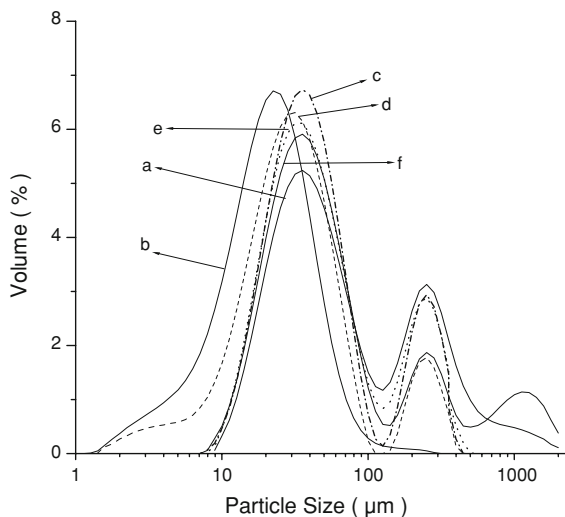


Fig. 1 continued

Table 1 The crystallite size and the microstrains developed in different MCC samples

Sample type	Reflection	Crystallite size (nm)	Microstrain
MCC 20	101	32.27	1.07
MCC 30	101	20.73	1.69
MCC 35	101	46.26	0.767
MCC 40	101	40.82	0.849
MCC 47	101	32.27	1.07
MCC 64	101	14.76	0.749

**Fig. 2** Particle size distribution of the MCC particles

cellulose microfibrils, indicating lower breakdown of the cellulose chains. Higher breakdown was evident in MCC 30 and MCC 35. In MCC 47, even smaller fragmentation was observed. In case of MCC 47 and specially for MCC 64, a powdery deposition was observed on the cellulose microfibrils.

Three sets of MCC particles (MCC 35, MCC 47 and MCC 64) in aqueous suspension were subjected to TEM analysis. TEM micrographs revealed that the particles generated were in nanometer range. The particles were found to be in 15–20 nm range for MCC 35 (Fig. 4a), 15–25 nm for MCC 47 (Fig. 4b) and 100–120 nm for MCC 64 (Fig. 4c). During drying, these nanoparticles were agglomerated to form larger particles in the micron range. However, it was evident that much finer particles were generated in case of MCC 35 and MCC 47 compared to MCC 64. This also corroborates well with Fig. 2, where MCC 35 and MCC 47 exhibited a fraction of very fine particles.

The bulk and tapping densities of the MCC particles have been shown in Fig. 5a and b, respectively. The bulk and tapping densities of MCC 35 and MCC 47 were highest compared to other MCC samples. As these particles were most fine in nature, hence their compaction was higher leading to higher densities. This supported our previous observations.

Microcrystalline cellulose pellets were subjected to nanoindentation test and the load-penetration graphs are shown in Fig. 6. The penetration of the nanoindenter on the surface of the MCC pellet was governed by many factors like degree of compaction of the MCC particles in the pellet, the structure of MCC particles, porosity of the particles etc. MCC 30, MCC 40 and MCC 47 showed almost similar nature of curves, indicating nearly same absorption of energy during loading/unloading cycle. In MCC 20, penetration was much less and the deformation was predominantly elastic type. Much smaller energy was absorbed for viscous dissipation. Much less breakdown of the cellulose chains and presence of larger sized particles might be responsible for such behavior. In MCC 64, penetration was slightly higher and some elastic energy recovery was also observed during unloading. In MCC 35, the depth of penetration was significantly higher than all other MCC samples and the viscous energy dissipation was very high. MCC 35, having a very wide particle size distribution, might have given rise to porous aggregates, which underwent fragmentation during nanoindentation, forming smaller plastically deformable MCC particles, which showed such a high viscous dissipation. Modulus and hardness of the MCC pellets obtained from the nanoindentation test, are shown in Fig. 7a and b, respectively. MCC 35 was found to have lowest modulus and hardness, which could be due to formation of porous aggregates as mentioned above.

The MCC particles were subjected to TGA. The loss in weight of the MCC particles with the rise in temperature and their rates of degradations are shown in Figs. 8 and 9, respectively. It was observed that MCC 35 and MCC 47 exhibited two degradation peaks unlike other MCC samples (Fig. 9). MCC 35 showed two peaks at 235 and 286 °C, respectively, while MCC 47 showed the two peaks at 242 and 282 °C, respectively. The first peak could be due to dehydration of cellulose to dehydrocellulose, while the second peak could be due to depolymerization of

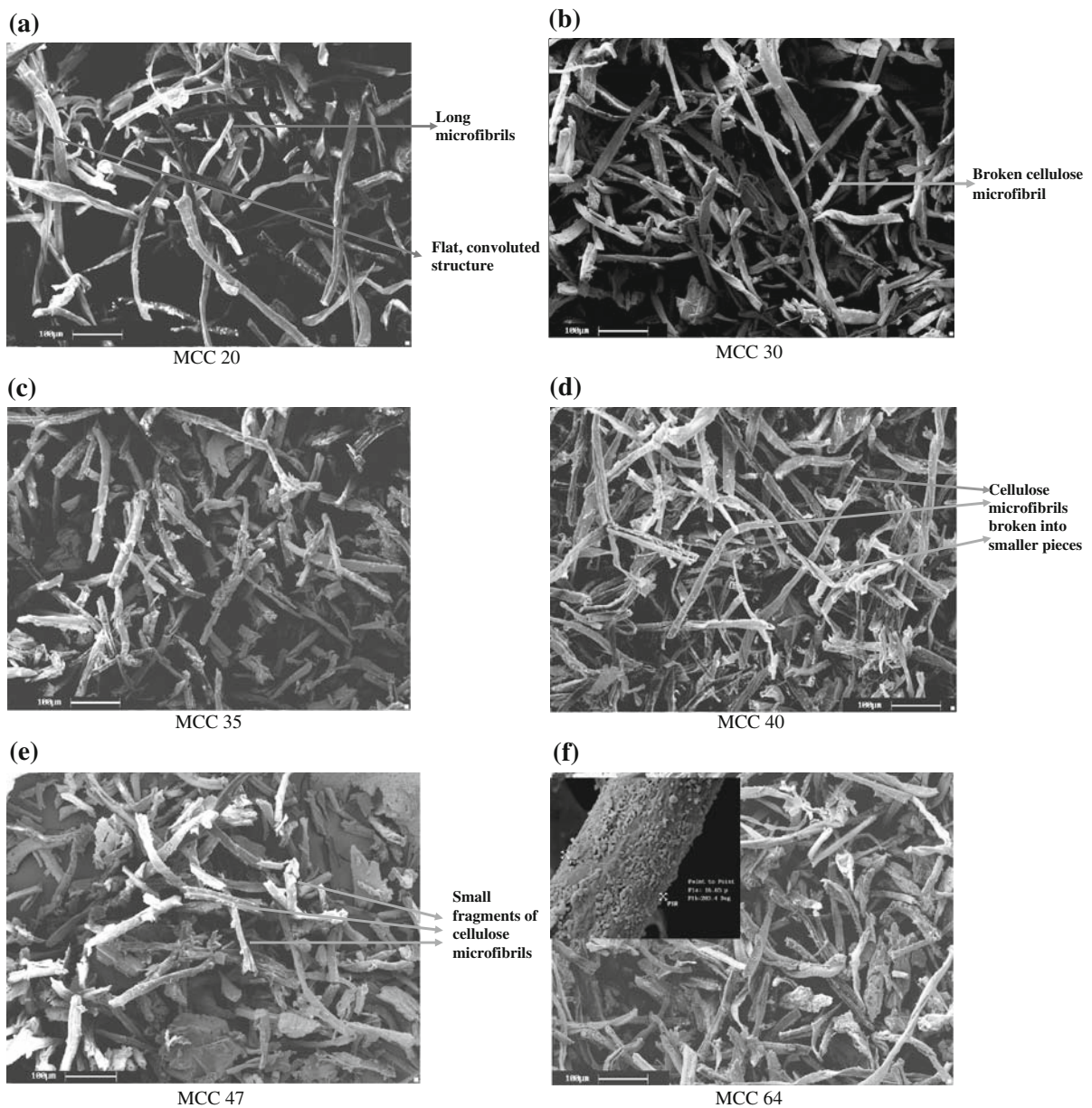


Fig. 3 Surface morphology of the MCC particles prepared **a** MCC 20, **b** MCC 30, **c** MCC35, **d** MCC 40, **e** MCC 47, **f** MCC 64

cellulose in competition of dehydration (Concise encyclopedia of wood and wood based materials; Klemm et al. 2004). The dehydration peaks were prominent in MCC 35 and MCC 47 only, which could be due to the presence of very fine particles in these samples (observed from Fig. 2). The rates of degradation of cellulose were also very low in both these MCC samples, yielding a large amount of residue (Fig. 8). The cellulose depolymerization peak

shifted to a much higher temperature 350 °C for MCC 40, 331 °C for MCC 64 and 302 °C for MCC 30, respectively. If the thermal stability of the samples is considered in terms of their char residue, then it can be said that all the MCC prepared from cotton had higher thermal stability than cotton. And also the MCC particles prepared by lower acid concentration (47–20%) showed higher thermal stability than MCC 64, highest being in case of MCC 35

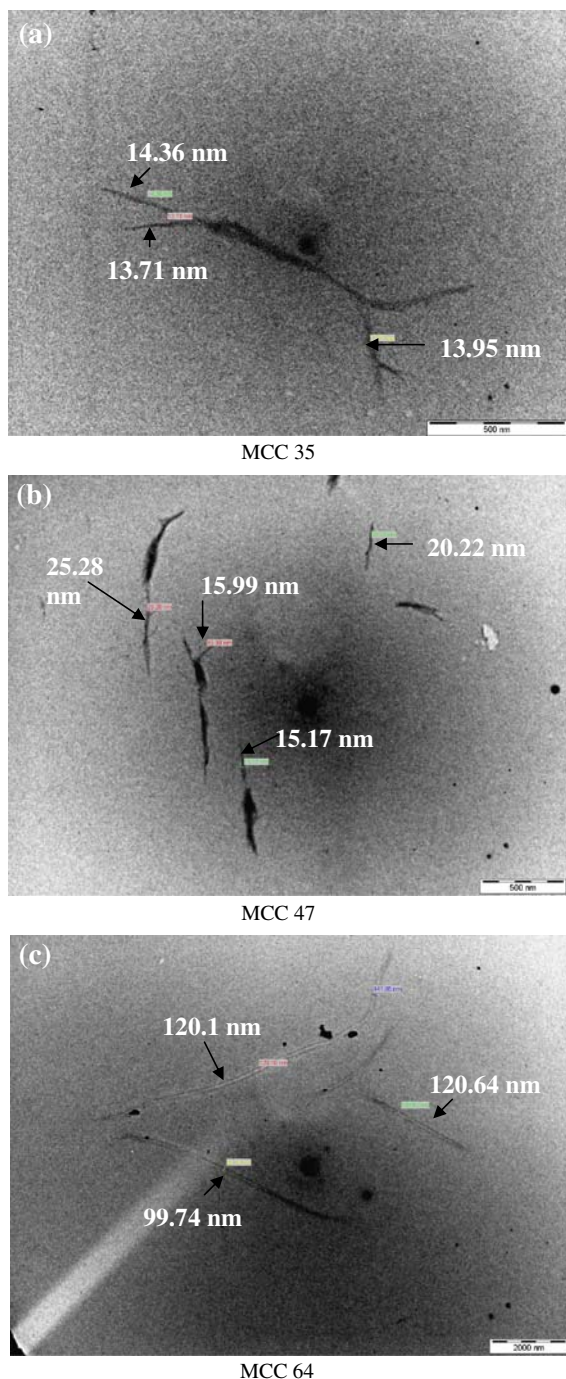


Fig. 4 Transmission electron micrographs of the MCC particles prepared **a** MCC 35, **b** MCC 47, **c** MCC 64

followed by MCC 47. The lower residue of MCC 64 could be due to the splitting of the sulfate groups during thermal degradation process, which are formed onto the cellulose chains during sulfuric acid

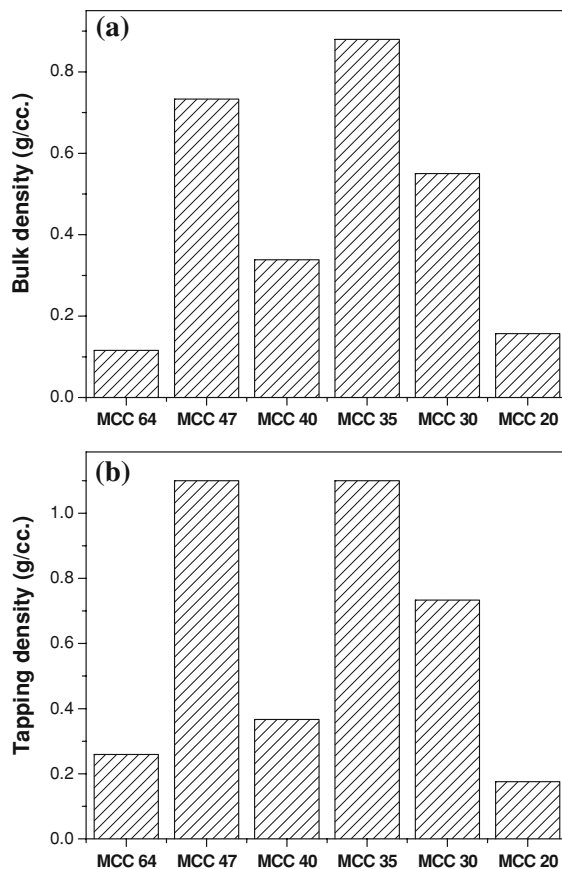
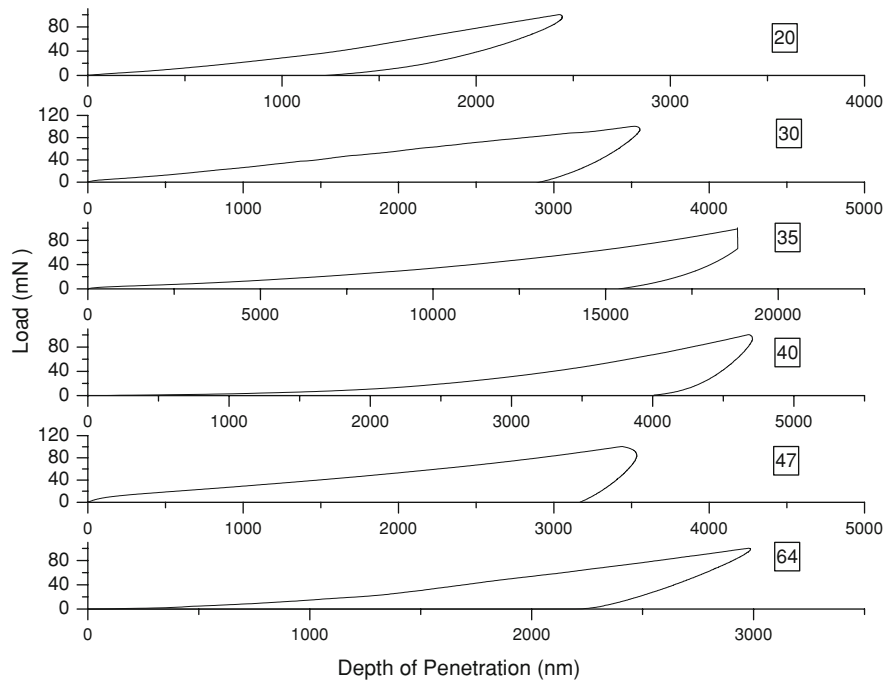


Fig. 5 **a** Bulk density of the different MCC samples. **b** Tapping density of the different MCC samples

treatment, which might have affected the degradation onset temperature, rate of thermal degradation and the residue left (Klemm et al. 2004).

Hydrolysis of cotton by H_2SO_4 is a heterogeneous reaction (Xiang et al. 2003). The reaction is influenced by the reaction conditions like acid concentration, temperature, time, mechanical agitation, etc., and also by the physical state of the cellulose. Among all the factors, concentration of the acid is one of the key parameters which determine the resulting nature of the microfibrils (Samir et al. 2004). From our observations, it was evident that MCC 35 was the most flexible one, showing significantly higher penetration during nanoindentation test compared to all other MCC samples. MCC 35 also showed lowest hardness and modulus values (Fig. 7a, b). Also, the crystallite size of MCC 35 was higher than the other MCC samples. All these observations were indicative of the fact that there was a significant

Fig. 6 Nanoindentation curve of the MCC pellets using 100 mN load



structural transition at this acid concentration. This has also been reflected in the XRD graphs (Fig. 1a, b). It is well known that the cleavage of glycosidic bonds during acid hydrolysis is counteracted by rearrangement of the tangling chain ends, which is favoured by release of internal strain (Xiang et al. 2003; Klemm et al. 2004). It is apparent from all the data that at 35% acid concentration, a rearrangement of the tangling chain ends might be predominant, which gave rise to higher crystallite size and released the internal strain. When this happens, the chains do not go back to their original orderly structured fibrillar form but form an irregular bundle (Xiang et al. 2003). This new rearrangement might be responsible for a very high penetration, lower modulus and lower hardness values compared to other samples. The higher thermal stability of MCC 35 samples (Fig. 8) could also be due to this tangling effect (Samir et al. 2004). With increase in acid concentration from 35 to 64%, the crystallite size gradually decreased. This is ascribed to the probability of stronger hydrolysis at higher concentration, which removed the amorphous domains more effectively and lowered the crystallite size (Samir et al. 2004).

The XRD graphs of the MCC samples revealed that the breakdown of the cellulose chains during acid

hydrolysis, their crystal packing, molecular conformation, intermolecular H-bonding pattern were significantly different in the different MCC samples depending on the concentration of acid used for hydrolysis. These differences also influenced their aggregation states during the drying process and gave rise to a different particle size and particle size distribution.

Conclusion

Microcrystalline cellulose particles are versatile reinforcements for the biocomposites. Experimental results indicate that 30–47% concentration of sulfuric acid can yield very fine structured MCC particles from cotton. These MCC particles can be explored extensively in modifying the properties of biocomposites. MCC 35 and MCC 47 had individual particles in the range of 15–25 nm as observed from TEM, which were agglomerated during drying. In the particle size analysis also, these two MCC samples showed the existence of very fine particles in 1–5 μm range, which was not evident in other MCC samples. Nanoindentation test of the MCC pellets exhibited lowest modulus and hardness for the MCC 35 samples. This could be due to the formation of a

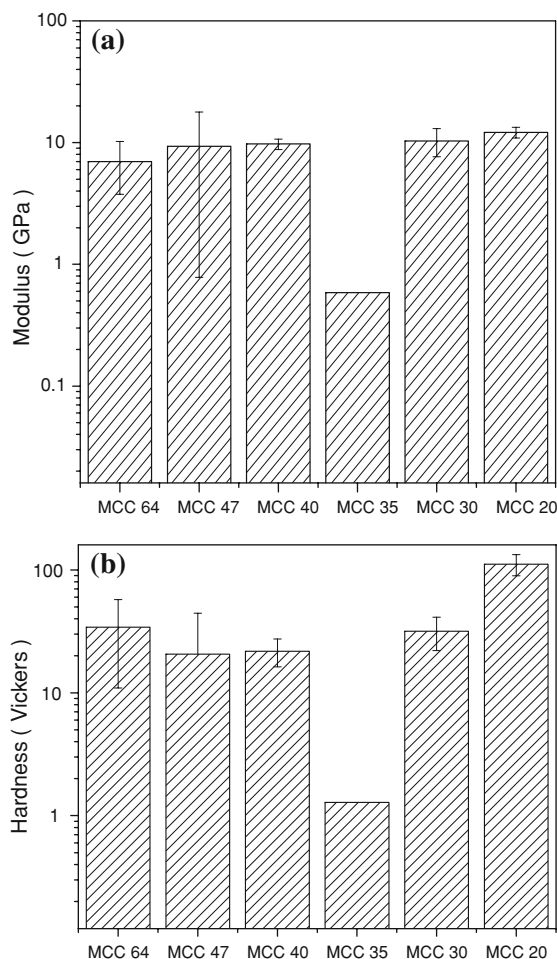


Fig. 7 The **a** modulus **b** hardness of the MCC pellets as measured from Nanoindentation test

porous aggregate during pelletization, which had facilitated a high plastic deformation of these MCC particles during the nanoindentation test. The thermal stability of all the MCC samples was found to be higher than their source cotton. The rates of degradations were lowest and the residue left were highest in case of MCC 35 and MCC 47. Thus, the MCC particles prepared by using different concentrations of acid showed significant differences in their properties. This work clearly indicates that sulfuric acid can be used successfully to yield MCC particles at a lower concentration (35–47%), compared to what is extensively practiced now (64%) and natural resources like cotton can be used as source for generating MCC particles, having tremendous potential as reinforcement for green biocomposites.

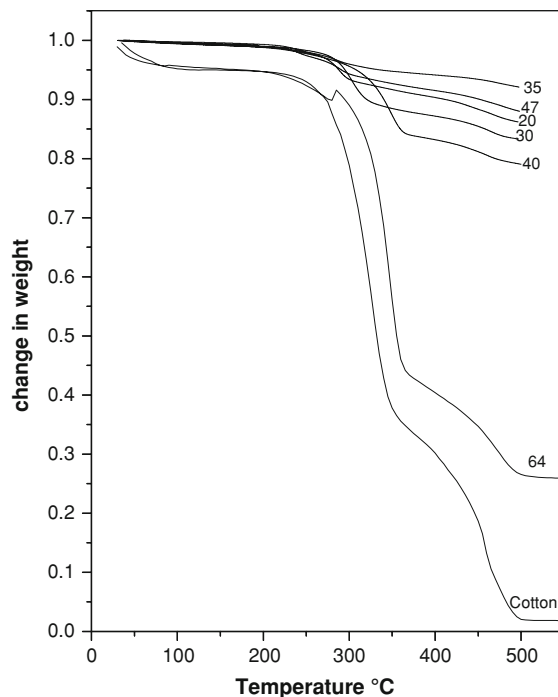


Fig. 8 TGA curve of cotton and different MCC particles as a function of temperature

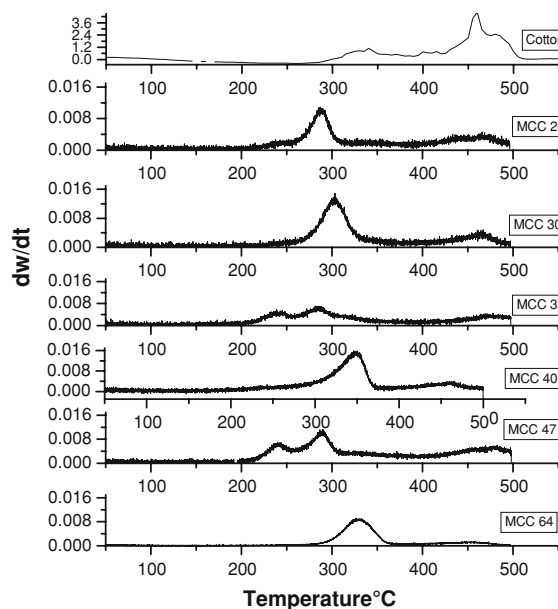


Fig. 9 Rate of degradation of the MCC samples with the rise in temperature

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