



Preparing Calcium Carbonate Nanoparticles from Biomass Waste and its Application as Fire-Retardant Agent

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Abstract

Biomass waste (calcium carbonate) nanoparticles were prepared from eggshell waste using ball mill treatment and characterized. These particles made from waste eggshell derived into nano calcium carbonate (WESNCC) were developed that could be easily integrated and effectively dispersed into polymers. Fire tests like ignitability, limiting oxy-index, and thermal stability were carried out using wood specimens painted with polymers where specimens showed good properties in fire retarding. The addition of biomass waste (calcium carbonate) nanoparticles was found to increase the flame retardant effectiveness of resin systems. The use of biomass waste (calcium carbonate) nanoparticles improved the physical characteristics of the char by increasing the amount of the insulating layer and reducing crack formation. The developed intumescent resin using Biomass waste (calcium carbonate) nanoparticles as an additive showed markedly improved results for time to ignition, heat absorbed, mass loss, and flame spread. The smoke from burned resin/graphite system was reduced compared to that obtained from the intumescent resin alone.

Keywords: Food waste, Calcium carbonate, Eggshell waste, Fires retardant agents.

Introduction

Flame retardants are defined as chemical agents that can withstand direct flame by stopping flame entry into the material, controlling its spread, and even extinguishing utterly. These materials can be added during or after the products fabrication for burning protection. The development of flame retardants allowed the safe usage of fabrics that cause flammable behavior by reducing flammability and the rate of burning. The compounds of phosphorus, nitrogen, chlorine, bromine, boron, and antimony are widely used for flame retardation [1-9]. Many materials with flame retardant properties have been known for many centuries. The earliest use of flame retardants was by the eastern civilizations, specifically by the Egyptians and Chinese. About 3000 years ago, the ancient Egyptians soaked grass and reed in seawater and rivers before they used it for roofing, so when the grass and reed dry, the mineral salts crystallized and acted as a fire retardant. The Egyptians and Chinese also used alum and vinegar to paint timbers in temples to protect them from fire [10-13].

As fires form a big problem, the increased solid waste is now becoming a challenge for a sustainable world. Improper management of those wastes leads to public health and environment related problems [14]. Huge amounts of solid wastes, including municipal, industrial and hazardous wastes have been generated worldwide. Food wastes are the major solid wastes causing problems in the environment. Industrialization and population growth are the major factors for the increase in solid wastes. Eggshell is a solid waste which contributes to degradation in the environment. Households, restaurants, and bakeries are the major source of eggshell [15]. The main component of egg shell is pure calcium carbonate with little porosity [16]. This waste can be transformed into valuable products like nano particles of calcium carbonate with different applications [17, 18], as it can be added to polymers to reduce cost and improve their fire retarding properties.

Materials and Methods

Toluene, Phenol, acetone, maleic anhydride, tetra bromo bis phenol-A, sodium hydroxide. Chloroform, dioxins, benzyl alcohol, styrene monomer. Benzoyl

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peroxide. Diol (1, 5-pentane diol), all chemicals were supplied by Sigma Aldrich Co. with purity 99, 9% and directly used. Biomass waste (egg shells) from surrounding environment.

Preparation of poly (tetra bromo bisphenol-A-co-maleic anhydride-co-1, 5-pentane diol) (copolymer 1) [19]:-

Bulk polyesterification reactions were carried out by the reaction of bis phenol-A, tetra bromo bis phenol-A and acid anhydride (maleic anhydride) with glycol (1, 5-pentane diol) in the molar ratio 1:2:1, respectively in the reaction flask which was dipped in an oil bath (thermostatically controlled) provided with a mechanical stirrer and dean-stark trap to collect the water. A pipette was inserted through a stopper down to the bottom of the flask to introduce as slow stream of dry deoxygenated nitrogen in order to facilitate the removal of water produced. A long reflux condenser was connected to the outlet of the effluent stream of nitrogen containing both water and glycol vapors to minimize the loss of glycol. The unreacted monomers and other by-products were removed from the reaction mixture by evacuation from half to one hour at the end of the reaction. The copolyester resin was purified by dissolving in diethyl formamide and precipitating into a large amount of rapidly stirred petroleum ether (40-60oC). The precipitated viscous co polyester was collected by decantation and then dried in a vacuum oven at 40oC. Then polyester resin was admixed with 50 wt% of styrene monomer and 0.2 wt% benzoyl peroxide (BZ2O2) to give the final dipping resin solution.[19]

Preparation of WESNCC:-

Waste chicken eggshells were gathered from local market and treated with hot water in a water bath at 100°C for 10 min to prepare clean eggshell waste. In the next step, clean eggshell waste was ground by mortar pestle to produce eggshell CaCO₃ particles. To prepare WESNCC, eggshell CaCO₃ particles were then treated in a planetary ball mill for 3.5 h. Grinding bowl (volume 250 mL) was made from zirconium dioxide. Grinding balls were made from zirconium dioxide with diameter of 10 mm. During ball mill treatment, the ball to powder weight ratio was maintained at 4:1 and the rotating speed of the mill was kept at 400 rpm. [20]

Preparation of Polymer/WESNCC Composites:-

WESNCC-filled polymer composites were prepared in a two-roll mixing mill at room temperature. The total mixing procedure was completed in 15 min. During mixing, the speed of the one roll was fixed at 20 rpm and that of the other at 24 rpm to obtain the friction ratio at 1:1.2. The compounded polymer sample was sheeted out using mold in a hydraulic hot press at a temperature of 160°C. [20]

Characterization:-

Fourier transform infrared (FTIR) spectrum of the polymer and WESNCC was recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{\max} in cm⁻¹) on KBr disks. X-ray diffraction (XRD) pattern of WESNCC was recorded on Xpertpro-Panalytical X-ray diffractometer; also ¹H-NMR spectrum was recorded on Varian Gemini 200 MHz spectrophotometer, limiting oxy-index test was proceeded on limiting oxy-index tester model ASIAN F701 and ignitability test was preceded on single flame source tester model manual/front (HDB/V). TGA test was proceeded on Perkin analyzer (TGA-8000).

Results and discussion

Characterization of polymer (1) based on tetra bromo bis phenol-A (TBBPA):-

In this work, unsaturated polyester containing maleate unsaturated polyester was prepared by reaction of tetra bromo bis phenol-A and maleic anhydride with 1,5pentane diol as shown in (scheme1).

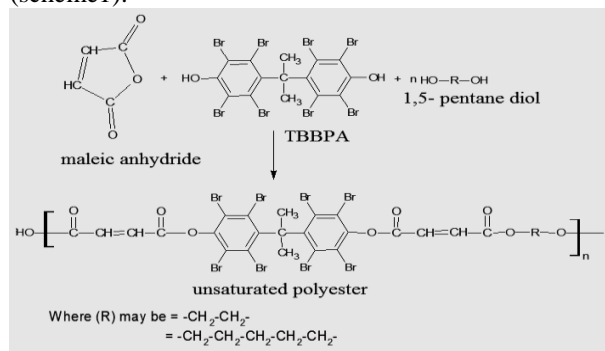


FIG .1. Scheme of preparation of unsaturated copolyester

The structure of the prepared copolyester based on TBBPA was established by studying its IR and ¹H-NMR spectra Figs. (2,3). The IR spectra of some prepared copolyester showed bands at (3450-3400 cm⁻¹) (ν OH), (2920-2900cm⁻¹) (ν CH₂) and (1720-1700 cm⁻¹) (ν C=O). The ¹H-NMR spectra of the copolyester showed bands at (σ 6.2-8) due to aromatic protons and (-CH=CH-), at (σ 4.2) due to (-CH₂-C=O-) group, at (σ 1.7) due to the two methyl groups of tetra bromo bis phenol-A, at (σ 1.2) due to the protons of (-CH₂-) group[21].

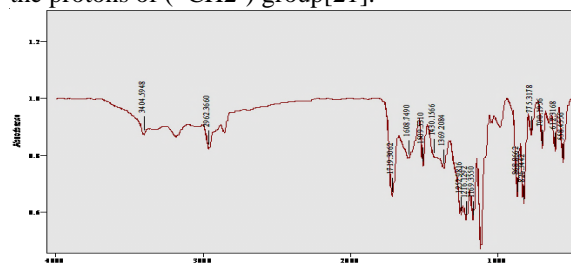


FIG. 2. FT-IR of the prepared polymer.

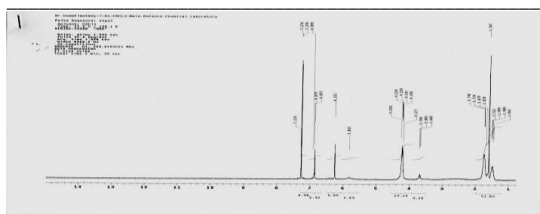


FIG. 3. ¹H NMR of the prepared polymer.

Characterization of (WESNCC):-

FTIR spectrum of WESNCC is shown in Fig. 4. FTIR spectrum of WESNCC showed some characteristic peaks of CaCO₃ at about 872 and 712 cm⁻¹ [8]. The peak around 2517 cm⁻¹ was due to the presence of HCO₃ [9]. The peaks around 2925 and 2875 cm⁻¹ were associated with the CH₂ asymmetric and symmetric stretching vibrations. Moreover, the strong peak around 3416 cm⁻¹ was associated with the amine group of organic protein part present at the WESNCC surface [22].

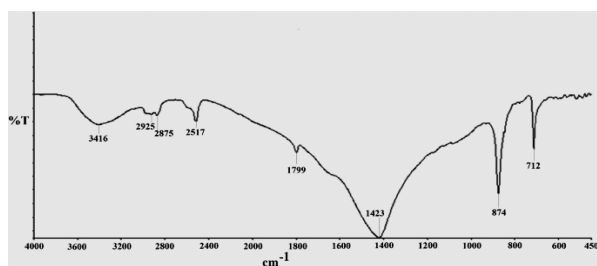


FIG. 4. IR of prepared WESNCC.

The X-ray diffraction (XRD) pattern of WESNCC is displayed in Fig. 5. The crystal lattice structure of WESNCC was rhombohedral according to JCPDS pattern 01-085-0849. The average crystallite size of eggshell nano CaCO₃ was determined from XRD analysis applying well established Scherrer equation. The Scherrer equation is written as:

$$C_s = K\lambda / \delta B \cos \theta$$

Here, C_s is the average crystallite size, K is a constant nearly about to unity, λ is the X-ray wavelength (0.154 nm for the CuKα), B is the integral half-width, θ is the Bragg angle (in degrees). The average crystallite size was found to be 30.31 nm for WESNCC nanoparticles.

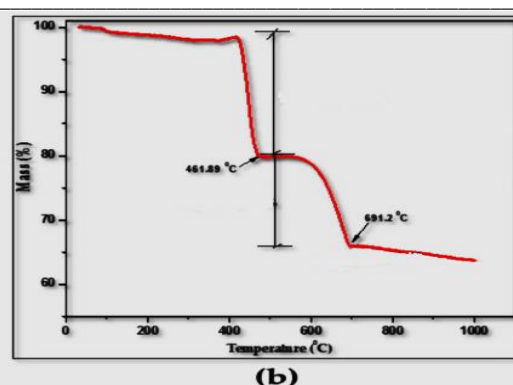
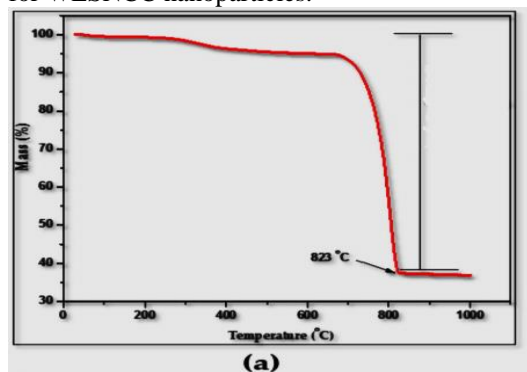


FIG 5. Thermogravimetric analysis (TGA) curve of (a) raw polymer, (b) (WESNCC/polymer) system SEM image as shown in Fig. 6, the CaCO₃ nanoparticles had strong tendency of agglomeration. This was due to the small particle size and high surface energy of waste eggshell-synthesized CaCO₃ nanoparticles. [23]

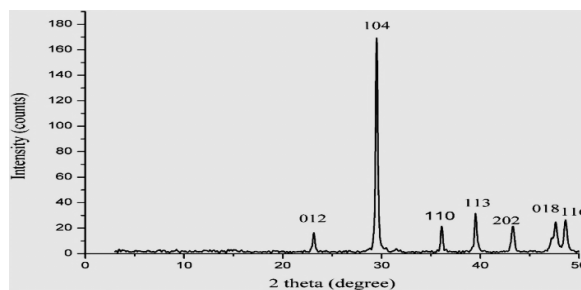


FIG. 6. XRD pattern of WESNCC.

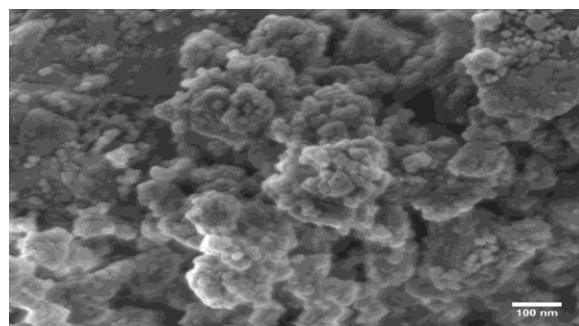


FIG. 7. SEM image of WESNCC.

Thermogravimetric test (TGA):-

Thermogravimetric analysis (TGA) curves of the polymer/WESNCC composite and the prepared polymer are illustrated in Fig 7 (a and b) respectively. In (polymer/WESNCC) composite, a total weight loss of 30% was noticed and at 823°C temperature CO₂ is released to the environment. In the case of polymer only, three major weight losses were observed in the analysis: 50°C 461.89°C, 461.89°C–691.2°C with mass changes of 18.49%, 21.51% respectively. The losses correspond to loss of moisture and decomposition of polymer to CO₂, CO and some other different gasses [24].

Limiting oxygen index: -**Table (1)**

Sample	Limiting oxygen index
Sample (1)	21%
Sample (2)	24%

In this test two specimens of wood the first was uncoated (sample1); the second was coated with (polymer/WESNCC) system (sample 2) with dimension of (80 mm x 10 mm x 4 mm). Limiting oxygen index test showed an increase in the amount of oxygen required for ignition process in the sample with CaCO_3 due to the need for high temperature to break it down to CaO and CO_2 . [25]

Ignitability test: -

In this test, two specimens of wood the first was uncoated (sample1); the second was coated with (polymer/WESNCC) system (sample 2) with dimension of (25 cm x 25 cm x 2.5 cm). Ignitability test was used to evaluate the fire retardancy of samples.

Table (2)

Sample name	MV transduce out	Heat flux applied	Temperature	Observation and Time to ignition
Sample (1)	1.6 Mv	10 Kw/m^2	433°C	flammable after 1 Min
Sample (2)	1.6 Mv	10 Kw/m^2	433°C	Not flammable after 5 Min
	2.5 Mv	15 Kw/m^2	505°C	Not flammable after 5 Min
	2.8 Mv	20 Kw/m^2	534°C	Not flammable after 5 Min
	4.3 Mv	25 Kw/m^2	623°C	Not flammable after 5 Min
	5 Mv	30 Kw/m^2	657°C	Not flammable after 5 Min
	6 Mv	35 Kw/m^2	700°C	Not flammable after 5 Min

Table 2 shows the time of burning of coated wood specimens. It is clear that the time of burning specimen is greater than that of uncoated plywood specimen. It is attributed to the presence of added particles in polyester chain that act as fire retardant which take long time to burn. [26]

Conclusions

In this paper, calcium carbonate nanoparticles were synthesized from waste eggshell. This technique has many key advantages, such as being simple, economic, requires no expensive equipment, ambient temperature. The FTIR and XRD results have clearly depicted the synthesis of calcium carbonates from eggshell. The SEM images of calcium carbonates

nanoparticles showed that the particles were almost spherical in morphology. The synthesized nanoparticles can be applied for future studies in heavy metal removal from industrial wastewater. Moreover, utilizing waste materials as a precursor for the synthesis makes the whole process cheaper, green and sustainable.

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