Green Blends and Composites From Renewable Resources

Yu L.*, Petimakis S., Dean K., Bilyk A., Wu D.
CSIRO Manufacturing & Materials Technology, Australia
*long.yu@csiro.au

Introduction
A special group of polymers, those from renewable resources, has attracted increasing amounts 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 (PFR) can be classified into three groups: (1) natural polymers, such as starch, protein, and cellulose; (2) synthetic polymers from natural monomers, such as polyactic acid (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB). Like many other petroleum-based polymers, various properties of PFR are also vastly improved through blending and composites formation.

The study and utilisation of natural polymers are an ancient science. Modern technologies provide powerful tools to elucidate microstructures at different levels and to understand the relationship between the structure and properties. Like most polymers from petroleum, polymers from renewable resource are rarely used as functional materials in a pure state today. Actually, the history of composites from renewable resources is far longer than that of conventional polymers. In the biblical Book of Exodus, Moses' mother built a small craft from rushes, pitch and slime, a kind of fibre-reinforced composite according to the modern classification of material. During the opium war in the 1800s, the Chinese built their castles to defend invaders using a type of mineral particle-reinforced composite made from glutin rice, sugar, calcium carbonate and sand.

Currently new blends and composites are extending the utilisation of polymers from renewable resource into new value-added products. This presentation briefly reviews recent advances in polymer composites from renewable resource, and introduces our research in this area, in particular the starch-based nanocomposites, biodegradable polyester/starch blends and cellulose-reinforced PLA composites.

Starch or Protein-Based Nanocomposites
Nature provides an impressive array of polymers; these are generally biodegradable polymers, as biodegradation is part of the natural biogeochemical cycle. Natural polymers, such as proteins, starch and cellulose, take on new importance in a world that is trying to navigate through the apparent conflict between technological development and environmental protection. 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 diffractogram for the ultrasonically treated protein/glycerol/water/Cloisite Na⁺ sample (Fig. 1) shows significantly different behaviour — the broad series of peaks had disappeared, indicating the nanocomposite formed was exfoliated.

![Fig. 1. WAXS diffractograms of the neat protein/glycerol, neat Cloisite Na⁺ and the resulting nanocomposite films.](image)

Biodegradable Polyester/Starch Blends

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 300% respectively when MDI was distributed in the polyester phase first rather than in the starch phase prior to blending.

Figure 2 shows SEM images of PCL/starch blends, in which the starch phase has been removed. Figure 2A shows the PCL/starch blend without MDI. It is seen that removed starch appears as spherical holes with smooth edges. A similar microstructure was also observed when MDI was distributed in the starch phase (see Fig. 2B). When the MDI was distributed in the PCL phase, the shape of the holes became irregular (see Fig. 2C). The spherical holes became random and the edges became rough and unclear. The results correspond with the mechanical properties.

![Fig. 2. SEM of PCL 70/starch 30 blends containing MDI (1%) distributed in different phases.](image)

Cellulose-Reinforced Biodegradable Polyester Composites

The focus of this work has been to investigate two techniques of improving the interface between PLA and wood flour: (1) surface treatment of wood flour; and (2) introducing a compatibiliser into the biodegradable polyester phase. The composites were prepared by melt compounding then injection moulding. Both techniques have improved the interface between PLA and wood flour, and also the mechanical properties significantly, even though the mechanisms are different. Surface treatment of wood flour has more influence on the tensile strength, while compatibiliser MDI improves the modulus of the composites more efficiently.

Conclusions

The study and utilisation of natural polymers is an ancient science. The application of these materials has rapidly evolved over the last decade primarily due to the issue of the environment and the shortage of oil. 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.

References