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Degradability of kenaf dust-filled chitosan biocomposites

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Abstract

Degradability of environmentally friendly of kenaf dust-filled chitosan biocomposites was investigated. Biocomposites of chitosan/kenaf was prepared via solution blending method. Diluted acetic acid was used as solvent for dissolving the chitosan powder. High speed homogenizer was used to assist the dispersion of kenaf dust in chitosan solution. Five types of composites containing different amounts of kenaf dust; 0%, 7%, 14%, 21% and 28% were fabricated. Degradability of each composites were evaluated against seven different solutions; (0.1, 0.5, 1.0) M of H_2SO_4, (0.1, 0.5, 1.0) M of NaOH and distilled water. Degradation behaviors were evaluated based on percent of weight gain, percent of water absorption and degree of swelling. It was noted that, chitosan film which contains higher kenaf dust content showed greater stability against seven different solutions due to lower degree of swelling compared to chitosan film having lesser amount of kenaf dust. It was observed that the composites showed greater resistance towards alkaline and acidic solution as compared to distilled water.

Keywords: Chitosan; Kenaf; Aqueous degradation; Biocomposites

1. Introduction

Chitin is a natural polysaccharide (*N*-deacetylated-2-acetamido-2-deoxy-β-D-glucan) that exists in considerable amount as the exoskeleton of arthropods and fungi [1]. The deacylated chitin is called chitosan. Chemically, chitosan is a linear polysaccharide, composed of glucosamine and *N*-acetyl glucosamine linked in β (1→4) manner (Fig. 1); the glucosamine/*N*-acetyl glucosamine ratio being referred to as the degree of deacetylation [2]. Chitosan is a virtually non-toxic polymer [3] with a wide safety margin. Moreover, chitosan is a biodegradable, biocompatible, positively charged polymer, [4] which shows many interesting properties, such as a biodegradable edible coating or film in food packaging [5], a dietary fiber, a biomaterial in medicine [6] either on its own or as a blend component, a medicine against hypertension because of its scavenging action for chloride ions, tissue engineering matrices [7] and membrane filter for water treatment [8].

In its crystalline form, chitosan is normally insoluble in aqueous solutions above pH 7; however, in dilute acids (pH < 6.0), the protonated free amino groups on glucosamine (Fig. 1) facilitate solubility of the molecule [9]. Therefore, according to [10], when chitosan dissolves in acidic medium, it becomes a kind of polyelectrolyte carrying positive charges due to the presence of amino groups, which may be protonated.

$$\text{Chit–NH}_2 + \text{H}_3\text{O}^+ \leftrightarrow \text{Chit–NH}_3^+ + \text{H}_2\text{O}$$

Degradation of chitosan can be classified based on the enzymatic [11,12], oxidation, hydrolytic, thermo-[13], radiation [14] photo-[15,16] and ultrasonic degradation [16]. Biodegradability test is done in order to predict the suitable condition which chitosan film will exhibit excellent degradation. Generally, factors such as nature of polymer and its composition, flexibility of the polymer chain, molecular mass of the polymer, crystal structure of the polymer and cross-linking affect the dissolution and swelling behavior of the polymer [17].

According to [18], the more quickly the degradation proceeds, the lower the molecular weight of chitosan, although there is no simple correlation between biodegradation rate and the molecular weight of chitosan. Chitosan can be degraded into non-toxic

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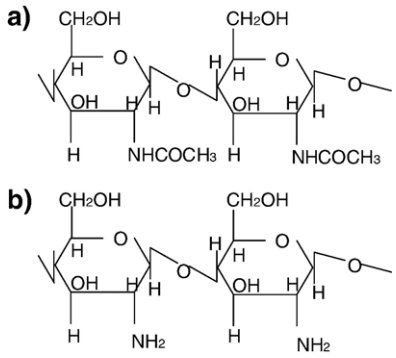

Fig. 1. Chemical structure of chitin and chitosan; (a) *N*-acetylglucosamine, (b) *N*-glucosamine (Source: Miranda et al. [4]).

products in vivo [7]. The rate of degradation is inversely related to the degree of deacetylation or crystallinity of the chitosan film [19]. Therefore, as chitin and chitosan are crystalline polymers, the crystalline ability of chitin and chitosan must be reduced by deacetylation and acetylation, respectively, resulting in an increase in the water content of the films [11]. However, a study by [12] found that, the enzymatic degradation of chitosan differs considerably even for chitosan of the same degree of deacetylation. This can be attributed to the source of which chitosan is derived or explored that hold on important explanation to the change of chitosan composition and behavior.

With that note, addition of rigid filler, plasticizer or natural fiber may also influence the biodegradability of chitosan in many ways. Thus, it is interesting to investigate how the filler naturally affects the biodegradability or antimicrobial activity of chitosan.

In this study, the kenaf dust-reinforced chitosan was prepared. The degradation of the composite was evaluated based on exposure to acidic, basic and neutral medium. Weight gain or weight loss was used as an indicator for the degradation.

2. Raw material

Kenaf fibers were supplied by Malaysian Agriculture Research Development Institute (MARDI). Details of the properties of the kenaf fibers used in this study are given in Table 1. Chitosan powder was purchased from HUNZA pharmaceutical with properties as shown in Table 2. Laboratory grade of (0.1, 05, 1.0) M sodium hydroxide, (0.1,0.5,1.0) M sulfuric acid and 0.2 M acetic acid were used as received.

2.1. Methodology

2.1.1. Kenaf dust preparation

Kenaf fiber is dried under the sunlight for about two days before it was ground into dust using grinding machine (Model: Grinder 3 phase induction motor type EEF).

2.2. Characterization of chitosan powder

2.2.1. Elemental analysis

The elemental composition of chitosan powder was determined using Perkin-Elmer PE 2400 CHN and CHNS elemental analyzer. The DD value of chitosan samples was calculated from Formula Eq. (1) [20]:

$$DD = \left[1 - \frac{C/N - 5.145}{6.816 - 5.145}\right] \quad (1)$$

2.2.2. XRD analysis

X-ray diffractograms on chitosan powder was obtained using a Bruker AXS D8 Advance X-ray diffractometer under the following operation conditions: 40 kV and 40 mA with Cu $K\alpha_1$ radiation at λ 1.54184 Å and acceptance slot of 0.1 mm. About 20 mg of the sample was spread on a sample stage, and the relative intensity was recorded in the scattering range (2θ) of 5–40° in steps of 0.1°. The crystalline index (CrI: %) was determined in two equations, Eqs.(2) and (3) [21]:

$$CrI_{100} = \left[\frac{I_{020} - I_{am}}{I_{020}} \times 100\right] \quad (2)$$

For comparison, another crystalline index was expressed as CrI_{110} by using the following equation:

$$Crl_{100} = \left[\frac{I_{110} - I_{am}}{I_{110}} \times 100\right] \quad (3)$$

2.2.3. Preparation of composites

Chitosan solution was prepared by dissolving chitosan powder in 0.1 M acetic acid at a ratio of 1:50. Kenaf dust was then added to the solution based on the weight percent of chitosan. Details of the composition of the composites used in the study are presented in Table 3. To minimize the formation of agglomerate in the mixture a homogenizer with high speed stirring between 10,000 to 29,000 rpm was employed. Despite of providing fast and efficient mixing of kenaf and chitosan, the homogenizer also generates a considerable amount of air bubble. In this study, the removal of air bubbles was done by employing vacuum oven at room temperature for a period of 1 h.

Prior to the solution casting process, a glass plate with dimensions of (200×200×9) mm was cleaned and 400 ml of the chitosan/kenaf dust solution was added. The film was oven dried for overnight at 60 °C. Once the film is dried, it is then neutralized using 0.1 M NaOH solution and further dried at room temperature for 5 h. The films are stored in desiccators until further use.

Table 1
Properties of kenaf dust [31]

Properties	Value
Density	1192.6 kg/m^3
Moisture content	5 to 10%
Cellulose content	60 to 80%
Lignin content	5 to 20%
Tensile strength	600–700 MPa
E-modulus	38
Elongation at failure	2 to 3%
Diameter	6 to 8 μm