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Study of Microstructure of Manganese (II) - Bakelite Composite after Carbonization

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ABSTRACT

This study reports the alteration in the microstructure and morphology of Mn (II) bakelite composite with variable salt concentration on thermal decomposition at high temperatures of 750ºC and 950°C for 6 hours through SEM, AFM and DLS. The structural characterization shows a decreasing trend in microstructure particle with increase in decomposition temperature.

1. INTRODUCTION

Metal Matrix Composites (MMC) are always preferred due to its low weight, high strength and high thermal conductivity attribute, but, its elevated cost makes it limited in daily requirements. The remarkable attributes of Polymer Matrix Composites (PMCs) such as low fabrication cost, low density is still secondary choice in fields requiring high thermal and electrical conductivity [1]. Lot of research work is done in designing and fabricating low-cost MMC with high strength, thermal and electrical conductivity which can serve in multiple fields. The MMC with polymer as reinforcement in producing low cost with several attributes of metal can help in overcoming the limitations [2].

High pressure impregnation carbonization method [3-6] on polymers [7,8] and composites [9] is used in generating innovative carbon products such as carbon nanotubes, Nanorods, spheroids, spherules, glassy carbons, onions, fullerenes with diameters of 30−70 nm and lengths of several micrometer by researchers to use them in diverse fields. The carbonized product hold promising in designing molecular sieves [10-13] and adsorbents [14] for enhancing mechanical attribute and electromagnetic interference shielding of cementitious materials [15]. But the HTHP method does not look economically attractive in large scale production due to its expensive nature [23]. Thermal decomposition of composites in muffle furnace at high temperatures can produce nanotubes [24] microparticles and magnetic nanocomposites [25] at low cost.

Bakelite is a synthetic polymer with multi-utilities due to its strength and ablative nature. The low cost of polymer and variable attributes such as high-temperature ablation and charring yield and high melting temperature [26] is expansively studied with various metal incorporation and its several modifications in form of composites [27]. The carbonized phenolic resin have found its application as polarizable electrodes of the electric double layer capacitors with high capacitance, high working voltage, high reliability and low leakage current [28]. Manganese polymer composite developed are extensively studied for its electrical and optical properties [29-30]. The carbonized product of Mn (II) bakelite composite formed by incorporating bakelite, in low-cost manganese salt which possesses highly unpaired electrons, is not yet reported. Thus the present investigation is focused on preparing Mn (II)-bakelite composites and to study its carbonized microstructure.

2. EXPERIMENTAL

2.1 Materials

Phenol was supplied by Fine Chemicals (India). Formaldehyde and Hydrochloric acid were supplied by Fisher Qualigens Scientific, Qualigens (India). Glacial acetic Acid was purchased from Central Drug House (P) Ltd (India). Manganese (II) Chloride tetrahydrate 98% ($MnCl_2.4H_2O$) was supplied by Sigma-Aldrich ACS reagent (India). Distilled water which was used to prepare composites was of chemically pure grade. Metal solutions were prepared by dissolving appropriate amount of its chloride salt in distilled water. The samples were decomposed using muffle furnace KLS 03/10 with T-max 1000^oC.

2.2 Sample preparation

The composites were prepared by stir casting method. The homogenous solution of matrix salt was prepared by adding 0.5gm and 2gm $MnCl_2.4H_2O$ in 5 ml distilled water. The metal matrix composites are prepared by adding the Bakelite reaction salts and chemicals as reported earlier [31]. The dried red lustrous MMC were mentioned as 0.5% Mn (II) bakelite and 2% Mn (II) bakelite composite. The 0.5% Mn (II) bakelite composite was decomposed at 750^oC and 2 % Mn (II) bakelite composite was decomposed at elevated temperature of 950^o C for 6 hours. The black carbonized product obtained was further crushed to powder using pestle and mortar and characterized to study its micro behavior.

1.3 Characterization

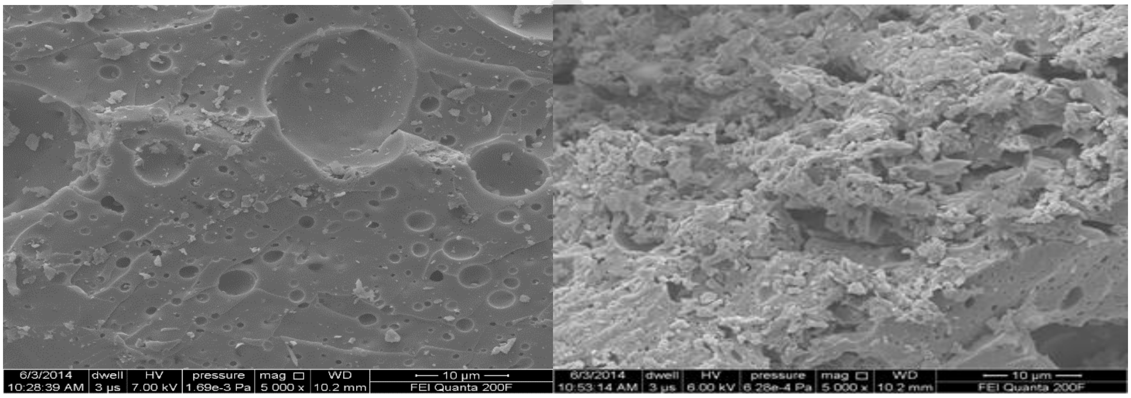
The morphology of the carbonized sample was characterized by Scanning Electron Microscope (SEM) using FEI Quanta 200F, with magnification 250 X to 1000X. Surfaces of the samples were coated with a thin layer of gold by the vacuum evaporation technique to minimize sample charging effects due to the electron beam. Atomic Force Microscopy (AFM) was done using AFM -XE 70, Park Systems - Korea in vibrating mode. Particle size was determined by Diffraction Light Scattering (DLS) Zetasizer Malvern, Nano ZS90 – UK.

3. RESULT AND DISCUSSION

3.1 Microstructure analysis of carbonized Mn (II)-bakelite composites

3.11 SEM of carbonized Mn (II) - bakelite Composite

SEM was used to investigate the effect of carbonization temperature on microstructure of 0.5% and 2% Mn (II) bakelite composite. SEM images suggest metal concentration and temperature dependence behavior on morphology of composite. Figure 1a revealed uniform distribution of $MnCl_2.4H_2O$ and bakelite in 0.5% Mn (II) bakelite Composite decomposed at 750°C with appearance of white spots due to aggregates of Manganese salt. This indicates interaction and complex formation of manganese salt with the polymeric matrixes [32]. There are evident voids seen on the surface of MMC due to water domain formed during condensation [33]. The fine metal particles are well encapsulated in bakelite. Figure 1b suggests that as the manganese salt content is increased in matrix and carbonization temperature is raised to 950°C, highly rough ganglia- like hills with some wrinkles (spherical longitudinal shapes) is observed [32]. It is observed that on increasing temperature the microparticle with size ranging in micrometers appears. The metal is firmly encapsulated in polymer network suggesting the firmness of material. The size and frequency of void appearance decreases with increase in concentration of metal salt and decomposition temperature.

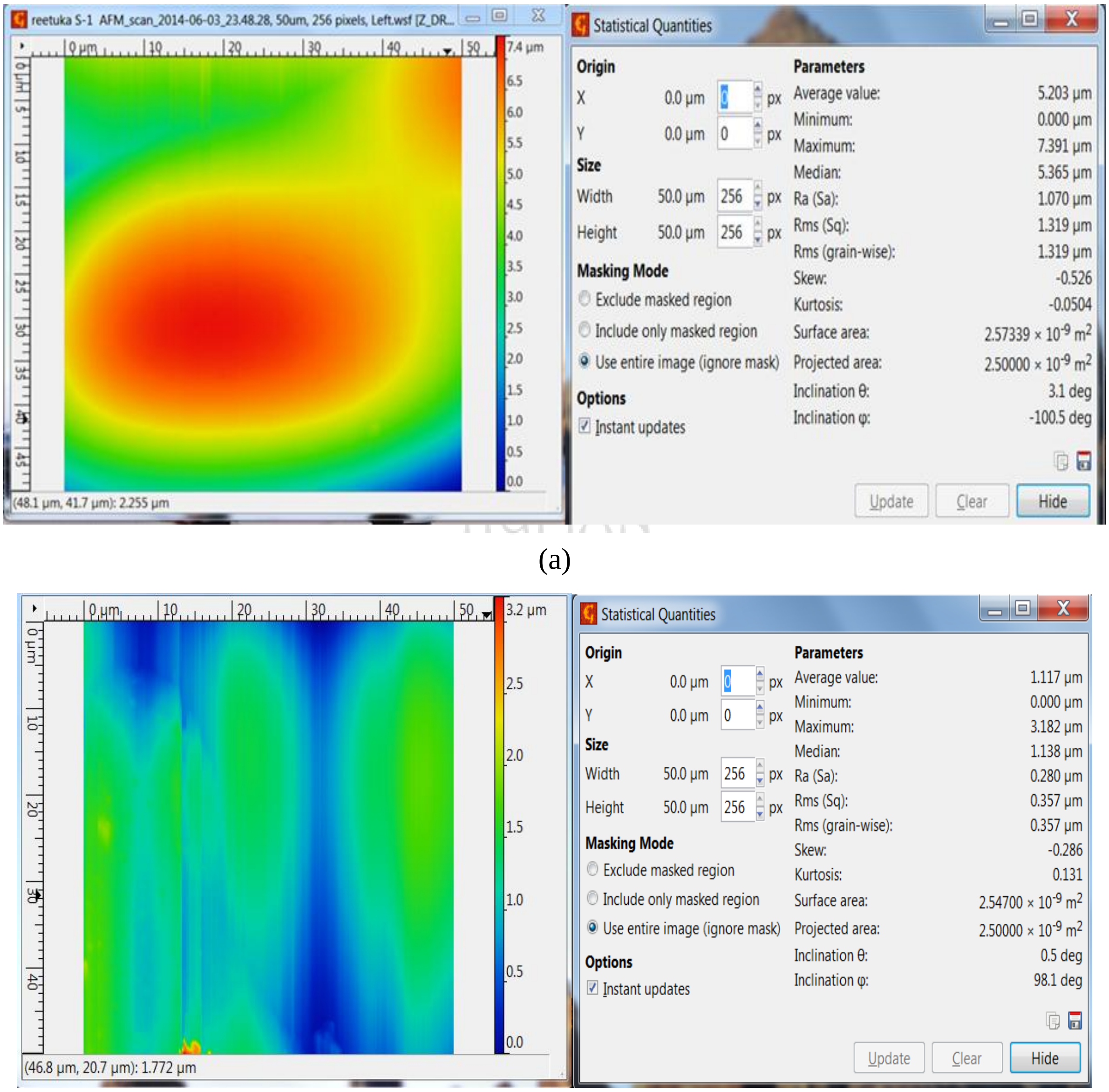


(a) (b)

Fig. 1: SEM images of (a) 0.5% Mn(II) bakelite composite (b) 2% Mn (II) bakelite composite.

3.12 AFM of carbonized Mn (II) bakelite composite

The surface morphology of Mn (II) bakelite MMC thin films were observed on 50 × 50 μm^2 area by AFM and particle size was analyzed. The AFM images Figure 2a display the film surface of 0.5%Mn (II) bakelite decomposed at 750°C and Figure 2b displays the film surface of 2% Mn (II) bakelite composite decomposed at 950°C which indicates that as the temperature is increased the size of particle get decomposed to form small microstructures. The photographs revealed that the average particle size of 0.5% Mn (II) bakelite composite to be 5.2µm which decrease to 1.117 µm in 2%Mn (II) bakelite with increase in decomposition temperature. This also accounts for proximity of metal and carbonized products with increase in decomposition temperature and be responsible for inculcation of new properties in the composite. Figure 3 a and 3b display particle height of 0.5% and 2% Mn bakelite composite decomposed at 750°C and 950°C respectively. It reveals that particle height also decreases with increase in temperature from 8.1µm to 3.2µm which confirm there is surface transformation and decrease in particle size with increasing temperature as corroborated in SEM.



Origin

X	0.0 µm	0 px
Y	0.0 µm	0 px

Size

Width	50.0 µm	256 px
Height	50.0 µm	256 px

Masking Mode

○ Exclude masked region
○ Include only masked region
● Use entire image (ignore mask)

Options

☑ Instant updates

Parameters

Average value:	5.203 µm
Minimum:	0.000 µm
Maximum:	7.391 µm
Median:	5.365 µm
Ra (Sa):	1.070 µm
Rms (Sq):	1.319 µm
Rms (grain-wise):	1.319 µm
Skew:	-0.526
Kurtosis:	-0.0504
Surface area:	2.57339×10^{-9} m^2
Projected area:	2.50000×10^{-9} m^2
Inclination θ:	3.1 deg
Inclination φ:	-100.5 deg

(a)

Origin

X	0.0 µm	0 px
Y	0.0 µm	0 px

Size

Width	50.0 µm	256 px
Height	50.0 µm	256 px

Masking Mode

○ Exclude masked region
○ Include only masked region
● Use entire image (ignore mask)

Options

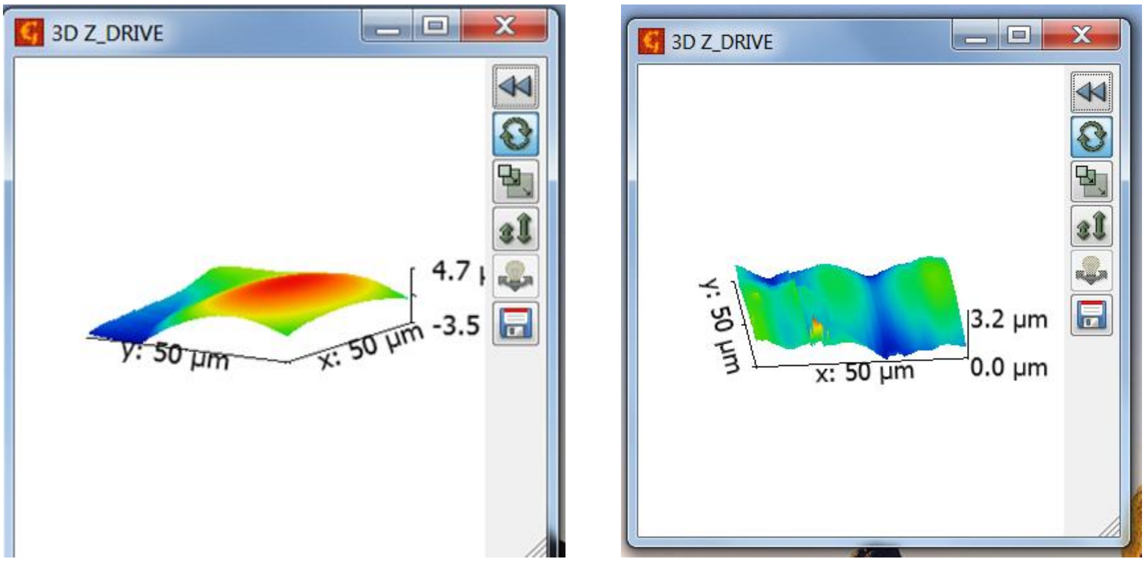
☑ Instant updates

Parameters

Average value:	1.117 µm
Minimum:	0.000 µm
Maximum:	3.182 µm
Median:	1.138 µm
Ra (Sa):	0.280 µm
Rms (Sq):	0.357 µm
Rms (grain-wise):	0.357 µm
Skew:	-0.286
Kurtosis:	0.131
Surface area:	2.54700×10^{-9} m^2
Projected area:	2.50000×10^{-9} m^2
Inclination θ:	0.5 deg
Inclination φ:	98.1 deg

(b)

Fig. 2: AFM images of particle size of (a) 0.5% Mn (II) bakelite composite (b) 2% Mn (II) bakelite composite

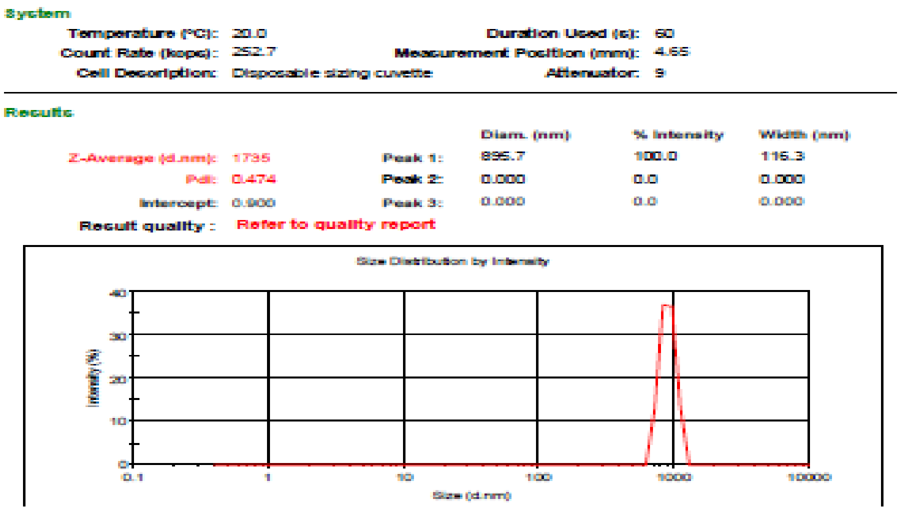


(a) (b)

Fig. 3: AFM images of particle height (a) 0.5% Mn-bakelite composite (b) 2% Mn–bakelite composite

3.13 DLS of carbonized Mn (II)-bakelite composites

The size distribution of 0.5% Mn (II) bakelite composite decomposed at 750^{o}C and 2 %Mn (II) bakelite composite decomposed at 950^{o}C dispersed in dimethyl sulphoxide (DMSO) is shown in Figure 4a and 4 b respectively. The Z- Average value from intensity overlay for higher decomposition temperature with higher concentration of MMC is 783.5 d.nm while with lower decomposition temperature with lower concentration of MMC is 1735 d.nm. The result illustrates decrease in particle size with increase in decomposition temperature.



System

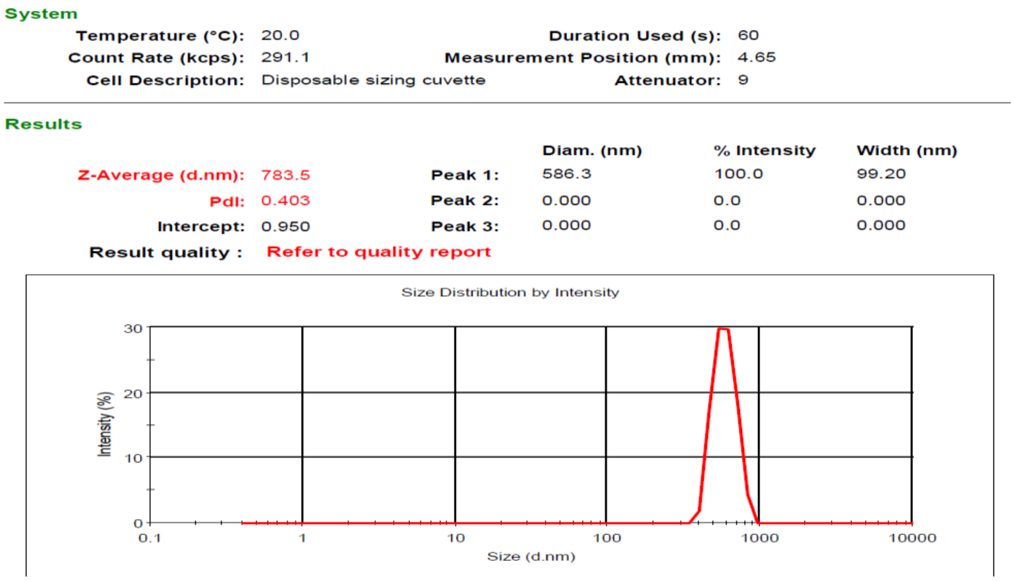
Temperature (°C): 20.0
Count Rate (kcps): 252.7
Cell Description: Disposable sizing cuvette
Duration Used (s): 60
Measurement Position (mm): 4.65
Attenuator: 9

Results

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	1735	Peak 1:	895.7	100.0	116.3
PdI:	0.474	Peak 2:	0.000	0.0	0.000
Intercept:	0.900	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report

(a)



System

Temperature (°C): 20.0

Duration Used (s): 60

Count Rate (kcps): 291.1

Measurement Position (mm): 4.65

Cell Description: Disposable sizing cuvette

Attenuator: 9

Results

Z-Average (d.nm): 783.5

PdI: 0.403

Intercept: 0.950

Result quality : Refer to quality report

	Diam. (nm)	% Intensity	Width (nm)
Peak 1:	586.3	100.0	99.20
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

(b)

Fig. 4: DLS Intensity overlay of (a) 0.5% Mn (II) bakelite composite (b) 2% Mn (II) bakelite composite

4. CONCLUSION

Mn (II)-bakelite with variable metal concentration, metal matrix composites were prepared by simple stir casting method. The low priced composites were further decomposed at higher temperature of 750°C and 950°C for 6 hours to study its microstructure properties on carbonization. The resulting decomposed composites were fully characterized by SEM, AFM and DLS. The carbonization of composite suggests that with the increase in decomposition temperature, there is decrease in the size of new microparticles formed. The carbonized Mn (II)-bakelite MMC can be used as adsorbents in clean water due to increased surface area. Further studies on electrical and magnetic nature of MMC can suggest its promising role in electronic devices as the proximity of metal particle in the composite also increased with rise in decomposition temperature.

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