AC 2011-447: DEVELOPMENT OF A LABORATORY MODULE IN HYBRID BIODEGRADABLE CORNSTARCH MATERIALS

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Development of a Laboratory Module in Hybrid Biodegradable Thermoplastic Cornstarch (TPS) Materials

Abstract

There is a global interest in replacing petroleum based synthetic composites with biodegradable hybrid materials in order to use renewable resources and to reduce the amount of persistent non-biodegradable plastics waste. Fillers (or reinforcements) play an important role to improve various characteristics in biodegradable hybrid composites. Various types of inorganic fillers are used to modify the properties of biodegradable composites in industrial applications. This study attempts to investigate the effects of inorganic fillers (such as halloysite nano clay and calcium carbonate ($CaCO_3$)) on the mechanical properties (tensile testing) and microstructures of hybrid thermoplastic cornstarch (TPS) material systems. The results of the study were implemented to develop a laboratory session for undergraduate students in manufacturing, mechanical engineering technology and packaging science programs at RIT

Introduction

The demand for bio-degradable polymers and hybrid materials in various product applications, such as; food packaging, personal care products, marine applications, automobile parts, and bio-medical products, has rapidly increased due to a combination of high crude oil prices, government policy, environmental concern, solid waste disposal cost, and public interest. There is a growing interest in the development of the biodegradable hybrid blends to replace many traditional petroleum-based materials; however, the biodegradable hybrid materials must meet the increasingly stringent requirements in industrial applications: such as, tensile, dynamic mechanical, thermal properties, and barrier properties of biodegradable composites in various applications.[1-3]

Recently, nano clay/thermoplastic cornstarch (TPS) composites have generated great attentions since they exhibit unique hybrid properties derived from multiphase components. The biodegradable hybrid materials tend to not only be suitable for a wide range of applications, but also be capable of undergoing decomposition process after intended lifetime.[1] For example, the thermoplastic starch-based hybrid materials showed improvements of the mechanical properties and stability over unfilled formulations.[1-4]

With the addition of a small amount of organically modified montrorillonite (MMT), Park et. al showed that the nano size of MMT clay filler (i.e., chemically modified montrorillonite (MMT)) improved the thermal, mechanical, and barrier properties in thermoplastic starch polymer blends, due to the formation of intercalated nanostructure.[3,4] In nano clay/thermoplastic starch blends, the inorganic surfaces of nano clays were modified by organic treatments to make the platelets of nano clays more compatible with the starch polymers and the melting process affected the degree of dispersion to improve the properties.[3,4]

Halloysite is a family of aluminosilicate ($Al_2Si_2O_5$ $(OH)_4 \cdot nH_2O$) which has a hollow tubular structure.[5] Halloysite naturally occurs as small cylinders which average 30 nm in diameter with lengths between 0.5 and 10 micrometers.[5,6] Many researchers have utilized halloysite nano tubes (HNT) as a nano filler to improve mechanical and thermal properties for polypropylene, polyvinyl alcohol, nylon, epoxy, etc.[5-8]

In engineering design, the performance of products is related to technical advances in materials. For example, polymers are the choice of materials in various applications because they provide low cost and high strength-weight ratio. In the last several decades, many discoveries have led to polymers with the high strength, conductivity or optical properties of other materials, often combined with unique processing and nanofabrication capabilities. Because of advances in technology and the growing demand for environmentally friendly products, manufacturing technology has become an increasingly important component of today's STEM education. Technology educators must impart competencies so that students can apply their knowledge and skills in relation to current engineering materials, as well as preparing students to work with the materials of the future in advanced manufacturing.

The primary goal of the study was to investigate the effects of inorganic fillers (halloysite nano clay and calcium carbonate ($CaCO_3$)) in the mechanical properties and microstructures of the thermoplastic cornstarch (TPS)/inorganic filler blends as biodegradable composites. Thus, the results of the study led to the development of a laboratory session in green materials for undergraduate students in the manufacturing, mechanical engineering technology and packaging science programs at RIT

Experimental

Materials

The thermoplastic cornstarch (TPC) material was prepared by blending the cornstarch (MP Biomedical: 75 wt.% amylopectin-25 wt.% amylose) with the ACS grade of glycerol (EMD Omnipur) in a laboratory mixer at 60 RPM for 30 min. Then, this cornstarch-glycerol blend was mixed with the inorganic fillers to produce the hybrid TPC materials (i.e., composites). The inorganic fillers for the experiment were halloysite clay (NaturalNano HMT) and the ACS grade of calcium carbonate (Acros: >99% $CaCO_3$). The cornstarch, nano clay, and calcium carbonate powders were dried in a dry oven before blending.

Sample Preparation

The ratio of the hybrid mixture of cornstarch/glycerol/inorganic filler was 6:3:1 by weight, respectively. Each batch of the hybrids of cornstarch/glycerol/filler was homogeneously blended in the laboratory mixer for 30 min. at 60 rpm. The mixed hybrid material was to swell in a laboratory oven for 30 minutes at 170ºC. The hybrid mixtures were coded for the extrusion and testing (Table 1).

Table 1: The samples of the thermoplastic cornstarch (TPC) hybrid materials

Sample names	Ratio of the hybrid mixture (cornstarch/glycerol/inorganic filler)	Filler type
CS730	7/3/0	No filler added
NCCS631	6/3/1	Halloysite nano clay powder
CCCS631	6/3/1	Calcium carbonate powder

The extrusion of hybrid TPC material was performed by a laboratory single screw extruder (30:1 of L/D ratio). The extrudate of the hybrid TPS was air cooled as it came out slow enough from the die. The processing temperatures were controlled at a constant of 125°C in most zones of the extruder and the screw speed was set at 45±5 RPM. The extrudate samples of the hybrid TPC materials were conditioned under two different controlled environments: 40±5% RH and 10±5% RH in dry nitrogen chamber.

Tensile Testing

The conditioned samples (ASTM D 618) were cut (3.175 mm dia. by 127 mm long) and tested to obtain the mechanical properties using a laboratory tensile tester. The ten samples of each type of hybrid materials were tested at a testing speed of 50 mm/min in tensile testing and the mean values of the tensile properties, such as tensile strength and fracture toughness, were analyzed for the investigation.

Results and Discussion

Figures 1 and 2 show the typical SEM morphology of halloysite nano clay. This halloysite clay consists of the various shapes of particles and agglomerates.

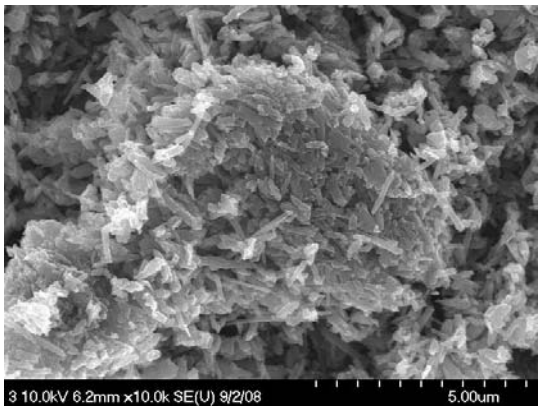

Figure 1: SEM morphology of the aggregates of halloysite nano clay.

The individually separated hollow nano tubes are aggregated with various shapes of particles and clusters; however, tubular shapes are dominant. The nano sizes in diameter are visible in Figure 2.

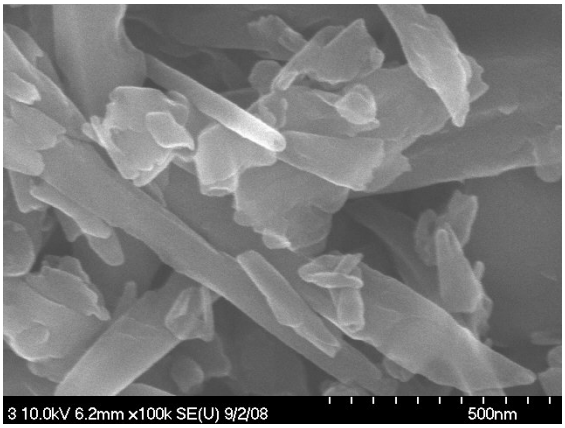

Figure 2: SEM morphology of tubular shapes of holloysite clay.

The SEM morphology of calcium carbonate powders is shown in Figure 3. The fine agglomerates, which consist of thin-plate-like $CaCO_3$, are observed and these individual thin plates are visually in nanometric magnitude (Figure 3).

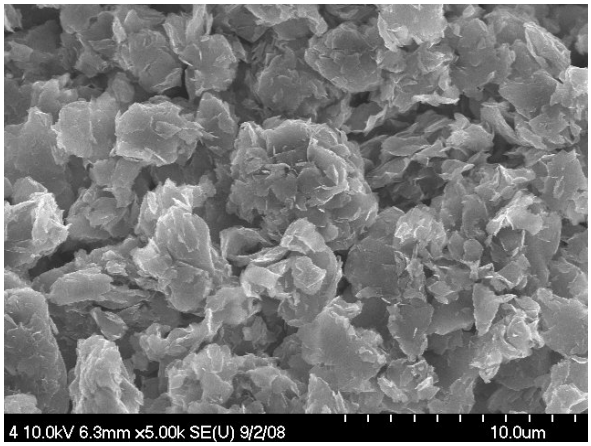

Figure 3: SEM morphology of carbonate ($CaCO_3$) powder

Figure 4 shows a SEM micrograph of the corn starch granules. Various sizes (5-15 µm) of the corn starch powder granules are observed in a dried batch before blending.

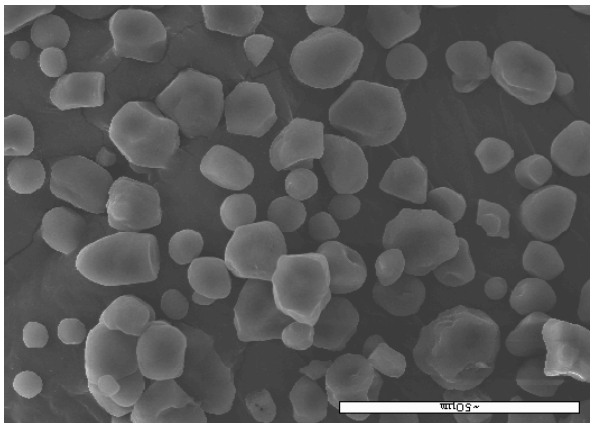

Figure 4: SEM micrograph of the corn starch granules

Figure 5 shows the SEM microstructure of the cross-sectioned area of thermoplastic corn starch (TPS)-nano halloysite nano clay; the TPS matrix is formed with an uniform distribution of halloysite nano particles.

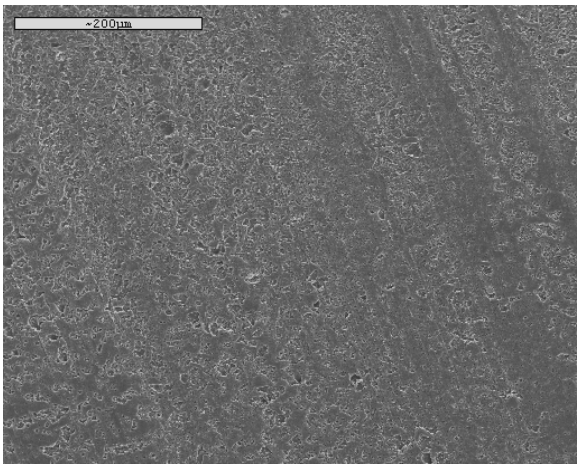

Figure 5: SEM micrograph of the thermoplastic corn starch-halloysite nano clay composite

The tensile properties of the hybrids (NCCS 631 and CCCS 631) are generally higher than the TPS blend (CS 730) in two different testing environments (Figure 6). For example, the mean values of the tensile strength of TPC/halloysite nano clay hybrid and TPS/$CaCO_3$ powder hybrid are 4.21 MPa and 3. 5 MPa, respectively, in a laboratory environment (40±5% RH). In comparison, the mean value of the tensile strength of TPS is 3.1 MPa at the same environment.

In Figure 6, the tensile strength of the hybrid materials substantially increases as the humidity of the sample conditioning environment decreases. The results indicate that the tensile properties are directly affected by humidity. In addition, it is noticed that the

TPS/halloysite hybrid material has the highest tensile strengths among them in both environments.

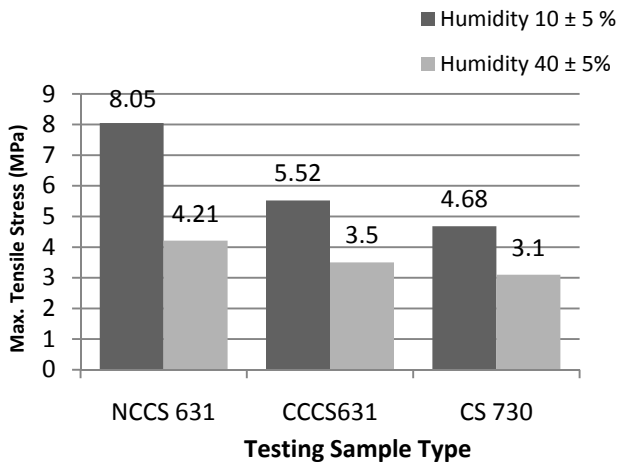

Figure 6: Tensile strength comparison for hybrid materials

The tensile toughness (i.e. fracture energy at break in tension) of the specimens was analyzed in Figure 7. The TPS is more brittle than the other hybrid materials; the inorganic fillers are effective to improve the tensile toughness in both low and high humidity environments. The results show that the toughness of the TPS/halloysite-nano clay hybrid is higher than the TPS/$CaCO_3$ hybrid material at 40±5% RH. This result may be due to the stronger interaction between TPS and nano inorganic fillers.[3,4]

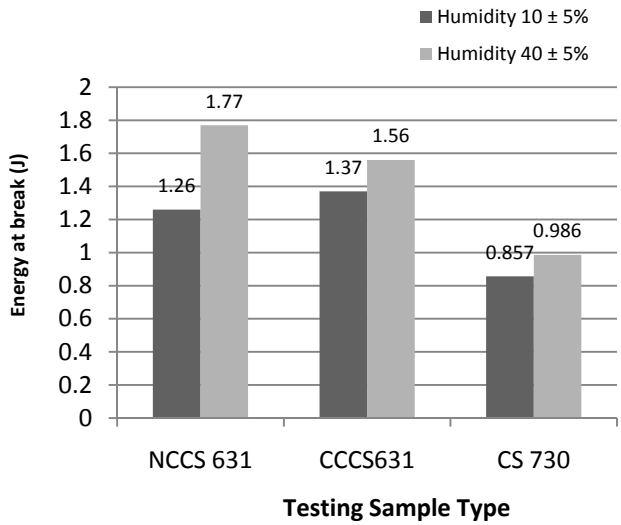

Figure 7: Energy at break (J) for hybrid materials

Undergraduate Research for Green Materials

The establishment of an undergraduate scholarship activity in materials for engineering technology education is difficult, although large engineering institutes may have no problem to provide opportunities for undergraduate students to be involved in various research projects. The project titled in "Hybrid Biodegradable Thermoplastic Cornstarch (TPS) Materials" was developed for undergraduate students to promote scholarship activity and to stimulate students' interests in green materials technology for the manufacturing and mechanical engineering technology programs.

Three undergraduate students conducted the research project under the guidance of Dr. S. Kim for approximately six months. Not only did this research project prove to be motivational for the students, but also it provided them an opportunity to seek work in the related industries. Student testimonials are presented as follows:

" I just wanted to send you a note as I said I would to update you on my fall plans. I have accepted a double block of Co-op with GE Global Research in the materials lab. I want to thank you for sparking my interest in the field and giving the opportunity to be in the lab, which gave me the confidence to go after a position like this. I will be returning to RIT in the spring. Thanks again Prof. Kim!"

"I would also like to thank you for the opportunity of working in the Plastics lab this summer. I have re-enforced much of my education through hands on application. I feel I have learned something of value that I could use to gain employment in industry. Also, I would like to say that through continued research I feel this lab has the ability and knowledge to produce formulas and/or processes that could be valuable to RIT as well as industry."

Implementation and Laboratory Design

The laboratory course in materials and processes needs to focus on the problem-solving-based approach interfaced with research experiences. The course titled "Mechanical Engineering Technology Laboratory II" is a materials laboratory course to provide basic principles in plastics testing for the 3rd or 4th year students in the Manufacturing and Mechanical Engineering Technology programs at Rochester Institute of Technology (R.I.T.).

The MET lab course is designed to introduce not only theories in plastic materials, but also to provide hands-on-experience in the ASTM (the American Society for Testing and Materials) standards testing. Students can utilize the testing apparatus and measurement techniques by obtaining and analyzing the data in the comparison of polymers: petroleum based materials, biodegradable polymers and composites. Thus, students learn how to draw conclusions from the results and develop skills to understand some fundamentals in the structure-property-process relationships in various types of engineering materials.

The development of lab contents recently emphasizes the needs to give proper preparation so that students can deal with inevitable changes in materials science and engineering. Some concerns reflected on the development of laboratory session are to enhance knowledge in green materials, to develop laboratory skills, and to synthesize the course goals. Since the newly developed lab session has been implementing in spring, the results of the assessment of the student performance will be documented.

Conclusions

- The tensile properties of the hybrids (NCCS 631 and CCCS 631) were generally higher than the TPC blend (CS 730). The tensile strength of the hybrid materials substantially increased as the humidity in the sample conditioning environment decreases. The TPC was more brittle than the other hybrid materials; the inorganic fillers are effective to improve the fracture strength in both low and high humidity environments.
- Students utilized the testing apparatus and measurement techniques by obtaining and analyzing the data in the comparison of polymers: petroleum based materials, biodegradable polymers and composites. Also students learned how to draw conclusions from the results and develop skills to understand some fundamentals in the structure-property-process relationships in various types of engineering materials.

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