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Development of biodegradable laminate films derived from naturally occurring carbohydrate polymers

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Abstract

In recent years, co-extruded laminate films have become increasingly important for many applications, especially in the food industry, where they are mainly applied in the packaging of products such as fresh pasta, meats and cut vegetables to extend the shelf-life of the goods. Commercial multilayer films currently comprise a number of layers (3–9) of different polymers. In most applications, the outer layers consist of cheap, water barrier polymers with good mechanical properties (polyethylene [PE], polystyrene [PS]); the inner layers consist of more expensive materials, which offer good gas-barrier properties (polyvinylidene chloride [PVdC], polyethylene terephthalate [PET]). However, the existing products are not biodegradable. Such conventional plastics, manufactured from fossil fuels, not only consume non-renewable and finite resources, but also impact heavily on waste disposal. For this reason, BioComposites Centre is collaborating in the development of new laminate films for the production of food packaging. These new materials include laminates based on modified starch and polylactic acid (PLA), which are anticipated to present good water and gas-barrier properties, as well as easily extruded and processed, and eventually (bio)degraded at the end of the product life.

Keywords: Modified starch; Polylactic acid; Biodegradable; Laminate films

1. Introduction

Annual European co-extruded sheet production destined for the food industry is estimated to be between 60 and 80,000 tons. If we include polyvinyl chloride (PVC) and PET laminates, the figure rises to over 160,000 tons. Germany, France, Italy and the UK are the main European consumers of multilayer sheets, and their use is growing continuously. Unfortunately, despite many great advantages, most of these polymers are traditionally designed for resistance to microbial attack and biodegradation (Corti et al., 1991). This gives rise to serious environmental effects allied to the accumulation of plastic products, as well as the potential leaching of associated plasticisers into the environment. Gluszynski (1997) reported that the conventional plastics, manufactured from fossil fuels such as oil, coal and natural gas, not only consume non-renewable and finite resources, but also contribute heavily to the global problem of waste disposal. Thus, it can take at least 50 years for them to break down and there is a limit on how often they can be recycled. Environmental concerns associated with the handling of plastic waste have emphasised the importance of developing biodegradable materials to alleviate the plastic waste disposal problems. In other words, the continuously increasing extent of pollution of the environment has recently given rise to demands for novel biodegradable polymers, mainly for applications related to food packaging and agriculture (Arvanitoyannis, 1999).

Our current work is focused on the use of natural materials, such as modified starch [MS] and PLA, to establish and prepare laminate films, which are anticipated to have equal or better performance characteristics to those of existing laminate films, but with the additional benefit of being degradable at the end of film life. The transformation from traditional to biodegradable laminate film systems is depicted in Fig. 1. Successful transfer of technologies would

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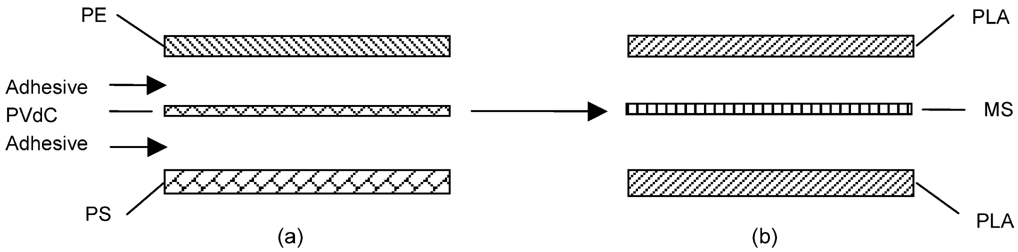

Fig. 1. Schematic laminate films for (a) non-biodegradable and (b) biodegradable system.

offer substantial benefits in all three key measures of sustainability: economic, social and environmental, by increasing the utilisation and value of starch and PLA and decreasing environmental problems associated with plastic waste disposal.

2. Materials and methods

Potato starch was provided by ABR Foods Ltd. Hylon VII was from corn which contained 70% amylose and was supplied by National Starch and Chemical Company. Lauroyl chloride, lithium chloride (LiCl) and pyridine were obtained from Lancaster Synthesis Ltd. *N*,*N*-dimethylacetamide (DMA) was purchased from Aldrich Chemical Company. All reagent grade chemicals were used without further purification.

Starch esters were prepared by acylation with lauroyl chloride using pyridine as a catalyst and base reacted in LiCl/DMA solution. The detailed method and characterisation were described in our previous paper (Fang, Fowler, Tomkinson, & Hill, 2002).

3. Results and discussion

The development of biodegradable plastics started more than 20 years ago. First generation products were conventional plastics blended with starch causing slow disintegration of the product in nature. Second generation products are emerging based on totally biodegradable polymers derived from synthetic or natural materials or blends of both. Important polymers from among the synthetic group include polycaprolactone (PCL), polyvinyl alcohol (PVA) and aliphatic polyesters (polytetramethylene succinate and polyethylene succinate). Major polymers of industrial interest include PLA, the polyhydroxyalkanoates (PHAs), cellulose and starch.

Starch is an inexpensive, totally biodegradable polymer that is readily available from agriculture (Thiebaud et al., 1997). It has a range of potential applications in the markets currently dominated by petroleum-based materials, because it is abundant, renewable, safe and economic. However, as a component of biodegradable laminate film, unmodified starch is unsuitable because it shows no plastic behaviour, thermally degrades at around 260 °C and does not have adequate mechanical properties.

Nevertheless, starch can be rendered thermoplastic in an extruder by combination with plasticisers such as water or glycerol, when it is generally described as destructurised. Under such conditions, starch granules are fragmented, crystallinity is lost by disruption of hydrogen bonds and partial depolymerisation occurs (Nayak, 1999). The thermoplastic, mouldable and amorphous material produced offers excellent oxygen barrier characteristic. However, the use of destructurised starch is limited by hydrophilicity. For example, such materials are too sensitive to environmental humidity and are liable to extremely rapid biodegradation.

Our research has focused on the chemical modification of starch to overcome issues of (1) thermoplasticity and (2) water sensitivity. Depending on the nature of the modification and on the degree to which the modification is made, the properties of the modified starch can be varied extensively. Modification of the abundant hydroxyl groups of native starch to form esters (at substitution levels of DS 1.5–3.0) afforded a material that can be extruded, processed and shaped like traditional plastic products. Plasticisers like glycerol triacetate and diethyl succinate are completely miscible with starch esters and can be used to improve processability. The water resistance of such starch esters is greatly improved over the unmodified starch. BioComposites Centre (Fang et al., 2002) has developed a technology platform from which to prepare chemically modified, hydrophobic starches. Briefly, the method comprises gelatinisation of the candidate starch in hot water, followed by introduction of organic solvent, and preferential removal of the water. The resulting anhydrous suspension is heated with lithium chloride that renders the gelatinised starch soluble in the organic solvent. In this homogeneous form, conventional esterification reactions are performed and

Table 1
Starches from different sources reacted with lauroyl chloride

Sample	Starch	Ester	DS-value
1	High amylose (70%)	Lauroyl	2.3
2	Potato	Lauroyl	2.3
3	75% high amylose:25% potato	Lauroyl	2.3
4	50% high amylose:50% potato	Lauroyl	2.3
5	25% high amylose:75% potato	Lauroyl	2.3

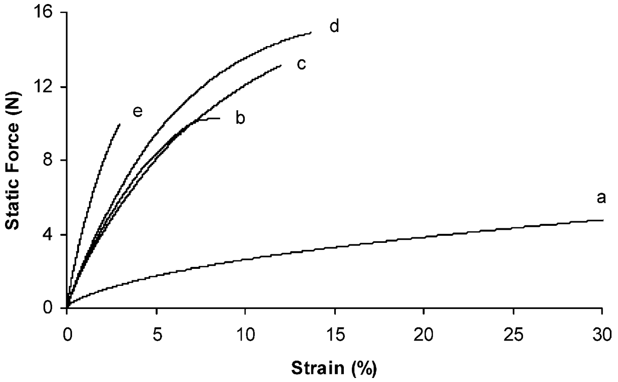

Fig. 2. Static force–strain curves for lauroylated high amylose (a), mixed potato starch containing 25% high amylose (b), 50% high amylose (c), 75% high amylose (d) and potato starch (e).

the modified starches are isolated after appropriate work-up. A range of substituted (Table 1) maize, potato and wheat starches has been prepared and in collaboration with colleagues at AIMPLAS (Valencia), films have been extended. Films are water resistant and flexible.

A broad, preliminary screen of a variety of starches modified with various fatty acid derivatives has led us to concentrate on the lauroylation of potato and high amylose starches as well as blends of the two in various proportions (Table 1). Native potato starch contains about 21% of amylose and 79% of highly branched amylopectin. The lauroyl ester of potato starch is easily extruded to form a film, but the resulting film is brittle. However, high amylose starch (amylose content of 70%) presents a linear component polymer that after lauroylation affords a film that is much more flexible than the corresponding potato-derived film. In combination, the two starches afford materials with desirable properties for the envisaged application.

The modified starches from different sources show much variety of their mechanical properties as shown in Fig. 2. The modified potato starch forms a strong film but is poorly extensible while the modified high amylose film gives good elongation but poor strength. However, the modified mixture of starches with 50% high amylose and 50% potato starch has greatly improved the tensile strength, which forms stronger films and shows good processability.

3.1. Polylactic acid

Our current project is focused on the use of modified starch film as a laminate component in combination with other polymers, such as polylactic acid (PLA). PLA may easily be produced fermentation of carbohydrate feedstock (Roper, 2002; Weber, 2000). Moore and Saunders (1997) reported that PLA is a versatile polymer made from renewable agricultural raw materials, such as sugar, cornstarch, potato starch and waste and plant juice, yielding a highly transparent material of high molecular weight, exhibiting good processability and resistance to water solubility. Transparency and water resistance have led to PLA polymers and copolymers finding applications in the packaging and coating fields. However, the good processability of this group has also led to much wider applications in the plastics industry. High molecular weight PLA exhibits the attractive properties of styrenes, enabling thermoforming without displaying the brittleness inherent in styrene polymers. It has also been found that prolonged exposure to moisture, such as high humidity conditions will lead to a breakdown of the hydrophobic integrity. The degradation occurs by hydrolysis to lactic acid, which is metabolised by micro-organisms to water and carbon monoxide (Oksman, Skrifvars, & Selin, 2003). Therefore PLA represents the major advantage to enter in the natural cycle implying its return to the biomass.

The contribution of PLA's mechanical strength and the gas barrier properties of starch are anticipated to lead to a viable biodegradable laminate film appropriate for modified atmosphere packaging.

4. Conclusion

Chemically modified starches have been prepared by esterification from which thermoplastic, transparent films are derived as components of a biodegradable laminate. It is anticipated that the use of chemically modified starches in laminate constructions could reduce the complexity and cost of a laminate film significantly. A tri- or even bi-layer laminate is envisaged since films cast from chemically modified starches are semi-structural and likely to be wholly compatible with the polylactic acid. This will avoid the use and cost of compatibilisers and additional adhesive layers. Furthermore, at the end of product life the laminate is expected to be degraded under normal composting conditions.

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