KOREAN JOURNAL OF PACKAGING SCIENCE & TECHNOLOGY
Vol. 28, No. 2 89~95 (2022)
https://doi.org/10.20909/kopast.2022.28.2.89

Biodegradable PLA-based Biocomposites with Spent Coffee Grounds as Degradation Accelerator: Hydrolytic Degradation and Characterization Research

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Abstract The goal of this study was to evaluate the effect of spent coffee grounds (SCG) biofiller on the morphological, thermal, mechanical and hydrolytic degradation characteristics of poly(lactic acid) (PLA) based biocomposites. The PLA-based biocomposite films were fabricated by using a high-viscosity kneading and hot-pressing machine. The PLA/SCG biocomposites were analyzed with SEM, DSC, TGA, UTM and hydrolytic degradation test. Aggregation in the PLA matrix is a result of increasing SCG concentrations. In the thermal properties, it was described that the cold crystallization temperature (T_{cc}) decreased as SCG was added to PLA. When SCG was incorporated to PLA, the degradation onset temperature (T_{onset}) revealed a diminish. The elastic modulus increased while tensile strength of PLA diminished as SCG was applied. Through hydrolysis analysis, the decomposition of PLA was accelerated with the addition of SCG. This research confirmed the possibility of devloping an eco-friendly packaging material with high degradability as SCG hasten the breakdown of PLA.

Keywords Poly(lactic acid), Spent coffee grounds, Hydrolytic degradation, Accelerate

Introduction

Plastics are so widely used everywhere in our daily life[1)]. Every year enormous volumes of plastics are generated, consumed, and produced as waste in a variety of industrial areas[2,3)]. The plastics made from petroleum resources are not biodegradable and have a major negative impact on the environment[4,5)]. Furthermore, the reduction and considerable cost of fossil fuels require alternative and sustainable resources for our future. As a result, there are many applications[6,7)].

After crude oil, coffee is the world's second largest traded commodity[8)]. Pulp, husk, silver skin, and SCG are the most common residues from coffee processing and use[9)]. Among them, SCG accounts for largest part of coffee by-products, most of which are disposed of in landfills[10)]. To utilize SCG, numerous investigations are being conducted. Research is being done on using lignocellulosic characteristics of SCG as a biofiller for polymers[11,12)].

PLA which is often used as a biodegradable polymer is being researched and empolyed in numerous fileds due to its superior mechanical qualities and high transparency. However, there are drawbacks, such as brittle characteristics, low elongation, high cost, and limited conditions for decomposition[13)]. These problems are being addressed through research into polymer blending and the use of additives to enhance physical properties[14)]. Additionally, researches have been conducted on whether the addition of biofillers can accelerate the decomposition rate of PLA[15)]. However, studies on whether SCG is applied as a biofiller to enhance the degradation of polymers are scarce.

According to ISO 16929, disintegration experiments is carried out during 12weeks under industrial composting conditions. Through sieving in a 2 mm screen, the standard for judging the degradation of plastic materials is established. The sample that obtained after screening should be washed and dried before being weighed and compared to the initial weight to determine how much decomposition has been progressed[16)]. In general, the initial mass is often measured while conducting a hydrolysis experiment, and the analysis is then carried out utilizing the reduction in mass as a measurement scale. However, the area change, not the weight change, served as the measurement scale in this hydrolysis experiment. As a result, it was determined that particles smaller than the usual mesh size of 2 mm employed in disintegration had undergone

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breakdown, and the degree of the decomposition was assessed using the residual surface area of film in this experiment.

In this study, the introduction of SCG to PLA is assessed for its morphological, thermal and mechanical characteristics, as well as whether it promotes hydrolysis. In order to ascertain whether SCG may be used with PLA as a biofiller and degradation accelerator.

Materials & Methods

1. Materials

Polylactic acid (PLA) (Ingeo™-4032D) was supplied by Nature Works LLC, USA It has average molecular weight (Mw) 190,000 g/mol, melt flow index (MFI) 7.6 g/10 min (at 190°C/2.16 kg) and density of 1.3 g/cm^3. Spent coffee grounds (SCG) were obtained from the local cafe dictionary in Korea. To remove moisture, SCG was dried for 48 hours at 105°C in a dry oven. Sodium hydroxide buffer solution (pH 12) was purchased from SAMCHUN, Korea.

2. Sample preparation

Prior to the experiment, PLA and SCG were prepared for 24 hours at 50°C in a dry oven. Table 1 below presents the content ratio of PLA-based biocomposites. Particle size of SCG is less than 140 mesh. Melt kneading was implemented for 6 minutes at 190°C and 80 rpm by using a high viscosity kneading machine (TEST-ONE, Seoul, Korea). The film was produced with a thickness of 120 ~ 160 ㎛ by using a hot-press machine (TEST-ONE, Seoul, Korea) at 200°C for 250 MPa for 3 minutes. With the fabricated films, SEM, UTM, and hydrolysis specimens were prepared and analyzed.

Table 1. Compounding ratio of PLA-based biocomposites with different SCG contents

Sample	PLA (wt%)	SCG (wt%)
PLA	100	0
PLA95SCG5	95	5
PLA90SCG10	90	10

3. Methods

3.1. Morphology analysis

The morphology of PLA-based biocomposites with SCG was observed with scanning electron microscopy (SEM) (Quanta FEG 250, FEI, USA). All samples were sputter-coated for 30 seconds with gold and analyzed the surface morphology of the biocomposites, as well as the particle shape and dispersity of the SCG in PLA matrix at 400 and 1,200 magnifications.

3.2. Thermal properties

The thermal characteristics of the compounding sample were measured using differential scanning calorimetry (DSC) (Q-20, TA Instruments, USA). The samples were heated at a rate of 20°C/min between –50°C ~ 230°C in a nitrogen environment. The thermal history was eliminated by repeating the cycle twice.

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the samples by using a TGA Instruments (TGA-4000, PerkinElmer, USA). The samples were heated from 30°C to 800°C at a heating rate of 20°C/min in a nitrogen atmosphere.

3.3. Mechanical properties

A universal testing machine (QM100T, QMESYS, Korea) was used to assess the tensile strength, elastic modulus, and

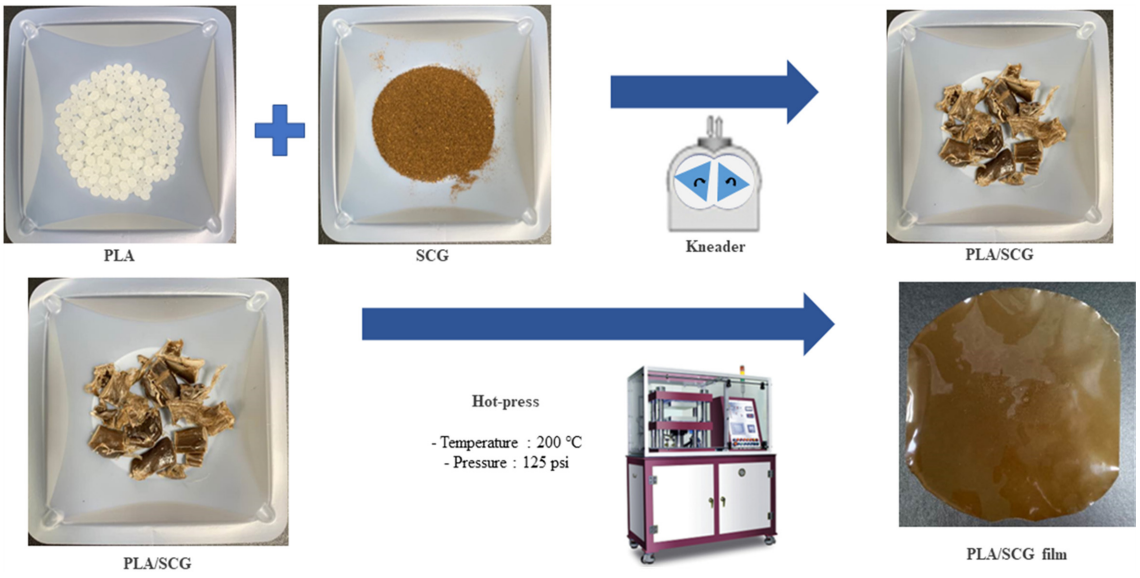

Fig. 1. Process of compounding and fabricating samples of PLA-based biocomposites with various SCG contents.

elongation at break of films at room temperature (RT) with operating at a crosshead speed of 20 mm/min with a 20 kgf load cell. The test specimens were manufactured using a mold that was made in the shape of a dumbbell in accordance with the ISO 527 standard. For each sample, the 10 specimens were measured, and the standard deviation was estimated.

3.4. Hydrolytic degradation test

The hydrolysis test was performed under accelerated conditions. It was carried out at pH 12 and 37°C, and the experiment was conducted for 5 days. The biocomposite films size is 2.5 cm × 2.5 cm and wrapped with 2 mm mesh. The average thickness of films was 150 ㎛. The area was calculated using ImageJ software (Java-based image processing program, National Institutes of Health, USA) as data for comparison of the degree of decomposition.

Results & Discussion

1. Morphology analysis

SEM examination was used to illustrate the surface characteristics of PLA-based biocomposites with diverse SCG concentration. The surface of neat PLA is shown in Fig. 2.(a), and it is clear that it is smooth. SCG has been added to images Fig. 2.(b) and 2.(c), and when the amount of SCG content increases, a rough surface is exhibited. Weak compatibility between SCG and PLA matrix may lead to deteriorate the mechanical properties. Aggregation of SCG is confirmed in Fig. 2.(c), which seems to have occurred due to the addition of a larger amount of SCG than in Fig. 2.(b). As the amount of filler increased, a similar trend to aggregate was observed in previous literatures.[17] Agglomeration caused a diminish in the elastic modulus.

2. Thermal properties

To evaluate the thermal behavior of the samples, such as melting and cold crystallization enthalpies ($\triangle H_m$ and $\triangle H_{cc}$), and also cold crystallization, melting, and glass transition temperatures (T_{cc}, T_m, and T_g), DSC analysis was conducted and the results were shown and gathered in Fig. 3 and Table 2. In the DSC graph in Fig. 3, T_g and T_{cc} of the neat PLA were obtained at 57.5°C and 109.7°C, repectively. The T_{m1} and T_{m2} of PLA is shown at 161.1°C and 166.7°C, respectively. The primary melting peak (T_{m2}) was followed by the T_{m1} peak. A

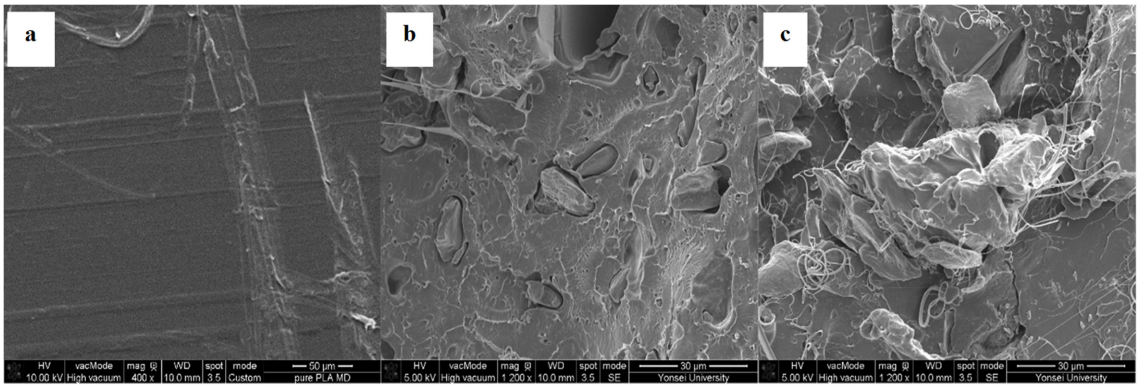

Fig. 2. SEM images present the dispersion of SCG of the PLA-based biocomposites with different SCG contents in (a) PLA, (b) PLA95SCG5 and (c) PLA90SCG10.

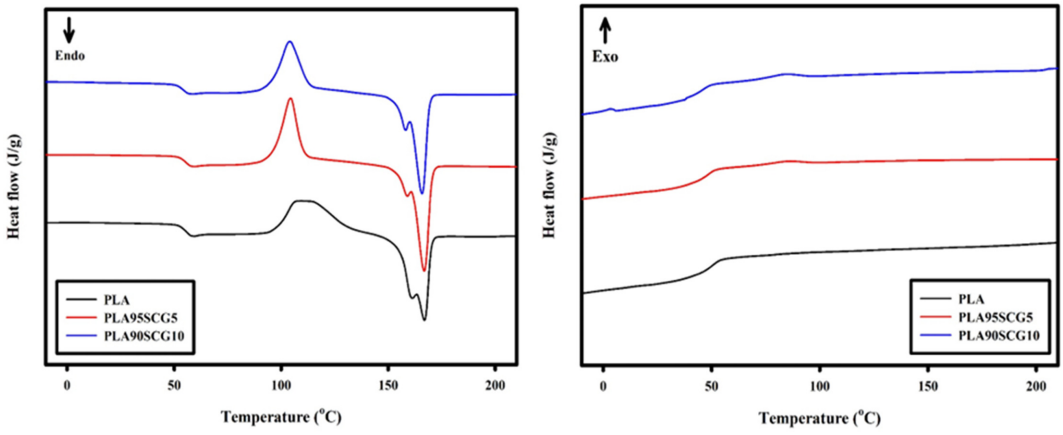

Fig. 3. DSC graph of PLA and PLA-based biocomposites with various SCG contents from second heating and cooling runs.

Table 2. DSC and TGA results of PLA and PLA-based biocomposites with various SCG contents

	Tg (°C)	T_{m1} (°C)	T_{m2} (°C)	$\triangle H_m$ (J/g)	T_{cc} (°C)	$\triangle H_{cc}$ (J/g)	T_{onset} (°C)	T_{max} (°C)
PLA	57.5	161.1	166.7	52.4	109.7	51.5	355.5	377.1
PLA95SCG5	55.9	159.1	166.8	50.9	104.4	43.3	357.5	377.5
PLA90SCG10	54.4	158.0	165.8	47.6	104.1	41	350.6	375.7

more perfect crystalline structure of PLA may be responsible for the melting peak at higher temperatures (T_{m2}) whereas a less perfect crystalline structure may be responsible for the shoulder peak at lower temperatures (T_{m1}).[18] A bimodal melting peak was reported in previous PLA studies.[19] The T_g and T_m of PLA/SCG biocomposite decreased slightly with increasing SCG contents. While $\triangle H_{cc}$ and T_{cc} decreased noticeably. The addition of 5 wt% and 10 wt% of SCG decreased T_{cc} by 5.3°C and 5.6°C when compared to neat PLA. When 5 wt% and 10 wt% of SCG were added, respectively, $\triangle H_{cc}$ reduced from PLA by 8.2 J/g and 9.5 J/g, respectively. A decreased cold crystallization temperature appears to be the result of SCG acting as a nucleating agent in the PLA matrix. Similar results in the previous research employing pecan nutshell as a biofiller in PLA contribute to validate this trend[20].

Fig. 4 has shown the TGA and DTG graphs. The T_{onset} and T_{max} of PLA/SCG composite were analyzed. The T_{onset} and T_{max} of PLA are 355.5°C and 377.1°C, respectively. With the addition of SCG, T_{onset} had a 350.6°C, which decreased by 5°C compared to PLA in PLA90SCG10. The introduction of SCG does not significantly alter T_{max}. Since SCG has lower thermal stability than PLA and a thermal decomposition temperature range of 200°C to 380°C, the T_{onset} of PLA/SCG composite drops when SCG is introduced.[17].

3. Mechanical properties

Mechanical properties of the PLA-based biomcomposites were evaluated under tensile strength, elastic modulus and elongation at break. The results were presented in Fig. 5 and Table 3. The neat PLA had 67 N/mm^2, 1091.7 N/mm^2 and 2.2% for tensile strength, elastic modulus and elongation at break, respectively. In the presence of SCG, in PLA/SCG composite, tensile strength and elongation at break decreased. It is determined, as supported by SEM, that the low miscibility of PLA and SCG induced loss of physical attributes. Previous study has shown a similar tendency, and a research that added wood flour showed mechanical properties degraded as content increased[21]. The tensile strength of PLA95SCG5 and PLA90SCG10 decrease 11.7 N/mm^2 and 25.5 N/mm^2 comparison to neat PLA, respectively. The elastic modulus of biocomposites increased with the addition of SCG. When SCG is added at 5 wt% and 10 wt%, the elastic modulus had 1523 N/mm^2 and 1221.8 N/mm^2, respectively, which is a 431.3 N/mm^2 and 130.1 N/mm^2 increase compare to neat PLA. The elastic modulus is lower when 10 wt% of SCG is added than when 5 wt% is added because the agglomeration of SCG causes a greater load to be applied to the aggregation area, which is validated by SEM. These results supported a

Table 3. Mechanical properties of PLA and PLA-based biocomposites with different SCG contents

	Tensile strength (N/mm^2)	Elastic modulus (N/mm^2)	Elongation at break (%)
PLA	67	1091.7	2.2
PLA95SCG5	55.3	1523	1.9
PLA90SCG10	41.5	1221.8	1.5

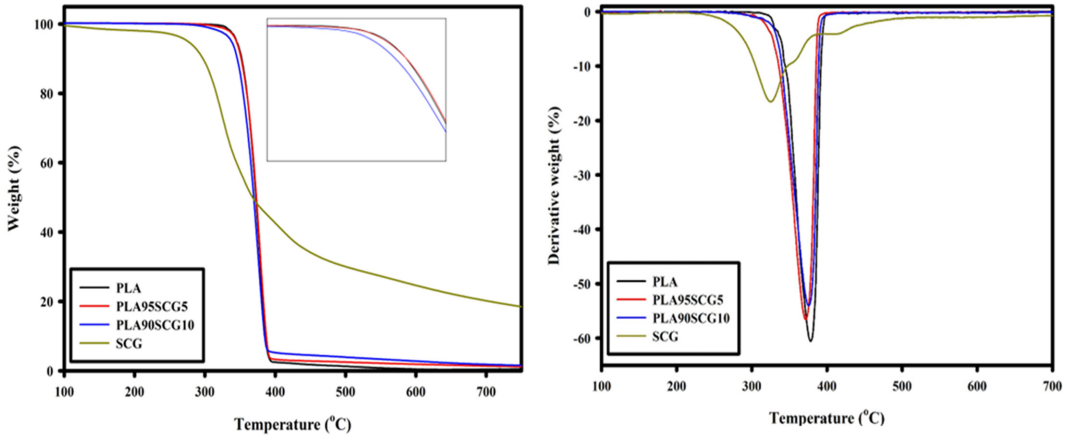

Fig. 4. TGA and DTG curves of PLA and PLA-based composites with diverse SCG contents.

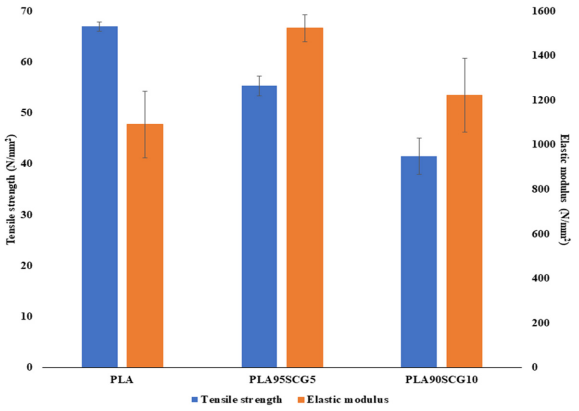

Fig. 5. Tensile strength and elastic modulus of PLA and PLA-based biomcomposites with different SCG contents.

tendency in the eariler study that added up to 5 wt% of egg shell powder to polypropylene carbonate[22].

4. Hydrolytic degradation test

Hydrolysis was performed under accelerated conditions of pH 12 and 37°C using sodium hydroxide buffer solution. When PLA is exposed to moisture, the ester groups in its main chain are cleaved, causing its molecular weight to drop and allowing the release of soluble oligomers and monomers[23]. Chain cleavage reactions are preferred in amorphous regions during the hydrolytic degradation of PLA[24]. In this case, neat PLA confirmed that disintegration did not occur significantly for 5 days. It was established that disintegration occurred in the sample which SCG was added, resulting in area change. The presence of SCG increases the wettability of the sample surface in addition to creating many permeation channels for moisture penetration. In Fig. 7, it was observed that disintegration started faster when SCG was added in 10 wt% compared to that in which 5 wt% was empolyed. As the decomposition test proceeded, the same decomposition occurred in the sample to which SCG was added, and the 100% disintegration was faster in the 5 wt% sample. The decomposition behavior of the PLA matrix was shown to accelerate the disintegration by penetrating the polymer due to the large penetration caused by SCG, and moisture permeating through the hole. Accodring to Wang et al. which also shows a similar tendency, the PLA hydrolysis was accelerated due to the holes caused by the poly(butylene succinate) (PBS) when PBS was added to the PLA matrix[25]. As shown in Fig. 6, it was verified that in the images corresponding to PLA95SCG5 and PLA90SCG10, disintegration of the film appeared as a result of degradation and holes in the polymer matrix, rather than decomposition due to erosion of the surface area. According to da Silva et al., it was found that the biofiller promotes the

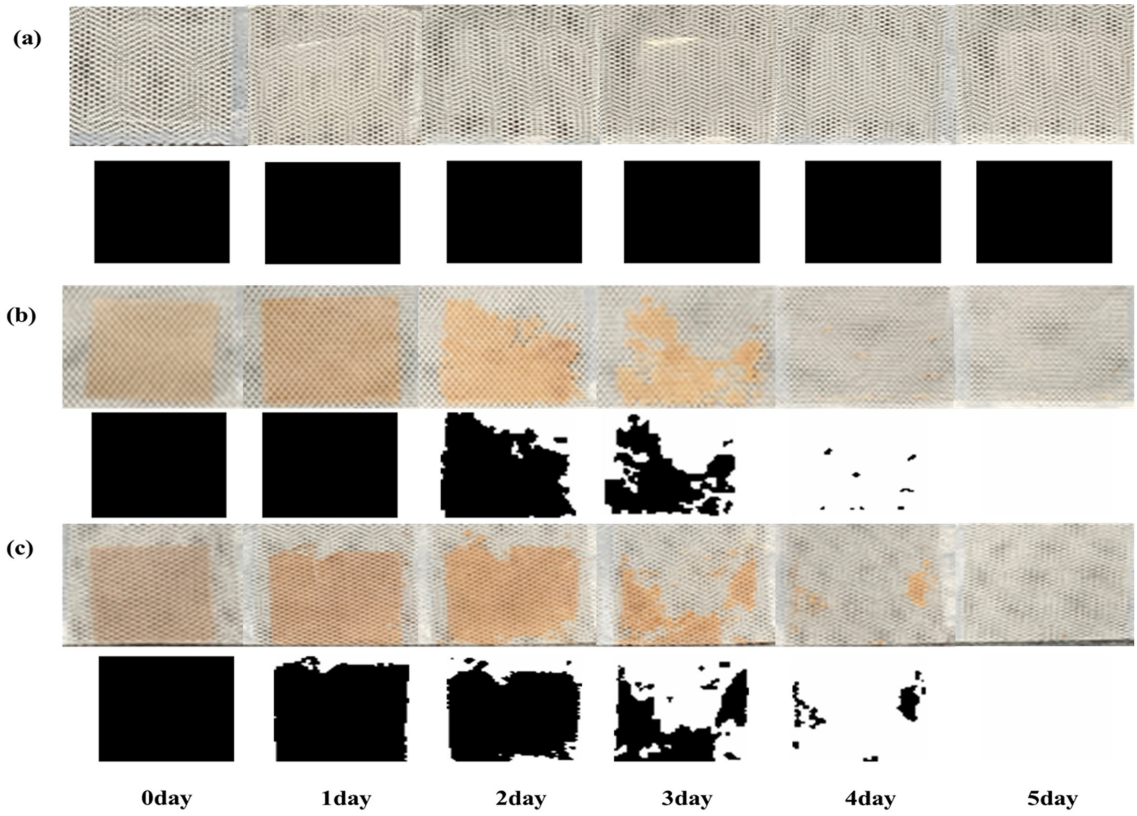

Fig. 6. Hydrolytic disintegration images of biocomposites films (a) PLA, (b) PLA95SCG5 and (c) PLA90SCG10.

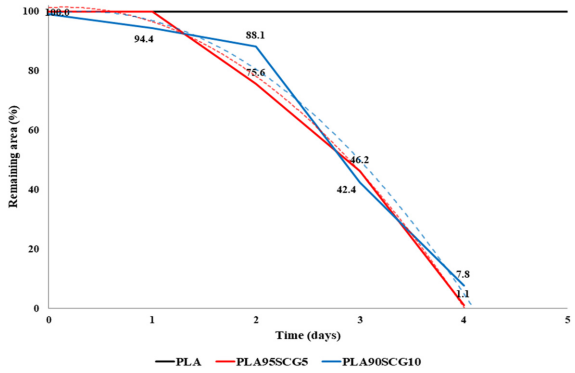

Fig. 7. Remaining area of hydrolytic degradation tests for PLA and PLA-based biocomposites films with various SCG contents.

biodegradation in soil and photolysis of the polymer[26].

Conclusions

In this study, biocomposites made with SCG incorporated to PLA were evaluated for morphological, thermal, mechanical properties and hydrolytic degradation. The surface of PLA-based biocomposites fabricated by SEM was analyzed. As SCG was added, it was established that SCG was added into the PLA matrix, and when 10 wt% was applied, it was confirmed that the aggregation phenomenon appeared as the amount of SCG increased. Through DSC analysis, it was demonstrated that the T_{cc} of PLA droped when SCG was integrated, and it was affirmed that SCG acts as a nucleating agent and causes the crystallization temperature of PLA to proceed from a lower temperature. The degradation max temperature of SCG occurred at a temperature lower than the decomposition max temperature of PLA, and it was proven through TGA analysis that thermal stability declined due to SCG. As for the mechanical properties, it was determined that the addition of SCG diminished the tensile strength of PLA while increasing the elastic modulus. As analyzed by SEM, it is discovered to have a lower elastic modulus due to the agglomeration phenomenon. The hydrolytic degradation test demonstrated that SCG accelerated the degradation of PLA.

Through this study, it was demonstrated that SCG hastened the decomposition of PLA, and it appears that in order to develop PLA/SCG composite packaging materials in the future, it will be necessary to supplement the physical qualities by using a compatibilizer. It is anticipated that this research will increase the possibilities of developing green composite packaging materials.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (Grant number 2021R1F1A1052004).

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투고: 2022.07.28 / 심사완료: 2022.08.12 / 게재확정: 2022.08.16