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Article

PLA/Coffee Grounds Composite for 3D Printing and Its Properties

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Abstract: Coffee is one of the most popular beverages in the world. It generates a waste known as coffee grounds. In this work, changes in mechanical properties, crystallinity index, and DSC characteristics of PLA/coffee grounds with different dosages were analyzed by XRD, DSC, and mechanical property tests. Statistical analysis showed that the modulus of rupture of PLA/coffee grounds 3D printing materials was maximal at 109.07 MPa and 3604 MPa when 3% coffee grounds were added. The tensile strength of the untreated PLA complex was 49.99 MPa, and the tensile strength increased from 49.99 MPa to 51.28 MPa after 3% coffee grounds were added. However, there was no significant difference between the PLA complex and PLA/coffee grounds 3D printing materials when the additions were lower than 3%. The statistical analysis showed that when the coffee grounds additions increased from 5% to 7%, the tensile strength of PLA/coffee grounds 3D printing products significantly decreased. For example, the tensile strength decreased from 49.99 MPa to 26.45 MPa with addition of 7% coffee grounds. The difference between the glass transition, cold crystallization, and melting temperatures of PLA coffee grounds 3D printing materials was almost negligible, which indicates that the thermal properties of PLA coffee grounds 3D printing materials are comparable to those of PLA, and that the processing temperature and FDM printing temperature of the PLA filament are suitable for application to the PLA coffee grounds 3D printing material system.

Keywords: additive manufacturing; 3D printing; cellulose-reinforced composite

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1. Introduction

Three-dimensional printing technology emerged in the 1980s and in 2012 was recognized as being highly valued by the general public, entrepreneurs, and governments as traditional manufacturing turned to new technologies [1]. Currently, research into 3D printing technology with broad market prospects is supported by government policies in many countries and regions. Three-dimensional printing technology mainly includes light-curing rapid prototyping (Stereo LithographySLA), fused deposition modeling (FDM), selective laser sintering (SLS), layered solid manufacturing (laminated object manufacturing, LOM), three-dimensional printing (3DP), and other processes [2]. Of these, fused deposition modeling is characterized by low equipment costs as does not require any rapid prototyping technology. Fused deposition modeling materials are relatively inexpensive, making fused deposition especially suitable for printing products with gaps. It saves materials, reduces printing time, has a small shell, and is pollution-free [3]. Currently, it is widely used in teaching, research, office work, model design, crafts, and other fields. There is considerable market demand for fused deposition materials [4]. As the most common thermoplastic polymer material, PLA is widely used in FDM 3D printing [5]. Over the years, PLA has attracted increasing attention from scholars and entrepreneurs and has been widely used in drug delivery systems, food packaging, 3D printing, and tissue engineering [6]. Unfortunately, its inherent shortcomings, such as low flexibility and toughness, seriously limit its application. Much research has been conducted into promising additives for modified PLA to enhance its mechanical properties [7].

Suryanegara et al. used cellulose as an additive for PLA to improve its high-temperature mechanical properties and applied modified bamboo cellulose additive in polylactic acid composite to improve its modulus and toughness [8]. Ballesteros et al. used a thermoplastic elastomer (SBS, styrene–butadiene–styrene plastic) to modify ABS in an attempt to improve the flow properties of ABS, increase the strength of the melt, and improve the toughness of the materials [9]. Utilizing iron and copper powder particles, Nikzad et al. modified ABS for FDM 3D printing by melt blending and significantly improved the thermomechanical and mechanical properties of ABS substrate [10]. Postiglione et al. combined an FDM 3D printer with a liquid-phase deposition (LDM) process to prepare polylactic acid/multi-walled carbon nanotube (PLA/MWCNT) composites and tested their electrical conductivity [11]. The composites showed a significant improvement in electrical conductivity compared to pure PLA [12]. The electrical conductivity of the composites reached its optimum when 5% carbon nanotubes were added. Huang et al. used coffee husks as an additive in a polyethylene matrix, which resulted in incremental modulus and thermal properties [13]. Moustafa et al. utilized coffee grounds as an additive for polymers to reduce the overall cost of the composite [12]. To sum up, graphene, carbon nanotubes, and metal powder evenly dispersed in the polymer matrix can effectively improve the electric conductivity and mechanical properties of composite materials, but there is little research on the fabrication of 3D printing wire using coffee grounds [14].

Increasing attention has been paid to functional additives and composite manufacturing technology based on the selection of green additives that are pollution-free, environmentally friendly, and economical [15]. Coffee, one of the most popular beverages in the world, is a truly global commodity. Total global consumption of coffee packaged in 60 kg units reached 160.9 million between 2016 and 2017 [16]. In this study, coffee residues were used to modify PLA for use as a 3D printing material and to investigate the enhancement effect of coffee residues on PLA. Coffee grounds can be added to polymers as pigment on account of their unique color and flavor, to produce a bright and coffee-colored product with a mild coffee aroma. In addition, coffee grounds are rich in antioxidants and alkaloids and have numerous tiny pores that absorb moisture and deodorize, which create a coffee aroma during printing. Research into PLA/coffee grounds 3D printing materials will not only increase the variety of printing materials but may also lead to the creation of unique printing materials [17].

In this study, coffee residue was used to modify PLA to produce a 3D printing material. The effect of different additions (1%, 3%, 5%, and 7%) on the mechanical properties, crystallinity index, and DSC properties of PLA/coffee grounds 3D printing materials was explored through XRD, mechanical property testing, and DSC.

2. Materials and Methods

2.1. Materials

Pulverized PLA powder (4043D, 60 mesh) was purchased from Filabot (Barre, VT, USA). Coffee grounds were provided by Singtex Industrial Co. (Nanjing, China).

2.2. Preparation Process

The pure PLA powder and dried coffee grounds were mixed at concentrations of 1%, 3%, 5%, and 7%, respectively. Each mixture weighed 100 g and was mixed for 4 h in a normal V-shaped powder mixer. The PLA was then dried in an oven at 50 °C for 4 h; a 3D printing filament was prepared using a precision drawing machine, and the diameter of the filament was kept to around 1.75 mm by adjusting the temperature, extrusion speed, and traction speed of the extruder. The drawing temperature was reduced to 140 °C during preparation. The drawing machine and FDM 3D printer are shown in Figure 1. The adjusted temperature, extrusion speed, and traction speed of the extruder were 195 °C, 60 mm/s, and 100 mm/s, respectively.

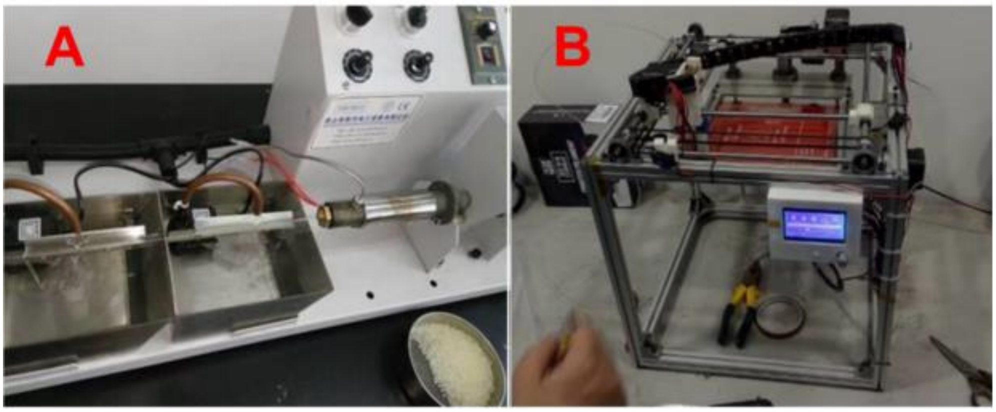

Figure 1. (**A**) Drawing machine; (**B**) FDM 3D printer.

2.3. Mechanical Property Test

Tensile strength was tested based on the ASTM D 638-2010 standard. The bending test specimens were cut to an average size of 150 × 10 × 4 mm. The mechanical properties of five repeat specimens in each group were tested. The average size of specimens used for testing the bending strength was 80 × 10 × 4 mm. The tensile and bending tests were performed with crosshead displacements of 1–2 mm/min and 2 mm/min, respectively. The 3D printing wire produced by the coffee grounds is presented in Figure 2A,B. The standard specimens for the mechanical properties test are shown in Figure 2C,D.

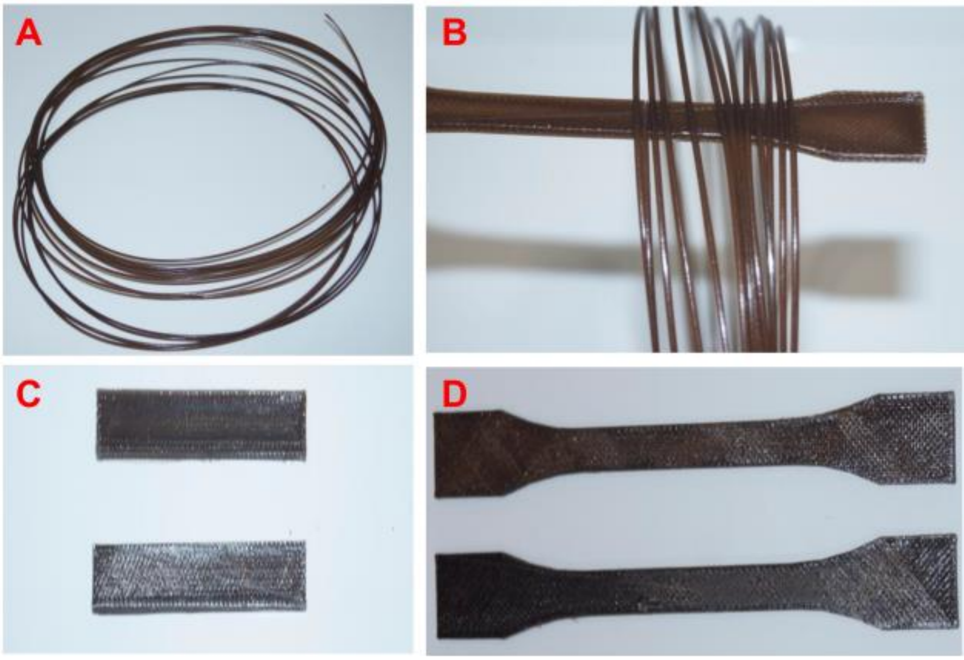

Figure 2. (**A**,**B**) Three-dimensional printing wire produced with coffee grounds; (**C**,**D**) standard specimens for the mechanical properties test.

2.4. Thermal Property Analysis

Differential scanning calorimetric analysis of the PLA was conducted in three stages during the specimen testing process. In the first stage, the temperature was increased from room temperature to 200 °C and was then held for 5 min. During the second stage, the temperature was reduced from 200 °C to room temperature and was then held for 5 min.

During the third stage, the temperature was increased from room temperature to 200 °C. The reference standards were GB/T 19466, ISO 11357, and ASTM D3418. The temperature was raised and lowered at a rate of 10 °C/min, and the specimen was placed in a crucible protected by nitrogen gas at a dosage of about 10 mg.

During the test, the DSC curves were recorded, and the glass transition temperature (T_g), cold crystallization temperature (T_{cc}), hot crystallization temperature (T_{hc}), and melting temperature (T_m) of specimens, as well as the enthalpy change corresponding to the cold crystallization peak ($\Delta \boldsymbol{H_{cc}}$), hot crystallization peak ($\Delta \boldsymbol{H_{hc}}$), and melting peak $\Delta \boldsymbol{H_m}$, were calculated. The crystallinity of specimens after the heating and cooling processes was calculated as below:

$$\chi_c = \frac{|\Delta H_m + \Delta H_{cc}|}{\varnothing \Delta H^*} \times \mathbf{100}\%$$

$$\chi_c = \frac{|\Delta H_{hc}|}{\varnothing \Delta H^*} \times \mathbf{100}\%$$

where $\Delta \boldsymbol{H_{cc}}$ is the cold crystallization peak, $\Delta \boldsymbol{H_{hc}}$ is the hot crystallization peak, and $\Delta \boldsymbol{H_m}$ represents the melting peak.

2.5. X-ray Diffraction (XRD) Test

Wide-angle X-ray diffraction of FDM specimens of PLA/coffee grounds 3D printing materials with different coffee grounds contents was analyzed by measuring the crystallinity of the FDM products and exploring the crystallization behavior and characteristics of the 3D printing materials.

2.6. Scanning Electron Microscope

The micro-morphology of the PLA/coffee grounds was first coated with a thin layer of gold using the sputter method and then studied using a scanning electron microscope (FEI Quanta 200F, Hillsboro, OR, USA) at an acceleration voltage of 20 kV.

2.7. Statistical Analysis

Tukey's tests were used to distinguish the differences between the different PLA/coffee samples using SPSS software. In addition, 12 replicates were used to measure the means for modulus of elasticity, modulus of rupture, tensile strength, and oven density. Capital letters have been used to represent significant differences between groups ($p < 0.05$).

3. Results Analysis

3.1. Mechanical Properties of PLA/Coffee Grounds Composite 3D Printing Products

As shown in Figure 3A,B, the modulus of elasticity (MOE) and modulus of rupture (MOR) of the untreated PLA complex were 81.86 MPa and 2336 MPa, respectively. Lowercase letters have been used to represent significant differences between groups ($p < 0.05$). The error bar represents the standard deviation. After the coffee grounds were added, the modulus of elasticity (MOE) and modulus of rupture (MOR) of PLA/coffee grounds 3D printing materials firstly increased and then decreased with incremental addition of coffee grounds. The statistical analysis results showed that the modulus of rupture of PLA/coffee grounds 3D printing materials reached its maximum value at 109.07 MPa and 3604 MPa when 3% coffee grounds were added, because of the stronger reinforcement effect of coffee grounds on PLA [8]. However, the modulus of elasticity and modulus of rupture decreased from 109.07 MPa and 3604 MPa to 51.04 MPa and 2044 MPa with the addition of more than 5% coffee grounds. Meanwhile, specimens of PLA/coffee grounds 3D printing materials were treated at 100 °C for 120 min to test their bending properties; the bending strength and bending modulus were found to be 115.4 MPa and 3948 MPa, respectively, indicating that thermal treatment significantly improved the bending properties of the 3D printing materials. The tested PLA/coffee grounds 3D printing materials are shown in Figure 4A,B. When 5% or more coffee grounds were added, the modulus of elasticity and modulus of rupture decreased, which was attributed to poor dispersion in the PLA composite [18].

Due to the increase in coffee grounds, coffee grounds were aggregated in the PLA complex, resulting in uneven dispersion [18]. In other words, when added coffee grounds were well dispersed, the mechanical properties of the PLA/coffee grounds composites improved. Well-dispersed coffee grounds can be associated with stress concentrations and are conducive to the formation of crazes during bending [19]. As a result, the mechanical properties of composites with higher coffee grounds contents deteriorated.

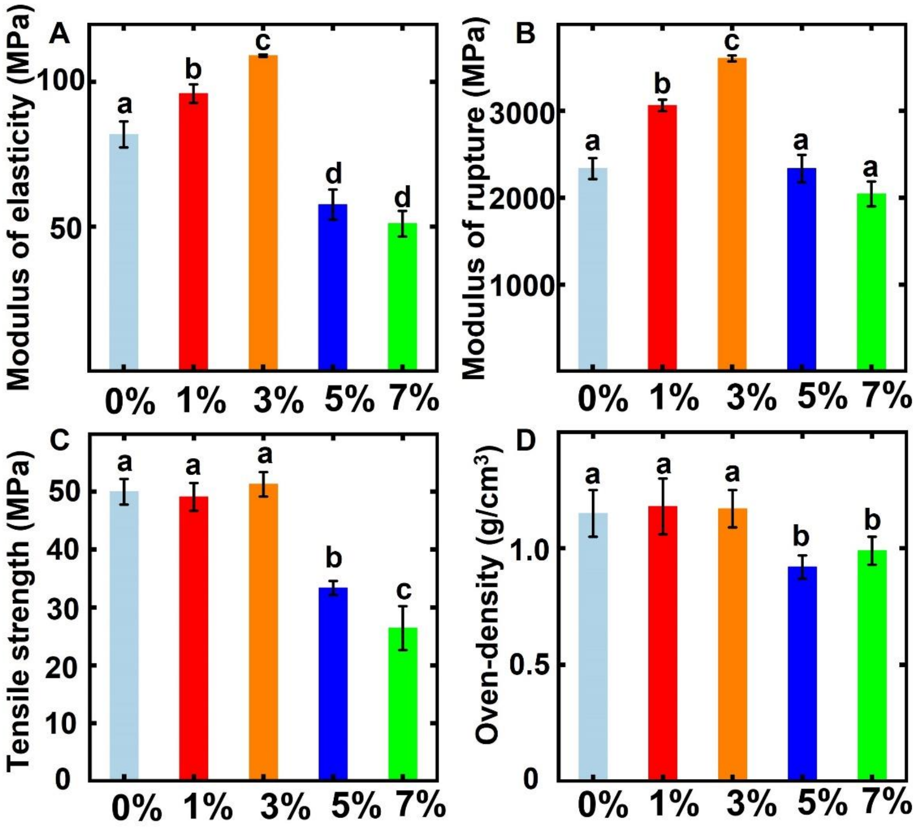

Figure 3. Physical/mechanical properties of PLA/coffee grounds composite 3D printing products: (**A**) modulus of elasticity; (**B**) modulus of rupture; (**C**) tensile strength; (**D**) oven density. The figure shows significant differences between groups ($p < 0.05$). The error bar in the figure represents the standard deviation.

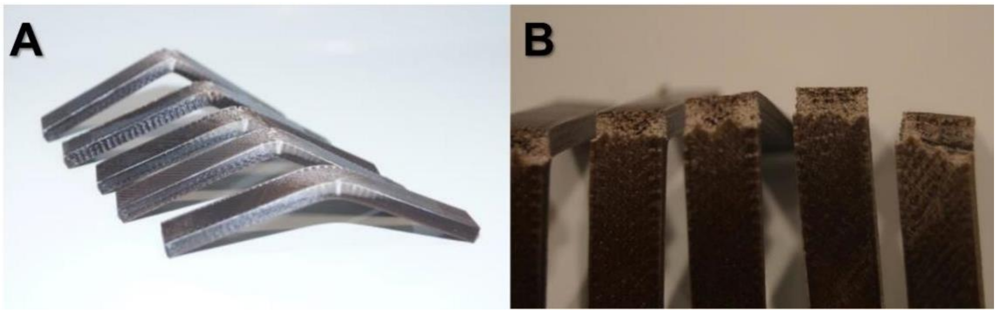

Figure 4. The standard bending specimen of PLA/coffee grounds after the bending test: (**A**) PLA/3% coffee grounds composite 3D printing products; (**B**) PLA/7% coffee grounds composite 3D printing products.

The tensile strength exhibited a similar pattern to bending strength. In detail, the tensile strength of the untreated PLA complex was 49.99 MPa, and the tensile strength increased from 49.99 MPa to 51.28 MPa after 3% coffee grounds were added. However, there was no significant difference between the PLA complex and PLA/coffee grounds 3D printing materials when the additions were lower than 3%. The statistical analysis showed that when the coffee grounds additions increased from 5% to 7%, the tensile strength of the PLA/coffee grounds 3D printing products significantly decreased. For example, the tensile strength decreased from 49.99 MPa to 26.45 MPa when the coffee grounds additions increased to 7%. Due to the increase in coffee grounds, coffee grounds were aggregated in the PLA complex, resulting in an uneven dispersion. In other words, when added coffee grounds were well dispersed, the mechanical properties of the PLA/coffee grounds composites improved. To be more specific, well-dispersed coffee grounds can be associated with stress concentrations and are conducive to the formation of crazes during bending. As a result, the mechanical properties of composites with higher coffee grounds contents deteriorated [20].

As shown in Figure 3D, the density of the untreated PLA complex was 1.15 g/cm^3. After the coffee grounds were added, the density of the PLA complex firstly increased and then decreased with incremental additions of coffee grounds. The statistical analysis showed that there was no significant difference between the PLA complex and PLA/coffee grounds 3D printing materials when the additions were lower than 3%. The statistical analysis showed that when the coffee grounds additions increased from 5% to 7%, the density of PLA/coffee grounds 3D printing products significantly decreased. For example, the density decreased from 1.15 g/cm^3 to 0.99 g/cm^3 when the coffee grounds additions increased to 7%. The increased coffee grounds content was aggregated in the PLA complex, resulting in uneven dispersion. In other words, when added coffee grounds were well dispersed, the density of PLA/coffee grounds composites improved. To be more specific, well-dispersed coffee grounds can be associated with stress concentrations and are conducive to the formation of crazes during bending. As a result, the density of composites with higher coffee grounds contents decreased. The SEM results for different PLA/coffee grounds are shown in Figure 5A–C. Figure 5C shows that the coffee grounds were poorly dispersed in the PLA composite. Thus, the change in modulus of elasticity, modulus of rupture, tensile strength, and density were confirmed by the SEM results.

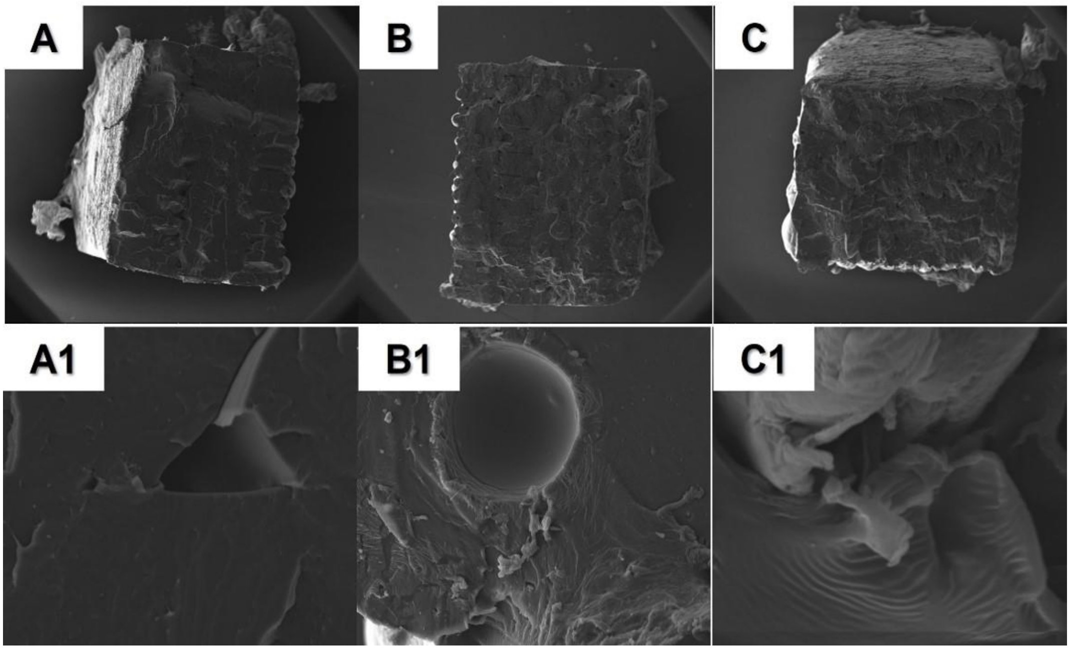

Figure 5. SEM images of PLA/coffee grounds composite 3D printing products with different coffee grounds additions: (**A**,**A1**) PLA composite 3D printing products; (**B**,**B1**) PLA/3% coffee grounds composite 3D printing products; (**C**,**C1**) PLA/7% coffee grounds composite 3D printing products.

3.2. XRD Analysis

An FDM filament was prepared by melting and co-blending 100 mesh coffee grounds in PLA. This was used for FDM 3D printing, and the obtained bending specimens were used for XRD diffraction analysis. The XRD patterns of PLA/coffee grounds 3D printing materials with different dosages of coffee grounds are shown in Figures 6a,b and 7.

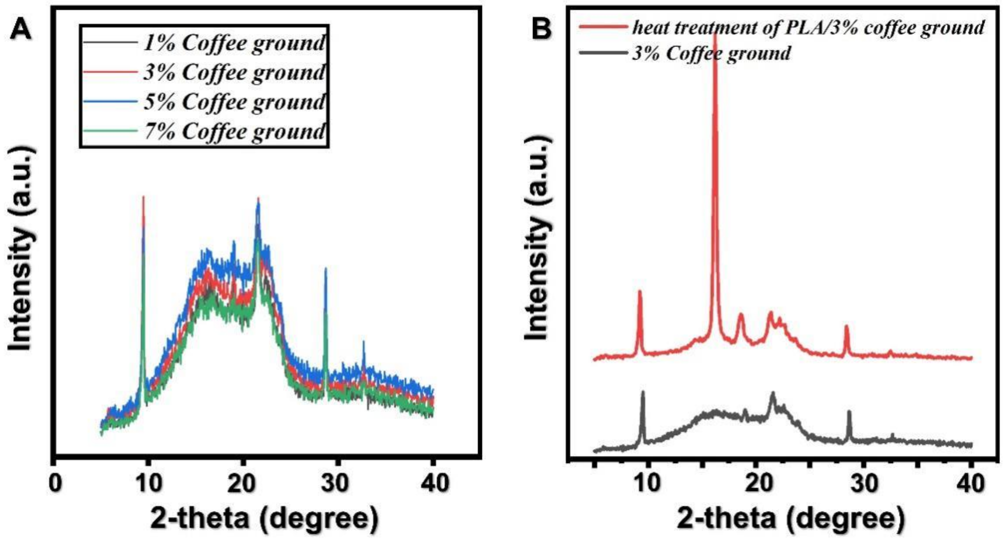

Figure 6. XRD curves of different PLA/coffee grounds 3D printing materials: (**A**) XRD curves of 1%, 3%, 5%, and 7% coffee grounds 3D printing products; (**B**) XRD curves of 3% coffee grounds 3D printing products and thermal treatment of PLA/3% coffee grounds 3D printing products.

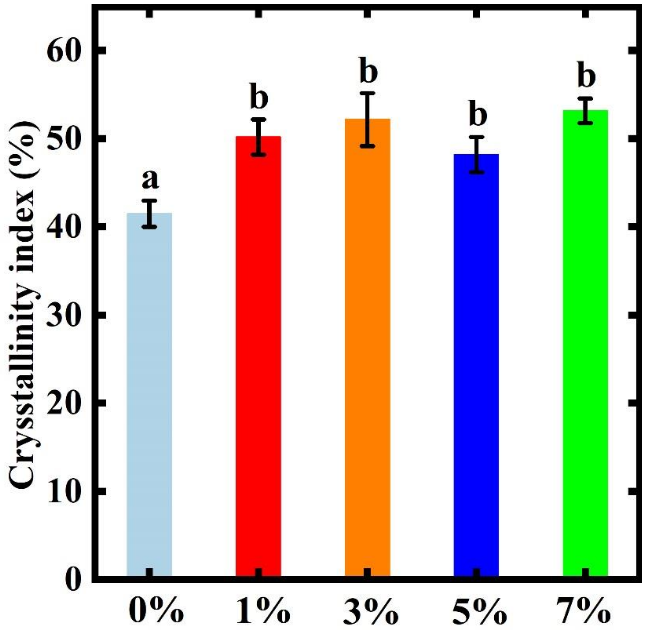

Figure 7. The crystallinity index of different PLA/coffee grounds 3D printing materials. Lowercase letters indicate significant differences between groups ($p < 0.05$). The error bar represents the standard deviation.

The XRD diffraction peaks of the PLA/coffee grounds 3D printing materials were large and broad (typical of amorphous plastics), and the (200)/(100) and (203) crystallographic features of the PLA were visible in the diffraction pattern, with corresponding diffraction 2θ angles of about 16.2° and 18.6° [21]. The intensities of these two characteristic diffraction peaks were close to those of the plastic matrix, and the high background noise of the XRD pattern indicated that PLA/coffee grounds 3D printing products obtained by FDM (with a nozzle temperature of 210 °C, print layer thickness of 0.3 mm, deposition angle of 45°, and filling rate of 100%) had low crystallinity. In addition, Figure 6a,b show that the XRD pattern of the samples did not change significantly when the dosage of coffee grounds was increased from 1% to 7%, indicating that the coffee grounds had little effect on the crystallization ability of the PLA matrix [22]. Crystalline regions are likely to suffer at high temperatures. In previous studies [23], thermal treatment of coffee grounds was found to cause increased crystallinity [22]. This could be attributed to elimination of water molecules in coffee grounds. Additionally, the transformation from α-polymorph to β crystal phase structures also contributed to changes in the crystallinity of coffee grounds [24].

As shown in Figure 6a,b and Figure 7, the crystallinity index of pure PLA 3D printing material was 41.5%. In these figures, lowercase letters represent significant differences between groups ($p < 0.05$). The error bar represents the standard deviation. Statistical analysis showed that after addition of coffee grounds, the crystallinity index of PLA/coffee grounds 3D printing materials significantly increased. For example, the crystallinity of PLA/3% coffee grounds 3D printed material increased significantly after thermal treatment in an oven at 100 °C for 120 min (to 50.18%). However, after incremental additions of coffee grounds, there was no significant difference between groups. The diffraction peaks of PLA (200)/(100) and (203) crystalline surface characteristics stood out from those of the plastic matrix, and the diffraction peaks of the PLA crystalline surface also became noticeable, indicating that thermal treatment was highly effective in improving the crystallinity of PLA/3% coffee grounds because PLA crystallized at 100 °C, and thermal treatment at crystallization temperature gave the PLA molecular chains enough time and energy to rearrange, thus increasing the crystallinity of the FDM products [7]. This is consistent with the results of the mechanical tests, which showed that the mechanical properties of the material are generally directly proportional to its crystallinity. The greater the crystallinity, the higher the mechanical strength. Thermal treatment also improved the crystallinity of the material, thus increasing its bending strength and modulus. The incremental crystallinity made the PLA/coffee grounds composites more rigid. According to the previous literature [15,25,26], small fiber-based particles such as coffee grounds can be used as a nucleation agent in PLA composite systems to enhance their mechanical properties.

3.3. DSC Curve Analysis

The DSC curves (and the characteristics of these) are presented in Figure 8 and Table 1, respectively. As can be seen from Table 1, coffee grounds had an insignificant effect on the crystallinity index of PLA (below 10%). The Tg of the pure PLA complex was 60.4 °C. However, according to our tests, the mechanical properties of the 3D printed material were greatly affected by adding coffee grounds. Thus, it can be concluded that the mechanical properties of PLA/coffee grounds 3D printing materials do not significantly affect their crystallinity index [16]. It can also be seen from Table 1 that Tg did not change significantly after PLA and coffee grounds were mixed together, mainly because of the large amount of coffee grounds. Even if they were dispersed in the PLA matrix, the spacing between the molecular chains of PLA did not increase, and the intermolecular forces remained basically the same, so the Tg did not change noticeably. This is because a small amount of coffee grounds and dispersion in the PLA matrix cause the spacing between the PLA molecular chains to increase; the force between the molecular chains decreases; there is more room for the PLA molecules to move about; the chain segment movement becomes easier; and there is a glass transition process involving a change in molecular movement from small moving units to chain segment movement, which means that glass transition occurs at a lower temperature. The melting temperature also decreased in our experiments because chain segments moved actively, meaning that less energy was required for melting. The decrease in viscosity of coffee grounds 3D printing material was not caused by the decrease in melting temperature of the 3D printing material but by the nanostructure of the carbon nanotubes and graphene itself, because of its lubricating effect [9]. Moreover, the force between PLA molecular chains, as well as frictional resistance, decreased, resulting in better fluidity [26]. In summary, it can be seen from Table 1 that coffee grounds had little influence on the crystallinity of polylactic acid (PLA), which was less than 10%, while the test of mechanical properties showed that the amount of coffee grounds had a significant influence on the mechanical properties of the 3D printing materials. Therefore, it can be concluded that the mechanical properties of polylactic acid/coffee grounds 3D printing materials have no significant relationship with their crystallinity. The difference between the glass transition temperature, cold crystallization temperature, and melting temperature of polylactic acid/coffee grounds 3D printing material is almost negligible, which indicates that the thermal performance of polylactic acid/coffee grounds 3D printing material is comparable to polylactic acid, and the processing temperature of polylactic acid wire and FDM printing temperature are suitable for application to the polylactic acid/coffee grounds 3D printing material system [27].

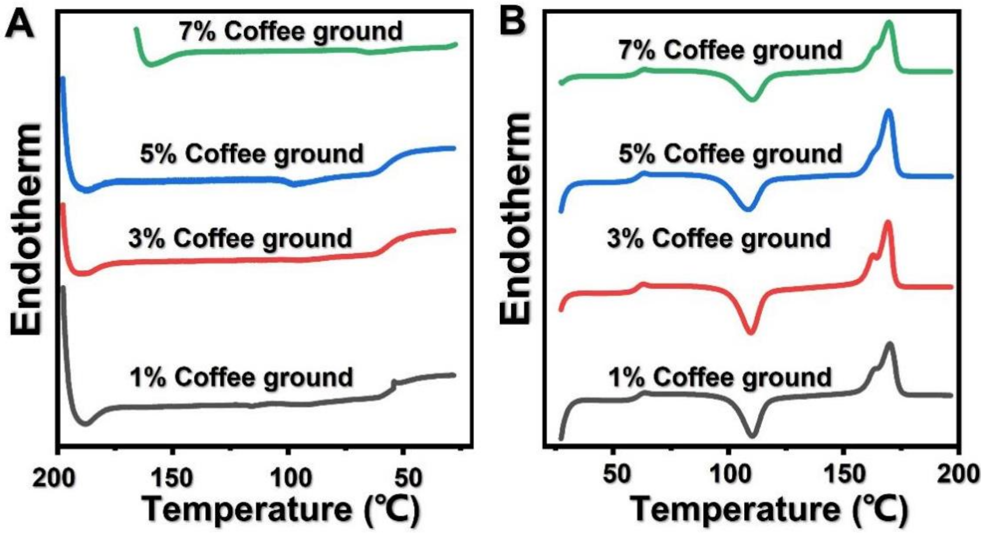

Figure 8. The DSC curves of different PLA/coffee grounds 3D printing products: (**A**) the cooling process of PLA/coffee grounds 3D printing products with different coffee grounds additions; (**B**) the second heating process of PLA/coffee grounds 3D printing products with different coffee grounds additions.

Table 1. Characteristics of DSC curves for PLA/coffee grounds 3D printing products with different coffee grounds additions.

Composition	Tg (°C)	Tcc (°C)	Tm (°C)	ΔHcc (J/g)	ΔHm (J/g)	X_c (%)
PLA	60.4	108.2	169.5	−29.6	35.0	5.8
PLA/1% coffee grounds	60.6	110.4	170.2	−25.0	29.8	5.2
PLA/3% coffee grounds	60.2	109.7	169.4	−28.8	31.8	3.3
PLA/5% coffee grounds	60.5	108.6	169.5	−25.2	33.3	9.2
PLA/7% coffee grounds	60.2	110.3	169.8	−21.2	26.5	6.1

4. Conclusions

Coffee grounds have attracted increasing attention on account of their unique color and flavor. In addition, as a residue, coffee grounds can be added to polymers to produce a bright, coffee-colored product with a mild coffee aroma. Changes in the mechanical properties, crystallinity index, and DSC characteristics of PLA/coffee grounds with different dosages were analyzed by XRD, DSC, and in mechanical property tests. Statistical analysis showed that the modulus of rupture of PLA/coffee grounds 3D printing materials peaked at 109.07 MPa and 3604 MPa when 3% coffee grounds were added because of a stronger reinforcement effect on PLA. However, the modulus of elasticity and modulus of rupture decreased from 109.07 MPa and 3604 MPa to 51.04 MPa and 2044 MPa when more than 5% coffee grounds were added. Tensile strength exhibited a similar pattern to bending strength. In detail, the tensile strength of the untreated PLA complex was 49.99 MPa, and the tensile strength increased from 49.99 MPa to 51.28 MPa after 3% coffee grounds were added. However, there was no significant difference between the PLA complex and PLA/coffee grounds 3D printing materials when the additions were lower than 3%. The statistical analysis showed that when the coffee grounds additions increased from 5% to 7%, the tensile strength of PLA/coffee grounds 3D printing products significantly decreased. For example, the tensile strength decreased from 49.99 MPa to 26.45 MPa when the coffee grounds additions increased to 7%. The difference between the glass transition, cold crystallization, and melting temperatures of PLA coffee grounds 3D printing materials was almost negligible, which indicates that the thermal properties of PLA coffee grounds 3D printing materials are comparable to those of PLA, and the processing temperature and FDM printing temperature of PLA wire are suitable for application to the PLA coffee grounds 3D printing material system. The introduction of coffee grounds to the PLA filament reduces the cost of traditional PLA filaments, as well as environmental pollution.

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