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IMECE2012-86393

SINTERING OF CHITOSAN AND CHITOSAN COMPOSITES

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ABSTRACT

Chitosan is a naturally-occurring polymer that is derived through the deacetylation of chitin. Chitin, found in the exoskeletons of invertebrates, is ubiquitous in nature and easily collected as waste and repurposed for a multitude of industrial and biomedical applications. Development of composites of chitosan and carbon are attractive due to their availability, compatibility, and mechanical properties. In the present work we construct a chitosan composite reinforced with 2 wt% carbon nanostructures using mechanical milling. The carbon nanostructures consist of amorphous carbon, graphene-like, and graphitic nanostructures synthesized by mechanical exfoliation. We demonstrate that the mechanical properties of this composite material can be altered by varying the sintering conditions. Preliminary thermal analysis showed a degradation temperature around 220 ± 5 °C but this was also influenced by the duration of temperature exposure. The material was strengthened by adding carbon nano-composites and through sintering. Better sintering conditions occurred at lower temperatures and shorter times. The new material properties are characterized by means of mechanical testing, electron microscopy, Raman spectroscopy, and X-ray diffraction.

INTRODUCTION

The development of multi-functional bio-composites is a topic of great interest in the fields of material science and bioengineering [1-2]. Low procurement and low production cost material are especially desirable as engineering materials with a great emphasis on recycled waste. Chitosan is one such tunable material that offers both bio-compatibility and can be reinforced with carbon nanotubes, graphenes, and other carbon species [3]. Researchers have demonstrated that these carbon species are effective reinforcements for structural materials [4-8]. Furthermore, the properties of chitosan can be improved by very simple heat treatments under the right conditions. In the present work we've prepared and sintered chitosan and chitosan composites reinforced with carbon nanostructures and evaluated the effectiveness of the material processes.

METHODS

Samples were prepared using 80 % deacetylated Chitosan (Carbomer Inc, San Diego CA) and commercially available fullerene soot (SES Research, Houston TX). Mechanical milling was conducted on a SPEX apparatus for 1.5 h for the chitosan and 3 h for the fullerene soot. The products were then mixed at a 98:2 ratio (chitosan-fullerene soot) and milled together for an additional 1.5 h. The sintering was performed on a custom made French press-heater system connected via PC to a high resolution thermal analysis system. The sintering was conducted at 180 and 220 °C for 3 and 12 h at 50 MPa. Hardness testing was performed on all samples using the Rockwell "A" method with a load of 15 kg. X-ray diffraction (XRD) was measured with a D5000 SIEMENS diffractometer at $K\alpha = 0.15406$ nm. The SEM observations were carried out on a FEI XL-30FEG on secondary electrons. Finally, a Raman analysis was done on a confocal micro-Raman microscope XploRA™, Horiba JY. A 638 nm diode laser was used for excitation.

RESULTS AND DISCUSSION

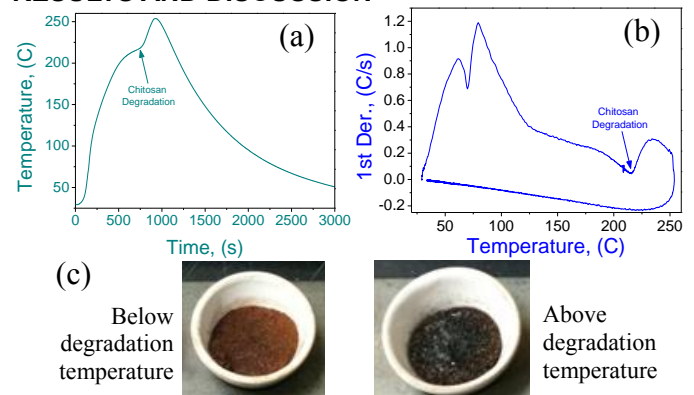


Figure 1. (a) Heating/cooling curve for chitosan and (b) the first derivative of the heating/cooling curve. Samples of pure chitosan before (c-left) and after (c-right) the degradation temperature.

Figure 1 shows the heating/cooling and first derivatives for one sample that was used to determine degradation temperature thresholds. Heating above 220 °C resulted in accelerated material breakdown as evidenced by the characteristic exothermic reaction or by the appearance of ash (cf., Figure 1).

The SEM micrographs of chitosan in raw and milled configurations are shown in Figure 2 (a-b). The raw chitosan particles have irregular morphology with sizes ranging from 10-50 μm . The milled composites exhibit agglomerations of smaller particles that are coated with the carbon nanostructures. The carbon nanostructures are mainly composed of graphitic carbon and graphene-like structures. Therefore, the milling process was an effective method to homogeneously cover chitosan. This effect is further confirmed by the Raman results shown in Figure 3. Bulk Raman measurements were taken for the composite structure, sintered chitosan, and the pressed control at 100x magnification. In the 1000x magnification the Raman clearly shows the D and G bands typical of carbon at approximately 1320 and 1600 cm^{-1} respectively. The D band shows that carbon nanostructures have a high density of defects having a quasi-amorphous structure. The G band indicates that most of this carbon is sp^2 forming five to seven fold rings [9].

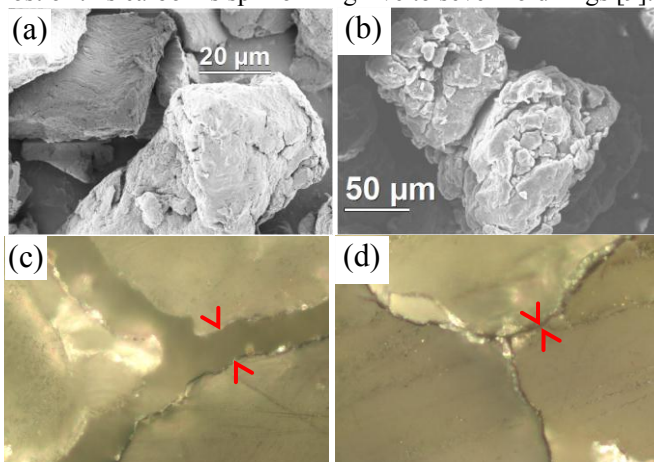


Figure 2. SEM micrographs of (a) raw chitosan (b) and chitosan-nanocarbon composite powders. Optical micrographs showing (c) sintered chitosan and (d) sintered chitosan-nanocarbon composite at 180 °C for 3 h. Arrows (in c&d) indicate grain boundaries.

The XRD results show that the sintering (180 °C; 3 h) shows no degradation of the crystalline structure of chitosan suggesting the time and temperature of this test were within safe thresholds. The presence of carbon is not evident by XRD for two main reasons: *i*) the amount added 2 wt% is very small and *ii*) the carbon nanostructures are quasi amorphous. Therefore, Raman and XRD results suggest that these sintering conditions (180 °C; 3 h) are adequate to prevent chitosan degradation. At the same time, the light optical microscopy images show the sintered microstructures with different characteristics along the grain boundary. The grain boundaries in the sintered chitosan are wider than the composite. Additionally, local Raman characterization (1000x) of the composites demonstrates that the grain boundaries are formed by carbon nanostructures.

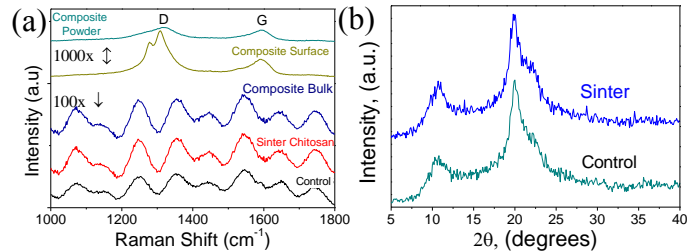


Figure 3. (a) Surface and bulk Raman characterization of pressed chitosan (control), sintered chitosan, and chitosan-nanocarbon composites. (b) XRD characterization of the control and sintered chitosan. In both images, the control has been pressed to 50 MPa and the sintered conditions were 180 °C for 3 h.

The hardness results for the sintering times and temperatures performed using these protocols can be seen in Table 1. The hardness was conducted using the ASTM procedures for Rockwell “A” hardness and is presented in relative values (1=softest). The composite structures show an increase in hardness compared to the chitosan only counterparts.

Table 1. Rockwell “A” hardness presented in relative values.

Description	Hardness	
Pressed chitosan (control)	1.67	
	Chitosan	Composite
180 °C; 3 h	1.67	107.41
180 °C; 12 h	1	n/a
220 °C; 3 h	5.23	42.14
220 °C; 12 h	13.04	10.49

CONCLUSIONS

Thermal analysis is an effective tool to determine sintering conditions. Chitosan degradation starts above 220 °C but can also occur at lower temperatures (180 °C) at longer sintering times (12 h). Shorter sintering times seem to favor the strength of the chitosan and chitosan composite. Carbon nanostructures are effective reinforcements for chitosan. Furthermore mechanical milling and sintering are useful methods to manufacture composites as well as to sinter pure chitosan.

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