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Rice husk agricultural waste-derived low ionic content carbon–silica nanocomposite for green reinforced epoxy resin electronic packaging material

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ABSTRACT

The present study focused on the preparation and characterization of a bio-based carbon-silica material derived from rice husk agricultural waste and its function in epoxy matrix for electronic packaging applications. X-ray diffraction (XRD) analysis, N_2 adsorption/desorption isotherms, and scanning electron microscopy were used to characterize the structure as well as morphology of the resultant carbon–silica material, namely black rice husk ash, called BRH. Thermogravimetric analysis results suggest that improved thermal stability can be achieved by reducing the ionic content of the BRH materials through the pre-acid-hydrothermal technique. The ionic content of [Cl^-], [Na^+], and [K^+] of the BRH sample respectively were 4.3, 9.8, and 9.0 ppm after further post-hydrothermal process. In addition, the XRD diagram shows that the structure of the calcined BRH material, is in amorphous form, which is non-toxic to humans. For packaging application, an improvement of 147% in storage modulus and 49% in CTE by the addition of 46% filler was realized. In addition, compared with pure polymer, the thermal conductivity values of the epoxy/*pre*-BRH composites were improved by 142%. From these results, it was concluded that this BRH filler derived from waste rice husks can promote the thermal stability, thermal-mechanical strength, and thermal conduction of the Epoxy/BRH composites.

1. Introduction

Rice husks are a major waste product of the agricultural industry, comprising over 22% of 700 million tons of world rice production [1]. Treatment or disposal of the rice husks result in a rather significant challenge for environmental protection. Generally, the major constituents of rice husks, at about 80–83 wt% on dry basis, are organic components consisting of lignin, hemicellulose, cellulose, and other organic matter, while minor components include silica at 17–20 wt% and other trace impurities, such as alkali oxides, alkali earth metals, aluminum and chloride [1–3]. In the past decade, many researchers have produced both silica-based white rice husk ash (WRH) and carbon–silica-based black rice husk ash (BRH), which owing to their superior mechanical properties are widely used in many fields. Moreover, such materials have been widely applied in insulating refractories, thermal dissipation materials, SiC production, toxic substance absorbents for water purification, and reinforcing filler in rubber and polymers [4–9]. However, WRH and BRH contain ionic impurities such as chlorides, sodium and potassium; and when moisture is present become the leading causes of corrosion and electrical failures in metal interconnections of an integrated circuit (IC), thereby resulting in a substantial impact on the reliability of electronic packaging [10].

For electronic packaging application, it has been reported that impurities boosts failures by increasing the chlorides-ion content in adhesives from 10 ppm to over 200 ppm. JEDEC J-STD-030 (Guideline for Selection and Application of Underfill Material for Flip Chip and other Micropackages) determined a specification for ionic content [Cl^-], [Na^+], and [K^+] in the underfill material, all of which were less than 10 ppm under aqueous extraction at 121 °C for 20 h [10]. Hence, different origins of rice husk have various impurities and, with proper pre-treatment and post-chemical modification, the surface or structure of the rice husk might not only be significantly changed, but could also provide excellent filler-matrix

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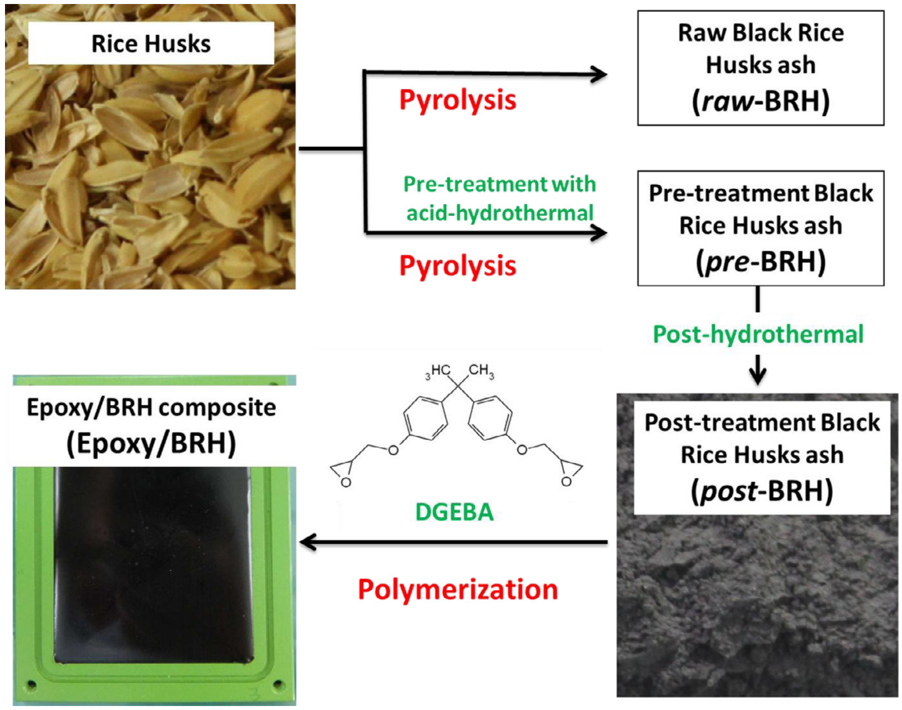

Fig. 1. Flow diagram of the process used to convert black rice husk into *raw*-BRH, *pre*-BRH, and *post*-BRH materials and the subsequent fabrication of the epoxy/BRH composites.

interaction so as to greatly affect its efficiency in industrial applications [11–16]. However, there is a lack of reports targeting the preparation and electronic packaging application of the carbon–silica fillers with low-ionic content derived from waste rice husk.

In general, utilization of biomass rice husk ash in the composites has provided several advantages, such as low cost, low density, greater deformability, and biodegradability. With this in mind, the present study focused on the preparation and characterization of a bio-based carbon–silica material derived from waste rice husks for the electronic packaging industry. The low-ionic content and good filler-matrix interactions of the as-prepared carbon–silica materials can be fabricated via the pre- acid-hydrothermal and post-hydrothermal techniques. The structural properties and morphology of the resultant carbon–silica material, namely BRH, were characterized by X-ray diffraction (XRD) analysis, N_2 adsorption/desorption isotherms, and scanning electron microscopy. The improved thermal stabilities of the epoxy/carbon–silica composites were confirmed by thermogravimetric analyzer (TGA) and thermo-mechanical analyzer (TMA) measurements. Furthermore, the thermo-mechanical properties of the storage modulus and coefficients of thermal-expansion (CTE), as well as the thermal conductivities of the epoxy/carbon–silica composites were evaluated by TMA, dynamic-mechanical analyzer (DMA), and thermal conductivity measurement, respectively.

2. Material and methods

2.1. Materials

The bio-based carbon–silica materials were derived from rice husk agricultural waste. The EEW (epoxy equivalent per weight) 188–192 of Diglycidyl Ether of Bisphenol-A epoxy resin (DGEBA, BE188) was procured from ChangChun Group, Taiwan. The curing agent, 4-Methyl-1,2-Cyclohexanedicarboxylic anhydride (MHHPA) and a catalyst, N-Benzyl-2-methylimidazole were purchased from Aldrich. All chemicals were used without further purification in this study.

2.2. Preparation of the bio-based carbon–silica materials

Fig. 1 shows the flow diagram of the process used in this study. The carbon–silica materials were produced using rice husk agricultural waste pre-treated with the citrate acid-hydrothermal process at 100 °C for 2 h [17]. Then, the dried husks were pyrolyzed at 900 °C for 2 h under a nitrogen atmosphere to prepare the pre-treatment BRH, which is denoted as *pre*-BRH. In order to further decrease the ionic content, the *pre*-BRH was treated with a post-hydrothermal process at 100 °C for 24 h and repeated three times, the obtained sample was named *post*-BRH. For comparison purposes, the rice husks without any pre-treatment were directly pyrolyzed and denoted as *raw*-BRH.

2.3. Fabrication of the epoxy/carbon–silica composites

To achieve micro-sized dimensions, the carbon–silica particles were milled with a mechanical grinding machine and after sieving through 40 and 100 meshes, respectively. Different amounts of the carbon–silica particles were well-mixed with the epoxy resin, at around 95 °C, a temperature above the melting point of the epoxy resin, for 12 h [18]. An appropriate amount of the anhydride curing agent in the stoichiometric ratio of 1:0.8 (DGEBA/MHHPA) was added to the slurry and mixed at 60 °C for 2 h. Then, 1 wt% of the catalyst was added to the curing agent and stirred at 60 °C for 10 min. The resulting composite was cast into a preheated aluminum mold and then degassed under a vacuum at 60 °C for 6 h. All samples for measurements in thermal-mechanical and thermal conductivity properties were cured at 100 °C for 1 h followed by post-curing at 150 °C for 3 h.

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