# Renewable resource-based green composites of surface-treated spent coffee grounds and polylactide: Characterisation and biodegradability

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A B S T R A C T

The morphology, mechanical properties, and biodegradability of composite materials containing polylactide (PLA) and spent coffee grounds (SCG) were evaluated. Maleic-anhydride-grafted polylactide (PLA-g-MA) and treated, i.e. cross-linked, spent coffee grounds (TSCG) were used to enhance the desired characteristics of these composites. PLA-g-MA/TSCG materials exhibited desirable mechanical properties relative to those of PLA/SCG. This effect was attributed to greater compatibility between the grafted polymer and TSCG. The dispersion of TSCG in the PLA-g-MA matrix was highly homogeneous due to ester formation and resulted in branched and cross-linked macromolecules. Additionally, the PLA-g-MA/TSCG composites exhibited lower melt viscosities and were therefore more easily processed. The water resistance of the PLA-g-MA/TSCG composite was greater than that of PLA/SCG and the mass losses following burial in soil compost indicated that both materials were biodegradable, especially at high levels of SCG substitution. The PLA/SCG and PLA-g-MA/TSCG composites were more biodegradable than neat PLA.

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## 1. Introduction

Increased consumption of goods has resulted in considerable waste of resources that has been increasing steadily [1,2]. The food and beverage (F&B) industry alone generates considerable unusable waste products, resulting in several environmental pollution issues [3,4].

Food waste residues consist mainly of starches, food fibres, and animal fats such as bagasse pith, tofu pulp, coffee grounds, tea dregs, etc. Most food waste residues are produced domestically and can be incorporated into compost to improve soil pH [5,6]. Recent studies have evaluated the use of food waste to produce animal feed [7] and biogas, which can be used for power generation or as a heat supply [8]. However, the disposal cost of such materials is generally very high. Most countries ship food waste into landfills [9,10], which require a great deal of land, pollute local environments, and can even limit the recycling of waste resources. Therefore, the development of biodegradable plastics and green additives is beneficial both economically and environmentally.

Polylactide is the most commonly used biodegradable plastic. It is produced by the polymerisation of lactic acid and is nontoxic, nonirritating, mechanically strong, easily processed, and highly biodegradable [11,12]. However, the relatively high cost of polylactide limits its marketability. Coffee grounds have been used as an additive to polylactide [13,14] as a means of reducing cost and alleviating environmental concerns. In this study, spent coffee grounds were added to biodegradable plastics to create composite materials. Spent coffee grounds are extensively available, low density, and do not irritate the skin. After decomposition in soil, coffee grounds are an effective plant fertiliser providing protein, cellulose, ash, calcium, and phosphorus [15,16]. However, the binding adhesion forces between spent coffee grounds and biodegradable plastics are weak, which prevents effective mixing. To enhance the compatibility between plastic matrices and spent coffee grounds, the grounds can be surface-modified. Moreover, maleic anhydride can be grafted onto the backbone of the biodegradable plastic matrix to act as an interfacial compatibility agent. The modified coffee grounds penetrate into the long pores of the polymer chain, thereby enhancing the mechanical properties of the resulting composite material [17,18].

## 2. Experimental

### 2.1. Materials

PLA composed of 95% L-lactide and 5% meso-lactide was used as supplied (Nature Works Corp., Minnetonka, NE). Maleic-anhydride

(MA) and di-cumyl peroxide (DCP) were obtained from Sigma-—Aldrich Corp. (Milwaukee, WI). Before use, the MA was purified by recrystallisation from chloroform. DCP was used as the polymerisation initiator, and was purified via dissolution in chloroform and re-precipitation from methanol. The other reagents were purified using conventional methods. SCG was obtained from Yunlin (Taiwan, R.O.C.).

## 2.2. PLA-g-MA copolymer

The grafting reaction of MA onto PLA was carried out in a round-bottom flask. In a preliminary test using xylene as a solvent, a mixture of MA and DCP was added in four equal portions to molten PLA at 2-minute intervals to allow grafting to take place. The reactions were performed in a nitrogen ($N_2$) atmosphere at $70\,^\circ C \pm 2\,^\circ C$. Preliminary experiments showed that equilibrium was attained in less than 12 h. Thus, reactions were allowed to progress for 12 h with stirring at 60 rpm. Samples of 4 g of the product were dissolved in 200 mL of refluxing xylene at $70\,^\circ C \pm 2\,^\circ C$, and the solution was filtered through several layers of cheesecloth. The xylene-insoluble product remaining on the cheesecloth was washed with acetone to remove the unreacted MA, and was then dried in a vacuum oven at $80\,^\circ C$ for 24 h. The MA loading of the xylene-soluble polymer was determined by titration, and expressed as the grafting percentage, which was determined using a titration method [19]. The grafting percentage was approximately 0.96 wt%. The loading of DCP was maintained at 0.3 wt%, and that of and MA was maintained at 10 wt%.

## 2.3. Processing of SCG and TSCG

The processing of the SCG consisted of purification by immersing 60 g of ground and dried SCG in 1000 mL of distilled water for 0.5 days to remove any water-soluble components. The product was then dried at $100-110\,^\circ C$ for 2 days under vacuum. The SCG was ground and sorted by passing samples through 300- and 400-mesh sieves, then air dried for 2 days at $100-110\,^\circ C$, and vacuum dried for a further 12 h at $120-130\,^\circ C$ until the moisture content of the fine brown powder was $2 \pm 0.5\%$.

The TSCG was made by dissolving a mixture of crosslinking agents in a stoichiometric solution of tetraethyl orthosilicate (TEOS), $H_2O$, and lactic acid catalyst in tetrahydrofuran, which was stirred at room temperature for 1 h and allowed to stand for 1 day. The molar ratios used were as follows: lactic acid/TEOS = 0.01, $H_2O$/TEOS = 2.2. The SCG and crosslinking agents were mixed at room temperature for 1 h at a rotor speed of 50 rpm. Samples were prepared at a mass ratio of SCG to crosslinking agent of 1—8. The final product was dried under vacuum at $105-110\,^\circ C$ for 1 day.

## 2.4. Composite preparation

Prior to composite fabrication, the SCG and TSCG samples were washed with acetone and dried in an oven at $105\,^\circ C$ for 24 h. Composites were prepared in a Brabender (Dayton, OH) "Plastograph" W50EHT 200-Nm mixer with a rotor blade. The blends were mixed at $170-180\,^\circ C$ for 15 min at a rotor speed of 50 rpm. The SCG and TSCG contents in the hybrid materials, i.e. PLA/SCG or PLA-g-MA/TSCG, were 0, 10, 20, 30, and 40 wt%. After mixing, the composites were pressed into thin plates using a hot press and placed in a dryer for cooling. These thin plates were cut into standard sample dimensions for further characterisation.

## 2.5. Characterisation analysis

Solid-state $^{13}C$ NMR spectra were acquired using an AMX-400 NMR spectrometer (Bruker, Madison, WI) at 100 MHz under cross-polarisation while spinning at the magic angle. The power decoupling conditions were set with a 90° pulse and a cycle time of 4 s. Infrared spectra were obtained using an FTS-7PC FT-IR spectrophotometer (Bio-Rad, Hercules, CA). X-ray diffractograms (XRD) were recorded using a Rigaku D/max 3V X-ray diffractometer with a Cu target and $K_\alpha$ radiation at a scanning rate of 2°/minute. The phase compatibility in the composites was evaluated based on dynamic mechanical analyses (DMA) (Model 2080, TA Instruments, New Castle, USA) operating in film tension mode. Test specimens were rectangular thin films measuring $25 \times 5 \times 1$ mm$^3$. DMA tests were performed at a frequency of 1 Hz and a strain level of 0.075% under conditions in which the temperature increased from 0 to 200 °C at a rate of 3 °C min$^{-1}$. Static forces were selected from the experimental results in the linear elastic region in the absence of drawing effects. To specify this force, several stress-strain experiments were conducted beforehand, so that the ratio of static force to dynamic force could be kept constant during the measurements. The glass transition temperature ($T_g$), melting temperature ($T_m$), and heat of fusion ($\Delta H_f$), were determined by differential scanning calorimetry (DSC) (TA Instruments Model 2010 DSC, New Castle, DE). The sample quantity was in the range 4—6 mg. Melting curves were recorded over the temperature range 0—210 °C at a heating rate of 10 °C min$^{-1}$. The values of $T_g$, $T_m$, and $\Delta H_f$ were extracted from the temperatures and areas of the melting peaks in the DSC heating thermograms.

## 2.6. Mechanical tests

A mechanical tester (Model LR5K; Lloyd Instruments, Bognor Regis, UK) was used to determine the tensile strength at failure in accordance with ASTM Standard D638. Test specimens were prepared in a hydraulic press at 80 °C and conditioned at a relative humidity of $50\% \pm 5\%$ for 24 h prior to taking measurements. The measurements were made at a crosshead speed of 10 mm min$^{-1}$. Five specimens were tested and mean values were calculated.

## 2.7. Composite morphology

A thin film ($150 \times 150 \times 1$ mm) of each composite was prepared using a hydraulic press and treated with hot water at 60 °C for 24 h. Specimens were cut according to ASTM Standard D638. Following rupture, a thin section of the fracture plane was removed, coated with gold, and the fracture surface morphology was imaged by scanning electron microscopy (SEM).

## 2.8. Water absorption

Samples were prepared for water absorption measurements by cutting the composites into $45 \times 25$-mm$^2$ strips ($150 \pm 5$ μm in thickness) in accordance with ASTM Standard D570. The samples were dried in a vacuum oven at $50 \pm 2$ °C for 12 h, cooled in a desiccator, and then immediately weighed to the nearest 0.001 g. This mass was designated $m_c$. Thereafter, the samples were immersed in distilled water and maintained at $30 \pm 2$ °C for a 60-day period, during which they were removed from the water at 10-day intervals, gently blotted with tissue paper to remove excess water from the surfaces, immediately weighed to the nearest 0.001 g three times, and then returned to the water. The average of the mass measured at 10-day intervals was calculated; these average masses were designated $m_w$. The percentage mass increase due to water absorption, $m_f$, was calculated to the nearest 0.01% as follows:

$$\%m_f = \frac{m_w - m_c}{m_c} \times 100\%. \tag{1}$$