KOREAN JOURNAL OF PACKAGING SCIENCE & TECHNOLOGY
Vol. 27, No. 2 85~90 (2021)
https://doi.org/10.20909/kopast.2021.27.2.85

Effect of Gamma Irradiation on the Mechanical and Thermal Properties of Biodegradable Packaging Materials

DaeGyu Lim, Youngsan Kim, Sangwoo Kwon, Hyunho Jang, and Su-il Park[1]*

Department of Packaging, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwon-do, 26493, Republic of Korea

Abstract The gamma irradiation was on to Poly(butylene sebacate-co-terephthalate) (PBSeT), Poly(butylene adipate-co-terephthalate) (PBAT), Poly(lactic acid) (PLA) and casting polypropylene (CPP) at dose levels from 0 to 50 kGy. The properties of gamma irradiated samples were analyzed using DSC, TGA, UTM and FT-IR spectra. The mechanical and thermal properties of PBSeT and PBAT after gamma irradiation were less affected than CPP. The tensile strength and elongation of PBSeT was not affected by gamma irradiation, while these of PBAT, PLA and CPP were significantly decreased at 50 kGy gamma-ray dose. The thermal stability of PBSeT, PBAT, PLA and CPP showed a similar tendency to tensile strength. The glass transition temperature(T_g) and melting temperature(T_m) of PBSeT and PBAT were not altered by increasing gamma-ray dose, while these of PLA and CPP decreased. The chemical composition of all samples was not modified by gamma irradiation, and it was confirmed by FT-IR spectra. Based on mechanical and thermal stability studies of gamma irradiation on bioplastics, tested biodegradable packaging materials showed a potential to be used in sterilization process up to 35 kGy.

Keywords Gamma irradiation, PBSeT, PBAT, PLA

Introduction

Plastics have been widely used in various industrial fields for their high processability, convenience and low price[1]. However, as the seriousness of environmental pollution has recently emerged, the use of petroleum-based resources which is the main material of plastics, has been avoided. Accordingly, countries around the world are realizing carbon neutrality and reducing the amount of petroleum based plastics[2].

In order to solve the problems related to environmental pollution, bioplastics are given prominence as the alternative of petroleum based plastics. As of 2020, the world has 211.5 million tons of bioplastics production capacity, which is expected to gradually increase and reach 285 million tons by 2024[3]. Also, the scope of using bioplastics is expanding for alternate petroleum based plastics and it is being used in the wide range of fields such as disposable cups and tableware, as well as medical plastics and 3D printer filaments[4]. For using plastics in medical and food packaging industrial field, the sterilization process must be essential[5].

*Corresponding Author: Su-il Park
Department of Packaging, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwon-do, 26493, Republic of Korea
Tel: +82-33-760-2370, Fax: +82-33-760-2760
E-mail: parks@yonsei.ac.kr

Gamma irradiation, one of the most effective sterilization methods to eliminate microorganisms[6], has become widely used in commercial sterilization method for the food and medical fields[7]. Because it has high penetrating power[8], providing packaging with improved storage stability and microbiological safety[9]. Gamma irradiation does not leave any residue such as ETO (Ethylene oxide), and it has better penetrating power than E-beam[6]. The gamma irradiation of polymeric materials with gamma rays lead to the formation of very reactive intermediates, free radicals, ions and excited states[10]. Furthermore, gamma irradiation affects the chemical structure itself by acting like cross-linking and chain scission[11].

Due to the increasing usage of bioplastics, not only petroleum based polymers, but also bioplastics such as PLA and PBAT have a chance to be sterilized through gamma irradiation. Accordingly, a lot of research which is the effect of gamma irradiation on existing commercial plastics has been done[12,13]. However, studies on the effect of gamma irradiation on the newly developed bioplastics such as PBSeT have not been sufficiently conducted and data is insufficient. The purpose of this study is to investigate the effect of gamma irradiation on bioplastics such as commercialized PLA, PBAT and synthesized PBSeT. In addition, these effects of gamma irradiation on the mechanical properties of commercial CPP film were compared with those of bioplastics.

Materials & Methods

1. Materials

Dimethyl terephthalate (DMT) (SK Chemical, Korea), bio-based sebacic acid and 1,4-butanediol (BDO) (Daejung Chemical&Metal Co. Ltd. Korea) were used for synthesizing PBSeT, and titanium butoxide (TBT) (Mereck Co, Germany) was used as a catalyst. PBAT was supplied by ANKOR Bioplastics (Korea) with average molecular weight (Mw) 162,000 g/Mol, a density of 1.2 g/cm^3 and melting temperature (T_m) 125°C. PLA (IngeoTM-4032D) was supplied by the Nature Works LLC (USA) with average molecular weight (Mw) 190,000 g/Mol, melt flow index (MFI) 7.6 g/10min (at 190°C/2.16 kg), density of 1.3 g/cm^3 and melting temperature (T_m) 170°C. Commercialized CPP with 30 μm film thickness was supplied by SungilChemical (Korea).

2. Sample preparation

PBSeT was synthesized with sebacic acid and DMT, and using TBT as a catalyst, using two steps. Esterification was using first step of synthesis of PBSeT and was conducted at approximately 200~210°C, 50 min. After esterification, polycondensation was progressed for second step. Polycondensation was progressed at 240°C and low vacuum level (0.5~1.5 torr) was maintained while polycondensation.[14] Synthesized PBSeT, PLA and PBAT films were fabricated by using Hot-press (TO-200, TEST-ONE, Korea) 100~180 μm of thickness.

Prepared sample films were irradiated with 15, 25, 35 and 50 kGy at a 5 kGy/h dose rate by a ^{60}Co γ-ray source. Sample irradiation was carried out with the use of a gamma irradiator (JS-8900) located at the Greenpia technology in Yeoju, Korea.

3. Measurements

3.1. Mechanical properties

The tensile strength and elongation at break values of films were measured using a universal testing machine (QM100T, QMESYS, Korea) operating at a crosshead speed of 50~500 mm/min at room-temperature (RT). The test specimens were prepared using a dumbbell-shaped mold manufactured as explained in the ISO 527 standard. The ten samples were measured for each polymer, and the mean and standard deviation were calculated. All samples were dried out at least 24 hr in a dry oven at 25 ± 5°C, under RH 50 ± 5% before the test.

3.2. Fourier transform infrared spectroscopy (FT-IR)

The changes of the chemical structure of a sample by gamma irradiation were analyzed by Fourier transform infrared spectrometer (Spectrum 65, PerkinElmer, USA) in attenuated total reflection (ATR) mode with 64 scans. Measurements were performed at room temperature and the range of obtained was 400~4000 cm^{-1}.

3.3. Thermal properties

Thermogravimetric was conducted by using a TGA Instrument (TGA-4000, PerkinElmer, USA). The TGA analysis was obtained in a nitrogen atmosphere at a heating rate of 20°C/min. The sample was maintained 5 min at 90°C to remove moisture and the temperature was then increased to 800°C.

The thermal properties of the films were carried out by Differential scanning calorimetry (DSC) (Q-20, TA Instruments, USA). The samples were heated under a nitrogen atmosphere in the –50°C~230°C temperature range at a heating rate of 20°C/min. The cycle was repeated twice to remove the thermal history.

Results & Discussion

1. Mechanical properties

The tensile strength and elongation at break were presented in Fig. 1. A commercialized CPP film was used to compare the properties. The tensile strength of PBSeT at 0 and 50 kGy were 5.6 N/mm^2 and 5 N/mm^2 respectively. But PBAT had noticeable altered. The tensile strength of PBAT decreased significantly from 21.6 N/mm^2 (0 kGy) to 16 N/mm^2 (50 kGy). PLA and CPP tended to decrease as the amount of gamma irradiation increased. The PLA showed a slight change in tensile strength as gamma irradiation dose increased, and decreased significantly at 50 kGy. The tensile strength of CPP also declined with increasing gamma irradiation dose. It showed a maximum value of 70 N/mm^2 at 0 kGy and decreased to 30 N/mm^2 at 50 kGy. Madera et al.(2016) reported that gamma irradiated PLA showed decrease in tensile strength and elongation at break, because of the aggravated brittleness of PLA by gamma irradiation[15]. The elongation of all samples showed a similar tendency to tensile strength. The elongation of PBSeT at 0 kGy and 50 kGy was 394% and 311%, respectively. Elongation of PBAT exhibited a similar tendency to its tensile strength. The elongation of PBAT had a maximum value of 475% at 0 kGy, which decreased significantly to 396% at 50 kGy. The chain scission may be occured in the amorphous phase of PBAT with gamma irradiation. Han et al.(2009) reported that gamma-ray induced chain scission and less chain entanglement in the amorphous phase of PBAT[16].

As the increased gamma irradiation dose, the elongation of PLA and CPP decreased. The elongation of PLA significantly decreased from 2.1% (0 kGy) to 1% (50 kGy). The reduced elongation of PLA films with by chain scission was reported in previous paper[17]. As the amount of gamma irradiation increased, the elongation of CPP continued to decrease from 279% at control CPP to 107% at 50 kGy dosed CPP.

2. Thermal properties

The DSC results were shown in Table 1. The PBSeT samples showed two melting peaks. The two melting peaks were

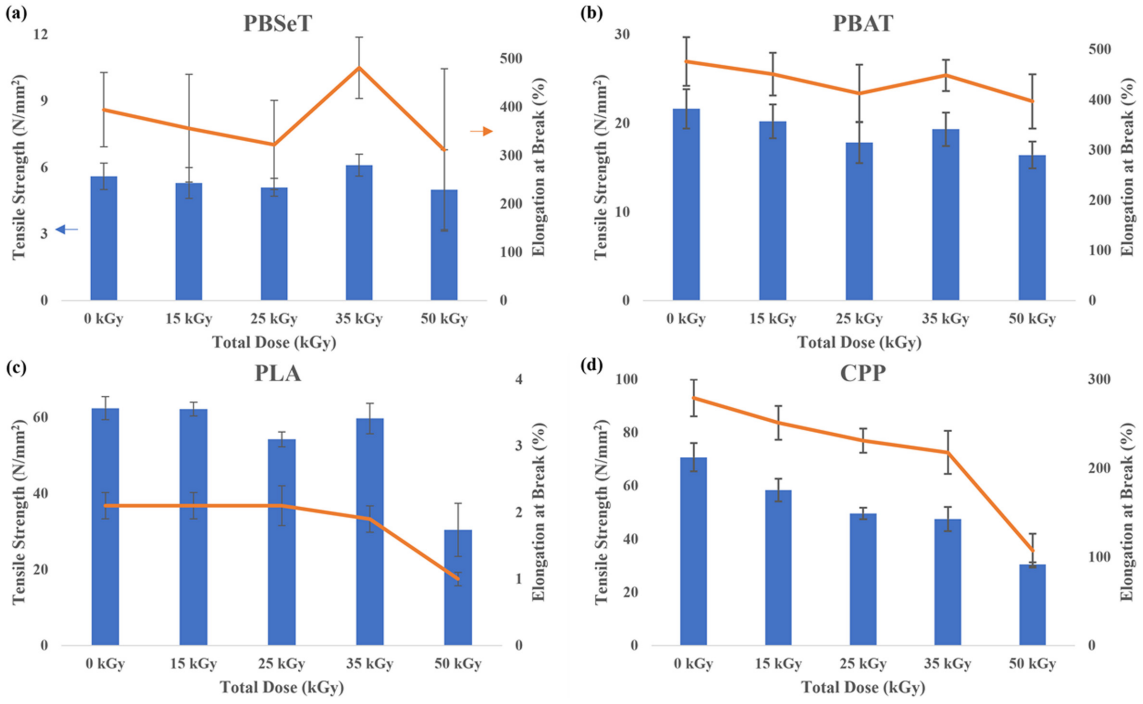

Fig. 1. The effect of gamma irradiation on tensile strength at break and elongation percent of (a) PBSeT, (b) PBAT, (c) PLA and (d) CPP.

Table 1. Thermal properties of PBSeT, PBAT, PLA and CPP with different level of gamma irradiation

Films		DSC			TGA	
Sample	Irradiation doses (kGy)	T_g(°C)	T_m(°C)	T_{cc}(°C)	$T_{5\%}$(°C)	T_{max}(°C)
PBSeT	0	−38.4	28.9 93.7	1.9 31.8	391.3	417.2
	15	−36.3	31.7 97.1	4.1 37.5	394.4	411.3
	25	−38.5	29.3 93.0	1.6 30.2	391.8	419.7
	35	−35.5	30.2 95.5	0.4 27.5	391.3	417.2
	50	−38.4	31.4 94.5	2.9 33.8	390.1	417.0
PBAT	0	−35.0	126.3	39.0	382.4	413.2
	15	−35.8	127.8	37.8	383.3	416.1
	25	−29.4	124.5	37.6	393.7	415.9
	35	−35.3	128.2	38.5	383.7	416.3
	50	−36.9	128.2	38.5	385.7	415.5
PLA	0	48.4	163.0	131.8	350.6	381.7
	15	46.3	161.4	127.5	347.7	379.7
	25	44.9	160.6	124.3	346.7	378.8
	35	44.9	161.6	108.2	342.8	379.0
	50	41.8	159.7	114.0	342.7	379.1
CPP	0	−20.8	161.7	109.3	394.0	460.0
	15	−23.4	162.4	106.2	384.8	458.0
	25	−23.1	154.4 159.9	109.7	378.7	459.2
	35	−22.8	159.5	108.4	373.4	458.2
	50	−24.4	150.6 157.9	108.1	371.6	413.1

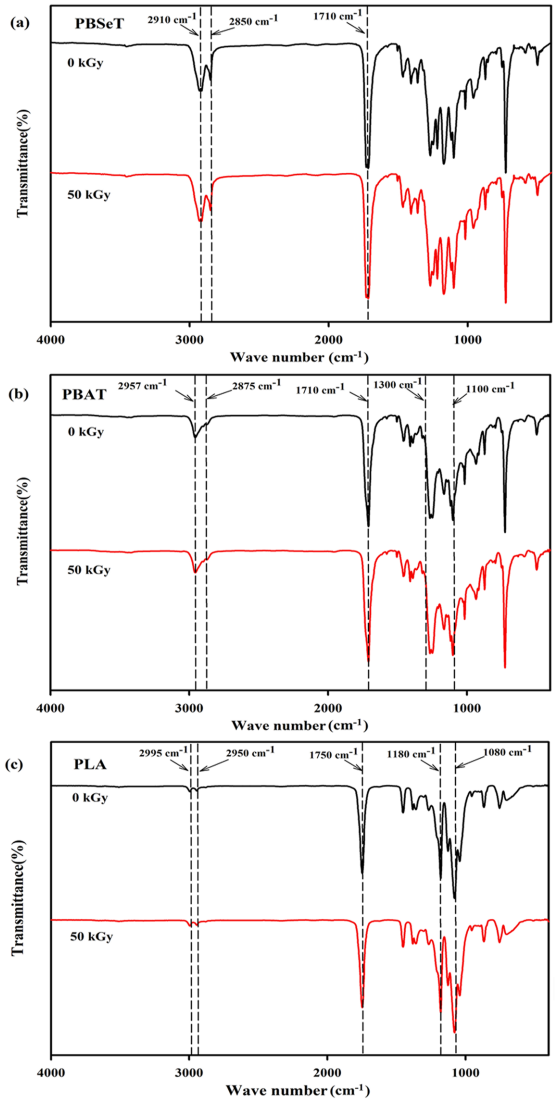

Fig. 2. FT-IR spectra of bioplastics irradiated at 0 and 50 kGy: (a) PBSeT, (b) PBAT and (c) PLA.

explained as phase change from a semicrystalline to amorphous state[1]. All of the DSC data of PBSeT had no significant effect with increasing gamma irradiation dose. PBAT 0 kGy sample indicated similar T_g and T_m values with other commonly used PBAT for research[18]. DSC values of all PBAT samples had no significant change. In this paper, the T_g value of PLA was measured to be lower than the basic thermal property value[19]. The T_g, T_m and T_{cc} value of PLA were slightly decreased as in increase gamma irradiation dose. These results may be explained by the chain scission of PLA due to gamma irradiation which were reported previously by other researchers[20]. The chain scission of PLA amorphous part occurred and the shortened chains became less entangled. Therefore, short chains had lower T_{cc} values than long chains because less energy was required for recrystallization[21]. The T_m value of CPP decreased with increasing gamma irradiation dose[22]. And the T_m value of CPP was splitted in two peaks after 25 kGy because additives which were added in processing PP were acted as a nucleating agent[23].

The $T_{5\%}$ and T_{max} values of TGA results were shown in Table 1. For PBSeT, the $T_{5\%}$ and T_{max} temperature of thermal degradation had not significant difference in the overall dose. So the thermal stability of PBSeT appeared to be maintained at the total gamma irradiation dose. The thermal degradation of PBAT showed an insignificant difference within the dose range up to 50 kGy[16]. And the change thermal stability was associated with chemical cross-linking and chain scissoring. The cross-linking and chain scissoring occurred simultaneously in the polymer by gamma irradiation[24]. Each ratio varies according to the amount of gamma irradiation. As for PLA, the $T_{5\%}$ and T_{max} values had insignificantly decreased. The $T_{5\%}$ value was reduced by 2°C from 0 to 50 kGy. On the other hand, the decrease in both $T_{5\%}$ and T_{max} values of CPP was higher than that of the above samples. The $T_{5\%}$ decreased by 23°C from 0 kGy (394°C) to 50 kGy (371.6°C), and T_{max} decreased by 47°C from 0 kGy (460°C) to 50 kGy (413.1°C). The thermal degradation of CPP was because gamma rays initiated degradation of the weak part of CPP, causing structural degradation and lowering the crystallinity[22].

3. Fourier transform infrared spectroscopy (FT-IR)

Since gamma rays induced various random decomposition and cross-linking reactions in polymers, it was expected that there would be changed in the intensity and wavenumber of the peaks of the FT-IR spectrum of each polymer after irradiation with gamma rays. To analyze the above-mentioned changed, FT-IR analysis was conducted. Fig. 2(a) was FT-IR spectra of PBSeT. The peaks location at around 2910 cm^{-1} and 2850 cm^{-1} was C-H stretching vibration of $–CH_2$. The peak around at 1710 cm^{-1} was C = O bending which was derived from ester carbonyl group[25]. The FT-IR spectra of PBAT was shown at Fig. 2(b). The peaks at 2957 cm^{-1} and 2875 cm^{-1} was CH_2 asymmetric stretching vibration[26]. The C = O stretching vibration was located at 1710 cm^{-1}, and 1100~1300 cm^{-1} associated with the stretching vibration of the C-O-C[27]. The FT-IR spectra of PLA was shown in Fig. 2(c). In the spectrum of PLA, the peaks which were located at 2995 cm^{-1} and 2950 cm^{-1} were stretching of $–CH_2$. The peak around at 1750 cm^{-1} was C = O bending. The symmetrical –C-O-C stretching was located at 1180 cm^{-1}, and asymmetrical stretching of $–CH_3$ was appeared at 1080 cm^{-1} [28]. It was expected that there would be a change in the chemical structure with the increase of the gamma irradiation dose. But comparing 0 with 50 kGy sample of the PBSeT in Fig. 2(a), there was no clear change in peak intensity or wavenumber. Besides PBAT in Fig. 2(b) and PLA in Fig. 2(c) also had similar tendency as a PBSeT in Fig. 2(a). This was because FT-IR is not sensitive enough to detect cross-linking or degradation of the polymer[17].

Conclusions

The effect of gamma irradiation on the properties of synthesized PBSeT, commercial PBAT and PLA was analyzed. As the amount of gamma irradiation increased, there were no significant changes in physical and thermal properties of the synthesized PBSeT. On the other hand, commercial PBAT, PLA and CPP showed significantly decreased tensile strength and elongation at break values especially at 50 kGy. The elongation of the synthesized PBSeT was better than that of PBAT, and more stable under gamma irradiation compared to other tested bioplastics. Tested bioplastics might be able to use as food and medical packaging materials up to a gamma irradiation dose of 35 kGy. Additional research is necessary to study the reason of PBSeT stability under gamma irradiation.

Acknowledgement

This work was supported by the Technology Innovation Program (or Industrial Strategic Technology Development Program-Technology Innovation Program) (20009837, Development of multilayer film for the manufacture of disposable bioreactor bags for biopharmaceutical production) funded by the Ministry of Trade, Industry & Energy(MOTIE, Korea)

References

1. Kim, S. J., Kwak, H. W., Kwon, S., Jang, H., & Park, S. I. 2020. Synthesis, characterization and properties of biodegradable poly (butylene sebacate-co-terephthalate). Polymers. 12(10): 2389.
2. 2019. Reducing UK emissions. 2019 Progress Report to Parliament. Committee on Climate Change
3. 2020. Global production capacities of bioplastics. European Bioplastics. Nova-Institute.
4. Liu, W., Zhou, J., Ma, Y., Wang, J., & Xu, J. 2017, December. Fabrication of PLA filaments and its printable performance. In IOP Conference Series: Materials Science and Engineering. 275(1): 012033.
5. Veiga-Malta, I. 2016. Preventing healthcare-associated infections by monitoring the cleanliness of medical devices and other critical points in a sterilization service. Biomedical instrumentation & Technology. 50(s3): 45-52.
6. da Silva Aquino, K. A. 2012. Sterilization by gamma irradiation. Gamma radiation. 9: 172-202.
7. Jipa, I. M. Stroescu, M., Stoica-Guzun, A., Dobre, T., Jinga, S. & Zaharescu, T. 2012. Effect of gamma irradiation on biopolymer composite films of poly (vinyl alcohol) and bacterial cellulose. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 278: 82-87.
8. Chuaqui-Offermanns, N. 1989. Food packaging materials and radiation processing of food: a brief review. International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry. 34(6): 1005-1007.
9. Parra, D. F., Rodrigues, J. A., & Lugão, A. B. 2005. Use of gamma-irradiation technology in the manufacture of biopolymer-based packaging films for shelf-stable foods. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 236(1-4): 563-566.
10. Chmielewski, A. G., Haji-Saeid, M., & Ahmed, S. 2005. Progress in radiation processing of polymers. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 236(1-4): 44-54.
11. Benyathiar, P., Selke, S., & Auras, R. 2016. The effect of gamma and electron beam irradiation on the biodegradability of PLA films. Journal of Polymers and the Environment. 24(3): 230-240.
12. Zaidi, L., Bruzaud, S., Kaci, M., Bourmaud, A., Gautier, N., & Grohens, Y. 2013. The effects of gamma irradiation on the morphology and properties of polylactide/Cloisite 30B nanocomposites. Polymer degradation and stability. 98(1): 348-355.
13. Cunha, E. L., Schimitberger, T., Oliveira, C. M., & Faria, L. O. Investigation of PBAT dosimetric properties for high gamma dose dosimetry.
14. Kim, S. J., Kwak, H. W., Kwon, S., Jang, H., & Park, S. I. 2021. Characterization of PLA/PBSeT Blends Prepared with Various Hexamethylene Diisocyanate Contents. Materials. 14(1): 197.
15. Madera-Santana, T. J., Meléndrez, R., González-García, G., Quintana-Owen, P., & Pillai, S. D. (2016). Effect of gamma irradiation on physicochemical properties of commercial poly (lactic acid) clamshell for food packaging. Radiation Physics and Chemistry. 123, 6-13.
16. Han, C., Bian, J., Liu, H., & Dong, L. 2009. Effect of γ-radiation on the thermal and mechanical properties of a commercial poly (butylene adipate?co?terephthalate). Polymer international. 58(6): 691-696.
17. Razavi, S. M., Dadbin, S., & Frounchi, M. 2014. Effect of gamma ray on poly (lactic acid)/poly (vinyl acetate-co-vinyl alcohol) blends as biodegradable food packaging films. Radiation Physics and Chemistry. 96. pp.12-18.
18. da Silva, C. G., Kano, F. S., & dos Santos Rosa, D. 2019. Thermal stability of the PBAT biofilms with cellulose nanostructures/essential oils for active packaging. Journal of Thermal Analysis and Calorimetry. 138(4): 2375-2386.
19. Coppola, B., Cappetti, N., Di Maio, L., Scarfato, P., & Incarnato, L. 2018. 3D printing of PLA/clay nanocomposites: influence of printing temperature on printed samples properties. Materials. 11(10): 1947.
20. Alsabbagh, A., Saleem, R. A., Almasri, R., Aljarrah, S., & Awad, S. (2020). Effects of gamma irradiation on 3D-printed polylactic acid (PLA) and high-density polyethylene (HDPE). Polymer Bulletin. 1-15.
21. Benyathiar, P., Selke, S. E., Harte, B. R., & Mishra, D. K.

2021. The Effect of Irradiation Sterilization on Poly (Lactic) Acid Films. Journal of Polymers and the Environment. 29(2): 460-471.
22. Krupa, I., & Luyt, A. S. 2001. Thermal properties of isotactic polypropylene degraded with gamma irradiation. Polymer degradation and stability. 72(3): 505-508.
23. Abiona, A. A., & Osinkolu, A. G. 2010. Gamma-irradiation induced property modification of polypropylene. International Journal of Physical Sciences. 5(7): 960-967.
24. Rahaman, M. H. A., Khandaker, M. U., Khan, Z. R., Kufian, M. Z., Noor, I. S. M., & Arof, A. K. 2014. Effect of gamma irradiation on poly (vinyledene difluoride)-lithium bis (oxalato) borate electrolyte. Physical Chemistry Chemical Physics. 16(23): 11527-11537.
25. Jaisankar, V., Nanthini, R., Karunanidhi, M., & Ravi, A. 2010. Study on biodegradable random copolyesters derived from 1, 4-butane diol, terephthalic acid and adipic acid/ sebacic acid. Asian Journal of Chemistry. 22(7): 5077.
26. Cardoso, E. C., Parra, D. F., Scagliusi, S. R., Sales, R. M., Caviquioli, F., & Lugão, A. B. 2019. Study of bio-based foams prepared from PBAT/PLA reinforced with bio-calcium carbonate and compatibilized with gamma radiation. In Use of Gamma Radiation Techniques in Peaceful Applications: 139.
27. Zhao, P., Liu, W., Wu, Q., & Ren, J. 2010. Preparation, mechanical, and thermal properties of biodegradable polyesters/poly (lactic acid) blends. Journal of Nanomaterials.
28. Awale, R. J., Ali, F. B., Azmi, A. S., Puad, N. I. M., Anuar, H., & Hassan, A. 2018. Enhanced flexibility of biodegradable polylactic acid/starch blends using epoxidized palm oil as plasticizer. Polymers. 10(9): 977.

투고: 2021.07.30 / 심사완료: 2021.08.09 / 게재확정: 2021.08.18