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Study of Changes of PMMA and PC Flammability Subjected to Aging

Matúš Adamčík [1,*], Emília Orémusová [2]

[1] Technical university in Zvolen, Faculty of Wood Sciences and Technology, Department of Fire Protection, T.G. Masaryka 24, 960 01 Zvolen, Slovakia; xadamcikm@is.tuzvo.sk

[2] Technical university in Zvolen, Faculty of Wood Sciences and Technology, Department of Fire Protection, T.G. Masaryka 24, 960 01 Zvolen, Slovakia; emilia.oremusova@tuzvo.sk

[*] Corresponding author: emilia.oremusova@tuzvo.sk

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Abstract

Today, plastics are used in every industry, from healthcare to the automotive industry. For their versatile use, it is necessary to deal with their fire-technical characteristics. The aim of the diploma thesis was to determine the effect of aging on the flammability of selected plastics polycarbonate (PC) and polymethylmethacrylate (PMMA), which main use is as a replacement for glass. Testing of plastics was performed according to the international standard STN ISO 1210, namely method A - samples placed in a horizontal position and method B - samples placed in a vertical position. From the point of view of fire-technical characteristics, the linear burning rate and the spontaneous burning time were monitored. In method A, the PC achieved lower flammability because the burning on the tested samples did not exceed the limit of 25 mm compared to PMMA samples, in which the burning of the samples exceeded the limit of 100 mm. In method B, the PC also achieved lower flammability because the samples were extinguished faster compared to PMMA, in which the combustion reached the sample holder. PC has achieved better fire performance and is less flammable than PMMA. The results show that the aging of the samples influenced the flammability of both plastics.

Keywords: fire properties; linear burning rate; polycarbonate; polymethyl methacrylate; spontaneous combustion time.

1 Introduction

Plastics are some of the most important parts of our daily lives. Products made of plastic range from the most sophisticated products such as prosthesis substitutes to auxiliary materials in the kitchen. One of the few reasons for the great popularity of plastics is the wide range of usability both in the home and in industry, due to the huge range of properties that individual plastics have and their ease of processing. The properties of plastics can be adapted to specific requirements by changing their structure, or by mixing them with other types. The first synthetic polymers were discovered in the first half of the 20th century, and Alexander Parkes was one of the discoverers. Nowadays, various materials such as wood, ceramics, glass are replaced by plastics, due to their ease of workability and wide range of usability. In general, plastics as well as products made from them are flammable polymeric materials, so it is important from the point of view of fire protection and safety to deal with their properties.

In the study, we were engaged in the evaluation of polymethyl methacrylate (PMMA) and polycarbonate (PC). Currently, both plastics have significant applications in the chemical, technological, electrical engineering industry. They have a significant presence in construction as various covers, spotlights, boards, roofs, parts, and others.

Polycarbonates belong to the polyesters of carbonic acid and dihydroxy compounds. Those are polyesters of carbonic acid and symmetrical aromatic dihydroxyls of fusion, which contain two phenolic nuclei connected by a bridge, derived from alkyl, or by an atom of oxygen or sulphur. Readily available and in terms of its properties, polycarbonates of 2,2-bis(4-hydroxyphenyl) propane, known by the name of dian or Bisphenol A. [1], are useful. Polycarbonate (PC) was first discovered in 1898 by German scientist Alfred Einborn at the University of Munich. In 1957, linear polycarbonate was patented at Bayer in Uerdingen, Germany, by Hermann Schenll. [2,3]

The PC is classified in class B of reaction to fire, which means that it contributes minimally to the spread of fire. It maintains dimensional stability up to approximately 140 °C and heat-resistant for a short period of time up to approximately 160 °C, and the block begins to deform, causing the material to sag or collapse from anything that holds it in place. It passes into the molten substance when tempered, at a temperature of approximately 220 °C, and the molten substance gradually drips in small quantities. Burning polycarbonate releases a sweetish odour and a yellowish flame coloration. The rate of spread in a fire is very slow, especially when compared to other flammable substances. The PC has an s1 classification, which means that it releases a low amount when burning. But at temperatures of approximately 380 °C, thermal degradation occurs with the formation of thick dark smoke without a special taste and odour. For humans, polycarbonate burning fumes are not physiologically dangerous.

Among other things, the PC is a self-extinguishing polymer and produces a small amount of burning droplets, therefore it receives a d0 rating according to EN 13501-1. However, even these small droplets can contribute to the spread of fire by igniting other objects. [4]

At a temperature of approximately 160 to 170 °C, the molten material is transformed when it begins to drip. This phenomenon can help extinguish a fire if it directly drips onto a source of flame. At the same time, this can detract from the impression when testing the PC, as it can drip onto the burner and stop the test before completing the classification, e. g., with a PC board more than 6 mm thick. For multilayer types, testing is possible to the will of more air and less material for melting. In the combustion products of polycarbonate, with increasing temperature, derivatives of phenols with a small number of elements of aliphatic and aromatic hydrocarbons and aldehydes, phenols, carbon monoxide and carbon dioxide are found. If polycarbonate burns in a room with insufficient burning, Bisphenol A is also found in the combustion products in a certain amount, which in increased quantities can have mutagenic effects on the human body. A burning PC is extinguished mainly with powders, CO_2, or medium and heavy foam. [5,6]

Polymethyl methacrylate is a polymer of methyl methacrylate (MMA) and a polymethracrylic acid ester) from chemical point of view. PMMA is usually synthesized by radical MMA polymerization, and anionic and coordinating polymerizations are also available. PMMA is one of the methacrylic resins, commonly called acrylic resin. PMMA is a transparent thermoplastic and is a widely used polymeric material in the fields of aerospace, engineering, medicine, and architecture, which has shock-, weather-resistant and chemical-resistant properties and is known as a substitute for inorganic glass. Since PMMA is strong, lightweight and has colour versatility, it is used in various applications in optical materials, automotive, electronics, displays and other industries. [1,7] Polymethyl methacrylate (PMMA) was first developed by the German chemist Otto Rohma in 1901. A few decades later, in 1943, Kulzer and Degussa ennobled PMMA into a form of a similar path. Their development led to the formation of cold-hardened PMMA. [8]

PMMA is a readily flammable polymer and begins to melt at around 120°C. The rate of flame on the surface is very low, and the coloration of the flame is blue and yellow. PMMA burnout is even and gradual. During burning, drip does not occur, but burning soft parts of the polymer may fall off. Burning has a sweetish smell. With the thermal degradation of PMMA, many esters are formed, but without the development of combustion products. It belongs to the group of polymers, after which no residues remain and there is no dripping. The substances contained in the combustion products include, first, methyl methacrylate, and others are methyl propinate, methyl acrylate, methyl isobutyrate. Alcohol substances, in particular ethanol and methanol, were also recorded at higher temperatures, as well as ethylene, carbon monoxide, acetylene and carbon dioxide when testing thermal degradation. To extinguish burning polymethyl methacrylate, it is adequate to use a compact or fragmented stream of water or water mist with admixtures of wetting agents. When using water foam, a two-sided reaction of the foam with the formed aldehydes and esters can occur, and such foam can further promote burning. [5,9]

Plastics change their properties over time due to aging.

The aim of the study was to determine the effect of aging on the flammability of PMMA and PC.

2 Material and Methods

The dimensions of the test samples (see Fig. 1 and 2) were laser cut to 125 x 13 x 3 mm. Subsequently, the samples were divided into two sets. One set of samples was stored indoors in a box in a dark place for 18 months, the second set of samples was exposed to weather conditions outdoors for 18 months, the samples were subject to natural aging.

The methodology used to deal with the experimental part of the work was constructed in accordance with STN ISO 1210:1996 [10]. It is an international standard characterizing a laboratory method for comparing fire characteristics in the horizontal (method A) and vertical (method B) position of samples of test plastics that are exposed to the action of a small flame initiator.

The test method is intended to determine the spontaneous flame/glowing time and the length of damage to the test sample. The use of the method shall be applied to lightweight or rigid materials with a specific weight of at least 250 kg/m^3. Testing of samples was in two ways according to the standard.

Method "A" – Determination of the linear burning rate of horizontal samples

For Method "A", marks are made on the samples and then the test device was prepared for the flammability test in a horizontal position. Underneath the sample a foil with filter paper was placed. The burner flame was adjusted so that it reached a length of 20 mm, was at an angle of 45° and touched the sample to a depth of approximately 6 mm. The flame was allowed to act on the sample for 30 s and subsequently delayed or immediately after reaching the marked line in less than 30 s. If the marked line was crossed, the second stopwatch was triggered. If the sample has burned without flame even after the burner has been delayed, the burning time in seconds was recorded. The damaged part of the sample was recorded and calculated according to the procedure in the standard.

Method "B" - determination of the period of spontaneous flame burning or glowing of vertical samples

For method "B", devices have been prepared for the flammability test in the vertical position. Underneath the sample a foil with filter paper was placed. The flame of the burner was adjusted so that it reached a length of 20 mm and was at an angle of 45°. The flame was applied for 10 s to the lower part of the sample at 10 mm below the lower end of the sample. After 10 s, the flame was delayed and at the same time the stopwatch was triggered to monitor the burning time t_1 in seconds.

If the combustion of the sample was interrupted after the flame has been delayed, the burner was re-placed under the sample at the same distance and left for 10 s. After 10 s, the flame was delayed again and the burning time t_2 and the glowing time t_3 were monitored. It was also recorded whether part of the sample had fallen off or dripped.

All samples were conditioned for 48 h prior to testing under the ambient laboratory conditions under which the experiment was carried out.

3 Results and Discussion

Fire properties are an important factor in the assumption of determining the fire behaviour of materials. The determination of the spontaneous burning time, the linear burning rate, describe more closely the supposed possibility of burning in real fires. The individual values of PC and PMMA vary, but there is a significant difference in the total time of spontaneous burning and mass loss before and after aging.

3.1 Method "A" results

When applying method "A", the samples were tested in a horizontal position. Demonstration of the combustion process of PMMA and PC samples is shown in Fig. 1-2.

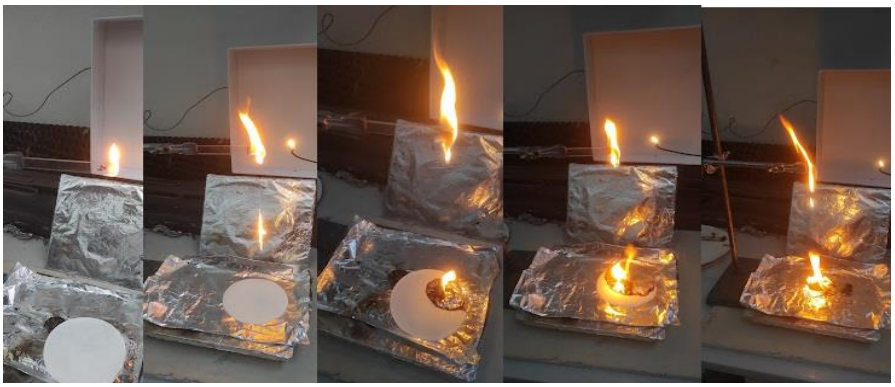

Fig. 1 PMMA burning pattern by Method "A"

Fig. 2 PC burning pattern by method "A"

The PMMA total time of spontaneous burning time is shown in Fig. 3.

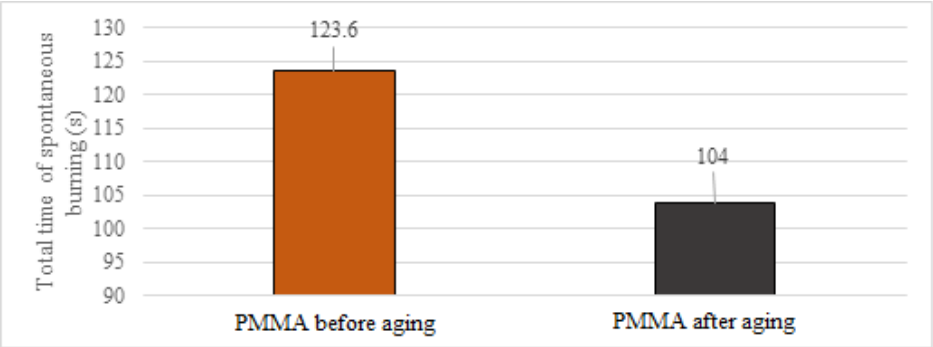

Fig. 1 Total time of spontaneous burning

The total spontaneous burning time shows that PMMA ageing has significantly influenced the comparative characteristics of the samples, with a difference of 19.6 s between PMMA samples before

and after ageing. The total spontaneous burning time of the PC could not be determined because the samples did not burn out the 25 mm limit from which the measurement begins.

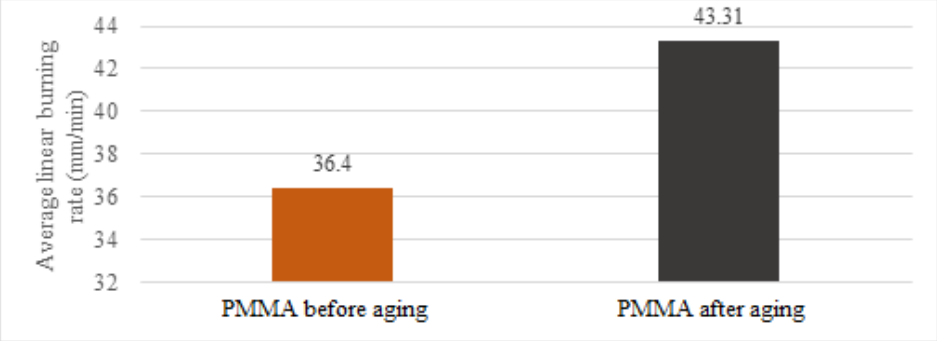

Fig. 4 Average linear burning rate

The graph (Fig. 4) shows that the lowest average linear burning rate was of 36.4 mm/min before ageing and the highest PMMA after ageing was of 43.31 mm/min. The linear burning rate of the PC could not be determined because the 25 mm boundary from which the measurement begins was not burned out for the samples.

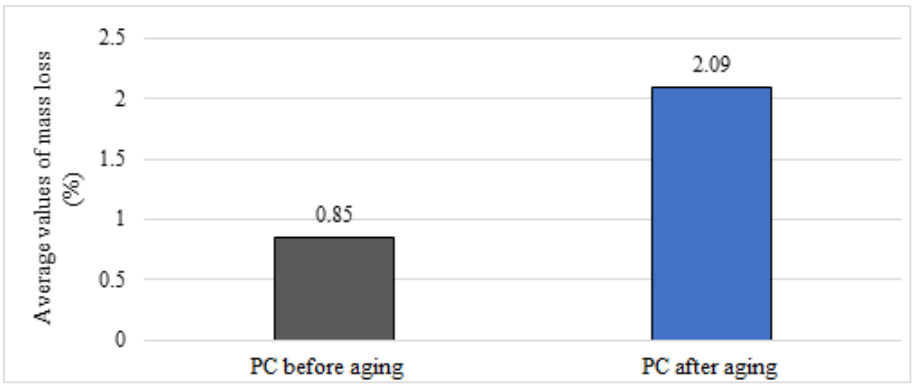

Fig. 5 Average values of mass loss

PC samples (Fig. 5) ahowed a significantly worse effect on the resulting average values of mass loss after aging. The average mass loss of PMMA samples is approximately 67% for both types of aging. However, here we must note that PMMA samples would burn out whole, however, the combustion stopped at the terminal block of the sample holder, therefore the values are removed from the graph. Samples after testing (before and after aging) are shown in Fig. 6.

Fig. 6 PMMA and PC samples after testing with method "A"

3.2 Method "B" results

When applying method "B", the samples were tested in an upright position. A demonstration of the burning process of PMMA and PC samples tested in an upright position is shown in Fig. 7-8.

Fig. 7 PMMA burning pattern by method "B"

Fig. 8 PC burning pattern by method "B"

The total period of spontaneous burning both before and after aging is shown in Fig. 9.

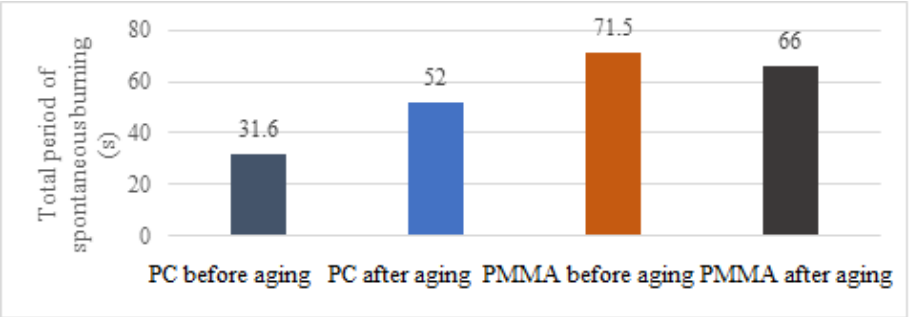

Fig. 2 Total period of spontaneous burning

With the total spontaneous burning time of PC and PMMA, aging has affected both the burning time of both PC and PMMA in a negative direction. As with method "A", the burning of the PC did not reach the upper limit (or sample holder). PC samples burned longer after aging than before aging. The self-extinguishing effect was more pronounced in the sample before aging, which also resulted in less mass loss. PMMA samples burned out after aging in less time than before aging. The mass loss of PC samples is shown in Fig. 10.

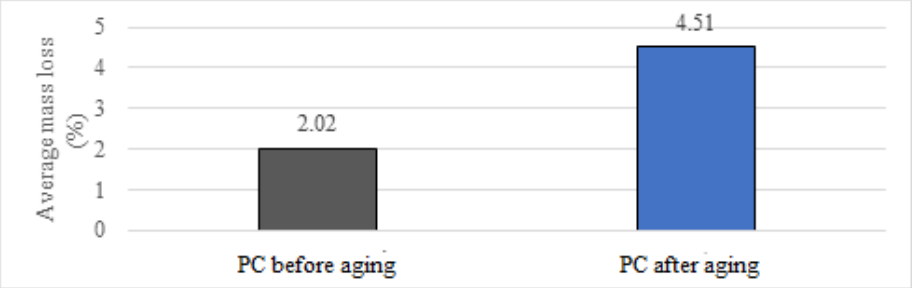

Fig. 3 PC average relative mass loss

For PC samples, aging has a significant impact on mass loss. The difference in mass loss before and after ageing was of 2.49%. The average mass loss of PMMA samples was approximately of 77% for both types of ageing. The same statement applies here as with method "A", that PMMA samples would burn out whole in this case, burning was stopped by the terminal block of the holder. Samples after testing are shown in Fig. 11.

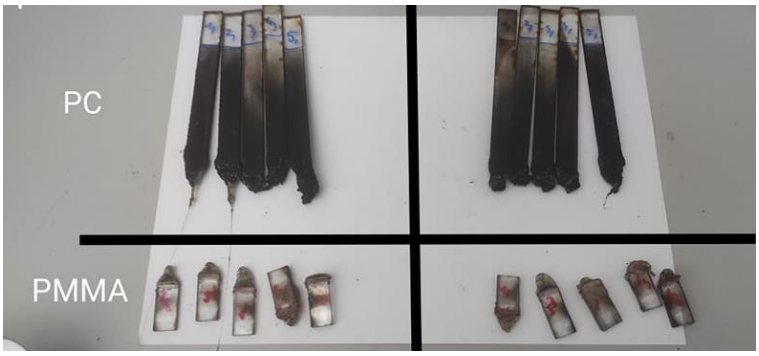

Fig. 4 PC and PMMA samples after testing with method B

In both methods, there is a difference in mass loss for PC samples before and after aging. When applying method "A", the difference in mass loss is 1,24 %, while in method "B" the difference is higher by 2,49 %. The average mass loss for PMMA samples by method "A" and method "B" is 67 % and 77 % respectively. However, for PMMA samples, by both methods, there would be a total burning out of the samples i.e., 100 %, if they were not in the holder which stopped burning.

When comparing the ignition of PC and PMMA samples, we found that PMMA had more negative results, which manifested themselves after just a few seconds, after attaching a flame. There was a sharp ignition, a large flame with the repeatable dripping of the melt, which is immediately ignited after contact with the filter paper.

By the PC, during the initial contact, there was a slower ignition, and its burning took a shorter time or until the melt drips, however, the filter paper did not ignite. In terms of ignition and the spontaneous spread of flame over the surface, the PC had significantly better results.

The linear burning rate assessment was done only by PMMA when testing using the method "A", while by PC the combustion did not reach the limit of 25 mm of the mark on the samples. The linear burning rate of the PMMA sample before aging showed lower values compared to PMMA after aging, which were exposed to weather conditions.

From the results obtained, we classified samples of PC and PMMA in both types of aging, in accordance with its fire-fighting characteristics, into a suitable class. For both types of aging, we have classified the PC in the FH-1 class. We classified pre-ageing PMMA in class FH-3-36.4 mm/min, and after aging, we classified PMMA in class FH-4-43.31 mm/min.

When using method "B", the total spontaneous burning time of samples in the vertical position was evaluated. From the results obtained, we found that the aging of the material has a significant impact on

the total time of spontaneous spread of the flame over the surface, which was shown in impaired results compared to the pre-aging condition.

Finally, based on the results of the PC and PMMA samples, we classified them in a special class according to the standard.

We classified PCs before aging in class FV-1, and PC after aging were classified in 4 class, since according to the standard it is not possible to classify PCs after aging by the "B" method, method "A" is used, according to which a PC is classified in class FH-1 after aging.

We have classified PMMA in 4 classes for both types of aging. According to the standard, PMMA cannot be classified according to method "B", therefore, a classification according to method "A" is used, according to which PMMA before aging is classified in class FH-4-71.6 mm/min and in FH-4-66 mm/min for PMMA after aging.

Audouin et al. [11] used the horizontal ignition and spread of flame test [12] and found that PMMA is easier to ignite than a PC, with the PC first melting and then burning, while by PMMA the melt drops.

According to Wang et al. [13], who dealt with dripping with both types of plastic polymers according to the UL-94 method, PMMA dropped faster than PC, with a PC converting the melt into carbon, while in PMMA it bubbled and gradually solidified.

Chow and Leung [14] found that the heat release rate as well as the total heat released by PMMA is several times greater than that of a PC.

We could not determine the linear burning rate of the PC due to not exceeding the limit of 25 mm. The same results were also released by Weaver [15] according to the ASTM D 635-14 [16] test. While for PMMA samples, we set the linear burning rate before aging at 36.4 mm/min and after aging at 43.31 mm/min.

Beňo [17], who in his work evaluated the fire properties of PC and PMMA material, found that in terms of linear burning rate and spontaneous burning time, PMMA has significantly worse properties compared to PC.

4 Conclusions

Nowadays, plastics are an integral part of human everyday life, including the work life. Plastics, according with their chemical composition, are flammable substances, and it is very important to deal with their behaviour also from a fire safety point of view. The aim of the study was to determine the impact of aging on the flammability of PC and PMMA. Flammability was assessed based on the fire properties as linear burning rate, spontaneous flame burning time and mass loss of sample before and after aging. The testing of the plastics was carried out according to the STN ISO 1210 standard, in which the plastics were evaluated using method "A" and method "B". Applying method "B", we tested three samples of each before and after aging. Applying method "A", five samples were tested before and after aging.

When applied method "A", we found that:

- When burning PC samples, a slight odour was felt and thick black smoke was released,
- PMMA samples showed a sharp, soot-free odour with slight turbulent smoke and regular dripping.
- The average mass loss of PMMA samples in both types of ageing reached 67%, with burning stopping at the holder terminal block.
- PC achieved a higher mean % mass loss after ageing of 2.08%, average % mass loss before ageing was of 0.85%.
- The average linear burning rate of PMMA samples before ageing reached 36.4 mm/min and PMMA after ageing reached 43.31 mm/min.
- For PC burning did not exceed the limit of 25 mm indicated on the sample and therefore it was not possible to determine the linear burning rate.

Next, using method A, we determined the total spontaneous burning time of a set of 3 PMMA samples (for PC the combustion did not reach the limit of 25 mm):

- PMMA before aging reached 123.6 s, while PMMA after aging burned for 104 s.

When applied method "B", we found that:

- When burning PC samples, there was a slight odour and thick black smoke.
- PMMA samples showed a sharp odour, with slight turbulent smoke and regular dripping.
- The burning pattern of PC samples was slow, while for PMMA it was very fast.
- The average mass loss of PMMA samples for both types of ageing were of 77%, with burning stopping at the holder terminal block.
- Average % mass loss of PC samples before aging was of 2.02% and of PC samples after aging was of 4.51%.

Further, using the "B" method, we determined the total time of spontaneous flame burning of PC and PMMA (before and after aging):

- For PMMA, better results we achieved for samples before aging (330 s), and worse for samples after ageing (358 s).
- For PC, better results were achieved for samples before aging (158 s) and worse for samples after aging (289 s).

Based on the results found, we can conclude that aging had an impact on the flammability of plastics. In terms of flammability, PC is more suitable than PMMA to be used in industry.

Besides, the results of the study can be beneficial in other PC and PMMA flammability studies as well as in various fire modelling calculations and can also serve for fire investigation needs.

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