PING WEI[1], SERGIO BOCCHINI[2)*], GIOVANNI CAMINO[3]

# Flame retardant and thermal behavior of polylactide/expandable graphite composites

**Summary** — In this article expandable graphite was used to produce fire retardant biobased polylactide. For this purpose, PLA blends with addition of 1, 5 or 10 wt. % of expandable graphite intercalated with sulphuric acid (GR) were obtained using co-rotating twin screw extruder. Thermal stability and flammability of prepared samples were examined by thermogravimetric analysis (TGA), cone calorimeter measurements and UL 94 test. Flammability UL-94 test shows the highest V-0 ranking from 5 % graphite loading, whereas 10 % is required for sensible decrease of rate of combustion in cone calorimeter forced combustion test.

**Keywords**: expandable graphite, polylactide, flame retardant, thermal stability.

## PALNOŚĆ I WŁAŚCIWOŚCI TERMICZNE KOMPOZYTÓW POLILAKTYD/EKSPANDOWALNY GRAFIT

**Streszczenie** — W artykule przedstawiono wyniki badań nad zastosowaniem zdolnego do ekspandowania grafitu do uniepalniania polilaktydu (PLA). W tym celu za pomocą wytłaczarki dwuślimakowej sporządzono mieszanki PLA z dodatkiem 1, 5 lub 10 % mas. ekspandowalnego grafitu interkalowanego kwasem siarkowym (GR). Otrzymane próbki badano metodą termograwimetryczną (TGA), a także wykonano pomiary z zastosowaniem kalorymetru stożkowego. Przeprowadzono również testy palności UL-94. Stwierdzono, że najskuteczniej uniepalnionym materiałem spełniającym kryteria klasy palności V-0 jest kompozyt zawierający 5 % mas. GR. Natomiast zapewnienie odpowiedniego zmniejszenia szybkości wydzielania ciepła (HRR) wymaga dodania 10 % mas. GR.

**Słowa kluczowe**: ekspandowalny grafit, polilaktyd, środek uniepalniający, stabilność termiczna.

Early biosourced polymers were used in short term applications, whereas now, environmental concerns and oil shortage worries expand their usage to longer term applications such as in construction, transport and electronics in which fire risk requires the use of fire retardant materials. Today, the most commercially developed biosourced polymer is polylactide (PLA) on which fire retardancy only a few papers have been published [1, 2]. Fire retardancy of PLA was not required, because packaging has been the typical PLA application so far.

Expandable graphite is an additive known to impart fire retardancy to various materials. Its structure consists of graphite layers within which a chemical compound is intercalated, generally an oxidizing acid (*e.g.* $H_2SO_4$, $HNO_3$), that induces abundant volume increase on heating, producing a protective foamed graphite covering onto the polymer surface (intumescence) [3].

Qu *et al*. [4, 5] studied expandable graphite-based intumescent flame retarded linear low density polyethylene (PE-LLD) and ethylene-vinylacetate (EVA) blends with magnesium hydroxide under different thermal-oxidative conditions. They evaluated combustion behavior of these materials by using cone calorimeter test, finding a consistent improvement in flame retardant properties. Awad *et al*. [6] investigated polyurea compounded with ammonium polyphosphate and expandable graphite obtaining a more thermally stable char than from polyurea, which traps volatiles, reducing flammability. In recent years, polymer based nanocomposites reinforced with expanded graphite have shown substantial improvement in mechanical and barrier properties in several polymers. Uhl *et al*. [7] studied the mechanical and fire retardant properties of polyamide-6/expandable graphite nanocomposites. Fukushima *et al*. [8] reported that PLA nanocomposites with expanded graphite showed considerable improvements in the thermal, mechanical and fire retardant properties of PLA.

To our best knowledge however, no much study on the effect of expandable graphite alone in biobased polymers has been reported so far in the literature. This work is devoted to an investigation using thermogravimetric analysis, UL-94 and cone calorimeter to test the thermal

---

[1] Shanghai Jiao Tong University, School of Chemistry and Chemical Engineering, Shanghai 200240, People's Republic of China.

[2] Istituto Italiano di Tecnologia, Center for Space Human Robotics@PoliTo, C.so Trento 21 10129 Turin, Italy.

[3] Politecnico di Torino Sede di Alessandria Viale Teresa Michel, 5 15121 Alessandria, Italy.

[*] Corresponding author; e-mail: sergio.bocchini@iit.it

stability and combustion behaviour of PLA-expandable graphite compounds.

## EXPERIMENTAL

### Materials

Polylactide of a commercial grade was supplied by NatureWorks (PLA, 3051D). Expandable graphite intercalated with sulphuric acid (GR) was supplied by INCA (HTEG 300) which main characteristics are reported in Table 1.

**T a b l e 1. Characteristics of expandable graphite HTEG 300**

| Property | Unit | Value |
|---|---|---|
| Density | g/cm$^3$ | 2.2—2.35 |
| Purity | % | >95 |
| Volume expansion | % | 150 |
| pH | — | 6—8 |
| Expansion temperature | °C | 280 |

Prior to melt blending, PLA was dried at 80 °C under vacuum to moisture content below 190 ppm, as measured by Karl-Fischer titration.

### Sample preparation

The materials were prepared using a Leistritz co-rotating twin screw extruder characterized by the following parameters: diameter $d$=18 mm, length/diameter ratio $l/d$=40, output of 4.0 kg/h, screw speed of 150 rpm and residence time 50 s. Prepared samples are denoted by symbols PLAXGR, where X gives the expandable graphite weight percent content.

### Methods of testing

Thermogravimetry analysis (TGA) was performed on a TA Q 500 instrument using platinum pans, with gas fluxes of 60 cm$^3$/min for sample gas (nitrogen or air) and 40 cm$^3$/min for balance protection gas (nitrogen). Analyses were carried out on ~10 mg sample at 10 °C/min heating rate, from 50 to 800 °C. Temperatures at which 10 % mass loss occurs ($T_{10\ \%}$) or the mass loss rate reaches the maximum ($T_{max}$) are reported. Experimental error was estimated to be typically less than 0.05 mg (approximately ±0.5 %).

Forced combustion tests were carried out on a Fire Testing Technology cone calorimeter according to the ISO 5660 standard, under the heat flux of 50 kW/m$^2$ in order to evaluate the fire properties of the materials in conditions comparable to a mild fire scenario. Specimens (100 mm × 100 mm × 3 mm) were contained in a tight aluminum boat placed on a ceramic backing board, exposing the upper sample surface to the radiant cone base (50 kW/m$^2$) at the distance of 25 mm.

UL-94 vertical test was carried out on strips 100 mm × 10 mm × 3 mm according to ASTM D635 standard. In this test, strips are ignited from the bottom and the material is ranked V-0, V-1, V-2 or non-classified, according to its behavior (burning time and dripping of burning material).

## RESULTS AND DISCUSSION

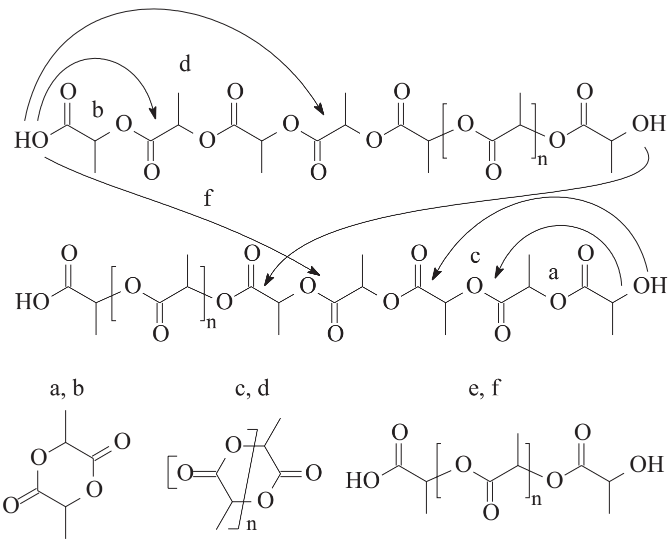
The results of thermal degradation and thermal oxidation, under nitrogen and air, respectively, for pure PLA and its compounds are reported in Table 2.

**T a b l e 2. Results of thermal degradation under nitrogen and thermal oxidation under air for PLA and its compounds**

| Sample | Under N$_2$ | | Under air | |
|---|---|---|---|---|
| | $T_{10\ \%}$, °C | $T_{max}$, °C | $T_{10\ \%}$, °C | $T_{max}$, °C |
| PLA | 338 | 368 | 323 | 353 |
| PLA1GR | 337 | 364 | 331 | 359 |
| PLA5GR | 333 | 356 | 331 | 364 |
| PLA10GR | 323 | 364 | 334 | 365 |

On the basis of literature it can be stated, that the main PLA pyrolysis mechanism involves intra- and intermolecular ester alcoholysis/acidolysis of polylactide chain ester groups by alcohol or acid chain end groups (Scheme A) [2, 9—12]. This dominant reactions pathway in the case of intramolecular reaction, leads to the formation of lactide and cyclic oligomers, whereas linear oligomers are formed by intermolecular reactions which may volatilise, depending on their molecular weight.

Ester alcoholysis and acydolysis are acid catalysed reactions, however the sulphuric acid intercalated between graphite layers is prevented from extensively reacting with the polymer as shown by the fact that weight loss takes place at similar temperatures and rates in PLA and



*Scheme A. Mechanism and products of PLA intramolecular alcoholysis or acidolysis according to [2]: lactide (a and b), higher cyclic oligomers (c and d), linear oligomers (e and f)* in graphite containing compounds, under nitrogen (Table 2). This behaviour further indicates that when graphite expansion occurs (*at ca*. 280 °C) and sulphuric acid is freed from the confined location, it undergoes mostly redox decomposition with formation of volatiles which are responsible of the volume increase [13].

Therefore a very limited acid catalysis of PLA chain scission takes place, which is responsible for a slightly lower degradation temperature observed in nitrogen for 5 and 10 wt. % of GR loadings.

As for many polyesters, the thermal stability of PLA in air is similar to that under inert atmosphere apart from some minor effects such as the decrease of about 10— 15 °C of $T_{10\,\%}$ and $T_{max}$ in air [9]. This small difference is an indirect confirmation that the main thermal degradation mechanism of PLA (alcoholysis or acidolysis induced chain ester bonds scission) is not a radical mechanism which would be strongly accelerated by oxygen of air. Thus, the role of oxygen is likely to be limited to a minor increase in the fragmentation of PLA, by a peroxide radical chain mechanism below 250 °C or hydrogen abstraction and radical chain fragmentation over about 250 °C, as usually happens for compounds containing aliphatic hydrocarbon structures [9, 14].

No detailed studies on thermal oxidation of PLA are available, except for those of Gupta *et al*. [15, 16] and Liu *et al*. [17] who however did not propose a thermal oxidation mechanism. Their only conclusions were that a small increase in the degradation rate and formation of carboxylic groups occurred by thermal oxidation. Addition of GR tends to increase $T_{10\,\%}$ and $T_{max}$ for mass loss of PLA in air (12 °C for PLA10GR, Table 2). This behavior is due to the gas barrier effect linked to graphite expansion and the formation of a foam that protects the polymer from the atmospheric oxygen, reducing the contribution of oxygen initiated pyrolysis to volatilization. Indeed, the temperature of maximum volatilization rate in nitrogen and air of PLA and PLA10GR is the same (364—365 °C) as if oxygen shielding by expanded graphite had been total.

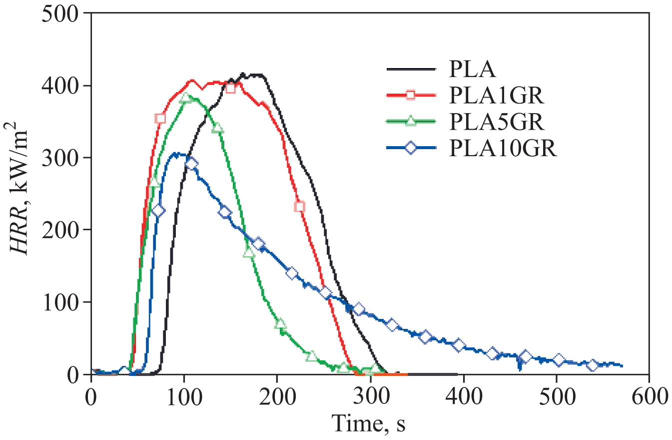


*Fig. 1. Comparison of the time dependence of heat release rate (HRR) curves for PLA, PLA1GR, PLA5GR and PLA10GR*

Cone calorimeter test is representative of a forced combustion, in which the material is forced to burn under exposure to external heat flux. Whereas the test supplies a complete set of combustion parameters, only the time to

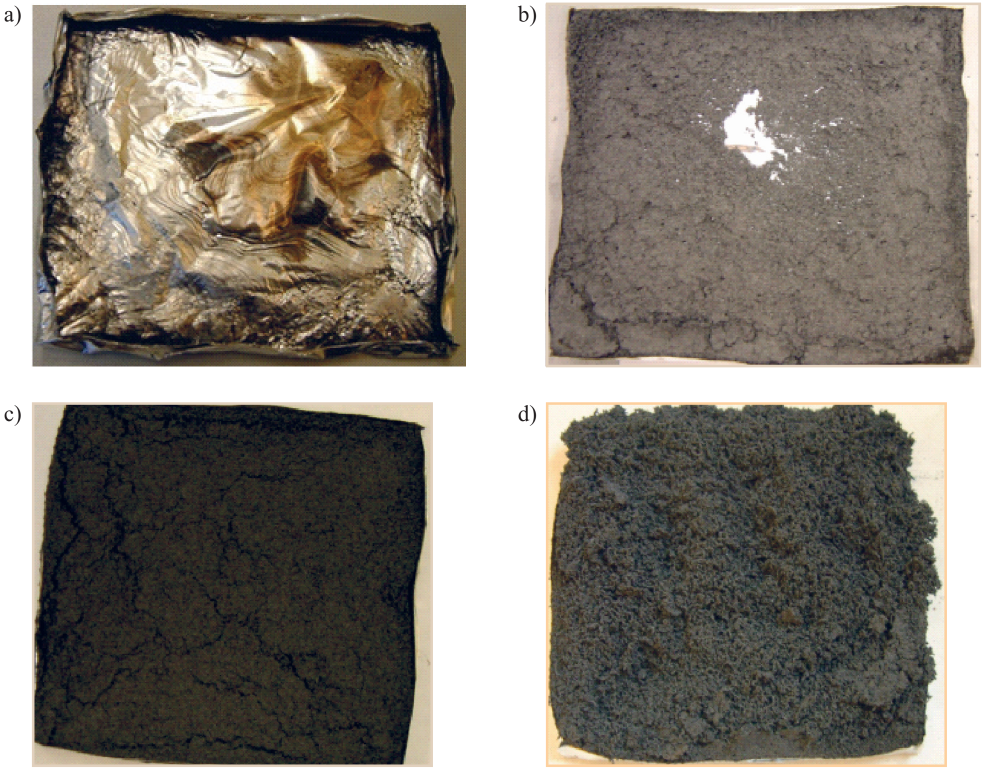


*Fig. 2. Residues after cone calorimeter test for: a) PLA, b) PLA1GR, c) PLA5GR, d) PLA10GR*

ignition (*TTI*), heat released rate (*HRR*) and total heat released (*THR*) are discussed here as the fundamental parameters for mechanistic understanding of the role of expanded graphite in PLAXGR compounds combustion.

**Table 3. Results of cone calorimeter measurements and UL 94 tests**

| Sample | *TTI*, s | *THR*, MJ/m$^2$ | p*HRR*, kW/m$^2$ | UL 94V |
|---|---|---|---|---|
| PLA | 64 | 64 | 425 | Non-classifiable |
| PLA1GR | 44 | 70 | 410 | V-2 |
| PLA5GR | 43 | 44 | 380 | V-0 |
| PLA10GR | 60 | 52 | 305 | V-0 |

The results presented in Figure 1 and Table 3 show that the addition of GR decreases the *TTI* of PLA in the compounds. This effect is probably related to the black color of the compounds that causes a greater absorption of radiant heat from the cone heater by PLAXGR compounds as compared to PLA. The higher quantity of heat absorbed causes a faster increase of the surface temperature of the graphite compounds and an earlier initiation of thermal degradation of PLA. This makes evolution of flammable PLA degradation products to reach the lower flammability limits above the sample surface, allowing for ignition by the igniting spark, in a shorter exposure time compared to PLA. Thus, the *TTI* of PLAXGR tends to be shorter than that of PLA. However the *TTI* values of PLA and PLA10GR compound are quite similar. In this case the concentration of GR is probably high enough to protect the sample from generating the intumescence before ignition occurs.

The maximal HRR value shows that graphite is quite ineffective at loading lower than 10 wt. %, at which 28 % reduction of peak *HRR* value (p*HRR*) is found, which is significantly outside 10 % experimental error, typical of *HRR* measurements in cone calorimeter and *THR* is reduced by 20 %. The suggested mechanism, by which expanded graphite acts as fire retardant reducing *HRR*, involves the formation of a char that serves as a potential barrier to both mass and energy transport between the flame and the burning polymer. Therefore, fire retardant effectiveness depends on barrier properties of the generated protective char as confirmed by Figure 2 in which it is shown that PLA burns leaving no residue, whereas in the presence of graphite a char is left which is compact and intumescent at 10 wt. % of GR content (Figure 2d). At lower graphite loading the protection fails either by the presence of holes (Figure 2b) or cracks (Figure 2c) in the char, through which volatile combustible PLA degradation products can feed the flame with poor or no restriction. Indeed, whereas the shape of *HRR* curves of PLA and PLA with 1 or 5 wt. % of GR loading is similar, at 10 wt. % loading the typical trend of surface protective intumescent char formation is shown, with delay of heat release.

UL 94 bottom ignited vertical test, on which application specifications are most often based, is widely used to evaluate materials flame retardant properties and to search flame retardant formulations. UL 94 test results of PLA and its expandable graphite compounds are reported in Table 3. PLA burns completely with flaming dripping, failing to be ranked with a fire retardant rating. In the presence of 1 wt. % of GR, the PLA combustion time is reduced within limits required by UL 94 test method for fire retardant ranking, which is set at V-2 level for PLA1GR. This is typical of materials that extinguish owing to flaming dripping, which eliminates heat from the burning polymer. From 5 wt. % of GR loading, the burning time is further reduced and dripping suppressed, leading to V-0 ranking which is the most challenging in UL 94 testing.

## CONCLUSIONS

PLA/expandable graphite compounds have been produced by melt-blending. The widely used vertical flammability UL 94 test gives the highest fire retardant ranking V-0, starting from 5 wt. % of expandable graphite loading.

Forced combustion tests indicate that the rate of combustion is sensibly decreased by the protective intumescent char created on the surface of the material, starting from 10 wt. % of GR.

## REFERENCES

1. Bourbigot S., Fontaine G.: *Polym. Chem*. 2010, **1**, 1413.
2. Bocchini S., Camino G.: „Flammability and Thermal Stability in Clay/Polyesters Nano-Biocomposites" in „Environmental Silicate Nano-Biocomposites" (Eds. Avérous L., Pollet E.), Springer London, London 2012, pp. 265—285.
3. Bourbigot S., Duquesne S.: „Intumescence-Based Fire Retardants" in „Fire Retardancy of Polymeric Materials", Second Edition (Eds. Wilkie C. A., Morgan A. B.), CRC Press 2009, pp. 129—162.
4. Xie R., Qu B.: *Polym. Degrad. Stab*. 2001, **71**, 395.
5. Li Z., Qu B.: *Polym. Degrad. Stab*. 2003, **81**, 401.
6. Awad W. H., Wilkie C. A.: *Polymer* 2010, **51**, 2277.
7. Uhl F. M., Yao Q., Nakajima H., Manias E., Wilkie C. A.: *Polym. Degrad. Stab*. 2005, **89**, 70.
8. Fukushima K., Murariu M., Camino G., Dubois Ph.: *Polym. Degrad. Stab*. 2010, **95**, 1063.
9. Mcneill I. C., Leiper H. A.: *Polym. Degrad. Stab*. 1985, **11**, 267.
10. Mcneill I. C., Leiper H. A.: *Polym. Degrad. Stab*. 1985, **11**, 309.
11. Wachsen O., Reachert K. H., Kruger R. P., Much H., Schulz G.: *Polym. Degrad. Stab*. 1997, **55**, 225.
12. Fan Y. J., Nishida H., Hoshihara S., Shirai Y., Tokiwa Y., Endo T.: *Polym. Degrad. Stab*. 2003, **79**, 547.
13. Camino G., Duquensne S., Delobel R., Eling B., Lindsay C., Roels T.: *ACS Symp. Ser*. 2001, **797**, 90.
14. Bensons S. W., Nangia P. S.: *Accounts Chem. Res*. 1979, **12**, 223.
15. Gupta M. C., Deshmukh V. G.: *Coll. Polym. Sci*. 1982, **260**, 308.
16. Gupta M. C., Deshmukh V. G.: *Coll. Polym Sci*. 1982, **260**, 514.
17. Liu X., Zou Y., Li W., Cao G., Chen W.: *Polym. Degrad. Stab*. 2006, **91**, 3259.

*Received 3 IX 2012.*