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Discussion on the feasibility of using proteinized/deproteinized crab shell particles for coating applications: Synthesis and characterization

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ABSTRACT

The discussion on the application of natural bio hybrid organic–inorganic fillers (crab shell particles) for coating application forms the focus of this work. The utilization of shells of marine organism is growing enormously in view of its mechanical and thermal properties. However, the application of proteinized crab shell particles (CSP) or deproteinized crab shell particles (DCSP) for coating field remains a question mark. Deproteinization is done by removing the organic matrix from the crab shell particles using the deproteinization/depolymerization method. Washburn capillary test, adsorption and hydro-stability of crab shell were conducted for studying the surface property of particles in hydro environment. The maximum adsorption capacity was observed for CSP in contrast to hydrophobic DCSP. Stability test had shown the dissolution of CSP. Thermogravimetric analyzer and differential scanning calorimeter results have shown the thermal instability of DCSP on the removal of organic matrix from the crab shell particles. Characterization was done extensively using Fourier transform infrared spectroscopy, X-ray diffractometer and scanning electron microscope.

1. Introduction

Surface coatings over the exposed steel surface are used for enhancing the corrosion, tribology and mechanical properties. Hence the recent research in surface engineering is primarily focused on increasing the property of the coating through use of suitable inorganic or organic elements [1–3]. However the effective combination of organic-inorganic fillers could be the most welcomed aspects [4] in the materials field because of both amorphous and crystalline structure. The combination of organic matrix with inorganic fillers is very keenly observed in the natural available crab shell which is considered as the strong competitor for the coating applications due to its good mechanical property, adequate strength, low cost and etc [5–8]. Crab shell is a by-product of crabs derived from the sea food industry, which generates millions of tons annually reported in 2006 [9]. However, more than 10^{11} tons of aquatic wastes are used for the extraction of chitin. Large amount of chitin is being synthesized worldwide and it is estimated at 1, 328,000,000 MT from marine ecosystem, 28,000,000 MT from freshwater ecosystem, and 6,000,000 MT from athalassohaline ecosystem [10]. Since the availability of crab shells is substantial, it creates an opportunity for the better utilization in the applications. Initially, majority of crab shells are thrown as waste in soil environment besides not knowing the importance of it. The decomposition of these waste residues could generate contaminants to the environment. So the effective way to overcome this problem is to convert this waste into useful products instead of disposing them in the environment. Several works have been taken up in the past on crab shells for the extraction of chitin, mechanical property, structure and etc., revealing the importance of using as a natural filler material [11]. At present, crab shell is used for the biosorption of heavy metals [12] and in the preparation of chitosan bio-fibers. The efficacy of crab shell as a bisorbent is attributed to its rigid structure, excellent mechanical strength and ability to withstand extreme conditions. With the objective of improving the thermal property of the composite materials, these crab shell powders are also used as filler in many works [13]. Some reports also suggest crab shell having excellent binding capacity towards different metal ions, which include lead [14], cadmium [15], nickel [16] and copper. The different types of waste produced by the marine organisms have distinct properties, among which the shells of crab and seashell waste are the important ones to be considered. Successful implementation of seashell particles as coating material with NiP matrix has been reported in a recent article [17,18] showing better wear property. However, the utilization of bio shells in presence and absence of

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Fig. 1. Images of crab shells a) before cleaning and b) after cleaning.

organic matrix is still contradictory, particularly with crab shells for coating applications. From the various studies, it is clear that organic matrix has a huge role to play on the mechanical property, thermal property and adsorption property. However, the role of protein and organic matrix in crab shells for coating applications has not been studied. To the best of our knowledge, challenges in developing a crab shell waste for coating application still remain without being met. As a new waste material for coating application, this study on the crab shell particle is necessary. Recent research primarily focuses on hybrid organic–inorganic base fillers as it is believed that their appropriate use can enhance their property. So, the objective of the present paper falls on investigating the role of organic matrix in crab shells for coating applications by examining their thermal stability, surface property and stability. The availability of enormous quantity of waste as a renewable material is the other advantage to consider the crab shell waste in the use of the coating applications.

2. Materials and methods

2.1. Preparation of crab shell powder

Fig. 1 shows the image of crab shells waste (Fig. 1a) collected from the seashore of the Marina Beach, Chennai, India. The collected crab shell was well soaked in the NaOH for 24 h and cleaned well in the Q-Milli water. Q-Milli water was supplied by Ipure distilled water industry, Redhills, Chennai, India.

Cleaned shells Fig. 1b were finally dried in the sunlight for two days and then pounded initially with a hammer in a stainless steel jar for 15 min and transferred into a ball milling machine. Later, shells were finely crushed into powder in a ball mill for 2 h. The crushed powder was directly used as CSP Fig. 2a.

2.2. Deproteinization of crab shell particles

Demineralization and deproteinization were generally used for the extraction of chitin from the crab shells. In this work, deproteinization process was used for the removal of the polymer and protein matrix from the crab shell powder. The crushed crab shell particles were first treated with low concentrated NaOH (1 N) and rinsed with the double distilled water.

Then the protein and polymer matrix were removed by treating the particles in the acetic acid solution [19] followed by a water rinse. This process eradicates the polymer and protein matrix from the crab shell particles. Fig. 2b shows the image of synthesized DCSP. Surface morphology of synthesized particles was also pictured using scanning electron microscope with a voltage of 10 kV. The images were then processed using image processing tool for better visualisation.

2.3. XRD analysis of CSP and DCSP

The diffraction pattern and structure of CSP and DCSP were analyzed using powder X-ray diffractometer in CuKα radiation

Fig. 2. Images of synthesized powder a) CSP and b) DCSP.