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Cone calorimeter study of high performance fibres—application to polybenzazole and p-aramid fibres

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Abstract

This work investigates the fire behaviour of high performance fibres. Poly-p-phenylenediamine-terephtalamide fibres (PPT) and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibres as knitted fabrics are evaluated using the cone calorimeter as fire model. The investigation of the fire performance of the PPT and PBO fibres shows the excellent behaviour of PBO in comparison with PPT. The contribution to fire growth of PBO is very low whatever the external heat flux is. In comparison with PPT, smoke obscuration of PBO is dramatically reduced as well as the production of carbon oxides during the combustion of the materials. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Zylon® is a new high performance fibre developed by Toyobo Co Ltd (Japan). It is Poly(p-phenylene-2,6-benzobisoxazole) (PBO) and it is one of polybenzazoles containing an aromatic hetero-cyclic ring. It is a rigid rod isotropic crystal polymer [1]. PBO fibre is registered under the trademark Zylon® and its commercial production started in 1996.

PBO has superior tensile strength and modulus compared to classical p-aramid fibres. As an example, current PBO fibre has a tenacity which exceeds 5.8 GPa. Furthermore, PBO shows excellent performance in such properties as creep, chemical resistance, that far exceeds p-aramid fibres [poly-p-phenylenediamine-terephtalamide fibres (PPT)] [2]. In our laboratory, we have recently shown that this fibre enables as knitted fabric to get very promising properties in cutting and perforation resistance [3]. The combination of various knitted layers gives exceptional results with PBO fibres (stab-resistance of 35 J for a textile structure of 2 kg/m^2).

PBO has good flame resistance and thermal stability among organic fibres and in particular, in comparison with p-aramid fibres. As an example, the limiting oxygen index of Zylon® is 56 vol.% [4] whereas that of p-aramid fibres is only 28 vol.% [5]. Nevertheless, the LOI test is not very representative of a fire even if it allows to rate quantitatively the materials. The approach that we have developed to evaluate fibres as knitted fabric, is to use the cone calorimeter as the fire model. The major advantage of the cone calorimeter is to measure the rate of heat release which is the quantity of most concern in predicting the course of the fire and its effect.

In this paper, we will compare and will discuss the fire behaviour of knitted PBO fibres in comparison with p-aramid ones using the cone calorimeter as fire model.

2. Experimental

2.1. Materials

PBO fibres were supplied by the Toyobo (Japan) and is registered under the trademark Zylon®. Poly-p-phenylenediamine-terephtalamide fibres (PPT) fibers are classical Kevlar®.

The yarns used in this study have the following characteristics: PBO, Nm 2/34 spun yarn; p-aramid:Nm 2/28 spun yarn.

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PBO and p-aramid fibres have been knitted on an automatic rectilinear machine gauge 7. The texture used is a woven rib. The two samples have the surface weight equalling 1.08 kg/m^2 (four yarns knitted together in the case of p-aramid and five yarns in the case of PBO).

2.2. Cone calorimeter

The Stanton Redcroft Cone Calorimeter was used to carry out measurements on samples following the procedure defined in ASTM E 1354-90. The standard procedure used involves exposing specimens measuring $100\times100\times2.5$ mm in horizontal orientation. External heat fluxes of 50 and 75 kW/m^2 have been used for running the experiments. These fluxes have been chosen because 50 kW/m^2 is the common heat flux in a mild fire scenario and 75 kW/m^2 represents flashover conditions [6][7].

The cone calorimeter is used to determine the following principal fire properties: rate of heat release (RHR), cumulative heat released (total heat evolved: THE), time to ignition (t_{ig}), and FIGRA (Fire Index of Growth Rate) [8], as well as CO and CO_2 production and smoke obscuration (volume of smoke production: VSP [9]). In particular, FIGRA provides an estimation of the rate of development of a fire and VSP measures the flow of smoke in a ventilated room. The data were computed using software developed in our laboratory. The experiments are repeated 3 times. When measured at 50 and 75 kW/m^2 fluxes, RHR and VSP values are reproducible to within 10% and CO, CO_2 are reproducible to within 15%. The results presented in the following are averages. The cone data reported in this paper are the average of three replicated experiments.

3. Results and discussion

Fire hazard is associated with a variety of properties of a material in a particular scenario. It is determined by a combination of factors including the material ignitability, the rate at which heat is released from it when it burns, the total amount of heat that is released, the flame spread, the smoke production and the toxicity of the smoke. It has now been established that the property which most critically defines a fire is the heat release, because two conditions are necessary for propagating a fire from the ignited material to another one and/or to the surroundings. First, sufficient energy, as heat, needs to be released to cause secondary ignition. Secondly, the heat release needs to be occurred sufficiently fast so that the heat is not quenched in the "cold" air. By using heat release equipment such as the cone calorimeter, the different parameters discussed above can be measured in the same instrument, in a manner generally relevant to real fires.

3.1. Heat release

RHR curves of knitted PPT and PBO fibres at two external heat flux (50 and 75 kW/m^2) show that PBO fibres present a very good fire behaviour in comparison with p-aramid fibres (Fig. 1). RHR peak of PBO at 50 and 75 kW/m^2 are respectively only 60 and 150 kW/m^2

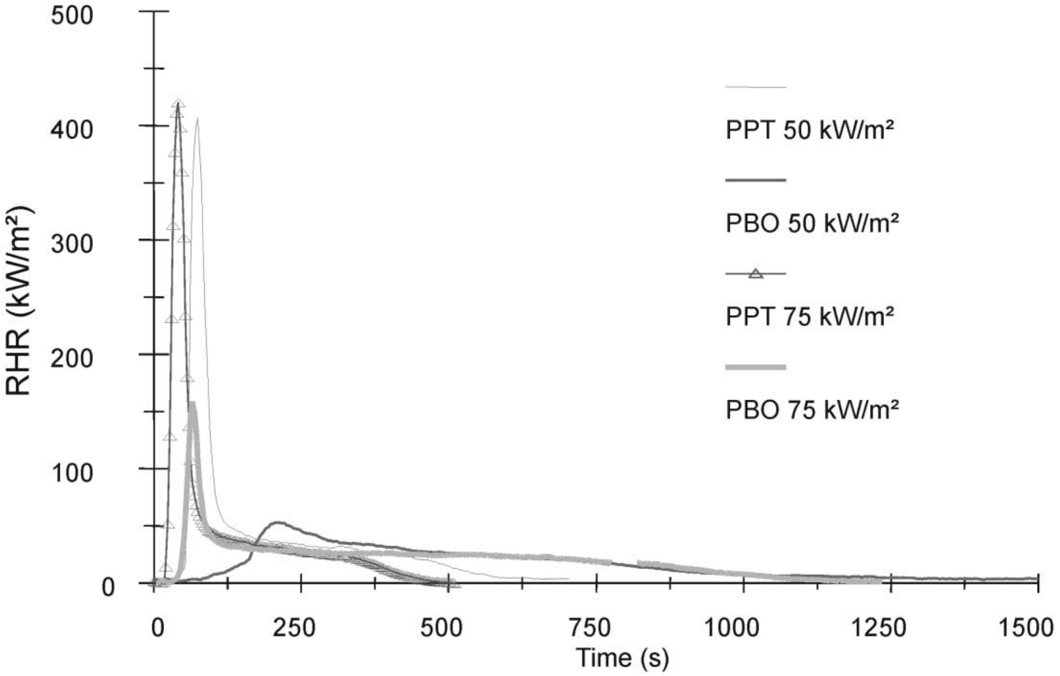

Fig. 1. RHR curves of knitted p-aramid and PBO fibres.

in comparison with 400 and 430 kW/m^2 for p-aramid fibres. It demonstrates therefore the high fire resistance of PBO.

Figs. 2 and 3 show the reaction to fire of p-aramid and PBO at an external heat flux equalling 75 kW/m^2. The time to ignition of PBO is twice as long as that of PPT (from 26 to 55 s). It shows the superior heat resistance of PBO compared with PPT. Between the ignition and the end of the RHR peak, the two behaviours are very different (see pictures on RHR peaks): p-aramid burns with high flames whereas PBO burns with small flames. After the RHR peak, glowing of the fibres occurs which leads to their degradation. Nevertheless, it is important to notice that the residues of the two materials at the end of the combustion are completely different. The residue of p-aramid consists of only some carbonaceous particles as compared to the residue of PBO which presents the same aspect as the beginning of the experiment except for the black colour, but this residue is crumbly and has no mechanical properties.

THE curves (Fig. 4) show that at the same heat flux the combustion of PBO is delayed in comparison with PPT. At the end of combustion THE values of PPT and PBO measuring at 50 kW/m^2 are close and they are

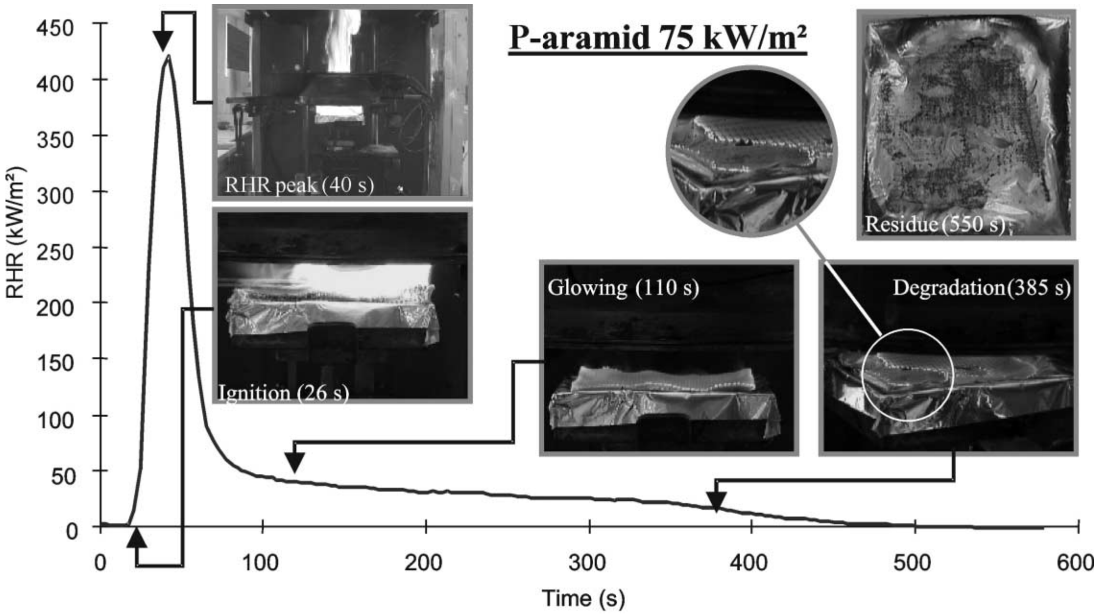

Fig. 2. Reaction to fire of p-aramid fibres in the conditions of the cone calorimeter (external heat flux equalling 75 kw/m^2).

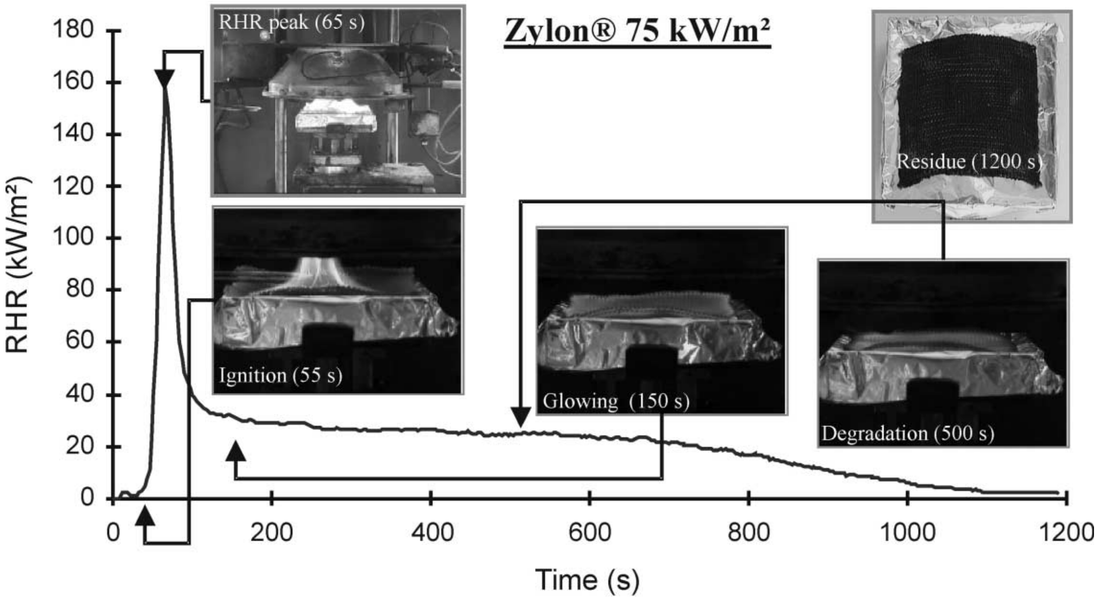

Fig. 3. Reaction to fire of PBO fibres in the conditions of the cone calorimeter (external heat flux equalling 75 kw/m^2).

different when measuring at 75 kW/m^2. In this last case, THE value of PBO is higher than PPT. It can be assigned to a post-glowing phenomenon which occurs at longer times in the case of PBO.

3.2. Fire index of growth rate

FIGRA is a good indicator of the contribution to fire growth of a material. FIGRA curves of PPT and PBO fibres are shown in Fig. 5. At an external heat flux of 50 kW/m^2, FIGRA of PBO is close to zero. It means that PBO does not contribute to the propagation of fire. FIGRA curve of PPT exhibits one peak at 75 s (FIGRA = 60 W/s) and from 150 s the FIGRA becomes close to zero. PPT contributes therefore to fire spread during its combustion and not when the sample is glowing.

At an external heat flux of 75 kW/m^2, FIGRA curve of PBO shows one peak at 65s (FIGRA = 25 W/s). Its contribution of fire growth is therefore comparatively very low. In the case of PPT, the peak of FIGRA (110

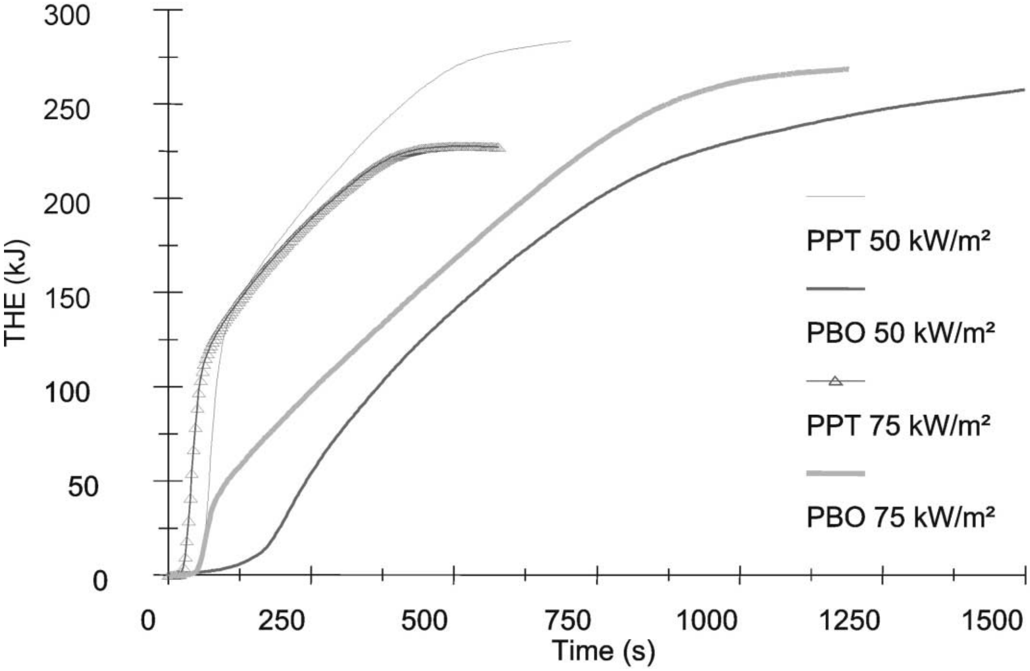

Fig. 4. THE curves of knitted PPT and PBO fibres.

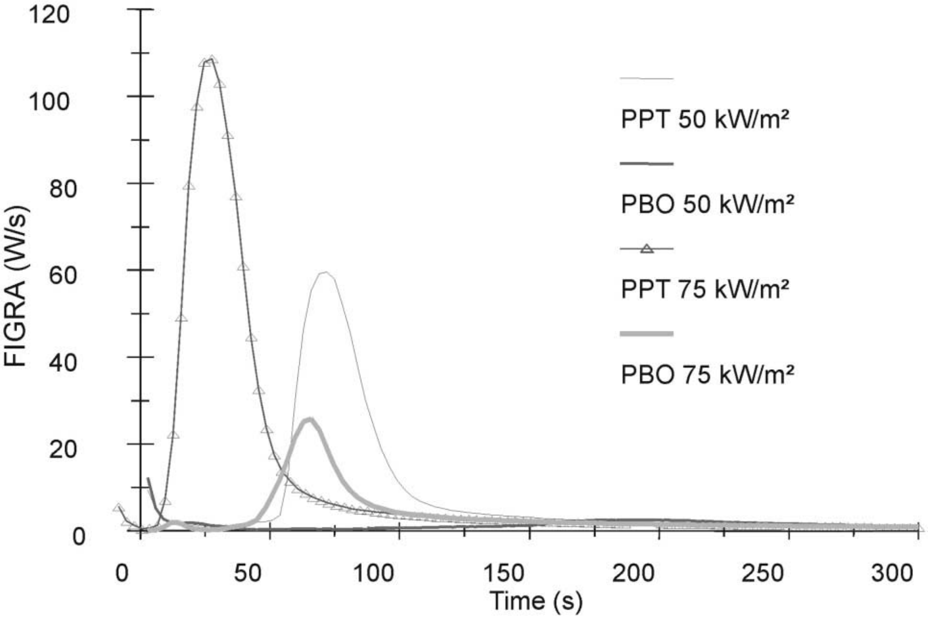

Fig. 5. FIGRA curves of knitted PPT and PBO fibres.

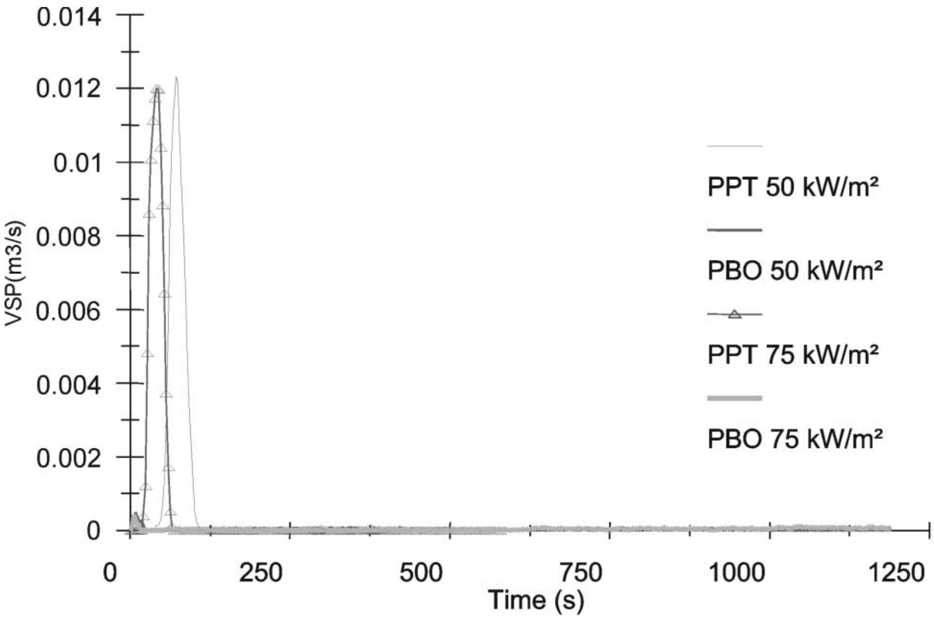

Fig. 6. VSP curves of knitted p-aramid and PBO fibres.

W/s) occurs at shorter times (40 s). It means that the contribution to fire growth of PPT is very fast. It is worth noting that in the two cases the contribution to fire growth is close to zero when the samples are glowing.

3.3. Smoke and carbon oxides evolution

Smoke obscuration is strongly lowered using PBO in comparison with p-aramid fibres (Fig. 6). PPT fibres evolve smoke with a peak at 0.012 m^3/s. This peak does not depend on the external heat flux except for the time when it occurs (42 s under 75 kW/m^2 and 72 s under 50 kW/m^2). PBO does not contribute to the smoke obscuration during fire whereas the smoke production of burning p-aramid material is comparatively high. It is very important in term of safety of people because the obscuration of a room or a corridor leads generally to a large panic effect. Indeed panic gives rise to more deaths than the fire itself [10].

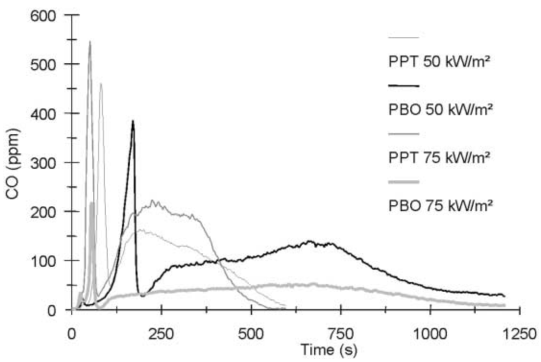

Fig. 7. CO curves of knitted p-aramid and PBO fibres.

Figs. 7 and 8 respectively present the CO production versus time and the total quantity of CO (TCO) evolved in the experimental conditions of the cone calorimeter, close to the conditions of a ventilated room. The amounts

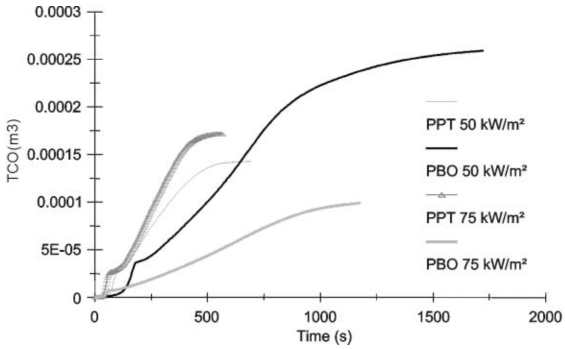

Fig. 8. Total evolved CO curves of knitted p-aramid and PBO fibres.

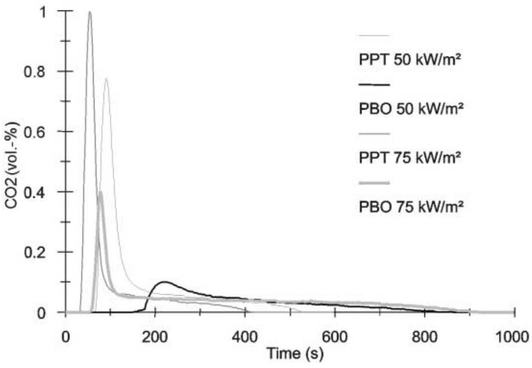

Fig. 9. CO_2 curves of knitted p-aramid and PBO fibres.

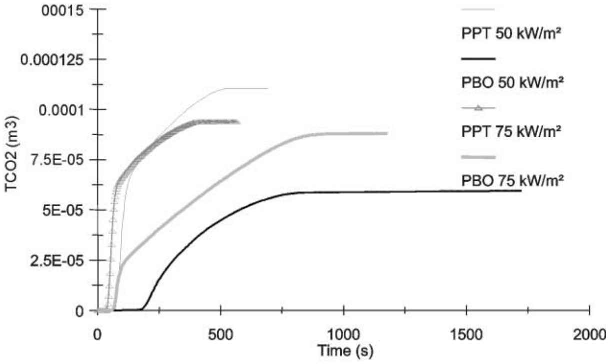

Fig. 10. Total evolved CO_2 curves of knitted p-aramid and PBO fibres.

evolved by PBO (CO peaks) are always lower than PPT and the event occurs later (Fig. 7). It is interesting to note that the production (peak and total production) of CO from the PBO fibres is decreased at an external heat flux of 75 kW/m^2. It means that incomplete combustion reactions of PBO are favoured at 50 kW/m^2. This phenomenon is not observed in the case of PPT. It should also be noted that the total amount of CO from PBO fibres at 50 kW/m^2 is high (2.6×10^{-4} m^3) in comparison with PPT (1.5×10^{-4} m^3 at 50 kW/m^2 and 1.75×10^{-4} m^3 at 75 kW/m^2) and PBO under 75 kW/m^2 (10^{-4} m^3).

The amounts evolved by PBO (CO_2 peaks) are always lower than PPT and the event occurs later whatever the external heat flux is (Fig. 9). The total CO_2 amounts (TCO_2) show the same trend except for PPT (Fig. 10). The quantity of CO_2 evolved by PPT under 75 kW/m^2 is lower than that at 50 kW/m^2. It means that complete combustion reactions of PPT are favoured under 50 kW/m^2.

4. Conclusions

The investigation of the fire performance of the PPT and PBO fibres using the cone calorimeter has shown the excellent behaviour of PBO in comparison with PPT. The contribution to fire growth of PBO is very low whatever the external heat flux is. In comparison with PPT, smoke obscuration of PBO is dramatically reduced as well as the production of carbon oxides during the combustion of the materials.

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