Anti-dripping flame retardancy and mechanical properties of polylactide/ammonium polyphosphate/rayon fiber composites

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Research Article

Keywords: polylactide, ammonium polyphosphate, rayon fiber, flame retardancy, mechanical properties, flame drip

Posted Date: September 20th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-893509/v1

Abstract

Polylactide (PLA) composites containing a flame retadant, ammonium polyphosphate (APP), and short rayon fiber were prepared by direct melting compounding in a brabender. The limiting oxygen index (LOI) of the neat PLA sample was only 20.5%, which was increased to 29% by adding 15 wt% APP and 15% rayon to the PLA matrix (sample A15R15) as an example. During the UL-94 vertical flammability test, flame dripping was further avoided by adding the rayon fiber, and a V-0 rating was achieved. The char residue determined by thermogravimetric analysis (TGA) increased with increasing APP content in the PLA composites. However, the PLA composite revealed a loss in mechanical tensile modulus and strength due to the APP addition, which was improved when rayon fiber was added to replace a portion of APP.

Introduction

Polylactide (PLA) can be produced from renewable resources such as lactic acid by fermenting starch. It is one of the most important biodegradable and environmentally friendly polymers that has been considered to relieve the problem of plastic disposal and can be used as an alternative to petroleum-based synthesized polymers (Ajioka et al., 1995; Farah et al., 2016). Therefore, PLA has been widely used for biodegradable packing bags and films, and it can be used as a thermoplastic matrix in composites (Auras et al., 2004; Haafiz, 2013; Hassan, 2019; Ncube et al., 2020). For example, the addition of glass or carbon fibers to polymers can improve the mechanical properties of materials, and fiber-reinforced composites have been applied in many applications such as electrical devices, sports goods, construction materials, automobiles and aircrafts. (Ramamoorthy et al., 2015).

For sustainability issues, many natural fibers have been chosen to replace synthetic fibers in polymer matrices. The tensile strength, Young’s modulus and impact properties of the composites can be improved by melt compounding PLA with different types of natural fibers such as cotton, hemp, jute, flax, or man-made cellulose. The mechanical properties depend on the characteristics of the fibers or the fiber content in the polymer matrix. (Bax & Müssig, 2008; Bledzk & Jaszkiewicz, 2010; Graupner et al. 2009; Kurokawa & Hotta 2019; Thangavelu & Subramani 2016; Zhao et al., 2020). PLA is a biodegradable thermoplastic polyester. PLA is highly flammable, which limits its high-end applications such as electronic or electrical materials. PLA can be blended with halogen-free flame retardants such as expanded graphite, aluminum hydroxide (ATH), magnesium hydroxide, and ammonium polyphosphate (APP) to improve the flame retardancy (Cheng, et al., 2012, 2018; Fukushima et al., 2010; Gao et al., 2020; Ke et al., 2010; Reti et al., 2008; Shukor et al., 2014).

In our previous studies, PLA nanocomposites were prepared by melt compounding PLA with aluminum trihydrate (ATH) and modified montmorillonite (MMT). The addition of the modified MMT indicated a synergistic effect with the ATH, and the flame retardant properties of the PLA composite reached the V-0 rating in the UL-94 test. The mechanical and flame retardant properties of the PLA/ATH/MMT nanocomposite could be further improved by adding short carbon fibers (CFs). Meanwhile, flame dripping was avoided during combustion (Cheng et al., 2012, 2015). Many PLA composites with various natural fibers have been reported, but most of them discussed the mechanical properties of fiber-reinforced PLA.

In this study, polylactide (PLA) composites with a flame retardant, ammonium polyphosphate (APP), and rayon fiber were prepared via direct melting compounding in a brabender. Rayon is a regenerated cellulose fiber that is produced from natural sources of regenerated cellulose, such as wood or other agricultural products. Because rayon fiber has more controllable and good uniform properties than natural fibers, it is an appropriate reinforced fiber in PLA composites (Bledzki et al., 2009; Graupner et al., 2017; Kobayashi et al., 2012; Rosli et al., 2019; Zhang et al., 2021). The limiting oxygen index (LOI) and UL94V flammability rating of the PLA composites at various contents of APP and rayon fiber were measured under combustion tests. The thermal degradation of the PLA composite was investigated by thermogravimetric analysis (TGA). The mechanical tensile impact properties of the test specimens were determined. The flame retardancy and mechanical properties of the PLA composites, which depend on the compositions of PLA, APP, and rayon fiber, were discussed.

Materials And Methods

Materials

Polylactide (PLA, PLA2002DTM) bought from Nature-Works, ammonium polyphosphate (APP, Application, Exolit AP 422, Clariant) with a size of approximately 17 μm, and rayon staple fiber (Formosa Chemicals & Fibre Corporation, Taiwan) with an average fiber length of approximately 76 mm were dried in a vacuum oven for 8 hours at 70°C before compounding.

Preparation and characteristics of the PLA composites

PLA, APP, and rayon fiber were mixed with a brabender (PLE-331, ATLAS) at 50 r.p.m. for 15 minutes at 170°C. To measure the tensile properties, the blended mixtures were formed into a type-IV example shape with a thickness of 2 mm, as indicated by ASTM D638, using an injection molding machine (HAAKE, MiniJet) at 170°C. The mold temperature was 60°C. The mechanical properties of the PLA composites were determined using a tensile tester (YM-H3501-A02, Yang Yi Technology Co.) at an extension rate of 5 mm/min. The Izod impact resistances of the samples were measured by a pendulum impact tester (GT-7045-MDL, Gotech) according to ASTM D256.

The limiting oxygen indices (LOIs) for various samples were determined under standard conditions as specified by ASTM D2863 (ON-1, Suga Test Instrument Co. Ltd.). The UL94V test of the specimen with a size of 120 mm x 13 mm x 3 mm was performed according to the ASTM D3801 testing process. During the tests, thermal images of the sample surfaces were captured by an infrared camera (TAS, Ching Hsing). The thermal degradation of the sample was examined using a thermogravimetric analyzer (TGA, TA Q-500) at a heating rate of 20°C/min under flowing air at 60 mL/min.

The water absorption of the PLA and PLA composite was measured according to ASTM D570. The test specimen was in the form of a disk 50.8 mm in diameter and 3.2 mm in thickness. The sample was first dried in an oven for 24 hours at 50°C and subsequently immersed in a container of distilled water for 24 hours. The percentage of water absorption of the sample was calculated by the ratio of the increase in weight after water immersion to the weight of the dried sample.

Results And Discussion

Flame retardant properties

Table 1 shows the limiting oxygen index (LOI) value and UL-94V rating of PLA and composites with APP or rayon fiber. The LOI of the specimen made of neat PLA was only 20.5. It was very inflammable and burned with flaming or glowing combustion up to the holding clamp during the UL-94V test. When the bottom part of the sample melted in the fire, a melt drip occurred and ignited a cotton indicator. The thermal decompositions of the PLA and the composites were inspected by TGA in air at a flow rate of 60 ml/min, as indicated in Figs. 1 and 2. The temperature at 5% weight loss, $T_{5wt\%}$, of the neat PLA was approximately 329°C, and the temperature at the local maximum rate of the main thermal decomposition, T_{max}, was 364°C, as listed in Table 2. Only a small amount of char residue remained at 600 ^{o}C, which implies that the PLA can be completely burned in air.

Table 1
Flame retardant properties of the PLA and PLA composites.

Sample	Composition (wt%)			LOI (%, ± 0.5%)	UL-94	Total flaming combustion time for all 5 specimens (sec)	Flame drips	Cotton ignited
	PLA	APP	Rayon					
PLA	100	0	0	20.5	Fail	**	Yes	Yes
A10R0	90	10	0	29.5	V-0	10	Yes	No
A0R10	90	0	10	22.5	Fail	156*	Yes	Yes
A20R0	80	20	0	32.0	V-0	0	Yes	No
A10R10	80	10	10	26.0	Fail	136*	No	No
A0R20	80	0	20	21.0	Fail	167*	Yes	Yes
A30R0	70	30	0	35.5	V-0	0	Yes	No
A20R10	70	20	10	32.5	V-0	0	No	No
A15R15	70	15	15	29.0	V-0	0	No	No
A10R20	70	10	20	28.0	V-0	0	No	No
A5R25	70	5	25	26.0	V-0	0	No	No
A0R30	70	0	30	21.0	Fail	160*	Yes	Yes
A0R35	65	0	35	20.0	Fail	180*	Yes	Yes
A10R25	65	10	25	28.5	V-0	0	No	No
A10R30	60	10	30	30.5	V-0	0	No	No

Fail: No rating of UL-94V test.

*: The specimen burned up to holding clamp.

**: The flame on PLA sample might drop away from the specimen during test.

Table 2
TGA data of PLA, APP, rayon fiber and PLA composites under air purge.

Sample	$T_{5wt\%}$ (°C)	T_{max}(°C)	Char residue at 600 °C (wt%)
PLA	329.2	363.5	0.9
APP	326.4	337.8	33.2
rayon	90.5	346.3	9.3
A30R0	361.9	404.3	25.5
A15R15	282.8	363.1	10.5
A0R30	292.1	347.4	0.9

Because water can be absorbed and retained in the rayon fiber, approximately 6% weight loss was observed by TGA at 100°C. Therefore, the rayon fiber ought to be dried before compounding with the PLA matrix. The main thermal decomposition of the rayon fiber occurred at approximately 346°C, which was lower than that of PLA. The LOI value of the PLA/rayon composite without the addition of APP, such as samples A0R10, A0R20, or A0R30, was not essentially increased. For the PLA compounded with 30% of the rayon fiber, A0R30, only limited char residue remained at 600°C. Consequently, those PLA/rayon composites remained highly flammable.

An IR camera was used to observe the surface thermal images of the PLA and PLA/APP/rayon composites during the UL-94V test. As shown in Figs. 3 and 4, when the ignition burner was removed, the temperature at the bottom of the PLA specimen increased to approximately 380°C, which is consistent with the temperature at the rate of maximum thermal degradation, T_{max}, determined by TGA. Sometimes, the flame at the end of the PLA sample might entirely drop down with melt dripping due to the high temperature. Therefore, the apparent maximum temperature of the PLA sample abruptly decreased during the test. The PLA composite with 30 wt% rayon and without added APP, i.e., sample A0R30, burned with flaming and glowing combustion up to the holding flame, whose apparent maximum temperature increased to approximately 400°C and was higher than the temperature of the main thermal degradation in air, which is approximately 347°C.

Because APP can be degraded at high temperature and produce polyphosphoric acid, it can catalyze the dehydration reaction of PLA and form char residues. This reaction will enhance the flame retardancy of the PLA composites (Fu et al., 2017; Jang et al., 2012). For example, when PLA was blended with 30% APP, i.e., sample A30R0, 25.5% char formed at 600°C. When we added 10, 20 and 30 wt% of the retardant APP into the PLA matrix to form samples A10R0, A20R0 and A30R0, the LOI values of the PLA/APP composites increased to 29.5, 32.0, and 35.5, respectively. During the UL-94V test, the flame very quickly self-extinguished, and the melt drip could not ignite the cotton indicator. This result indicates that the flame retardant properties of those samples were improved to a V-0 rating.

Once the rayon fiber was added to replace a part of APP, e.g., samples A20R10, A15R15, A10R20, and A5R25, the LOI values and char residues measured by TGA were less than those of sample A30R0, but the UL-94V test remained at the V0 rating. Moreover, the flame drip was avoided by adding rayon fiber. The thermal IR images of samples A30R0, A15R15 and A10R20 revealed the apparent maximum temperature that decreased to less than 250°C one second after the ignition burner was removed. It was lower than the temperature at 5% weight loss of the thermal degradation measured by the TGA under air purge, and the burning very quickly ceased.

Mechanical Properties

The mechanical tensile properties of the PLA and PLA composites are shown in Table 3 and Fig. 5. The tensile modulus, yield strength, and impact strength of the neat PLA were approximately 1.54 GPa, 63 MPa, and 4.6 kJ/m^2, respectively. The impact strength of the sample increased with the addition of the flame-retardant ammonium polyphosphate, which could be increased to 7.5 kJ/m^2 by adding 30% APP into the matrix PLA to form sample A30R0. However, the PLA/APP composite revealed a loss in mechanical tensile modulus and strength.

Table 3
Mechanical properties of the PLA and PLA composites.

Sample	Tensile modulus (GPa)	Yield Strength (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Impact strength (kJ/m2)
PLA	1.54 (± 0.14)	63.0 (± 2.3)	55.0 (± 2.0)	7.0 (± 0.7)	4.6 (± 0.6)
A10R0	1.53 (± 0.01)	42.0 (± 1.6)	36.0 (± 2.7)	4.2 (± 0.4)	5.9 (± 0.7)
A0R10	1.59 (± 0.09)	63.1 (± 0.8)	58.3 (± 3.2)	6.5 (± 1.2)	6.4 (± 0.4)
A20R0	1.49 (± 0.01)	35.1 (± 1.3)	22.5 (± 4.4)	13.0 (± 5.2)	7.3 (± 1.2)
A10R10	1.47 (± 0.06)	44.9 (± 2.9)	42.6 (± 3.4)	5.6 (± 0.8)	6.7 (± 1.1)
A0R20	1.84 (± 0.15)	*	74.6 (± 2.2)	5.5 (± 1.0)	7.3 (± 0.4)
A30R0	1.28 (± 0.09)	29.0 (± 0.8)	21.0 (± 1.2)	19.0 (± 4.4)	7.5 (± 1.4)
A20R10	1.28 (± 0.02)	44.0 (± 0.8)	42.9 (± 0.6)	5.6 (± 0.2)	7.1 (± 0.2)
A15R15	1.79 (± 0.04)	*	63.0 (± 2.5)	5.3 (± 0.1)	6.4 (± 0.8)
A10R20	1.58 (± 0.28)	*	65.9 (± 3.0)	5.0 (± 0.3)	6.7 (± 0.8)
A5R25	1.66 (± 0.07)	74.5 (± 1.7)	72.5 (± 2.6)	4.9 (± 0.3)	7.7 (± 0.8)
A0R30	1.81 (± 0.09)	80.2 (± 3.6)	79.1 (± 3.3)	5.2 (± 0.1)	7.7 (± 0.3)

*No apparent yield stress was observed.

When rayon fiber was added to replace a portion of the APP at a certain composition, the mechanical properties of the PLA composite improved. For example, by adding 15% rayon and 15% APP, the tensile modulus of PLA composite A15R15 was increased to approximately 1.8 GPa, and the tensile yield strength became 63 MPa. Thus, the addition of rayon fiber into the PLA/APP composite can resolve the loss in mechanical tensile modulus and strength from the APP loading. Meanwhile, the classification rating of UL-94 remained at V0, and flame dripping was further avoided by adding rayon fiber.

Water absorption of the PLA composite

The water absorptions of the PLA and PLA composites were evaluated by the weight change after 24 h of water immersion. The percentage of water absorption of the neat PLA sample was approximately 0.33%, and it increased to 0.44% when 30% APP was added to the PLA matrix. Once rayon fiber was added to replace a portion of APP, the water absorption slightly increased to approximately 1.1% due to the hydrophilic property of the rayon fiber.

Table 4
The percentages of water absorption of the PLA and PLA composites.

Sample	Water absorption (%)
PLA	0.33 (± 0.01)
A30R0	0.44 (± 0.01)
A20R10	1.15 (± 0.11)
A15R15	1.07 (± 0.08)
A10R20	1.13 (± 0.04)
A0R30	1.11 (± 0.05)

Conclusion

Flame-retardant ammonium polyphosphate (APP) was added to the PLA matrix to improve the flame retardant properties of the PLA composite. This was verified by increasing either the limiting oxygen index (LOI) or the char residue in a combustion test. Therefore, the V0 rating determined by the UL-94 vertical flammability test was reached for the PLA composite that contained a small amount of APP, e.g., 5 wt%. The mechanical tensile modulus and strength of the PLA composite decreased with the APP addition. When a part of the APP in the PLA composite was substituted with rayon fiber, which was made from regenerated cellulose, the mechanical properties increased, and the flame retardancy remained at the UL-94 V0 rating. Moreover, flame dripping could be stopped during the combustion test due to the addition of rayon fiber.

Declarations

Acknowledgements

We thank the Ministry of Science and Technology of Taiwan for their financial support of this study under Contract: MOST 109-2221-E-027-112.

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Figures

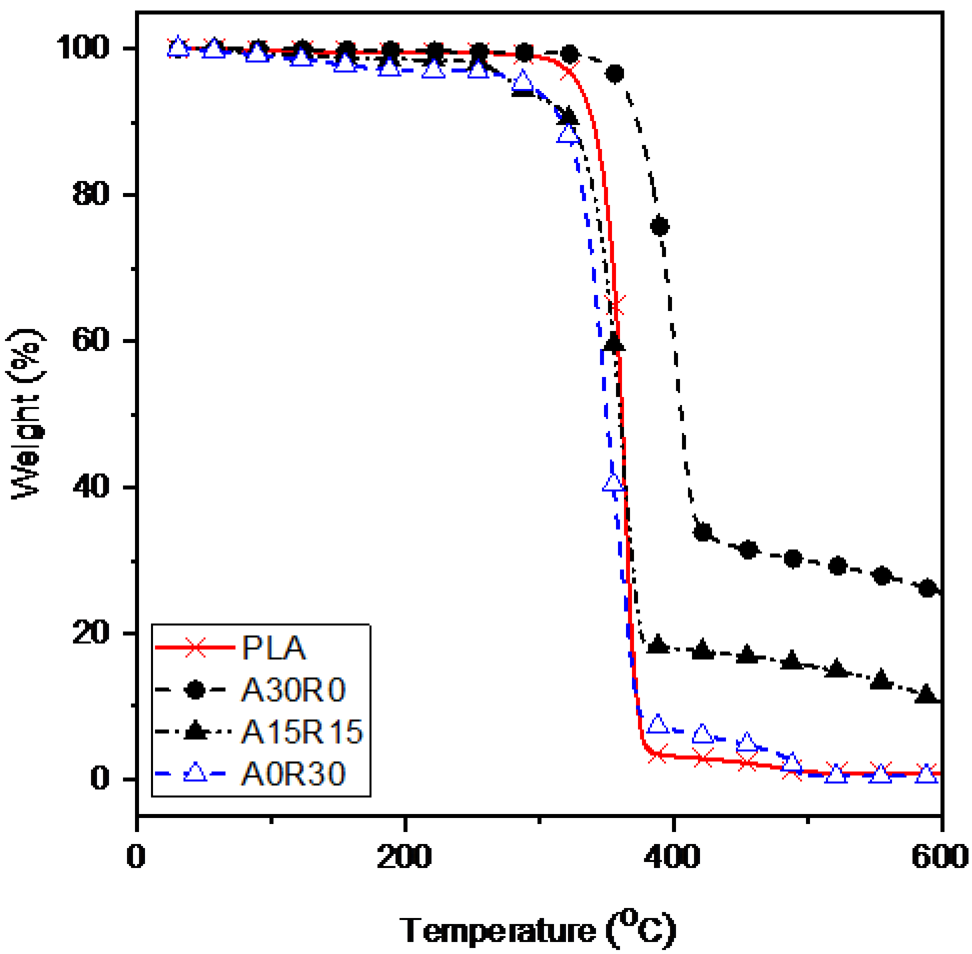

Figure 1

TGA curves of weight loss dependent on temperature for the PLA and PLA /Rayon composites under air purge.

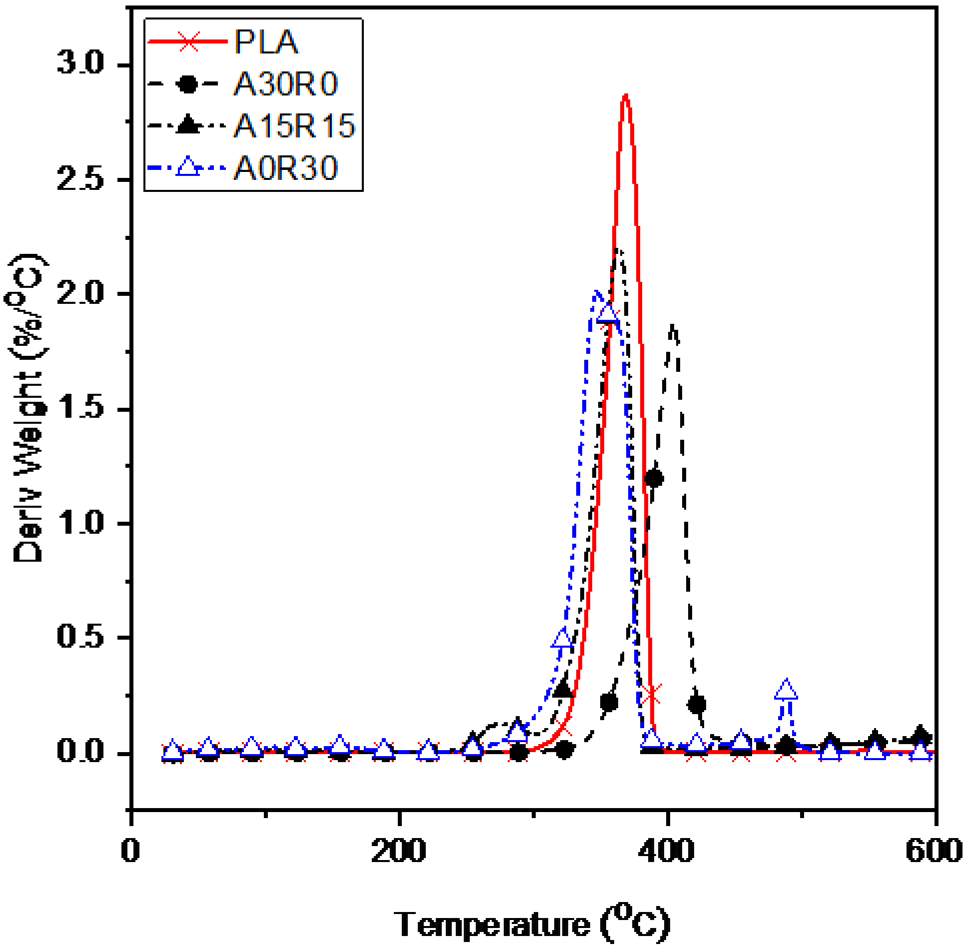

Figure 2

Derivative weight loss curves for the PLA and PLA /Rayon composites under air purge.

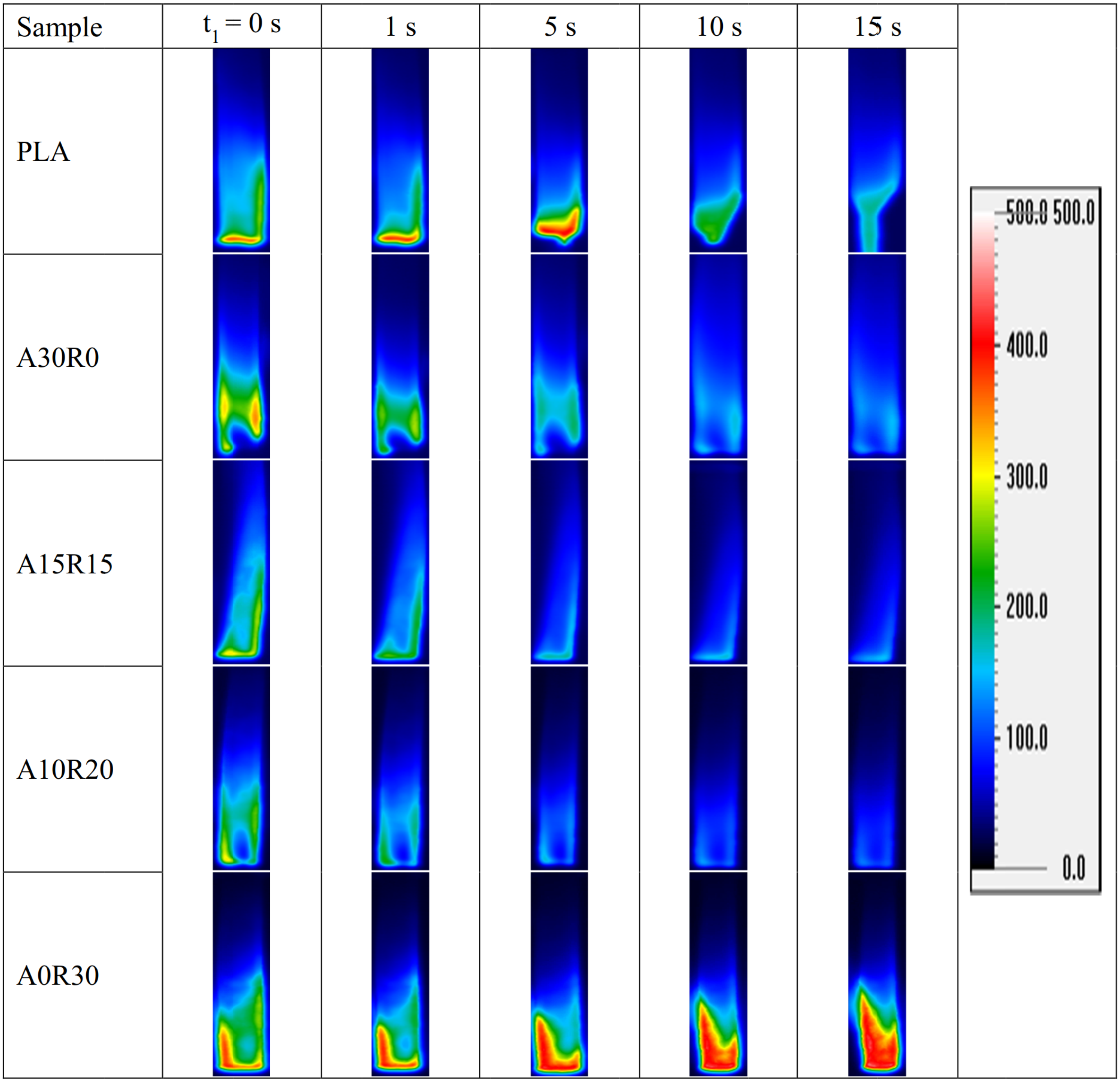

Figure 3

Thermal images of the samples when the ignition burner had been moved away for one second.

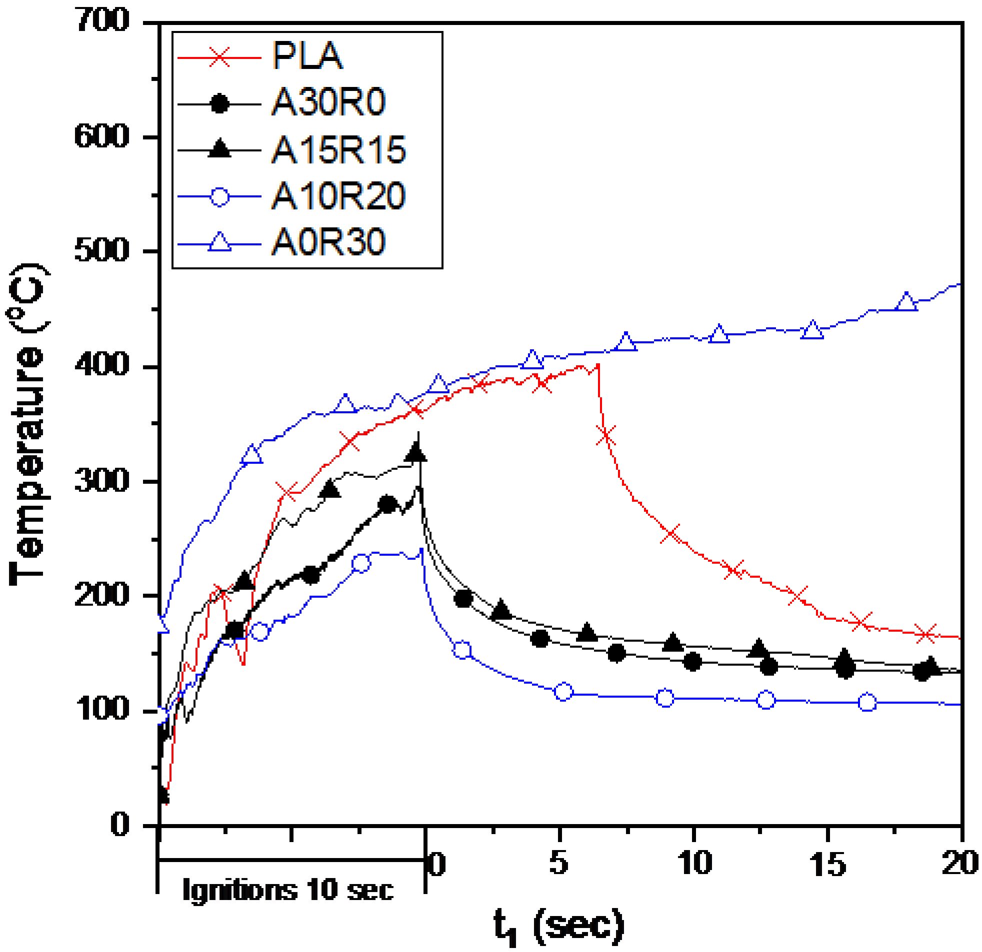

Figure 4

The highest temperature curves dependent on time determined by thermal images of the PLA and PLA composites in the first ignited.

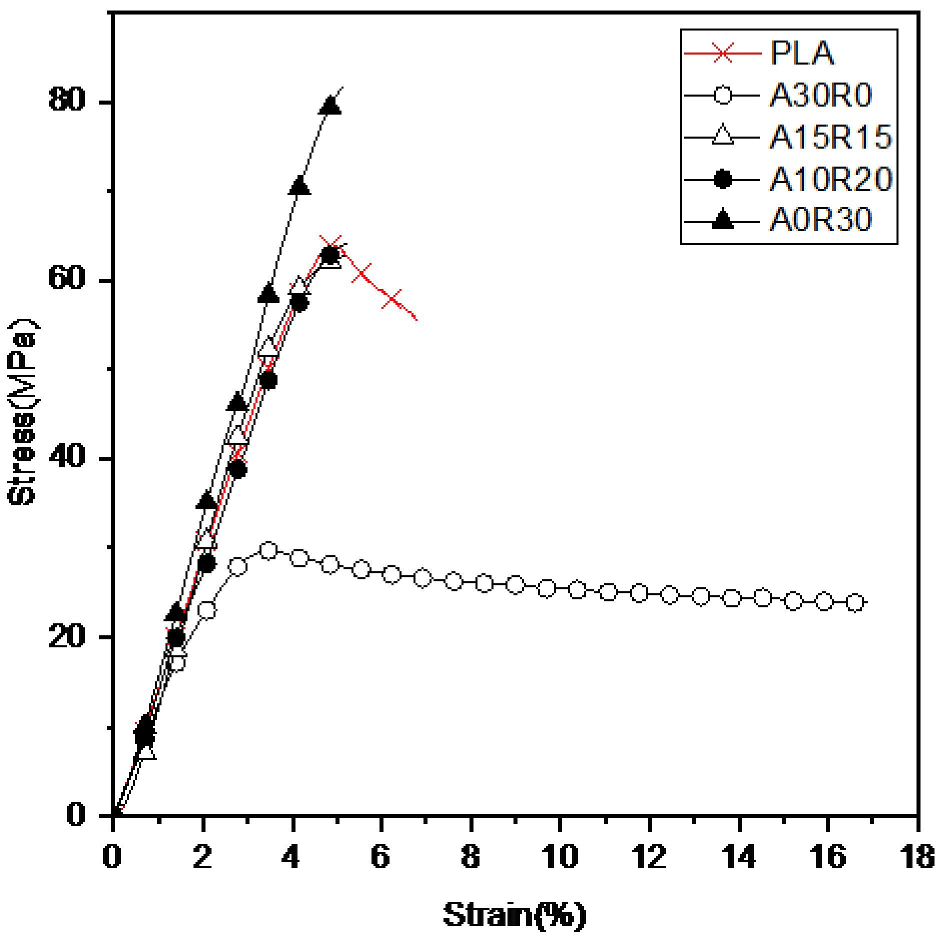

Figure 5

Stress-strain curves of the PLA and PLA composites under tensile tests.