SELF-REINFORCED POLYLACTIC ACID (PLA) BIOCOMPOSITES WITH DEGRADATION SENSING

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Abstract

In this paper a new family of self-reinforced polymers (SR-Ps) are developed which are based on the biopolymer polylactic acid (PLA). A biodegradable biobased plastic with improved mechanical properties and the potential to sense biodegradation is obtained. The influence of processing and solid-state drawing on the mechanical properties of PLA tapes has been investigated. The results show that 180 ^{o}C is the optimal processing temperature as it limits degradation. Compared to isotropic PLA films, a 3 and 4 times increase in Young's modulus and tensile strength have been achieved for the oriented tapes, respectively. Finally, carbon nanotubes (CNT) where used for the development of a smart composite system that can sense biodegradation. Electrical conductivity of these PLA/CNT nanocomposites increased with biodegradation and was correlated to mechanical property loss in a realistic application.

1 Introduction

"Self-reinforced polymer (SR-P)" composites or "all-polymer" composites [1, 2], in which a polymer matrix is reinforced with oriented fibres or tapes, or particles of the same polymer, are an interesting materials concept. This technology makes the end product much stronger and stiffer without any weight gain. SR-Ps have been developed to replace traditional fibre reinforced plastic (FRP) with high volume fraction of reinforcement, a better interfacial adhesion, and enhanced recyclability. In previous work, our group co-developed technology based around polypropylene (PP) [3, 4], which is now commercialized under the names of PURE® and Tegris®. Following on from these successes our research into all-polymer composites has moved towards other polymer systems such as polyethylene (PE) [5], poly (ethylene terephthalate) (PET) [6], cellulose [7] and aramid [8].

In this paper, a new family of SR-Ps is being presented which are based on the biopolymer polylactic acid (PLA). These SR-PLA composites are compostable high performance bioplastics which are fully biobased and biodegradable. The concept is based on PLA tapes and a thin layer of PLA matrix, which are combined using a film-stacking technique into a 'brick-and-mortar' structure. The reinforcing tape is solid-state drawn under tension at temperatures below the melting point of the polymer to orient the polymer chains along the tape's axis to improve strength and stiffness. This layer is then sandwiched between two thin

outer layers of a PLA matrix specially formulated with a lower melting point than the reinforcing core. During hot-pressing, the matrix layers are selectively melted to weld the high-strength PLA tapes together to form a composite structure. Through the introduction of CNTs and formation of conductive networks, the PLA matrix layers can be used for sensing biodegradation to make a smart composite. Ultimately these high strength PLA tapes can be woven into fabrics, which subsequently can be moulded into sheets and thermoformed into complex shaped 3D products, such as shell structure, beams or even sandwich panels when combined with a PLA foam core. In this research, the influence of draw ratio and processing condition on the mechanical properties of PLA tapes has been investigated. Efforts have also been made to create conductive networks into these materials for monitoring PLA degradation.

2 Experimental

2.1 Preparation of PLA reinforcement tapes and PLA/CNT matrix films
Dried pellets (PLA Natureworks 4032D) were compression moulded into thin films with an approximate thickness of 100 μm. Samples of dimensions 40 mm x 4 mm are cut from these films and drawn in a temperature controlled chamber attached to an Instron 5584 machine. The draw ratio (λ) of the core tape is calculated by the following equation:

$$\lambda = \frac{Extension}{Original\ Length} \qquad (1)$$

Multiwalled carbon nanotubes (MWNT) were supplied by Nanocyl (Belgium). A masterbatch (15 wt.% CNT loading in PLA Natureworks 3051D) was prepared by melt blending in a DSM mini-extruder at 180 ^{o}C and 100 rpm for 3 min. This masterbatch was then diluted with pure PLA using the same processing conditions to produce nanocomposites with a CNT concentration of 1 and 3 wt.%. After pelletizing and drying, these nanocomposites were hot pressed into matrix films at 180 °C and 50 bars.

2.2 Welding of PLA tapes and matrix films
A single drawn PLA tape was stacked onto a section of matrix grade PLA film and constrained to prevent shrinkage. A mass was used to apply a low pressure onto the tapes to encourage adhesion. To suitably determine the bonding characteristics of a wide range of different tapes, two interfacial failure modes: T-peel tests (Mode I failure), and single lap shear tests (Mode II failure) were performed. For Mode I, the specimens, which were 4 mm wide with a 40 mm long bonded area were peeled along the tape direction in a universal tensile machine equipped with a 100 N load cell at a cross-head speed of 150 mm/min. The peeling force is defined as a force per unit width. The single lap shear specimens were tested similarly to the T-peel specimens except that opposite ends of the bonded regions are pulled apart. Figure 1 illustrates the schematic of both.
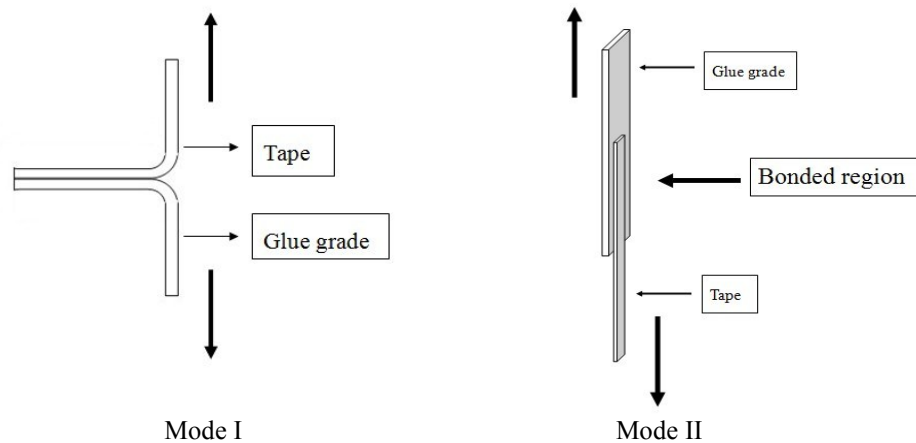
Figure 1. Diagrammatic representation of the evaluation of adhesive properties.

2.3 Hydrolytic degradation of matrix films

Pre-weighed tensile test samples with dimensions 60 mm × 4 mm × 0.15 mm were dried and immersed in vials of distilled water or phosphate-buffered solution (PBS) at pH 7.0 ± 0.2. The vials were then placed in a hot water bath at the degradation temperature 50 ^{o}C. At selected immersion periods, specimens were removed from the vials, washed several times with distilled water and dried until constant weight. The solutions were changed every week to ensure a constant pH value.

2.4 Characterization techniques

Weight average molecular weight (M_w) was determined by means of Gel Permeation Chromatograph (GPC). The measures were made at 30 ^{o}C in chloroform with an AGILENT Technologies 1200 series, equipped with 2x Agilent PLgel Mixed D column and a pre-column. 200 ml of polymer solution with a concentration of 5 mg/ml were injected at 1 ml/min. The molecular masses were calculated using a polystyrene standard.

For the electrical conductivity tests the compression-moulded films were cut into bars with dimensions of 60 mm × 4 mm × 0.15 mm. Silver paste was coated on the left and right plane surfaces of the sample to ensure good contacts of the surfaces with the electrodes of the electrometer. The resistance between two silver paste marks along the specimen length direction was measured at room temperature. The volume resistivity was calculated in relation to the specimen dimensions. The measured volume resistance, R_V, was converted to volume conductivity, using the formula:

$$\sigma = L / (R_V A) \qquad (2)$$

where A is the effective area of the specimen and L is the specimen length. Three specimens for each composite were tested.

Tensile tests were performed using an Instron 5586 at room temperature, equipped with a 1 kN load cell at a crosshead speed of 8 mm/min. The reported values were calculated as averages over six specimens.

3 Results and Discussion

3.1 Influence of processing conditions and solid-state drawing on the properties of PLA tapes
For the creation of reinforcing tapes, optimal hot pressing conditions have been investigated, resulting in the following standard procedure (see Figure 2). The pellets were pre-heated for 6 min, followed by applying a pressure of 50 bars for 3 min, and then releasing the pressure and removing the specimen until cooling below T_g. For process optimization two temperatures (180˚C and 200˚C) were used to prepare the films.
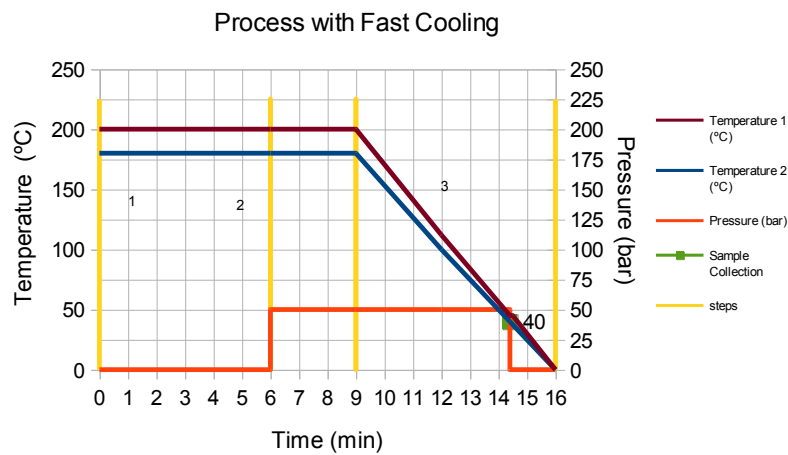

Figure 2. Graphical representation of compression moulding methods.

To produce all-PLA composites with competitive mechanical properties, it is essential to maximize the mechanical properties of the reinforcing PLA tapes. Tapes were produced with a range of draw ratios, λ, to determine the effect of draw ratio on the mechanical properties of the tapes. With increasing draw ratio there is a noticeable change in appearance of tapes as illustrated in Figure 3. Below a draw ratio of $\lambda = 7.5$, the tapes appear transparent, whereas above this draw ratio they become opaque. This phenomenon may be due to a transition from a homogenous to a highly micro-fibrous void-rich structure, established during so-called overdrawing, as well described for polypropylene and polyethylene [9], poly(ethylene terephthalate)–polyethylene films [10] and poly(oxymethylene) [11].
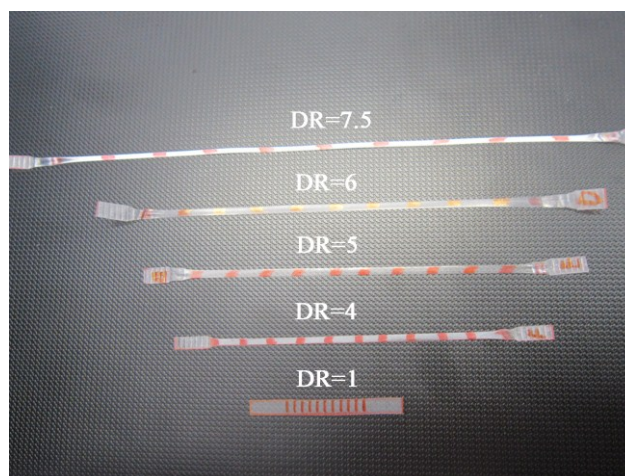

Figure 3. Photograph of tapes drawn at increasing draw ratios.

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It is highly possible that degradation occurs during processing, especially in the case of PLA. GPC results show a clear reduction in molecular weight with increasing temperature, which corresponds to degradation during processing (Table 1).

The effect of degradation on mechanical properties was therefore evaluated. As expected, a lower processing temperature (less degradation) has a positive effect on the modulus and strength of the drawn tapes, as shown in Figure 4. Little difference was seen in the values of strain at break. If closely examined, Figure 4 also shows a slightly reduced maximum draw ratio for the higher molecular weight (lower processing temperature) tapes. This fits with the well understood effects of higher molecular weight on drawability.

Table 1. Molecular weight of two initial grades at different processing temperatures.

Grade	Processing Temp. [˚C]	Molecular weight [g/mol]
4032D	180	3.30 e4
4032D	200	2.07 e4

As seen in Figure 4, increasing draw ratio leads to a large decrease in strain to failure. As expected, tensile strength increases with increasing draw ratio up to $\lambda = 8$, but decreases after that. This can be explained due to the formation of weak void-rich areas as a result of over-drawing, possibly leading to stress concentrations and early failure of the tapes. Thus in the production of high strength tapes where strength is critical, a draw ratio of 8 is sufficient. On the other hand, modulus increases almost linearly with draw ratio.
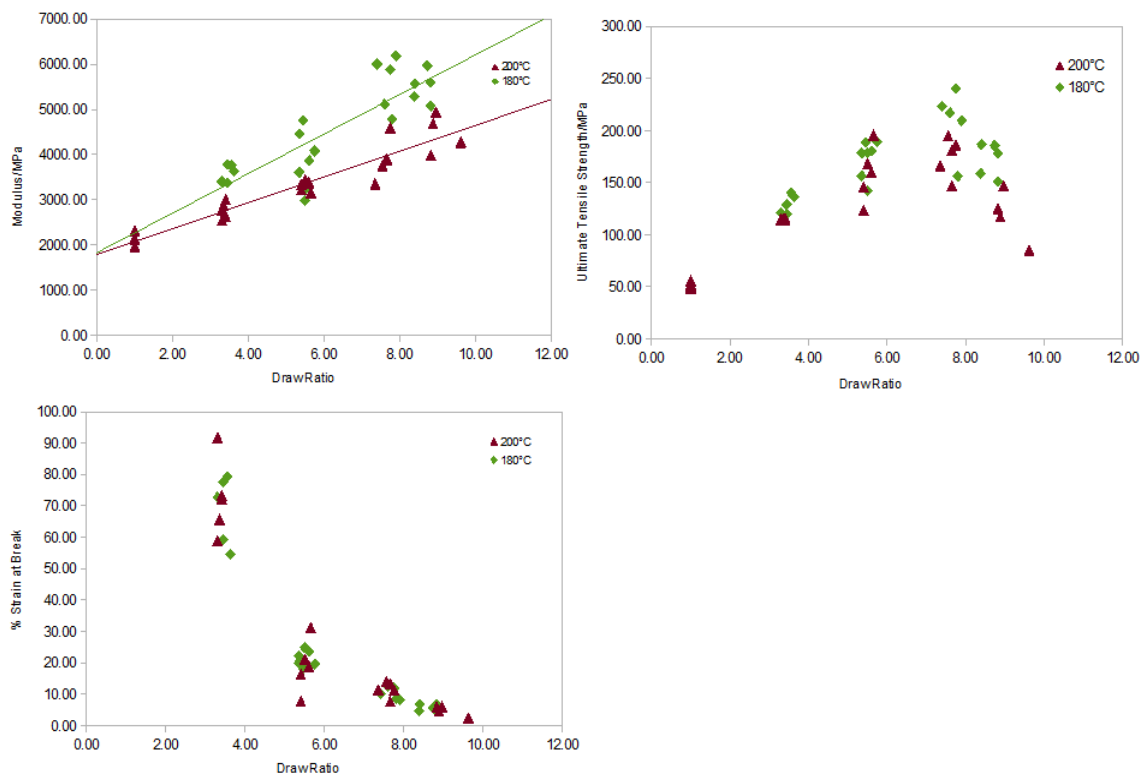

Figure 4. Young's modulus, ultimate tensile strength and strain at break versus draw ratio for solid-state drawn tapes from isotropic films hot presses at two different temperatures.

3.2 Biodegradation sensing of PLA film

Changes in the electrical conductivity of PLA/CNT nanocomposites can occur due to external stimuli such as temperature, strain, liquid and vapour [12]. Here we try to use the evolution of electrical conductivity as a means to monitor PLA degradation.

Figure 5 shows the change in conductivity with MWNT loading. The conductivity of the composites with 3 wt.% MWNTs is about 3-4 orders of magnitude higher than that with 1 wt.% MWNTs. However, it should be noted that composites containing 1 wt.% MWNTs have already a conductivity greater than 1×10^{-2} S/m, indicating that at these low concentrations already efficient percolation networks have been formed. Hence, the percolation threshold is probably below or near 1 wt.%.
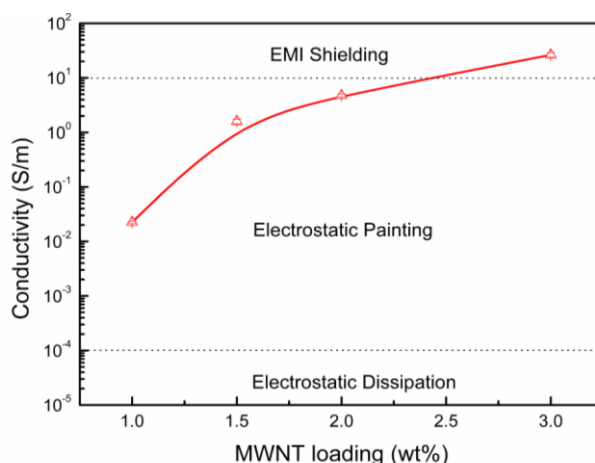

Figure 5. Conductivity of PLA/MWNT composite versus nanotube loading. Dashed lines represent the approximate conductivity lower bounds required for typical electrical applications.

Figure 6 shows the change in conductivity of composites during degradation. Changes in conductivity for composites degraded in PBS or water are fairly similar. However, different nanotube concentrations lead to significant differences in electrical conductivity with degradation. Conductivity increases with degradation for PLA nanocomposites with 1 wt.% CNT, while no significant changes are measured for PLA nanocomposites with 3 wt.% CNT.
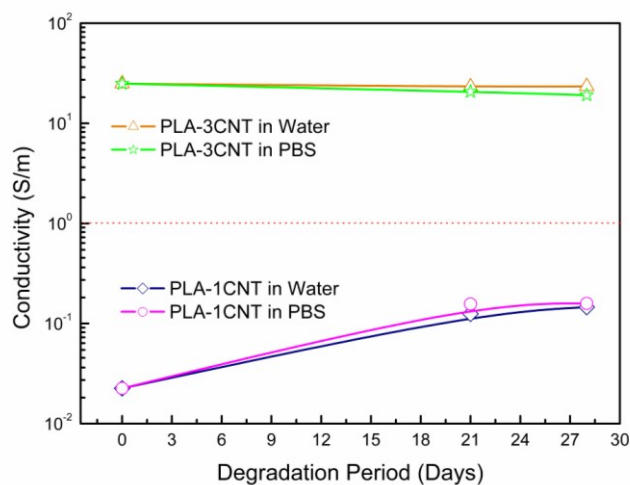

Figure 6. Conductivity of composites containing 1 and 3 wt.% MWNTs as a function of degradation period.

Clearly, the composite with a CNT loading around the percolation threshold gives the highest sensitivity. The increase in conductivity is probably due to an increased MWNT network density after removal of (amorphous phase) polymer. Composites containing 3 wt.% MWNTs have already a very strong network and hence, polymer degradation does not lead to major changes in local nanotube densities.

3.3 Tailoring the adhesive properties between PLA tapes and matrix film
The role played by the matrix film is crucial to the processability and performance of the all-PLA composite. The adhesive properties of the matrix film can be tailored not only by the choice of polymer but also by the compaction process parameters. The effects of compaction temperatures and draw ratio on the peel strength are plotted in Figure 7a. At 160 ^{o}C, good fusion bonding is not yet obtained. The film-stacked sample could be easily peeled apart at the interface. However, at 170 ^{o}C, the peel force is two times higher. It should also be noted that there is a decrease in peel strength with increasing tape draw ratio.
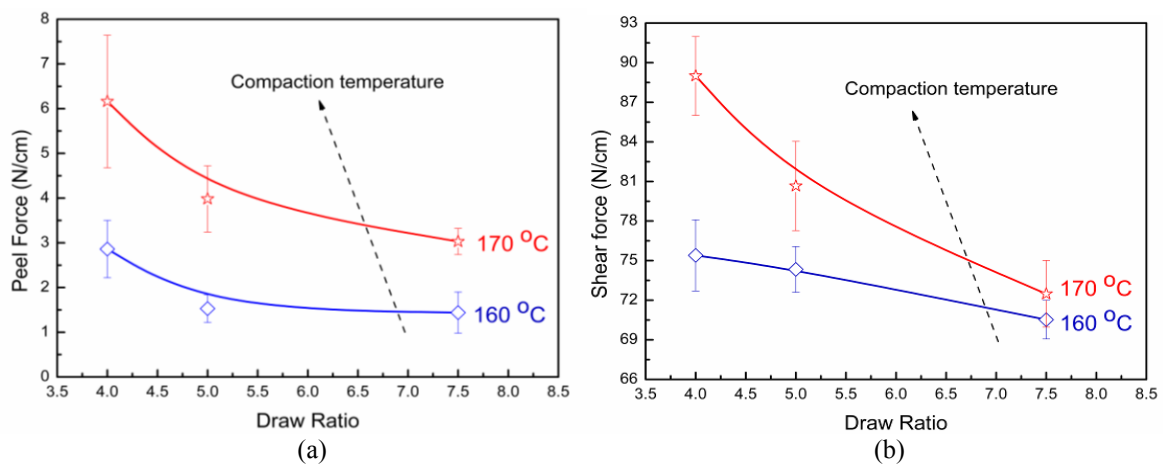

Figure 7. Peel force (a) and single lap bond strength (b) as a function of draw ratio with increasing temperature.

The bond strength for single lap shear specimens shows a similar trend as the peel force. (Figure 7b) Again interfacial strength increases with increasing compaction temperature. The high bond strength values for tapes with lower draw ratios is of less interest to this research due to the inherent lower stiffness and strength of such tapes. Tapes below $\lambda = 4$ and 5 show similar behaviour, but there is a clear transition to a much lower peel force at $\lambda = 7.5$. This also coincides with the creation of microvoids, as observed in Figure 3. However, this superior adhesion has to be balanced against the loss in mechanical properties resulting from compaction at elevated temperatures. The tensile properties of the tapes with $\lambda = 7.5$ before and after compaction are summarized in Table 2. Although the tensile modulus and strength of these tape used to manufacture the bi-directional plates decrease after welding at 170 $^{\circ}$C, modulus and strength are maintained at 87% and 92%, respectively. Moreover, the ductility of these tapes is better which expands the potential application of these all-PLA composites.

Table 2. Mechanical property loss during hot compaction for $\lambda = 7.5$ tapes.

Sample	Young's Modulus [MPa]	Tensile Strength [MPa]	Stain at break [%]
Before welding	5596 ± 108	209 ± 32	10.3
Welding at 160 ^{o}C	4958 ± 81	195 ± 24	29.6
Welding at 170 ^{o}C	4903 ± 120	192 ± 10	33.7

4   Conclusions

All-PLA composites with degradation sensing have been successfully developed in this pilot research work. The results show a 3 to 4 times increase in Young's modulus and tensile strengths for the oriented tapes compared to isotropic PLA film. Moreover, through the evolution of electrical conductivity during PLA/CNT compound degradation, we are able to monitor the biodegradation of these polymer composites. Electrical conductivity of the PLA nanocomposites increased with degradation, due to increased interconnecting conductive pathways after removal of amorphous polymer. Higher compaction temperatures resulted in better adhesive properties between the tapes without significant mechanical property loss. These initial results indicate that all-PLA composites may provide a promising green alternative to commercial polymer composites with embedded smartness.

5 Acknowledgement

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