Green Polymeric Blends and Composites from Renewable Resources

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Summary: Currently new blends and composites are extending the utilisation of polymers from renewable resources into new value-added products. This paper briefly discusses the development in this area, and introduces our research, in particular the starch-based nanocomposites, biodegradable polyester/starch blends and cellulose-reinforced PLA composites. It can be seen that hydrophilic character of natural polymers has contributed to the successful development of environmentally friendly composites, as most natural fibers and nanoclays are also hydrophilic in nature. On the other hand, hydrophobic property and moisture sensitivity of biodegradable polyesters are challenge to be reinforced by the natural materials.

Keywords: biodegradable; blends; composites; renewable resources

Introduction

A special group of polymers, those from renewable resources, has attracted an increasing amount of attention over the last two decades, due to two major reasons: environmental concerns and the limitations of our finite petroleum resources. Generally, polymers from renewable resources (PFRR) can be classified into three groups:[1] (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB). Like most polymers from petroleum feed stock, polymers from renewable resource are rarely used as functional materials in a pure state today. Blending and the formation of composites is often used to improve specific properties of PFRR as similar to strategies used for. Natural polymers are green materials often with preorganised micro and molecular structure that is guided by the organism they originate from. The advantages of natural polymers include the renewable resources from which they originate; their biodegradability; and the environmentally friendly compost products of degradation which are produced. The development of synthetic polymers using monomers from natural resources provides a new direction to develop biodegradable polymers from renewable resources. One of the most promising polymers in this regard is PLA, because it is made from agricultural products and is readily biodegradable.

Fibers are widely used in polymeric materials to improve mechanical properties. Cellulose is the major substance obtained from vegetable fibers, and applications for cellulose fiber-reinforced polymers have again come to the forefront with the focus on renewable raw materials. Hydrophilic cellulose fibers are very compatible with most natural polymers. The reinforcement of starch with cellulose fibers is a perfect example of PFRR composites. However, the hydrophilic cellulose fibers provide a challenge to be compatible with hydrophobic polyesters, such as PLA. Various techniques, such as surface treatments, compatibilizers and coupling agents, have been developed to improve the interface between cellulose and hydrophobic polyesters. The reinforcement of polymers

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using fillers is common in the production and processing of polymeric materials. The interest in new nanoscale fillers has rapidly grown in the last two decades, since it was discovered that a nanostructure could be built from a polymer and a layered nanoclay. This new nanocomposite showed dramatic improvement in mechanical properties with low filler content.

These new blends and composites are extending the utilization of polymers from renewable resource into new value-added products. In the following examples some of the new materials we have been working on are introduced and discussed. This paper will introduce our research in this area, in particular the starch-based nanocomposites, biodegradable polyester/starch blends and cellulose-reinforced PLA composites.

Experimental Part

Materials and Specimen Characterization

Commercial PLA (3051D, injection grade) from NatureWork was used in this work. The starch used in the work is cornstarch from Penford (Australia). The starch is pregelatinized using a twin-screw extruder (Ø 30, LD 40). Wood flour was obtained from Cheap with size about 500 μm. Methylenediphenyl diisocyanate (MDI) (purity 99.9%) was used as compatibilizer in the starch/PLA blends. In this work 0.5 MDI was used in various blends.

The blends and composites were firstly compounded using a twin-screw extruder (Ø 30, LD 40). The highest barrier temperature set up for extrusion is 190 °C and screw speed is 120 RPM. The specimens used for testing mechanical properties were prepared using a Battenfeld injection molder. The injection temperature is 190 °C and mould is 90 °C.

Characterization

Tensile properties were evaluated in accordance with ASTM D5938 standard on an Instron tensile testing apparatus (5565). Impact testing was carried out according to ASTM 256 on a Radmana IRT 2000 instrumented impact tester in Izod mode with impact strain rate 3.5 m/sec.

A Leica Stereoscan 360FE SEM was used to investigate the fracture surfaces and morphologies of the blends. The fracture surface was obtained from impact testing and coated with gold. Morphologies of the blends were studied using cryo surfaces in which starch had been removed. Cryo fracture surfaces were prepared by immersing the specimens in liquid nitrogen for 3 minutes followed by manual fracture. The broken specimens were then immersed in water and placed in an ultrasonic bath for 30 minutes at a temperature of about 45 °C to dissolve and remove the starch phase on the surface. A lower voltage of 2K was used in the experimental work to avoid damaging the surface. Wide-angle X-ray scattering (WAXS) was used to study the delaminating of clay.

Results and Discussions

Biodegradable Polyester/Starch Blends

Hydrophobic aliphatic polyesters and hydrophilic starches are thermodynamically immiscible, which leads to poor adhesion between the two components, and poor and irreproducible performance. Various compatibilizers and additives have been evaluated to improve the interface between starch and the biodegradable polyesters. Methylenediphenyl diisocyanate (MDI) is one of the well studied compatibilizers, in particular for the blends of starch/polylactic acid (PLA). Blends containing MDI have been shown to exhibit enhanced mechanical properties, which may be explained by the in situ formation of a block copolymer that acts as a compatibilizer.

Starch is a highly hydrophilic material that contains anhydro-glucose units linked by α-D-1, 4-glycosidic bond. The water absorbed by starch granules is mainly bound in the amorphous phase. At certain temperatures, shear stress and pressure in an extruder the gelatinization processing disrupts the crystalline and ordered structure in starch granules to produce an amorphous phase. Previous research has shown that the highly reactive isocyanate group in MDI could be consumed by the water absorbed in starch granules which results in weakening the coupling function at the interface between starch and polyester phases.

In this work, various blends of gelatinized cornstarch and biodegradable polyesters were blended to demonstrate the effect of compatibilizer distribution on the microstructure and mechanical properties[2] of the subsequently formed materials. The blends were prepared through compounding via twin-screw extrusion followed by injection moulding. Methylenediphenyl diisocyanate (MDI) was used as compatibilizer to improve the interface between starch and polyesters. The distribution of MDI was controlled through processing and its effect on microstructure and mechanical properties were studied by SEM, DSC, TGA and mechanical testing. Various blends of gelatinised cornstarch and biodegradable polyesters (PCL, PLA or PBSA) were prepared via melt processing using a twin-screw extruder. Distribution of a compatibiliser (MDI) was controlled through the processing conditions employed. Modulus, yield strength and impact strength were increased by more than 35%, 40% and 200% respectively when MDI was distributed in the polyester phase first rather than in the starch phase prior to blending.

Figure 1 shows the morphologies of PLA/starch blends observed by SEM, in which the starch phase has been removed by ultrasonic irradiation in hot water. Figure 1a shows the morphology of PLA/starch blend with MDI distributed in the starch phase. It is seen that removed starch appears as spherical holes with smooth edges. When the MDI was distributed in the PLA phase, the shape of the holes became irregular (see Figure 1b). The holes became random and the edges became rough and unclear that indicates the interface between PLA and starch has been improved when MDI was distributed in PLA phase. The results correspond well with the mechanical properties.

Cellulose-Reinforced Biodegradable Polyester Composites

PLA reinforced with various cellulose fibers have been widely reported. Cellulose fibers have successfully improved modulus and tensile strength of PLA when the loading is lower than 30%. The poor interface between hydrophobic PLA and hydrophilic cellulose fiber results in poor mechanical properties when the content of cellulose fiber is higher than 30%. In order to improve the interface between PLA and cellulose-based fibers, various surface treatments have been developed, such as esterification, alkali treatment, cyanoethylation. Our approach was to use

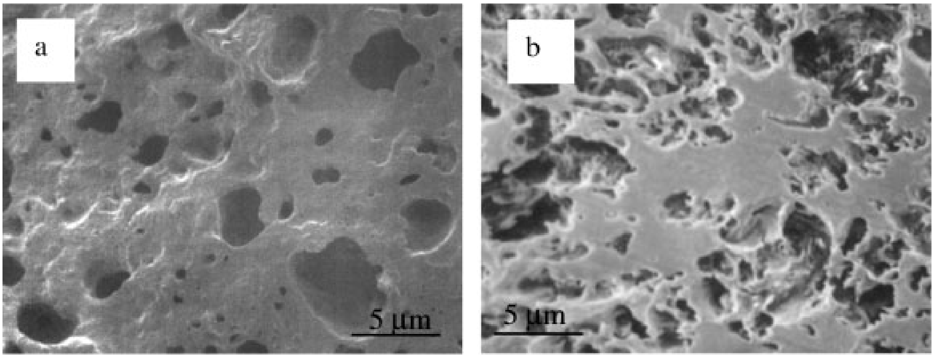

Figure 1.
Morphologies of PLA 70/starch 30 blends containing MDI (1%) distributed in different phases observed by SEM: (a) in starch phase; (b) in PLA phase.

compatibilizers that has been used to improve the compatibility between PLA and another carbohydrate materials. Methylenediphenyl diisocyanate (MDI) is one of the well studied coupling agents.

The focus of this work has been to investigate and compare three techniques of improving the interface between PLA and wood flour: (1) surface treatment of wood flour; (2) adding coupling agent and (3) introducing compatibilizer into PLA phase. The microstructure, mechanical properties and fracture of the composites prepared by melt compounding then injection molding were studied. The influence of wood flour content and techniques for improving the interface between PLA and wood flour were investigated to gain a better understanding of important mechanistic aspects for controlling the structure and properties of these composites. It was found that wood flour increased both modulus and toughness. In the PLA/wood flour systems interfacial improvement was shown to be more efficient at improving mechanical properties compared with toughening the matrix. Figure 2 shows the fracture surfaces of PLA 70/wood flour 30 composites with raw and chemical treated wood flour. Figure 2a shows the fracture surface of the composite with untreated flour. It can be seen that the wood flour has been removed and only the marks of wood flour can be see on the fracture surface, which indicate poor interface. Figure 2b shows the fracture surface with treated wood flour. Some broken wood flour can be found on the fracture, which clearly indicates the wood flour is strongly bound to the PLA matrix.

Natural Polymer-Based Nanocomposites

Nature provides an impressive array of polymers which are generally biodegradable, as biodegradation is part of the natural biogeochemical cycle. Natural polymers, such as proteins, starch and cellulose have the potential to replace many current polymers if new materials composites can be prepared to rival the performance of existing composites. Polymer nanocomposites have attracted an increasing amount of attention. They, in particular polymer/silicate nanocomposites, have been shown to exhibit significant improvements in properties compared with pure polymers or conventional composites. The inclusion of well-dispersed nanosilicates in polymers has led to a vast array of changes in properties, including increased storage modulus, increased tensile and flexural properties, and decreased permeability and flammability. We have been combining the two new technology approaches, nano- and bio-, to developed natural-based biodegradable polymeric nano-composites.

Water is commonly used in the processing of many natural polymers, and it also interacts strongly with the ions generally found in the intergallery spacing of layered nanoclays. Ultrasonics can produce tiny bubbles, which can collapse violently, relea-

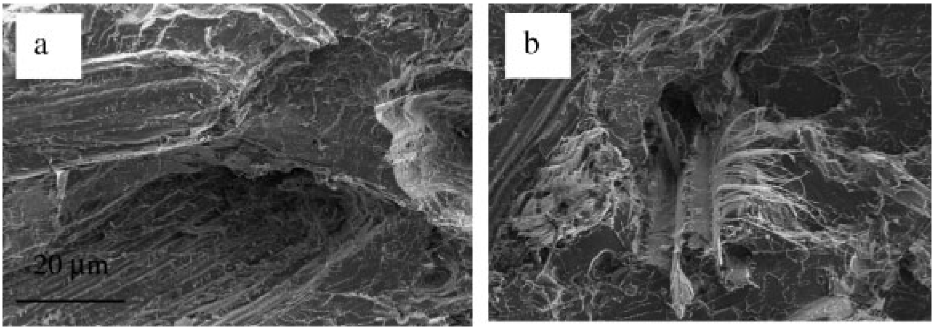

Figure 2.
Fracture surfaces of PLA 70/wood flour 30 composites: (a) without surface treatment; (b) with chemical treatment.

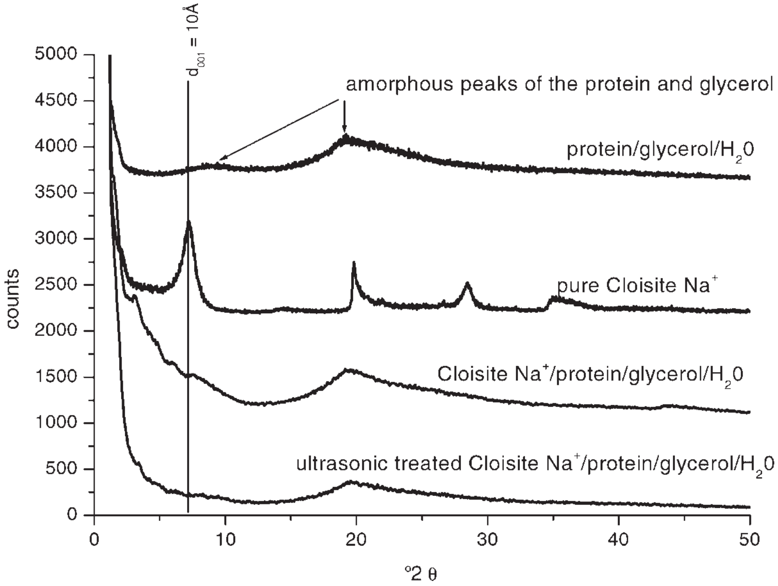

Figure 3.
XRD traces of the neat protein/glycerol, neat Cloisite Na+ and the resulting nanocomposite films.

sing significant energy that can be used to exfoliate clay. A unique technology to exfoliate nanoclay using a clean additive (water) and clean energy (ultrasonics) has been developed. In studies on[3,4] a number of plasticized soy protein/clay and starch/clay nanocomposites and through the use of high-powered ultrasonics, an exfoliated-type nanocomposite produced with significant improvement in modulus was prepared.

The X-ray diffractogram for the ultrasonically treated protein/glycerol/water/montmorillonite clay sample (Figure 1) shows significantly different behaviour – the broad series of peaks had disappeared, indicating the nanocomposite formed was exfoliated.

Conclusions

The development and application of green materials have rapidly increased over the last decade primarily due to the issue of environmental pollution and the shortage of oil. The hydrophilic character of natural polymers has contributed to the successful development of environmentally friendly composites, as most natural fibres and nanoclays are also hydrophilic in nature. On the other hand, the hydrophobic properties and moisture sensitivity of biodegradable polyesters ensure reinforcement using natural materials is a challenge. Modern technologies provide powerful tools to elucidate microstructures at different levels, and to understand the relationships between the structure and properties. However, there is still a long way to go in research to obtain ideal polymeric blends and composites from renewable resources. The future growth and sustainability of polymers and composites from renewable resources is reliant on continued research, in particular in the fields of compatibilizing mechanisms, surface modification and advanced processing techniques, and it is through an understanding of these that they are expected to replace more and more petroleum based plastics.

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