XV International Conference on Durability of Building Materials and Components
DBMC 2020, Barcelona
C. Serrat, J.R. Casas and V. Gibert(Eds)

Fire Properties of Novel Cellulosic Material Modified with Expandable Graphite

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Abstract. *Expandable graphite (EG) is an intumescent additive known to improve fire properties of various materials. Intumescent fire retardant (IFR) based on EG is a protection method for flammable materials taking the attention of researchers in the past few years (Xie et al., 2000). New studies indicate that EG is a good source of carbonization agent for effective and environmentally friendly intumescent systems (Feng et al. 2013). Although EG is used in a growing number of IFR systems as a blowing agent that will suppress flammable gases up to 75%, while reducing the flame spread index, its application to cellulosic material is not so popular in the cellulose industry today (Krassowski et al., 2012). The current study focuses on flammability, concerning cellulose modified material (CMM). The objective of this work was CMM encrusted with EG. The general aim of the research was to determine its basic fire resistance properties. The scope of the research included measurement of the following parameters: time to ignition (T_i), time to flame out (T_f), total heat peak (THR) and mass loss (ML). Samples of CMM sheets were manufactured with the use of hydropulper and rapid-koethen devices. Two types of EG (i.e. ES20 C200 and ES100 C10) were used. Sodra Black Cellulose fibres (700 kg/N^3) was used in this experiment. Cellulose milling time was 30 min. and drying time of 40 min. The drying temperature of the final sheets was controlled and kept at 93^0C to avoid graphite activation. Final sheets were conditioned at room temperature at 20^0C and relative humidity 60%. With heat flux of 35 kW/m^2, all samples were tested on MLC apparatus. The addition of EG was found to increase the flame retardant effectiveness of cellulosic material. Although T_i for all CMM species were lower than that of control samples, this fact actually favored the promotion of char forming, which led to a longer combustion process for all CMM.*

Keywords: *Mass Loss Calorimeter, Char, Expandable Graphite Cellulose, Flammability.*

1 Introduction

Fire retardant formulation (FRF) based on expandable graphite (EG) is a fire reinforcement method for flammable materials taking the attention of researchers in the past few years (Xie and Qu, 2000). As a carbon-layered crystal, EG consists of sheets of carbon atoms strongly bound to each other (Kruger, 2017). The literature indicates that EG is a good source of carbonization agent for effective design of environmentally friendly intumescent systems (Feng *et al.,* 2013). There are insufficient detailed reports in literature on the behaviour of EG-intumescent fire retardants (IFR) systems concerning cellulosic materials. Although EG is used in a growing number of IFR systems as a blowing agent that will suppress flammable gases up to 75%, while reducing the flame spread index, its application to cellulosic material is not so popular in the cellulose industry today. Depending on the processing methods, fire retardants (FR) are often categorized as: Additive or non-inert compounds. Additive FRs are often mixed inside the matrix of the polymer during its processing. These FR are usually inert

to de polymer. Reactive FRs are dose polymerized with a resin during processing of cellulosic material to become integrated into its molecular network structure. These FRs are also known as chemically modified FRs (Jesbains *et al.,* 2011). The footprints of fire retardants points to an effective ideal fire retardant that should be thermo-stable, compact with the protected polymer, should not change the physical-chemical properties of the protected polymer, and have low toxicity under heat exposure or during burning (Camino and Costa, 1987). In order to understand the dynamics of fire retardants it is required to have detailed knowledge of the mechanism of the thermal-degradation progress related to the polymer.

Inventions related to EG are usually linked to its thermal properties, therefore related to reducing the flammability and/or combustibility. In fact, the use of expandable graphite as part of flame retardant agents and fire protection is being promoted by laws and regulations that push the prohibitions of halogenated based fire retardants due to environmental concerns related to the emission of toxic gases from the thermal degradation of halogenated base flame retardants. The European Union is one of the organizations promoting the development of new halogen-free flame retardants (Acuna *et al.,* 2019). EG is a novel product in use in various inventions. Many patents claim that EG properties can be used for diverse of applications. Not only in the field of fire retardants where EG is used to protect fibrous materials, but also in electrical applications. As solid composite, EG was used in lithium/Sulphur batteries as cathode; the solid composite comprised of up to 75wt-% of expanded graphite (Schmidt *et al.,* 2017). Rubber melded body material with enhanced fire resistance. In this rubber composition, one of the main components was EG (Sakai and Nakano, 2019). EG is also used in devices of heat recovery unit, on this invention due to its heat resistance, EG was installed as a retention membrane (Murata and Koga 2019). EG is a multi-porous material with an average pore size distribution of about ~2 nm, this structure allows EG to accommodate other chemical espies in between is sheets to form other composites, it has been found to improve the conductivity properties of the polymer structure. From the exfoliation process of expandable graphite, we can obtain a good electrically conductive material, this is leading to several study of the electrical conductivity of some EG composites (Celzard, *et al.,* 2000). In solar energy storage researches, EG is one of the materials that can enhance the thermal conductivity of solar cell. In the works of Xiao *et al.,* (2013), sodium nitrate, potassium nitrate and their solution were used as the base material. The conductivity of the based material was of about 10 wt.%. With the addition of expanded graphite that has high thermal conductivity, the conductivity of the final material increased at about 40%. In his work, Xiao *et al.,* (2013) agreed that the theoretical results and the experimental results are in agreement. It is clear that the novel product has a diversity of fields/research areas to contribute with its property in this literature review we consider that the thermal conductivity properties and the potentially electrical conductivity properties are at the top potential characteristics that researchers at observing. Most articles do not address the aesthetic aspect of their final product. When combining EG with other additives the appearance of the final product is not so attractive the final application, especially when it is related to coatings fire retardants formulations. Other concern is related to cost of EG. The market to this product is growing at a fast speed. According to the Markets and Markets (2019), the global graphite market is projected to reach 29.05 billion dollars by 2022. This is a considerable amount that indicates that the global market is interested on these eco-friendly products. In the academy it is conclusive that the use of EG will increase as novel products

are developed.

To achieve this goal, the present preliminary experiment will use Mass Loss Calorimeter (MLC) infer the thermal stability of the CMM. MLC is frequently used to explore flammability properties of different type of materials, delivering a suitable sort of technical data (Krassowski *et al.,* 2012). Recent analysis of thermal stability of lingo-cellulosic materials under controlled conditions showed the decomposition temperatures (T_d) for lignin, hemicelluloses and cellulose. This last component, with $T_d = 320^0$C, char 6% by mass (Mazela *et al.,* 2018; Fox *et al.,* 2012). The current study focuses on flammability concerning cellulose component only.

The objective of this work was cellulose-based model material (CMM) encrusted with expandable graphite (EG). The general aim of the research was to determine its basic fire resistance properties. The scope of the research involved measurement of the following parameters: time to ignition (Ti), time to flame out (Tf), total heat release peak (THR) and mass loss (ML).

2 Methods

Samples of cellulose sheets were manufactured with the use of hydropulper and Rapid-Koethen devices. Cellulose sheets were encrusted with two types of EG (ES100 C10 and ES20 C200). EG was dispersed in a cellulose pulp at the preparation stage. ES20 C200 had higher amount of fine-grained fraction (90% <75µm) and thus was characterized by lower expansion volume (20 ml/g) in comparison to ES100 C10 type. Three variants of cellulose sheets were prepared: control sheets (pure cellulose) and sheets encrusted with graphite ES200 C20 or ES100 C10. Sodra Black Cellulose fibres (700 kg/m^3), with the following dimensions of fibers: 2.05 mm length, 30.0 µm width, were used for the process of cellulose sheets manufacture. The cellulose milling time was 30 minutes and the drying time 40 minutes. The drying temperature of the final sheets was maintained at 93^{0}C to avoid graphite activation notwithstanding the manufacture of EG advises that activation temperature is at about 320^{0}C. The final sheets were conditioned at room temperature at 200^{0}C and relative humidity 60%. All the samples were subjected to MLC measurements (Fig. 1). Heat flux at 35 kW/m^2 was estimated as suitable level for all tested samples. This work inferred conclusions on flammability properties of CMM by measuring time to ignition (Ti), time to flame out (Tf), total heat release peak (THR) and mass loss (ML). It was possible to account for all important aspect mentioned above however it was not possible to account for repeatability the samples. This led to some discrepancy in some sample properties (i.e. thickness) as shown on table 1. bellow.

Table 1. Characterization of samples.

Samples	Thickness	THR (MJ/m^2)	T_i (s)	T_f (s)	THR peak (MJ/m)
Cellulose 01	0.89	9	25	94	230.72
Cellulose 02	0.88	7.2	21	79	222.41
Cellulose 03	0.89	8.3	24	89	236.05
EG200-01	1.45	6.7	22	100	98.03
EG200-02	1.4	6	21	102	89.55
EG200-03	1.4	6	20	99	97.61
EG100-01	1.4	4.4	19	108	73.32
EG100-02	1.5	4.4	19	107	75.42
EG100-03	1.4	4.8	19	123	74.96

It is clear that the mass (g) of each sample are not the same. With the standard deviation calculated to be 0.1 for cellulose samples, 0.5 for EG200 and 0.3 for EG100.

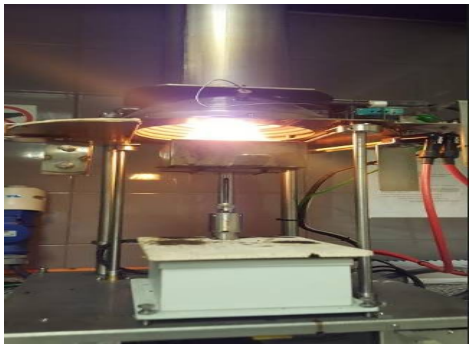

Figure 1. MLC apparatus set at 35kW/m^2.

3 Results

T_i for CMM encrusted with ES100 C10 and ES20 C200 was estimated at the average on 19.0 and 21.0s respectively. This corresponds to T_i of ES100 C10 2s faster than that of ES20 C200, while for control samples it was estimated on 23.3 s, control samples resisted 22% more time than the more "fragile" sample (ES100 C10). As we can confirm in the figure 2. In average, T_i for CMM encrusted with ES100 C10 and ES20 C200 were observed to ignite 4.3 s and 2.3 s, respectively faster than control samples.

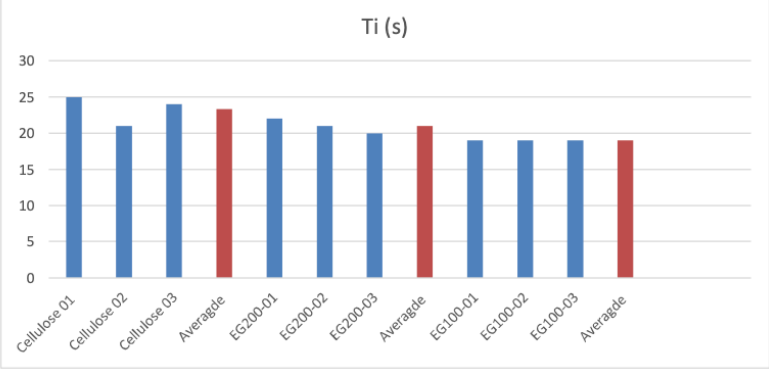

Figure 2. Time to ignition of all samples.

Figure 3. shows among others, the average T_f value for CMM encrusted with ES100 C10 was112.7 s, while pure cellulose and CMM with ES20 C200 did register an average of 87.7 and 108.0 s, respectively. In this case however, ES100 C10 showed a resilient behaviour, taking 28% more time to terminate its combustion process. ES100 C10 showed earlier char formation, this fact can help on fire protection properties.

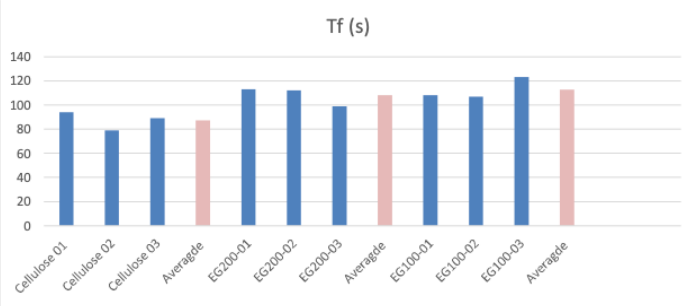

Figure 3. Time to flame out of all samples.

Maximum THR was observe to be 229.72 kW/m^2 for pure cellulose, 91.87 kW/m^2 for CMM with ES20 C200 and 71.51 kW/m^2 for CMM with ES100 C10, as presented in the in figure 4. ES100 C10 is a material that burns with a resilient behaviour. That is, this material suppresses better the refuel of the combustion process. Less heat released from the combustion process is redirect to the fire feed. One can observe that ES100 C10 have a more attractive fire property.

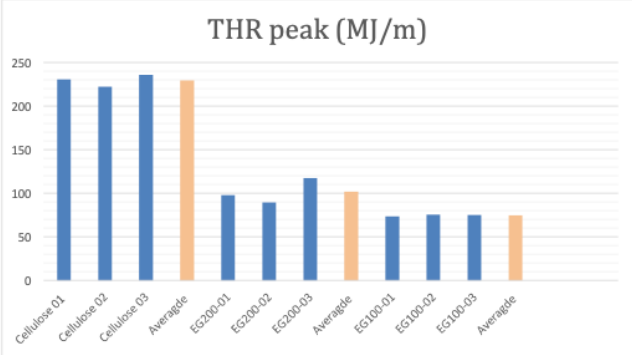

Figure 4. Time to flame out of all samples.

4 Conclusions

- The addition of EG was found to increase the flame-retardant effectiveness of cellulosic material.
- Although T_i for all CMM species were lower than for control samples, this fact actually favored the promotion of char forming. The improved physical characteristics of char is achieved by increasing the amount of the insulated layer and reducing crack formation. This aspect allowed the combustion process of CMM with ES100C10, to be 25s longer than combustion process of pure cellulose and almost 5 s longer than that of CMM with ES20 C200. In addition, the maximum HRR for CMM with ES100C10 was 69% smaller than its compared value for pure cellulose and 22% smaller than its compared value for CMM with ES20 C200.
- CMM with ES100 C10 is consequently the best performing system in terms of the observed parameters.

Acknowledgements

The work was financially supported by the Ministry of Science and Higher Education as the Project No 507.423.09. with subsidies for maintaining the research capacity and the paper was partially financed within the framework of Ministry of Science and Higher Education programme "Regional Initiative of Excellence' in years 2019-2022, Project NO. 005/RID/2018/19". Part of the above mentioned results were also presented on two scientific conferences in year 2019: INPAP 2019 - The future of papermaking, 10-12th of June, Augustów Poland and Wood Science Economy – International scientific conference, 21-22nd of October Poznan, Poland.

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