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► **To cite this version:**

Yann Carpier, Benoît Vieille, Nicolas Delpouve, Eric Dargent. Isothermal and anisothermal decomposition of Carbon fibres polyphenylene sulfide composites for fire behavior analysis. Fire Safety Journal, 2019, pp.102868. 10.1016/j.firesaf.2019.102868 . hal-02279988

HAL Id: hal-02279988

<https://hal.science/hal-02279988>

Submitted on 20 Jul 2022

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1 **Isothermal and anisothermal decomposition of Carbon fibres polyphenylene sulfide composites for**
2 **fire behavior analysis**

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7
8 **Abstract**

9 This work was aimed at studying the influence of severe temperature conditions representative of fire
10 conditions on thermal decomposition of both plain PPS thermoplastic resin and C/PPS laminates. The
11 investigations on the relationship between local temperature resulting from the local balance energy
12 exchange, the local atmosphere and the mass losses are essential in understanding the influence of fire on
13 polymers and polymer matrix composites. This involves first identifying the thermal decomposition
14 phenomena involved by means of thermogravimetric analyses conducted in both isothermal and
15 anisothermal testing conditions, as well as under inert and oxidizing atmospheres. As far the heating
16 conditions (isothermal and anisothermal) are concerned, an increase in the testing temperature leads to
17 increasing decomposition rates, as expected. In anisothermal conditions oxidation starts before the end of
18 pyrolysis, whereas, pyrolysis is complete before oxidation in isothermal conditions. Regarding the
19 influence of fibers on the thermal decomposition mechanisms in PPS-based composites, the cross-linking
20 may be promoted by the presence of fibers resulting in delaying the onset of pyrolysis under oxidizing
21 atmosphere. Such cross-linking is not significant enough to observe such a delay under air. Finally, MT-
22 TGA tests under inert atmosphere seem to reveal three different mechanisms during pyrolysis in agreement
23 with conclusions drawn in the literature on the same material: depolymerization, random chain scission and
24 ultimately cyclisation (char formation).

25
26 **Keywords:** fire; thermal decomposition; thermoplastic; isothermal; anisothermal

27 **1. Introduction**

28 In aeronautics fire is one of the most critical conditions in service for materials. When plane parts consist of
29 Polymer Matrix Composite (PMC) materials, the criticality is even higher because most PMCs usually
30 cannot bear significant mechanical loading at temperature higher than 200-250°C. High-performance
31 thermoplastic-based (TP) composites (e.g. PEEK, PPS, PEI...) are promising materials for structural
32 applications in aeronautics as they are resistant to impact. They have a good damage tolerance as well as
33 they have a very good retention of their mechanical properties under fire conditions. Among the most
34 common PMCs used in load-bearing aircraft structures Carbon/epoxy (thermosetting) composites are
35 flammable and readily decompose when exposed to heat and fire. In the literature most of the studies
36 dealing with the fire behavior of composite materials focus on thermosetting-based composites [1] but very
37 few on thermoplastic-based composites [2][3]. To better understand the changes in the thermal and
38 mechanical behaviors of polymer-based composites under fire exposure the first step usually is to
39 investigate the influence of thermal heat fluxes, hence temperature, resulting from a fire. Such heat fluxes
40 lead to significant temperature differences within composite structures. From thermal analyses it is
41 therefore possible to study the decomposition mechanisms as well as their kinetics under different testing
42 conditions (heating rate, isothermal and anisothermal, inert or oxidizing atmosphere). The decomposition
43 mechanisms are closely associated with the chemical nature of the polymer [4].

44
45 Figure 1 presents the characteristic behaviour of a thermoplastic material subjected to a heat flux on one
46 side. The heat conduction within the material causes physical and chemical transformations. Through the
47 thickness there are different transformations such as thermal degradation and thermal decomposition in a
48 cross section called the "mesophase". When the material undergoes a thermal decomposition there are
49 changes in the chemical composition and the structure of the material depending on the atmosphere (inert
50 or oxidizing) in which the decomposition occurs (see Fig. 1). Pyrolysis of polymer matrix produces a liquid
51 called tar and a non-condensable gas. Char is produced by repyrolysing the tar [5] and results from the
52 thermal decomposition of organic resins and fibres. It is a highly porous material that can consist of

53 crystalline (i.e. graphitic) and/or amorphous regions [6]. Under oxidizing atmosphere decomposition gases
54 can ignite and cause the material to ignite. All these chemical changes are accompanied by sudden changes
55 in physico-chemical and mechanical properties [7].

56 In the mesophase gas bubbles form within a phase whose viscosity decreases with temperature. On the
57 surface the bubbles burst and release combustible gases that may fuel the flame. If portions of material
58 remain non-gasified, then they form viscous tars that accumulate on the surface. From a thermal point of
59 view this thermal decomposition has many consequences. Indeed the chemical mechanisms of
60 decomposition (pyrolysis, oxidation, inflammation) are accompanied by heat exchanges, which influence
61 the energy balance: endothermic reaction for the first, exothermic for the other two. The resulting change in
62 properties is also accompanied by a significant perturbation of heat exchanges within the material. The
63 effective conductivity decreases through the thickness due to the formation of porosity but also on the
64 exposed surface due to the change in material emissivity.

65

66 **1.1 Thermal decomposition in PMCs**

67 First of all polymers have diverse chemical compositions and structures, which involve various thermal
68 decomposition mechanisms [8]: (i) depolymerization, (ii) random chain scission, (iii) chain stripping, (iv)
69 cyclisation. Although the thermal decomposition of a polymer can theoretically be observed according to
70 only one of these mechanisms, it is generally the combination of several of them as the temperature
71 increases and results in the formation of many decomposition products. It can be considered complete when
72 any solid residue is fully vaporized or gasified. Among the commonly used polymer materials for
73 aeronautics applications epoxy resin is known for its poor fire resistance [1], phenolic resins are also
74 widely used as thermal protection whereas fire-improved epoxy resins are sometimes considered as
75 ablative protection for internal thermal insulation [9]. Compared to common thermosetting resins (phenolic
76 and epoxy) used for high temperature conditions polyether-ether-ketone (PEEK) and PolyPhenylene
77 Sulfide (PPS) thermoplastic resins known for their high-temperature stability proved to have higher thermal
78 performance, particularly with a higher decomposition temperature [6]. In TP polymers, melting is a

79 general stage of char formation and their decomposition results in the production of char [10]. In addition
80 to temperature, the thermal degradation of a material is highly dependent on the atmosphere in which it
81 occurs. The presence of dioxygen greatly modifies the reaction kinetics, which generally accelerate
82 although the opposite effect is sometimes observed [11]. but it can also induce the formation of new
83 reaction products that would not be observed under an inert atmosphere [12]. Thermogravimetric analyses
84 (TGA) conducted on PPS resin show that decomposition under inert atmosphere begins 20°C later than in
85 air [11] but results in a slightly greater mass loss. When its formation is completed the char begins to
86 decompose at a slow rate (12% in 300°C), as shown by Yao et al. who observed slow rate decomposition in
87 PEEK-based composites [13]. Indeed pyrolysis (i.e. the first stage of decomposition) does lead to a greater
88 mass loss under inert atmosphere, but this is only because it is completed. Conversely, due to oxidation,
89 decomposition under air results in the total gasification of char at 750°C.

90 Second of all the presence of fibres in an organic matrix greatly influences thermal decomposition, since
91 fibres have a higher thermal resistance than polymers. For example glass fibres begin to soften between
92 700 and 1000°C [14]. Carbon fibres have a particularly high thermal resistance with a sublimation
93 temperature above 3000°C in an inert atmosphere. However they are very sensitive to oxidation with
94 complete decomposition when the temperature rises to 950°C under air [15]. Under isothermal conditions
95 the oxidation of carbon fibres starts at 500°C and results in their total decomposition in 3 hours at 650°C. A
96 thermal degradation study was carried out by Tadini et al. [16] on carbon fibres reinforced composites
97 (PEKK- and phenolic-based). To evaluate the PEKK behavior and to understand the impact of composite
98 nature in terms of structural strength under fire TGA tests were performed under different non-isothermal
99 heating conditions (between 30 and 1000°C). Under inert atmosphere PEKK-based composites are
100 characterized by one single global reaction between 500–700°C. Phenolic-based composites are
101 characterized by two reactions and earlier pyrolysis (around 200°C). The better performance of PEKK
102 composites is attributed to the ether and ketone bonds between the three aromatic groups of the monomer.

103

104 **1.2 Thermal decomposition of PPS**

105 The anisothermal thermal decomposition of PPS has been specifically addressed by different authors [17-
106 25]. Depending on the heating rate, it starts between 450 and 500°C and initially leads to a mass loss of
107 between 45 and 65% depending on the considered atmosphere. The chemical mechanisms of this
108 decomposition were studied using different characterization techniques: Pyrolysis (Py) - Mass
109 Spectrometry (MS) [19], Gas Chromatography (GC) [20], Py-GC-MS and TGA-MS coupling [21], etc. Not
110 all studies agree on the chronology of chemical mechanisms probably because of the different formulations
111 of the PPS resin. Nevertheless the decomposition seems to be a competition between depolymerization and
112 random chain scission resulting in the formation of benzenethiol and hydrogen sulfide H₂S, carbon
113 disulfide CS₂ and benzene respectively [21,22]. Cyclisation reactions between different decomposition
114 products then lead to the formation of char [19]. The latter, like what is observed during the decomposition
115 of the PEEK, then undergoes a slow thermal decomposition, which results in a relatively small mass loss.
116 This observation is only true for decompositions in an inert atmosphere. Under air, char undergoes
117 oxidation leading to its complete volatilization before 800°C.

118
119 As shown by Patel et al. in PEEK-based composites, the first stage of pyrolysis is relatively unaffected by
120 the atmosphere [23]. When it comes to thermal decomposition, T_{5%} refers to the temperature at the onset of
121 decomposition often defined as the temperature corresponding to a mass loss of 5%. Nevertheless in PPS-
122 based composites, mechanisms of cross-linking under air, occurring at temperatures lower than T_{5%}, can
123 increase the thermal resistance of PPS and delay the onset of its decomposition [24]. This phenomenon has
124 been highlighted by Ma et al. [11]. The study of isothermal decomposition between 410 and 470°C reveals
125 that from 440°C, the mass loss after 2 hours is higher under N₂ than under air (see Fig. 2b). This result
126 explains why mass loss begins later in TGA (anisothermal conditions) under air (see Fig. 2a). Note that the
127 inflection in the residual mass under air, which is a characteristic of a new decomposition mechanism (here
128 oxidation), is observed for residual mass of PPS around 75%, far before the end of pyrolysis under inert
129 atmosphere, suggesting an overlap of the two mechanisms.

130

131 **1.3 Objectives of the study**

132 The study of fire resistance aims to understand and characterize how and for how long the composite
133 material can bear a mechanical loading when one face is subjected to heat fluxes. It results in temperature
134 differences transversely on the sample exposed surface as well as through the materials thickness. The
135 knowledge of the temperature distribution on both exposed and back surfaces is required to determine the
136 temperature range within the materials with respect to its characteristic temperatures (glass transition,
137 melting, pyrolysis onset). Before considering the combined influence of heat and mechanical loadings, it is
138 also necessary to investigate the influence of temperature on the thermal decomposition of C/PPS
139 composites and its constitutive materials depending on the testing conditions. Thus TGA tests were carried
140 out for different heating rates, in both isothermal and anisothermal conditions, under inert or oxidizing
141 atmospheres.

142

143 **2. Material and methods**

144 **2.1 Materials and specimens**

145 The studied composite materials are carbon fabric reinforced laminates consisting of a semi-crystalline
146 high-performance PPS supplied by the Ticona company. The woven-ply prepreg, supplied by SOFICAR,
147 consists of 5-harness satin weave carbon fiber fabrics (T300 3K 5HS) whose weight fraction is 58%. The
148 prepreg plates are hot pressed according to a quasi-isotropic [(0,90)/(±45)/(0,90)/(±45)/(0,90)/(±45)/(0,90)]
149 stacking sequence (see Fig. 3). The glass transition temperature of the material is $T_g=98^{\circ}\text{C}$ and its melting
150 temperature $T_m=280^{\circ}\text{C}$, as measured by DSC [26]. The degree of crystallinity of PPS matrix is close to
151 30% and the porosity ratio is very small (less than 2%).

152

153 **2.2 Experimental set-up**

154 **2.2.1 Radiative heat flux exposure and temperature measurements**

155 To study fire resistance a cone calorimeter is usually used. A rectangular sample (100*150mm² and a
156 2.2mm thickness) is placed under a fume hood and subjected to different heat fluxes (30-40-50kW/m²)

157 resulting from the radiation of a conical heating resistor. The temperature distribution within the material
158 must be measured in order to understand thermally-induced phenomena such as the thermal decomposition
159 and degradation of mechanical properties [27]. Temperature measurements are conducted on the exposed
160 and the back surfaces of the specimens. In the present study, two methods are used to measure the
161 temperature: by infrared thermography (back surface) or by means of thermocouples (exposed surface).
162 The first method is the most accurate because it provides the temperature mapping over the entire surface.
163 The infrared thermography measurement was carried out using a Thermacam camera PM 575
164 manufactured by FLIR Systems. To estimate the temperature, the camera requires the knowledge of the
165 material emissivity. The value was set at 0.90 according to the value frequently used in the literature for
166 composite materials with carbon fibres [28]. However infrared thermography measurement is difficult to
167 implement on the exposed surface because it requires the measurement of the temperature by observing the
168 specimen through the cone calorimeter. Such measurement presents many sources of errors: hot
169 atmosphere, pyrolysis gas, reflection of a part of the radiation on the surface of the sample. As a result type
170 K thermocouples are used to measure the temperature distribution on the exposed surface.

171

172 **2.2.2 Thermogravimetric Analysis (TGA)**

173 To carry out these experiments a thermo-gravimetric analyzer TA Instruments Discovery is used. Thermal
174 decomposition is characterized under three atmospheres: nitrogen, air and dioxygen. The gas flow rate is
175 set at 20 mL.min⁻¹. The extent of decomposition is characterized by a degree of progress in the reaction
176 defined by the following expression [29]:

$$177 \quad \alpha = \frac{m_i - m}{m_i - m_f} \quad (1)$$

178 With m_i the initial mass of the sample, m is the mass at a time t and m_f is the mass after decomposition.
179 When the analysis is carried out in an inert atmosphere, α corresponds to the degree of pyrolysis and its
180 value is 1 when all the pyrolysis is completed. Under oxidizing atmosphere, it corresponds to the degree of
181 decomposition and its value is 1 when the entire solid residue is completely gasified.

182 The study of the PPS thermal decomposition has been conducted using anisothermal heating from room
183 temperature to 700°C. These analyses are extremely useful for determining the primary steps of the
184 decomposition: $T_{5\%}$ refers to pyrolysis onset, which is the temperature at which 5% of the polymer mass
185 has decomposed and T_{\max} refers to the maximum peak of decomposition rate. Such analyses can also be
186 considered for studying the thermal decomposition kinetics. However they are not suitable for clearly
187 identifying the chemical mechanisms involved. Two types of analyses were conducted on samples whose
188 initial mass is about 8mg:

- 189 • Anisothermal conditions at a heating rate of 10°C/min: linear evolution of temperature as a
190 function of time. These experiences are supposed to be representative of the increase in material
191 temperature during the transient phase of its thermal response.
- 192 • Isothermal conditions at a heating rate of 100°C/min: rapid temperature increase to a value of
193 which is maintained for a period of 1h30 and 5h, depending on the test temperature. These
194 experiments aim to characterize decomposition when the temperature of the material has reached its
195 permanent state.

196

197 2.2.3 Modulated TGA

198 Derived from the modulated DSC analyses proposed by Flynn [29] and Reading [30], the MT-TGA
199 method consists in subjecting a sample to a sinusoidal temperature ramp. It depends on the evolution of the
200 degree of conversion between the peak (maximum heating rate) and the trough (minimum velocity) of a
201 cycle. The activation energy E_a can be calculated [31] and related to the main decomposition mechanisms
202 from a single experiment [32,33]:

$$203 \quad E_a = \frac{R (T^2 - A^2) \ln\left(\frac{d\alpha_p}{d\alpha_v}\right)}{2 A} \quad (2)$$

204 Where T is the average value of oscillatory temperature; A is the amplitude of the temperature oscillation;
205 and $\frac{d\alpha_p}{d\alpha_v}$ is the ratio for adjacent peaks and valleys, of the periodic rate of reaction. The modulation
206 parameters were: amplitude = 5K, period = 200s and heating rate = 5K/min.

207 **3. Results and discussion**

208 **3.1 Radiative heat flux exposure**

209 On the exposed and the back surfaces the changes in the surface temperature depend on the applied heat
210 flux. The thermal response starts with a transient phase during which the temperature increases rapidly. On
211 both surfaces temperature eventually becomes constant when the balance is reached between heat sources
212 (radiation from the heat source) and losses (radiation of the material, convection and thermal
213 decomposition). The lower the heat flux is, the longer it takes to reach this steady state (see Fig. 5a).
214 Finally, by comparing the temperature profiles on both exposed and back surfaces of C/PPS laminates
215 subjected to 50kW/m² heat flux, the through-the-thickness temperature difference can be estimated (see
216 Fig. 4). In the steady state a significant difference (about 320°C) is observed through-the-thickness but also
217 on the back surface (see Fig. 5b). The onset of decomposition temperature is reached on the exposed
218 surface but not on the back surface. **It is therefore reasonable to assume that the temperature profile**
219 **through-the-thickness is nonlinear and that the laminates thickness increases as the material decomposes.**
220 The knowledge of the temperature difference is of the utmost importance to determine: (i) the gradient in
221 both thermal and mechanical properties, (ii) gradient in the chemical composition, (iii) thermally-induced
222 damages.

223
224 To better understand the influence of a heat flux on the temperature difference on the outer surfaces and
225 within the laminates it is necessary to investigate the influence of temperature on the thermal
226 decomposition of C/PPS composites and its constitutive materials depending on the testing conditions (see
227 Fig. 1). TGA provides information on the temperatures at which the matrix is pyrolyzed and possibly at
228 which the char and then the fibres oxidize in the composite. This will be useful in the future to establish a
229 temperature profile according to thickness. Thus, TGA experiments were carried out in both isothermal and
230 anisothermal conditions, under inert or oxidizing atmospheres (see Fig. 1) to identify the characteristic
231 temperatures on the outer surfaces as well as within the materials.

232

233 3.2 TGA under anisothermal conditions

234 3.2.1 Inert atmosphere

235 Under nitrogen the pyrolysis of the PPS starts at 503°C and ends around 640°C resulting in a mass loss of
236 about 55% (Figure 6a). Over this temperature range the evolution of the decomposition rate or Mass Loss
237 Rate (often abbreviated MLR) has a virtually symmetrical peak with a maximum close to 550°C (Figure
238 6b). The presence of a single peak may indicate that pyrolysis occurs according to a meta-mechanism, a
239 combination of random chain scission and depolymerization failures (see Section 1.1). The product of this
240 decomposition, representing 45% of the initial mass, is char which is resistant at high temperatures with a
241 mass loss of only 11% at 900°C (5% of the initial polymer mass – see Fig. 6a).

242
243 In C/PPS, consisting of 43% by weight of PPS, pyrolysis only results in a mass loss of 26% with a
244 maximum decomposition rate at 550°C. Indeed the thermal decomposition of carbon fibres under inert
245 atmosphere does not occur at this temperature level [15]. It is thus possible to calculate the mass loss of the
246 matrix in the composite material, as well as its decomposition rate, assuming that only it decomposed while
247 the fibres remained intact. It is interesting to note that despite the high thermal resistance of carbon fibers
248 the decomposition of the matrix starts 20°C earlier in the composite material ($T_{5\%} = 483^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$) as
249 fibre/matrix interfaces are preferential areas for initiating a degradation mechanism. It could also be caused
250 by the higher thermal conductivity of carbon fibres compared to the PPS matrix, bringing heat in the
251 sample at a faster rate. Decomposition is also slightly more extensive with a polymer residual mass after
252 pyrolysis of 60% compared to only 55% in the plain PPS. The presence of fibres also results in a
253 decomposition rate of the matrix slower than for the resin alone (Figure 7a). The residue, consisting of char
254 and fibres, is also very different from the decomposition of the plain PPS. Fibres limiting the swelling
255 associated with the formation of pyrolysis gas, the residue of C/PPS is a highly porous fibrous network but
256 only slightly thicker than the composite at room temperature (see Fig. 8a) while the product of the
257 decomposition of the PPS (see Fig. 8b) is in the form of a bubble resulting from the "swelling" of the

258 material under high internal pressure. Although fibres do not decompose they have a significant influence
259 on matrix decomposition.
260 Another illustration of this phenomenon concerns the evolution of the activation energy of decomposition
261 mechanisms as a function of the pyrolysis degree [32, 33], studied here by modulated TGA (Figure 7b).
262 Comparison of curves $E_a = f(\alpha)$ shows that the activation energy required to initiate decomposition ($<$
263 0.1) is much lower in the case of C/PPS, which could explain why it takes place at a lower temperature.
264 During most of the decomposition, E_a is higher for PPS alone resulting in an ever higher decomposition
265 rate (Figure 7a). Finally, we can observe that the last peak of activation energy, associated with char
266 formation, starts later in C/PPS ($\alpha = 0.84$ compared to 0.76 for matrix). This may explain the lower residual
267 polymer mass in the case of PPS only. The curves representing the activation energy is divided into three
268 parts supposedly associated with the mechanisms of PPS pyrolysis: depolymerization, random chain
269 scission and ultimately cyclisation through char formation.

270

271 **3.2.2 Oxidizing atmosphere (Dioxygen and air)**

272 As indicated in section 1.1 the decomposition of carbon fibre-reinforced composites under oxidizing
273 atmosphere is faster than the one of other fibers-reinforced composites such as glass fibres for example,
274 because carbon fibres are sensitive to oxidation phenomena just like polymeric matrices. For practical
275 reasons decomposition under air has been little studied. The oxidation phenomena are here mainly
276 characterized with TGA analyses under dioxygen.

277 Under dioxygen, the thermal decomposition of PPS begins at 502°C, approximately the same temperature
278 as under an inert atmosphere (see Table 1). The curve representing the Mass Loss Rate of plain PPS resin
279 as a function of temperature $MLR = f(T)$ is characterized by 3 peaks (see Figure 9). The first peak
280 corresponds to a mass loss of about 15%. Thus it may be associated with the first pyrolysis mechanism,
281 depolymerization (Figure 10b). Following this reasoning, the second peak, which extends to $\Delta m = 37\%$,
282 may be associated with the second pyrolysis mechanism. Even before the pyrolysis ends a new mechanism
283 starts and may be associated with the simultaneous oxidation of PPS matrix and the pyrolysis residue as it

284 extends until the entire initial material is carbonated (Figure 10a). The maximum oxidation rate is virtually
285 3 times higher than the pyrolysis rate.

286 In C/PPS thermal decomposition begins at 515°C, i.e. 10°C later than under N₂ (see Table 1). Similar
287 observations have already been made by Ma et al. in the study of the decomposition of C/PPS under air and
288 can be explained by the behaviour thermoplastic-thermosetting PPS [11]. Indeed when heated in an
289 oxidizing atmosphere above its melting temperature PPS can crosslink like a thermosetting polymer thus
290 having a higher thermal stability. If the delay in the onset of decomposition is only observed in C/PPS
291 composite, this suggests that these phenomena are promoted by the presence of fibres. As for the PPS
292 matrix alone pyrolysis and oxidation of char overlap in the C/PPS. Nevertheless the fact that the second
293 peak of MLR ends with a mass loss of 43% equivalent to the matrix mass in the composite, it tends to
294 indicate that oxidation of char and fibres occurs separately and not simultaneously (Figure 10a). Analysis
295 of the evolution of the activation energy E_a indicates a rather good correlation with decomposition rate
296 except when the material is strongly degraded as the MLR decreases with E_a . It is also possible to infer that
297 the oxidation mechanisms are broken down into several sub-mechanisms represented by different peaks on
298 the E_a vs polymer mass loss (Figure 10b). Finally, pyrolysis under oxidizing atmospheres requires higher
299 E_a than under nitrogen, which might be consistent with the cross-linking hypothesis (Figure 11).

300 The decomposition of PPS begins at 508°C at 20°C/min under air, which is the only experimental condition
301 tested under this atmosphere. For the same heating rate, decomposition begins at 523°C and 530°C
302 respectively under N₂ and O₂ (see Table 2). Pyrolysis results in a mass loss of 39%, which is lower than
303 that observed under inert atmosphere (Figure 12a), which is consistent with the observations made in the
304 case of a PEEK resin by Patel et al [23][34]. As under dioxygen, oxidation begins before the pyrolysis
305 ends. Nevertheless the appearance of the characteristic peak of pyrolysis on the MLR curve $MLR = f(T)$
306 indicates that pyrolysis is almost completed when oxidation begins under air (Figure 12b) while it did not
307 even reach its maximum rate when this transition occurs under O₂. In C/PPS, decomposition begins at
308 517°C compared to 525 and 526°C under N₂ and O₂ (see Table 2). Thus the mechanisms of crosslinking and
309 improvement of thermal resistance observed under O₂ do not appear to occur under air. During isothermal

310 tests under air, the latter have not been observed in C/PPS by Ma et al. However the decomposition
311 temperatures cannot be readily discussed from one atmosphere to another as the operating conditions differ
312 in term of heating rate and testing machine. Oxidation appears to start faster under O₂ simply because there
313 are more reactive species and the atmosphere is more oxidizing.

314

315 **3.3 TGA under isothermal conditions**

316 **3.3.1 Inert atmosphere**

317 The isothermal decomposition of C/PPS under N₂ was studied for a temperature range between 465 and
318 545°C. Lower temperatures than in an oxidizing atmosphere were chosen. Indeed the inert atmosphere is
319 representative of what the specimen undergoes at core whose temperature is lower than that of the exposed
320 side subjected to an oxidizing atmosphere (see Fig. 1b). In addition the temperature profiles measured in
321 section 3.1 are considered here to justify the choice of isothermal temperature conditions. As expected the
322 mass losses are at least equal to or greater than those observed during anisothermal decomposition (Figure
323 13) for all test temperatures except one (530°C). At 465°C for example, while only 2% of the mass of
324 polymer in C/PPS are gasified under anisothermal conditions, mass loss reaches 12% (28% of the matrix)
325 after 30 minutes of exposure and 29% (69% of the matrix) at the end of the test. The higher the test
326 temperature, the higher the mass loss. Indeed whereas for high temperatures (530 and 545°C), the mass loss
327 seems to reach a plateau, which is not the case for lower temperatures (at least over the temperature range
328 studied). However the isothermal conditions are not really isothermal for the highest temperatures at which
329 the decomposition has already clearly started at lower T_{5%} decomposition temperatures (whose accurate
330 estimate is difficult), which calls into question the possibility of direct comparison.

331

332 **3.3.2 Oxidizing atmosphere (Dioxygen and air)**

333 Under oxidizing atmosphere isothermal decomposition was studied for four temperatures: 520, 550, 580
334 and 610°C. The second and fourth were chosen because these are the maximum temperatures measured on

335 the front panel for specimens of C/PPS exposed to flux densities of 40 and 50 kW/m² (see Section 3.1).
336 One of the difficulties of the analysis is that the material can be quite significantly decomposed during the
337 temperature rise up to the test temperature. Nevertheless this temperature ramp is partially representative of
338 what the material undergoes during fire exposure and thus contributes to the understanding of fire
339 behaviour. Fire exposure combines both radiative and convective fluxes leading to heat fluxes
340 higher than 100kW/m², whereas the fluxes resulting from cone calorimeters are usually lower than
341 80kW/m². The oxidizing atmosphere in the vicinity of the surface exposed to a cone calorimeter
342 allows the combustion of pyrolysis gases. On the contrary, there is very little dioxygen in the
343 vicinity of the sample surface exposed to a flame. Under real fire conditions, it is therefore
344 expected that the thermal decomposition of C/PPS laminates would differ from the one observed
345 under a radiative heat flux.

346 As under inert atmosphere, the same decomposition mechanisms as under anisothermal conditions may be
347 at stake. However the times required for decomposition are shorter than under N₂ (Figure 14). The
348 distribution of decomposition rate peaks and therefore the decomposition mechanisms change with
349 temperature. For example, under the air, the lower the temperature, the more pyrolysis is characterized by a
350 low mass loss (Figure 15). The air crosslinking mechanisms highlighted by Ma et al. could partly explain
351 this phenomenon [11]. However this is no longer true when pyrolysis starts. For lower temperatures, as the
352 PPS matrix decomposition is slow, a partial crosslinking of the matrix occurring at the same time could
353 result in less extensive pyrolysis and therefore explain an earlier oxidation. Decomposition rates differ
354 under the two atmospheres. Under air, they are approximately 4 times lower than those observed under O₂,
355 which can be related to the percentage of dioxygen in the air. The fastest mechanisms are also different
356 under both atmospheres. Under air, pyrolysis occurs more rapidly while under dioxygen it is the oxidation
357 of char that occurs faster.

358

359

360 **4. Conclusion**

361 The investigations on the relationship between local temperature resulting from the local balance energy
362 exchange, the local atmosphere and the mass losses are essential in understanding the influence of fire on
363 polymers and polymer matrix composites. The main objective of this work was to better understand the
364 thermal decomposition mechanisms in both PPS plain resin and PPS thermoplastic-based composites
365 subjected to radiative heat fluxes representative of fire exposure.

366
367 The first step consisted in investigating the influence of thermal heat fluxes (hence temperature)
368 resulting from fire of medium intensity. Such heat fluxes (typically 50kW/m²) lead to significant
369 thermal gradients within composite structures, leading to (i) a gradient in both thermal and
370 mechanical properties, (ii) a gradient of chemical composition and (iii) thermally induced
371 damages.

372
373 By comparing the temperature profiles on both exposed and back surfaces of C/PPS laminates subjected to
374 a 50kW/m² heat flux, the through-the-thickness temperature gradient has been shown to be significant
375 (about 320°C in the steady state). For such temperature level, the onset of decomposition temperature is
376 reached on the exposed surface but not on the back surface, leading to a significant gradient of the chemical
377 composition through the thickness.

378
379 In order to predict the evolution of properties for other heat fluxes, decomposition mechanisms as well as
380 their kinetics and their activation energy under different heating conditions (isothermal and anisothermal),
381 or testing atmosphere (inert and oxidizing), have been studied by means of TGA and MT-TGA tests. If the
382 influence of the atmosphere has shown similar behaviors to what is conventionally observed on other
383 materials and corroborated by other studies on the PPS [21][31], questions were raised about the influence
384 of the heating rate in anisothermal conditions. Even if the heating rates tested in this study (10 and
385 20°C/min) are low compared to those observed in a real fire (several hundred degrees per minute),

386 differences were observed in the increase of $T_{d,onset}$ when the heating rate increases, whether the testing
387 atmosphere is oxidizing or not.

388
389 Considering the influence of heating conditions in isothermal conditions, an increase in the testing
390 temperature leads to increasing decomposition rates, as expected. Oxidation starts before the end of
391 pyrolysis under anisothermal conditions, whereas pyrolysis is complete before oxidation under isothermal
392 conditions. As far the influence of fibers on the thermal decomposition mechanisms in PPS-based
393 composites is concerned, the cross-linking may be promoted by the presence of fibers resulting in delaying
394 the onset of pyrolysis under oxidizing atmosphere. Such cross-linking is not significant enough to observe
395 such a delay under air. In agreement with conclusions drawn in the literature on PPS and PPS-based
396 composites, MT-TGA tests suggest the existence of three different mechanisms during pyrolysis under
397 inert atmosphere: depolymerization, random chain scission and ultimately cyclisation (char formation).

398

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477

478

479

480

481 **List of figure**

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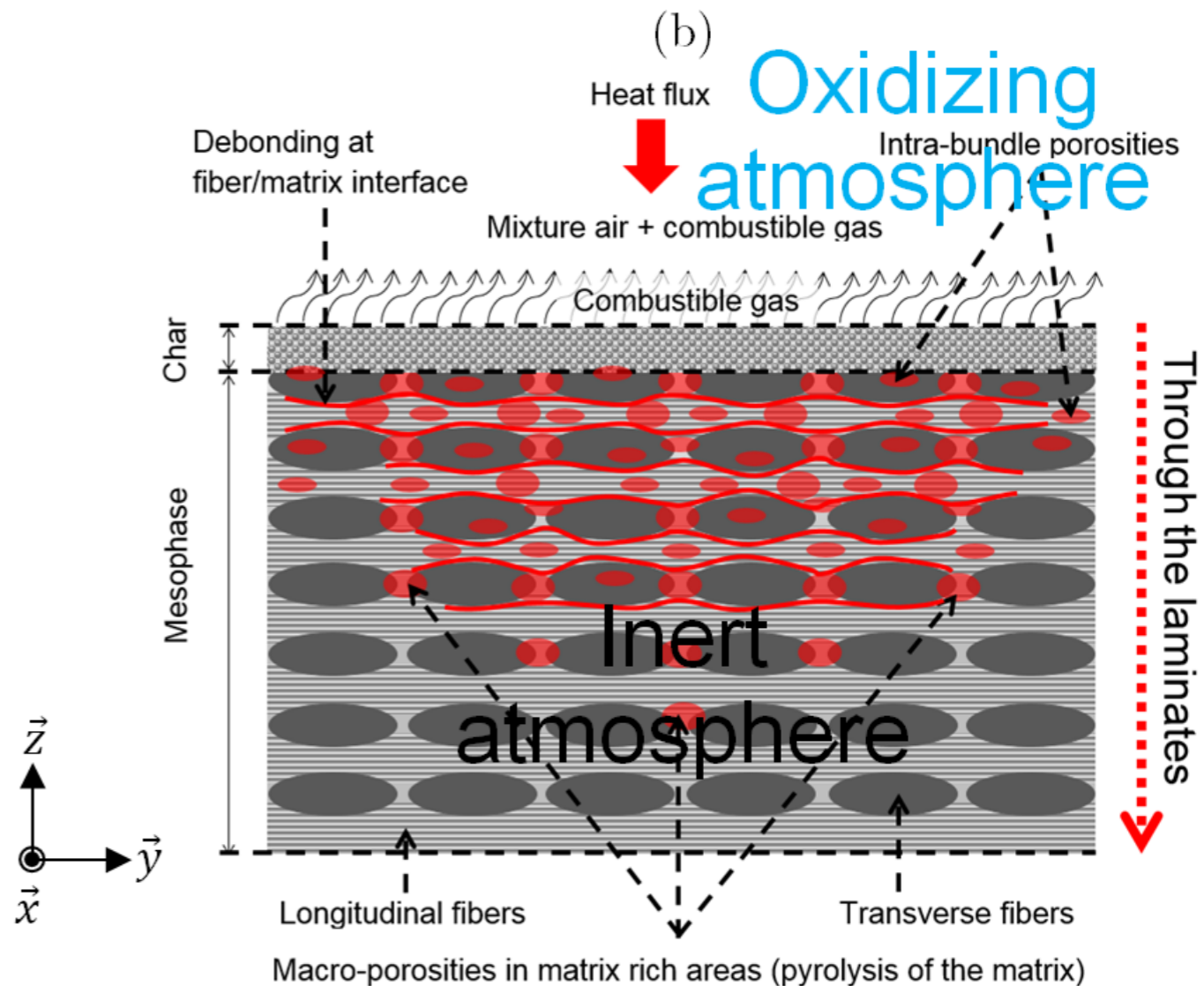
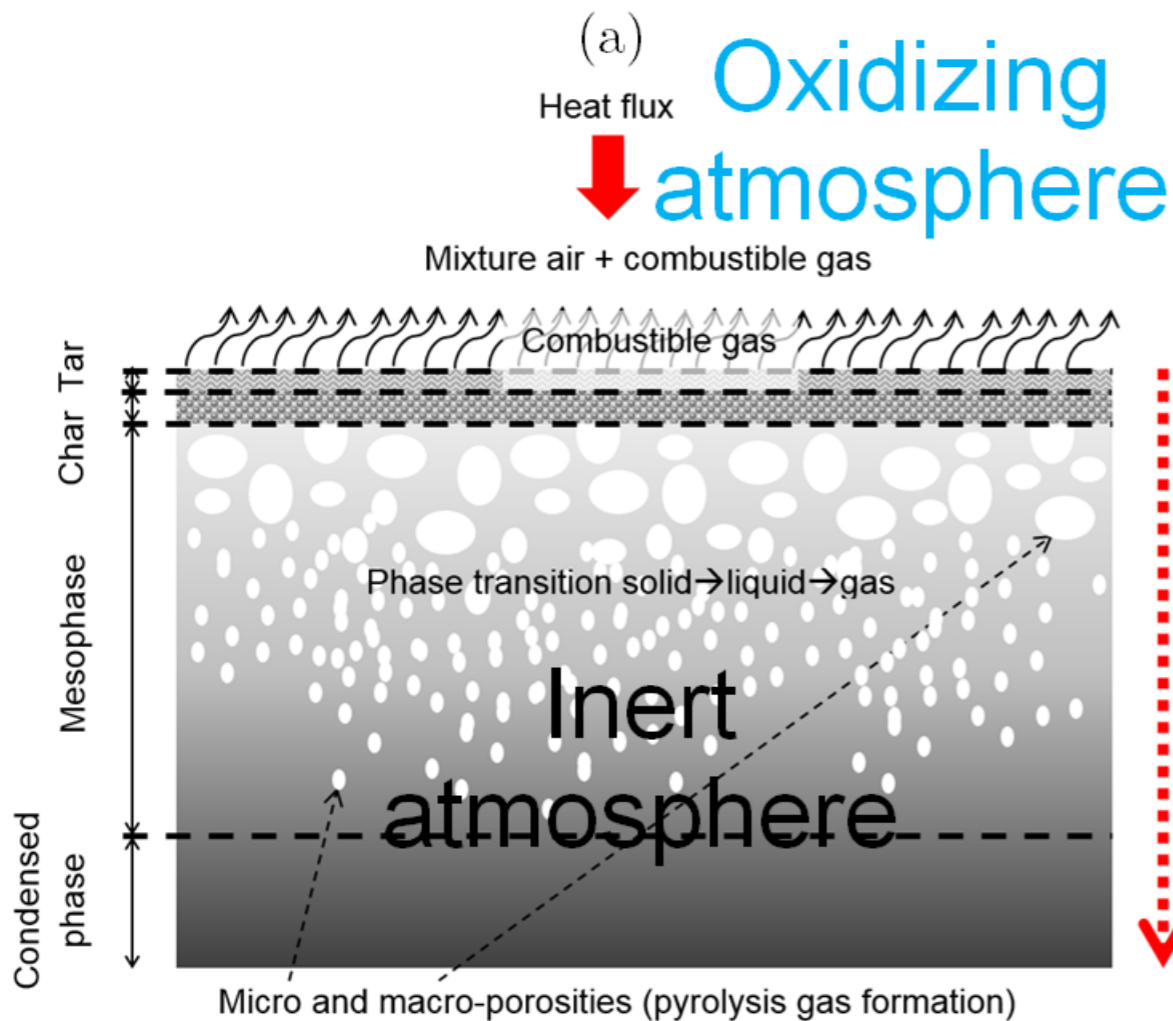
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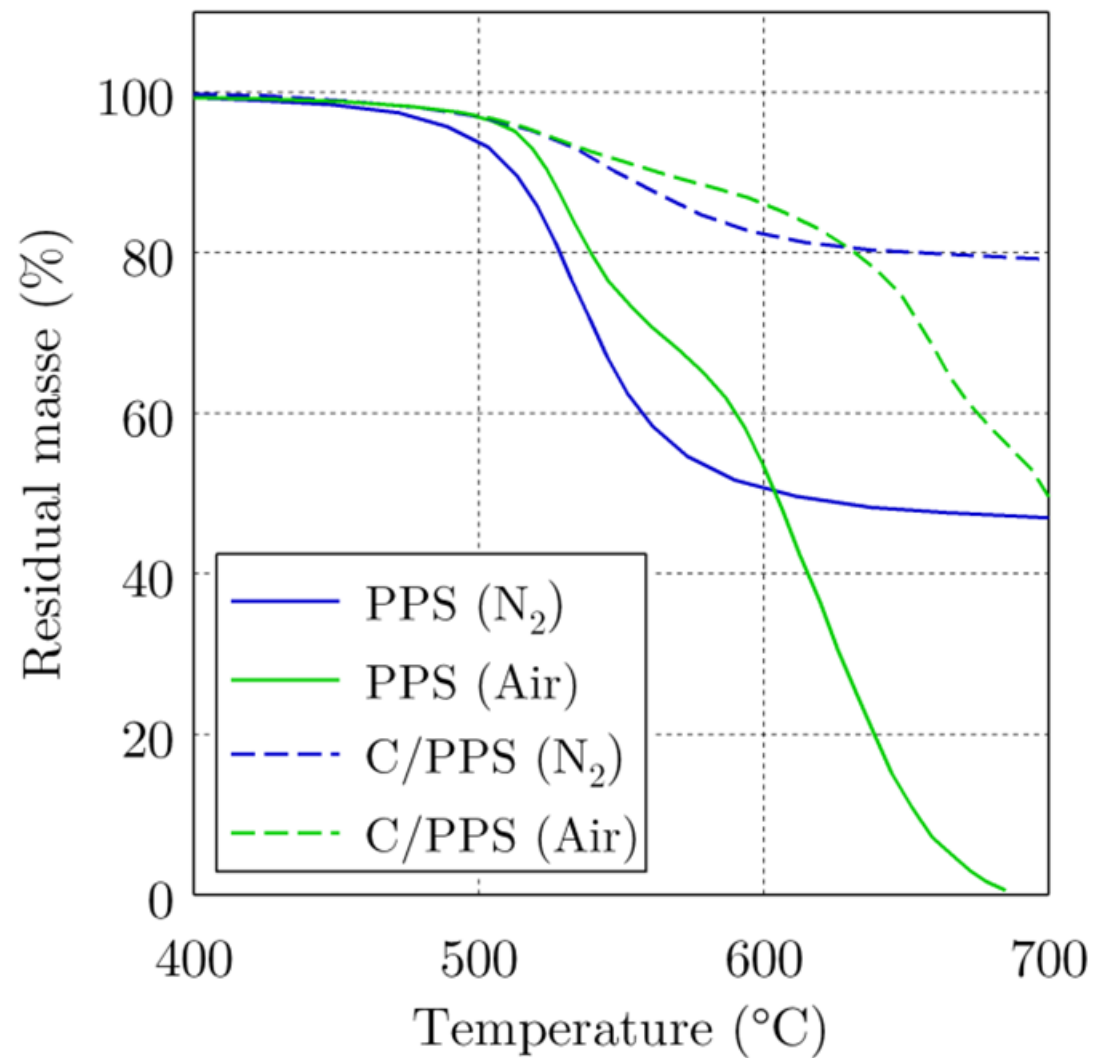
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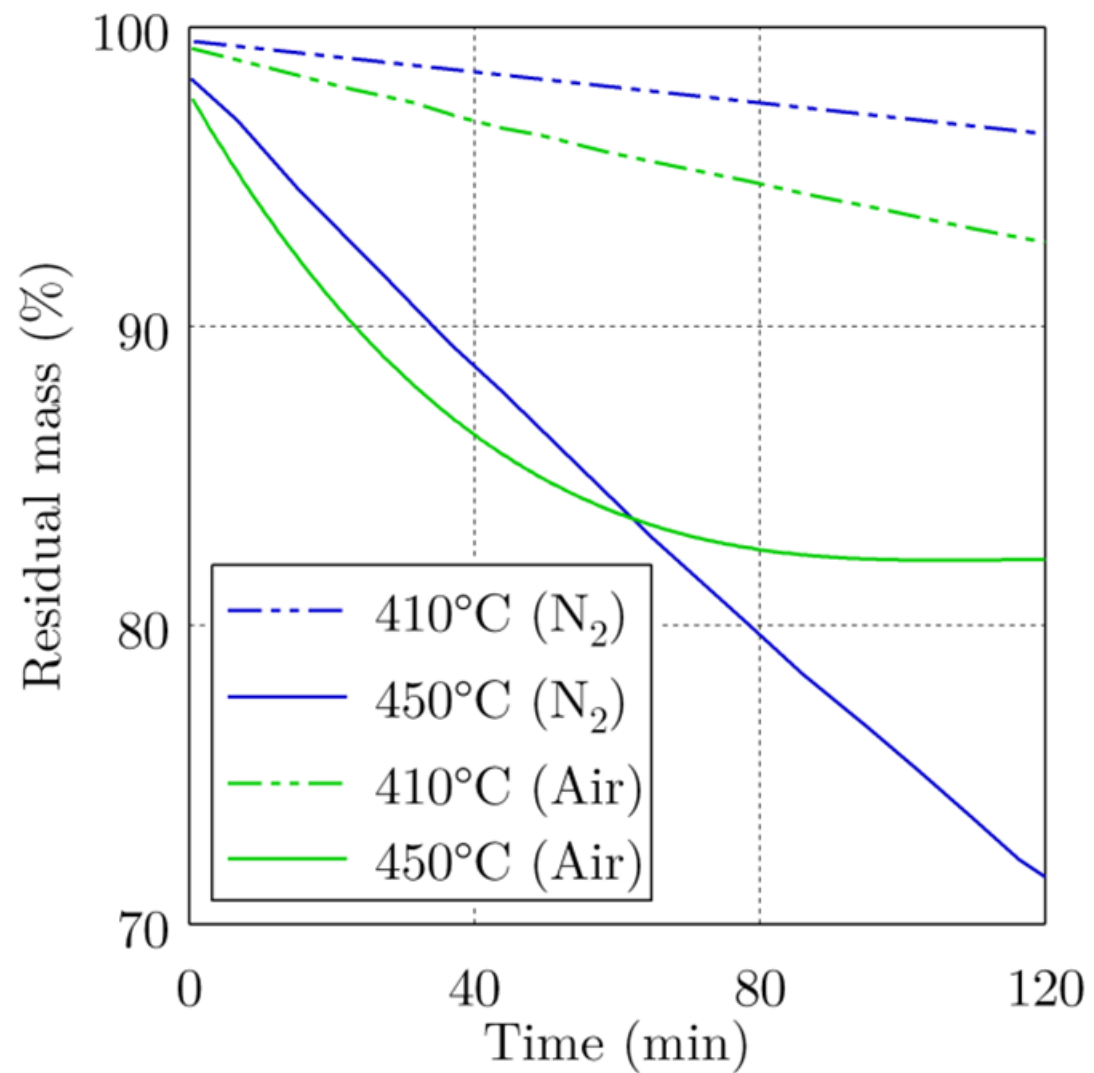
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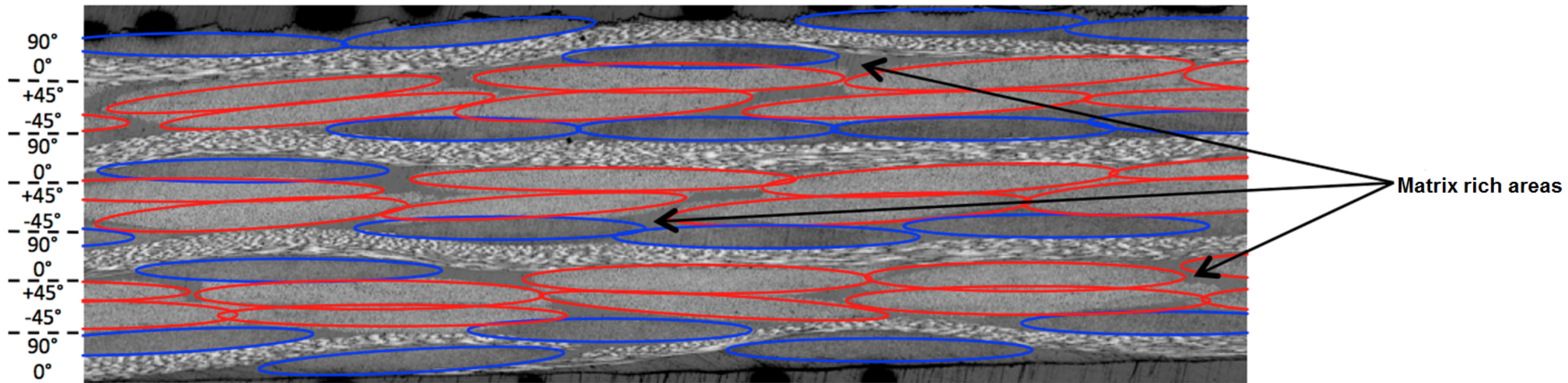


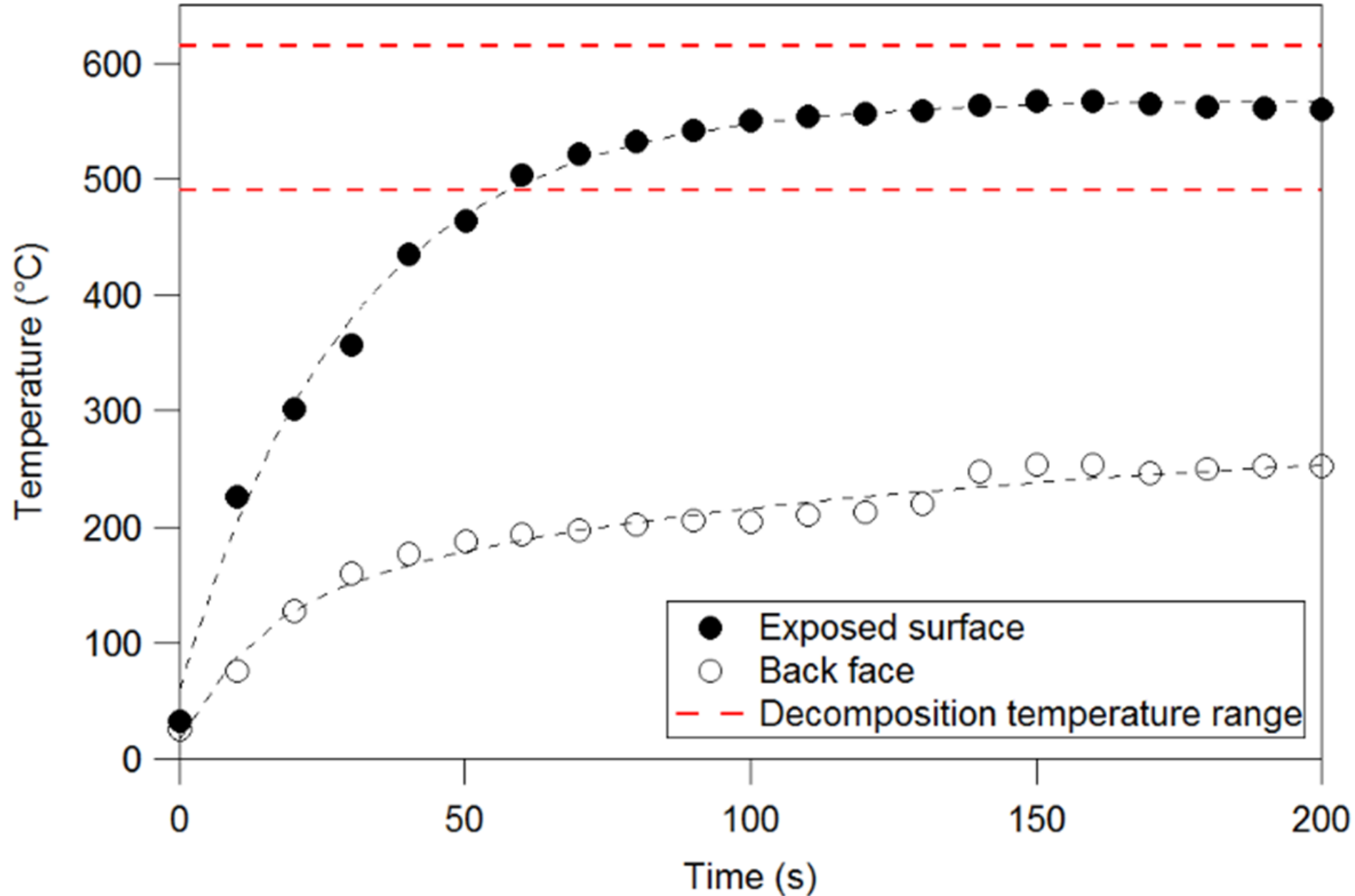
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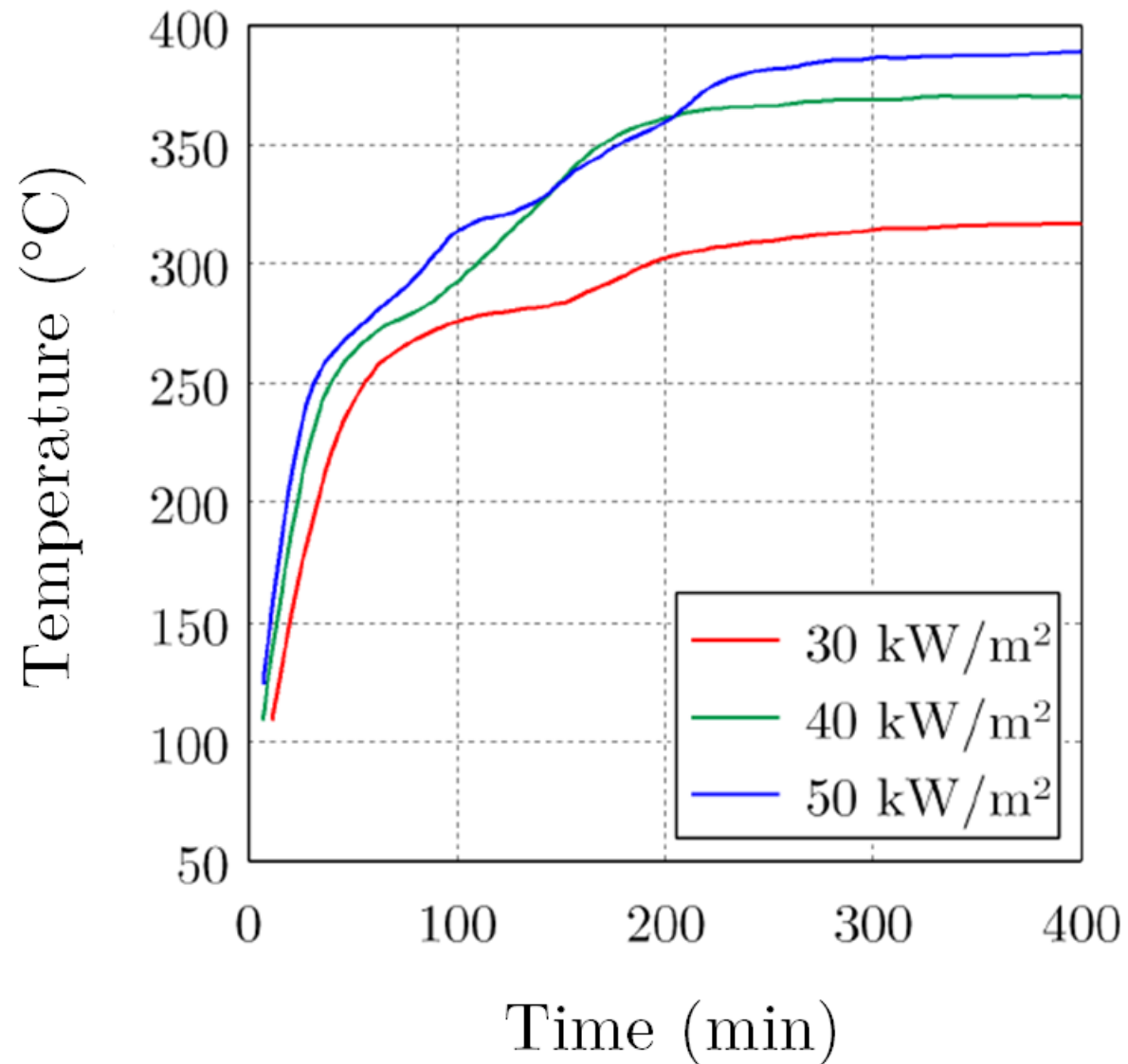
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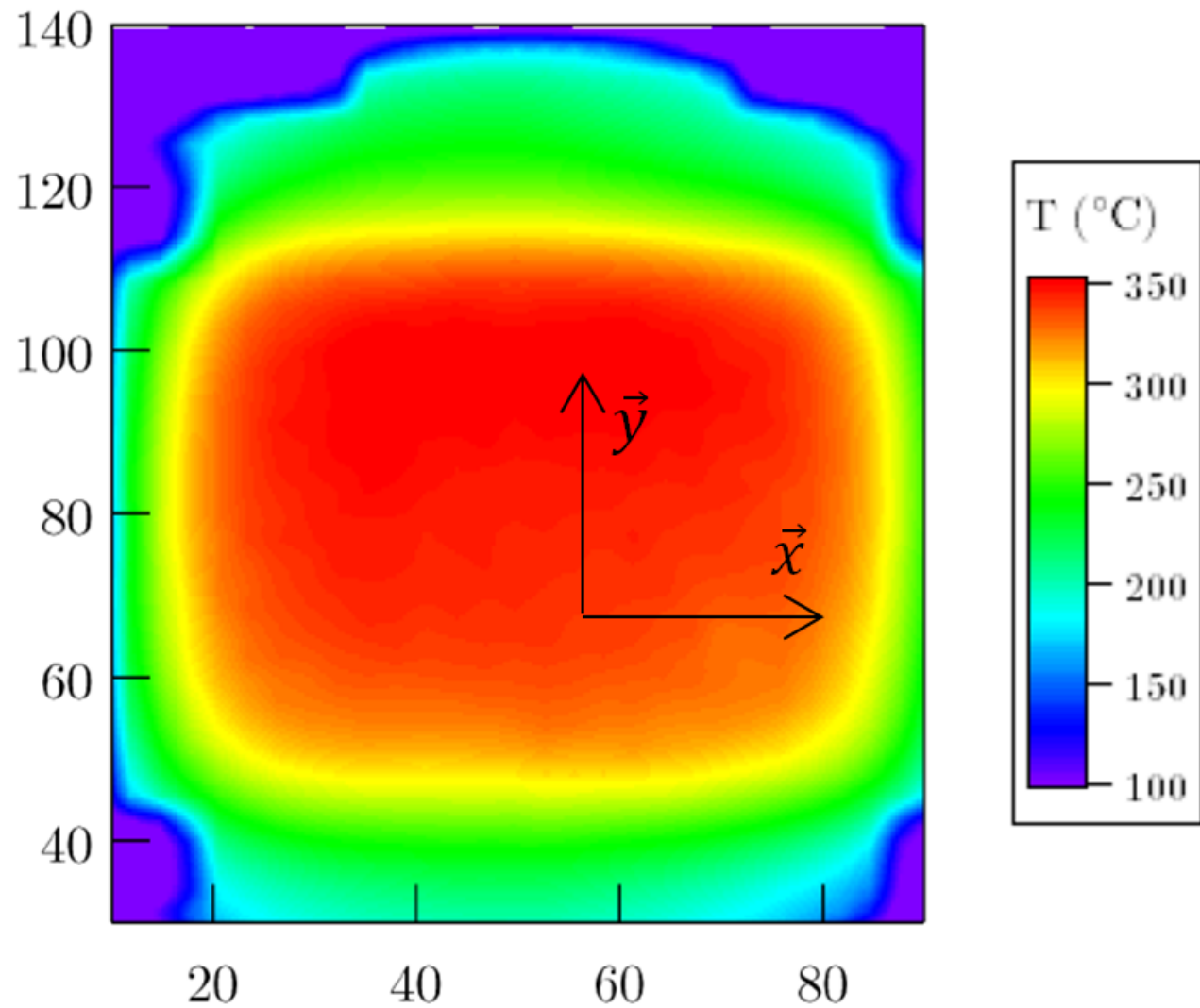




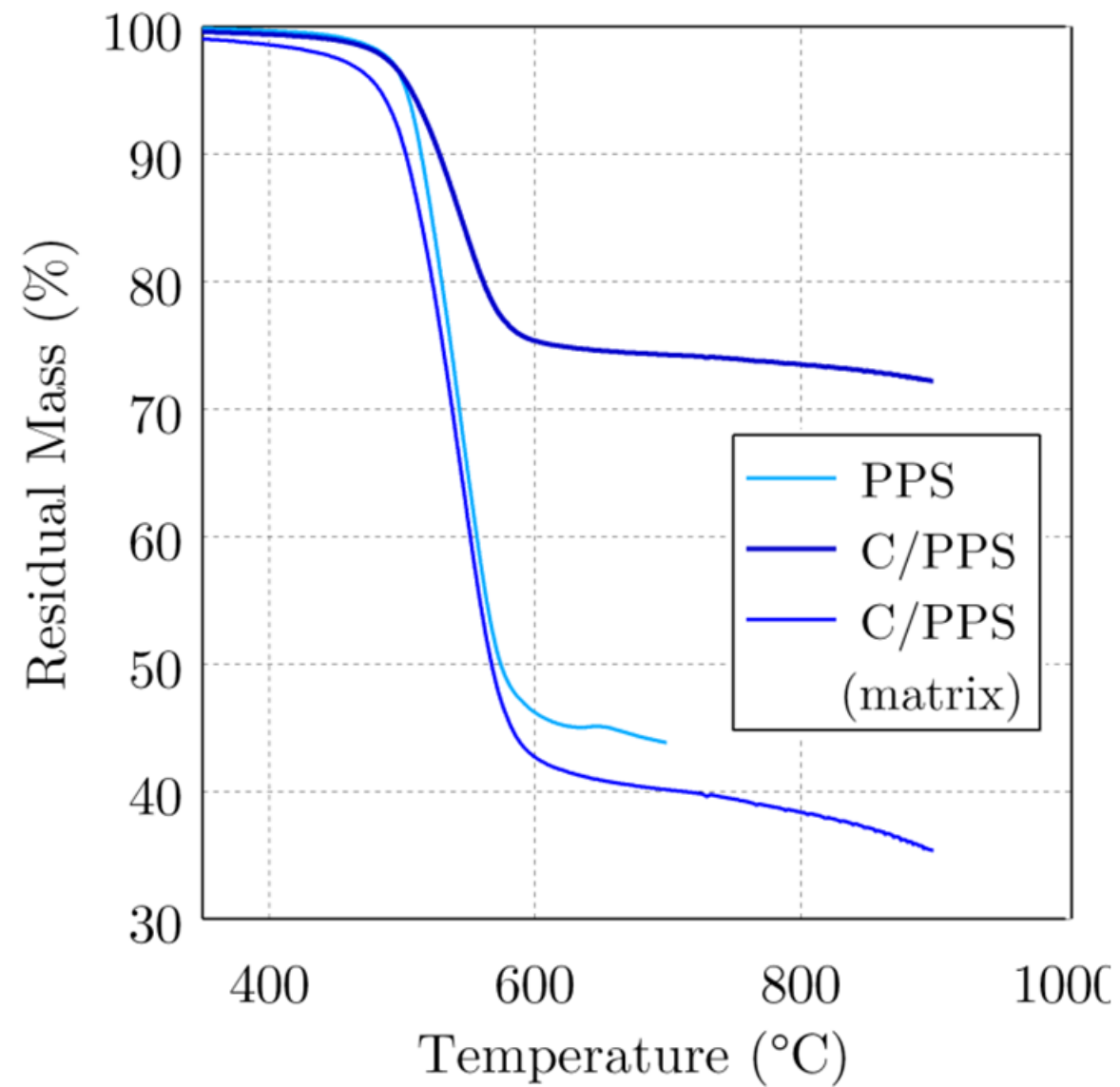
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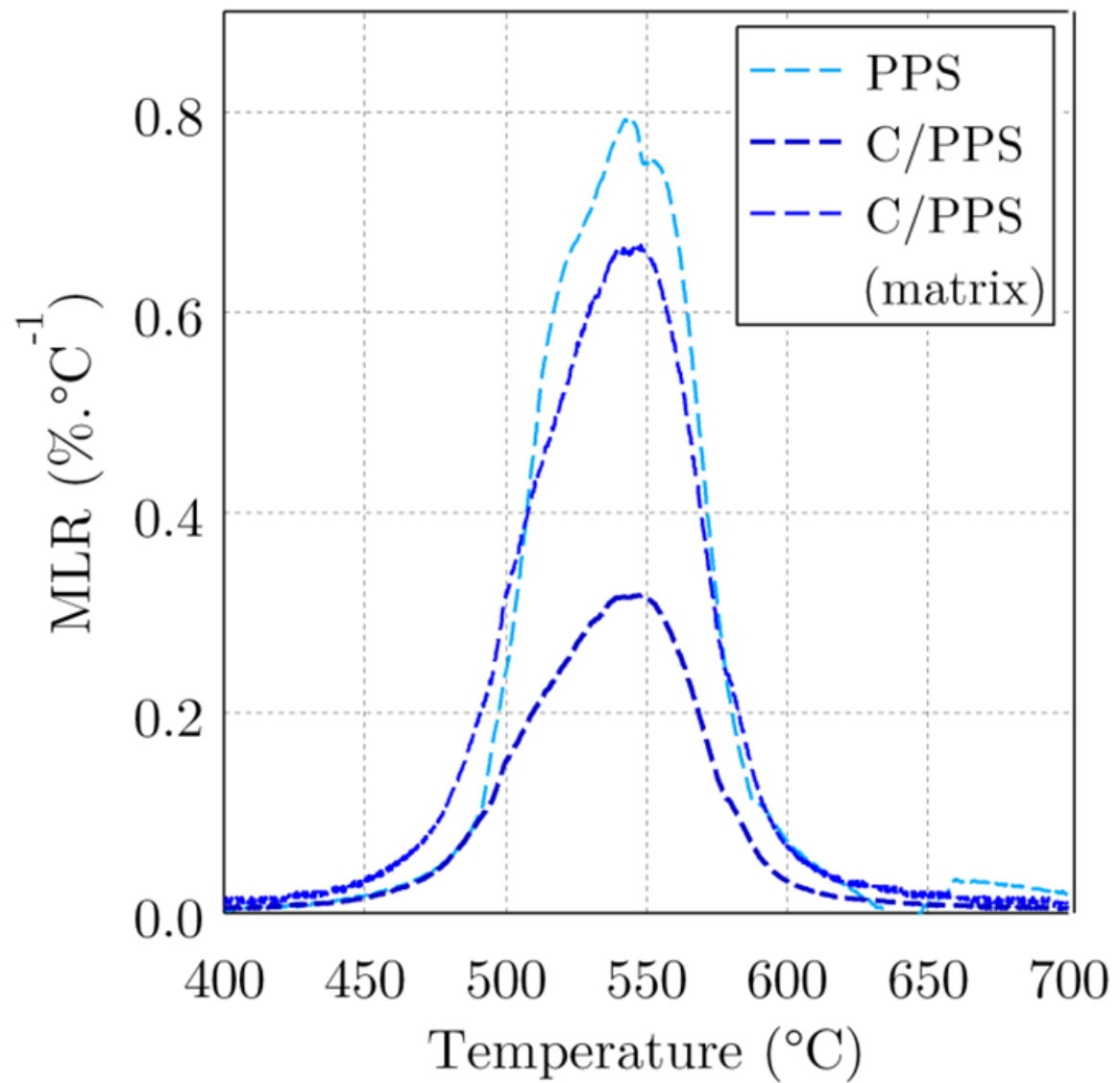
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(a)

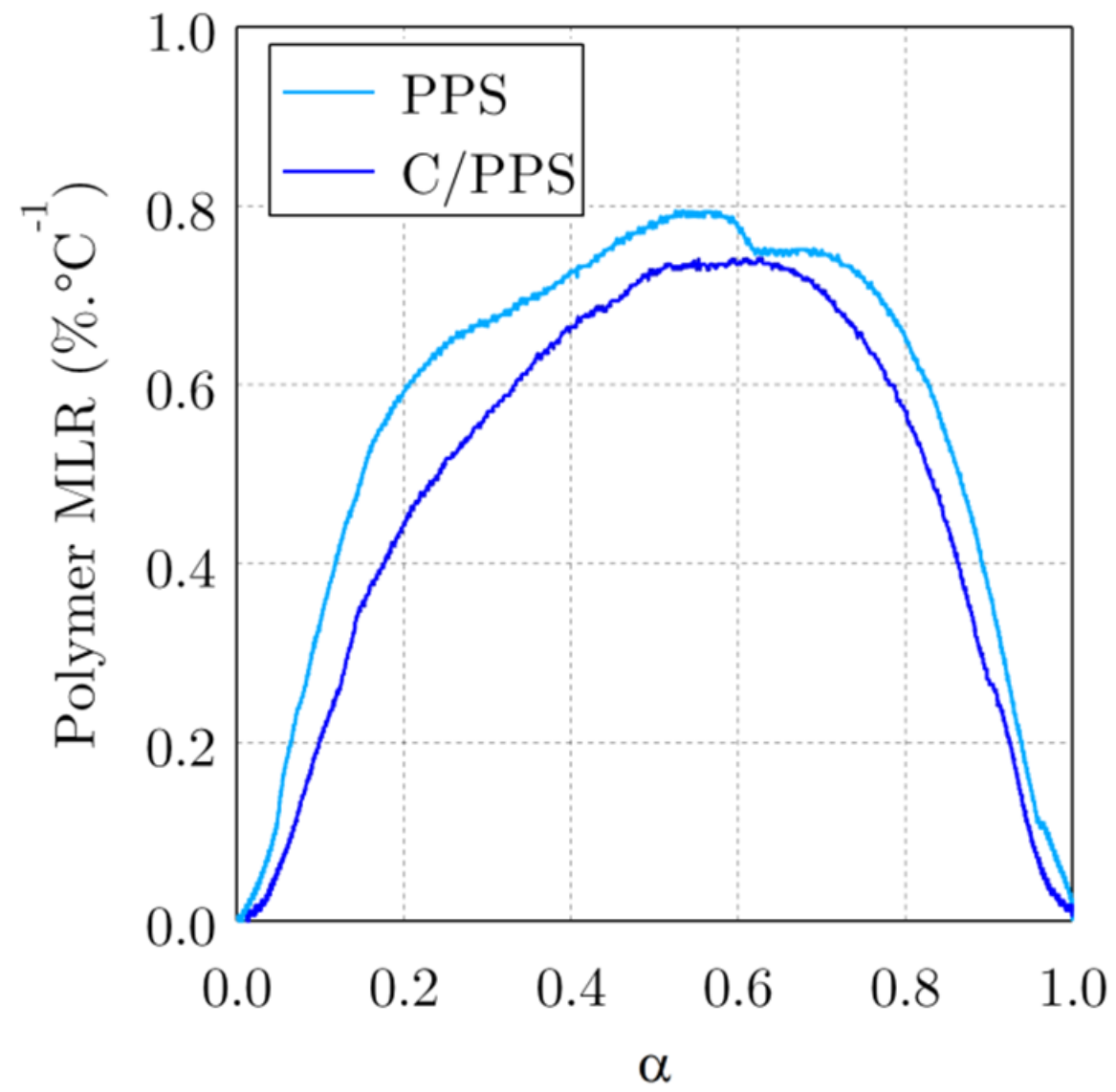


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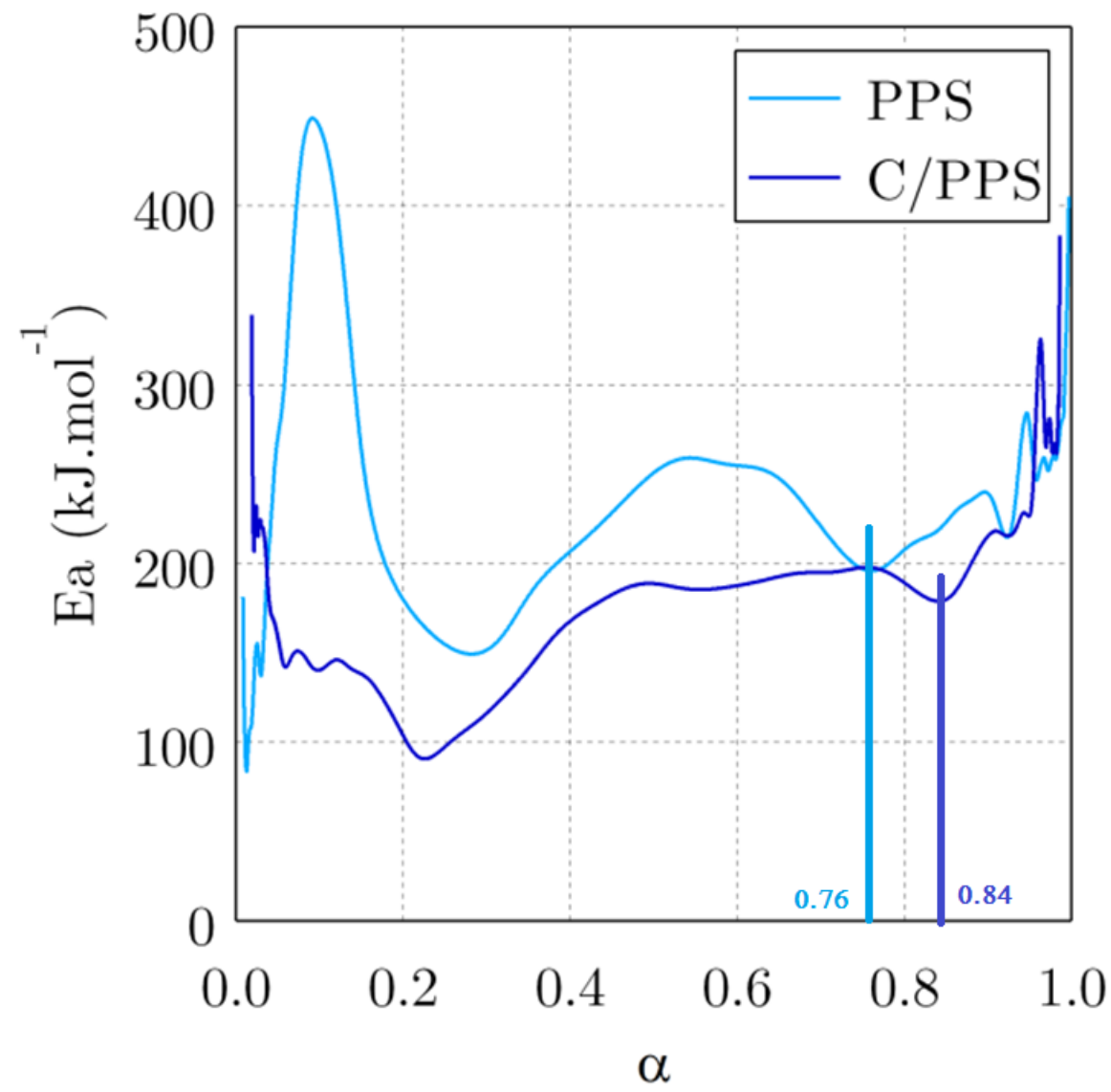


α

(a)



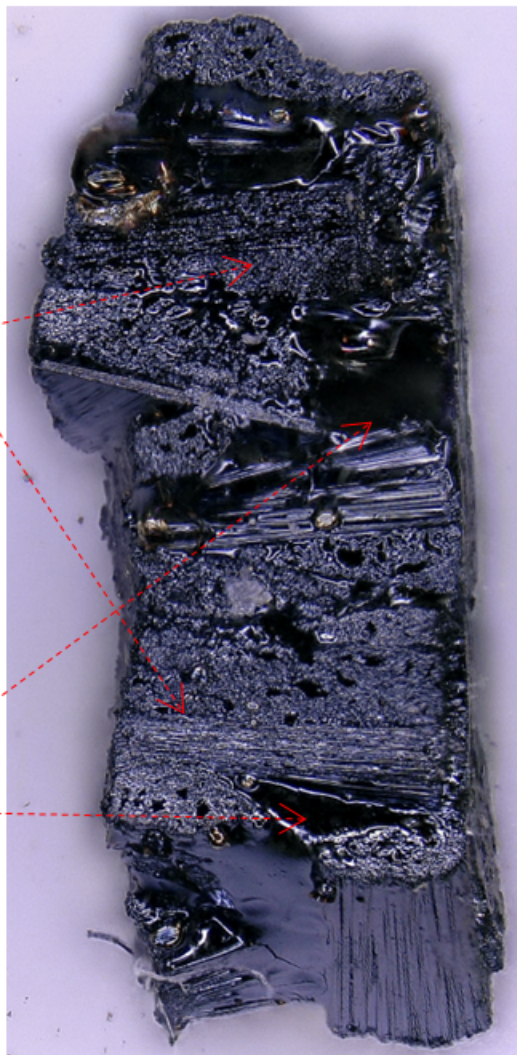
(b)



(a)

Carbon fibres

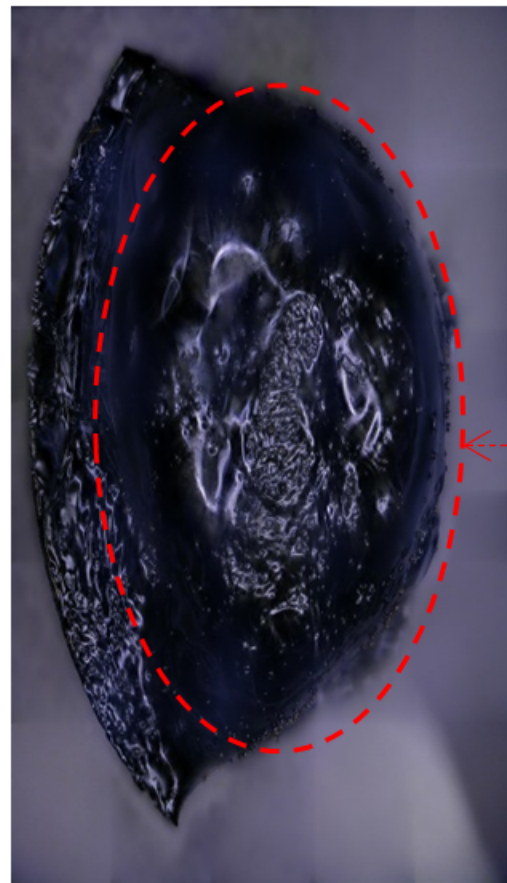
Melt PPS
matrix



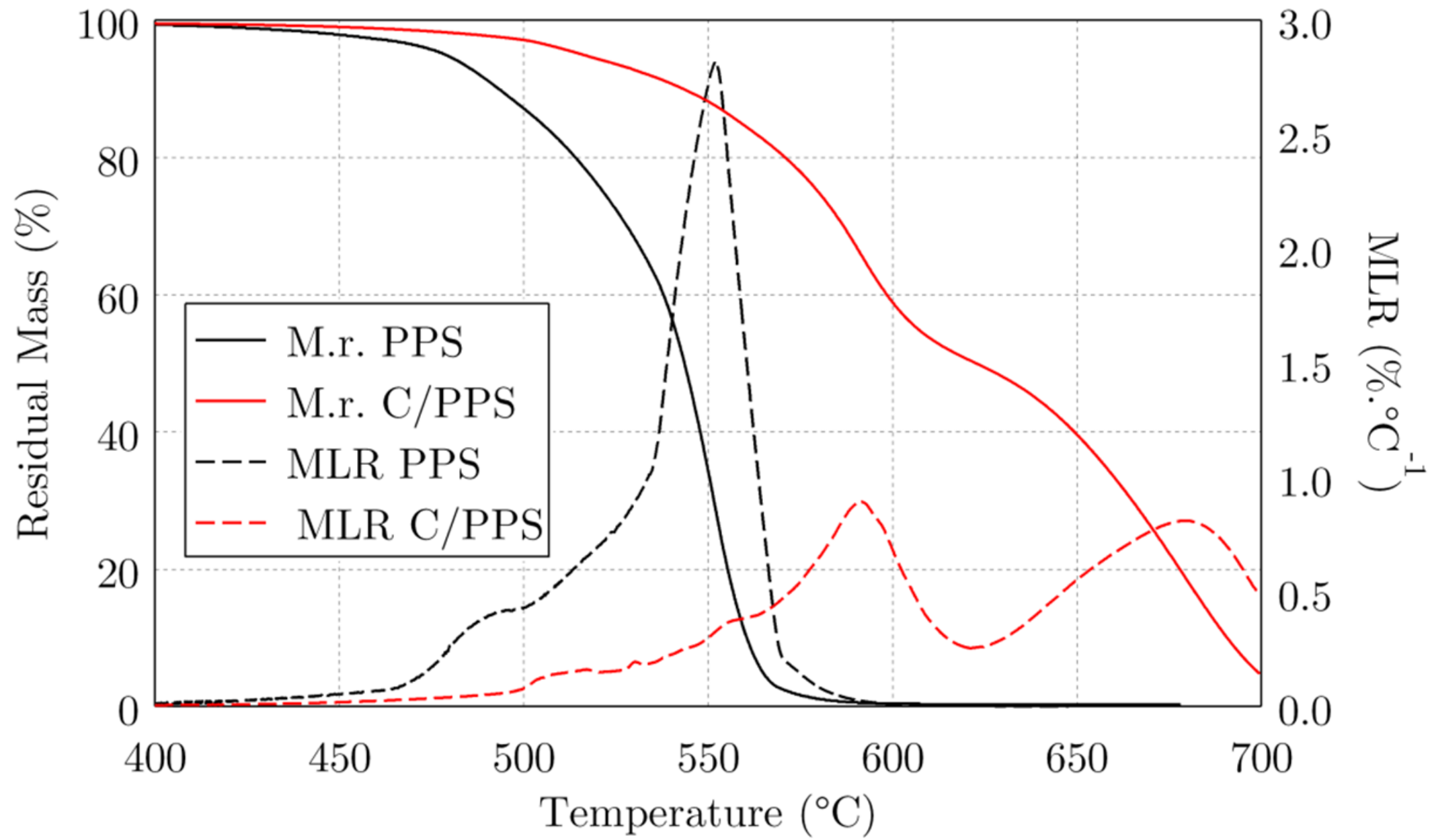
500 μ m

(b)

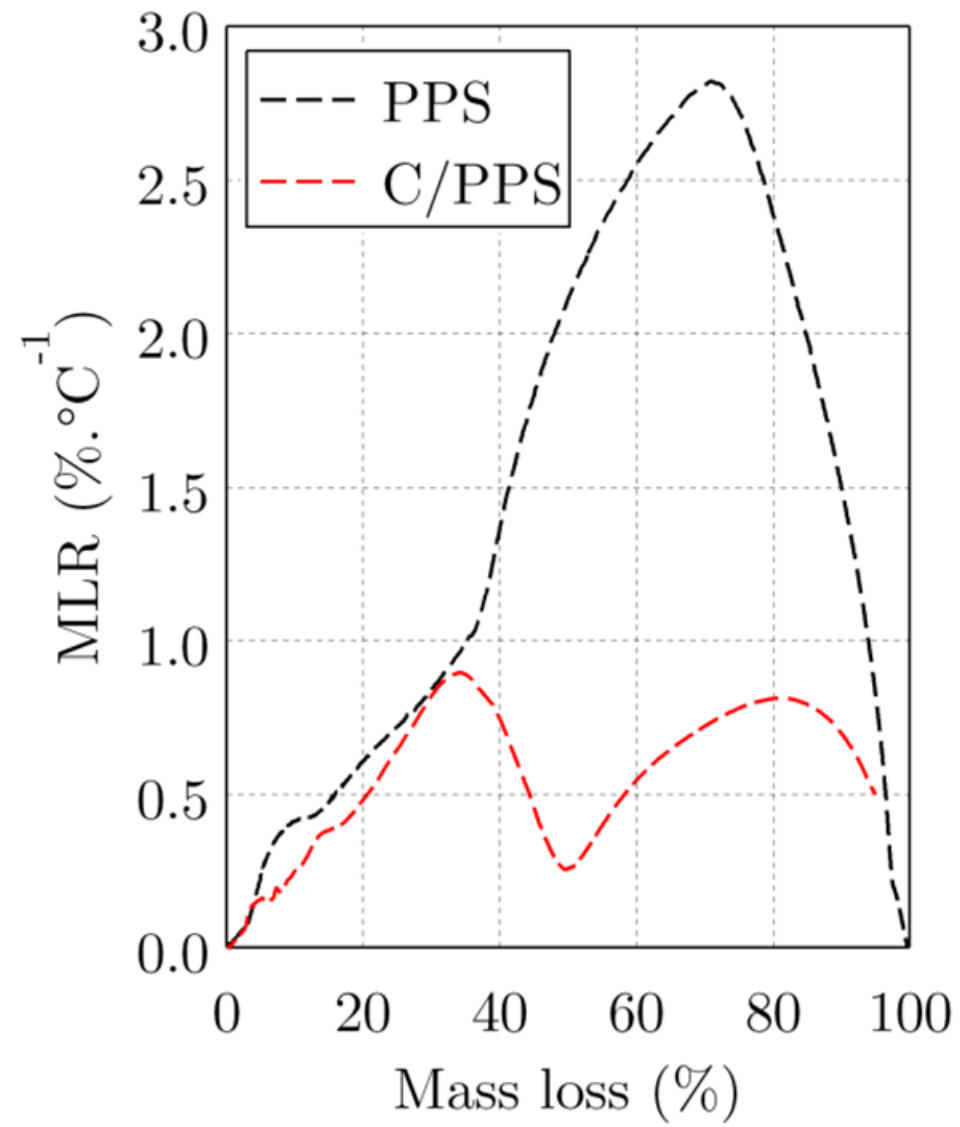
Bubble of melt
PPS resin
(swelling of
pyrolysis gas)



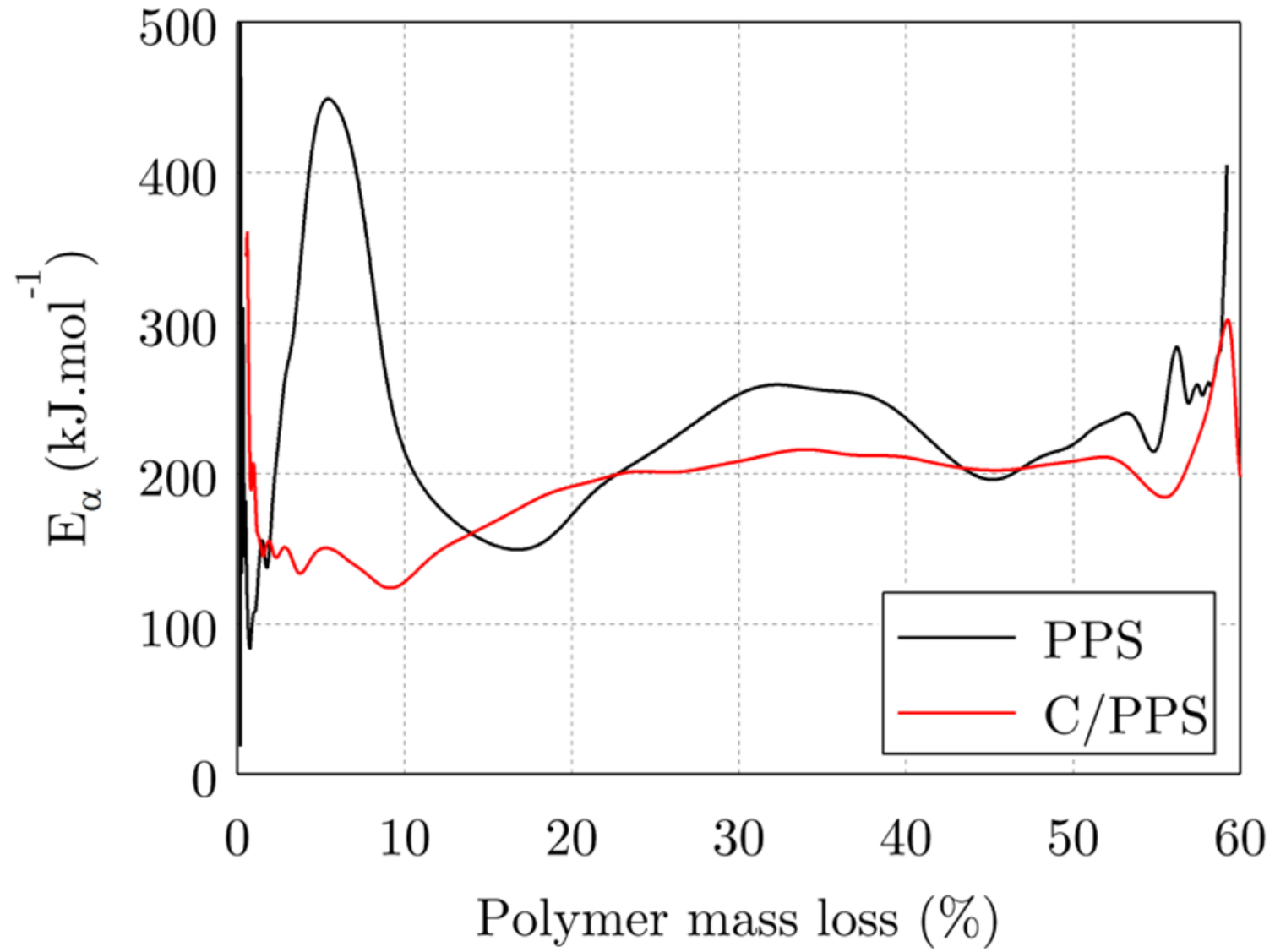
1mm

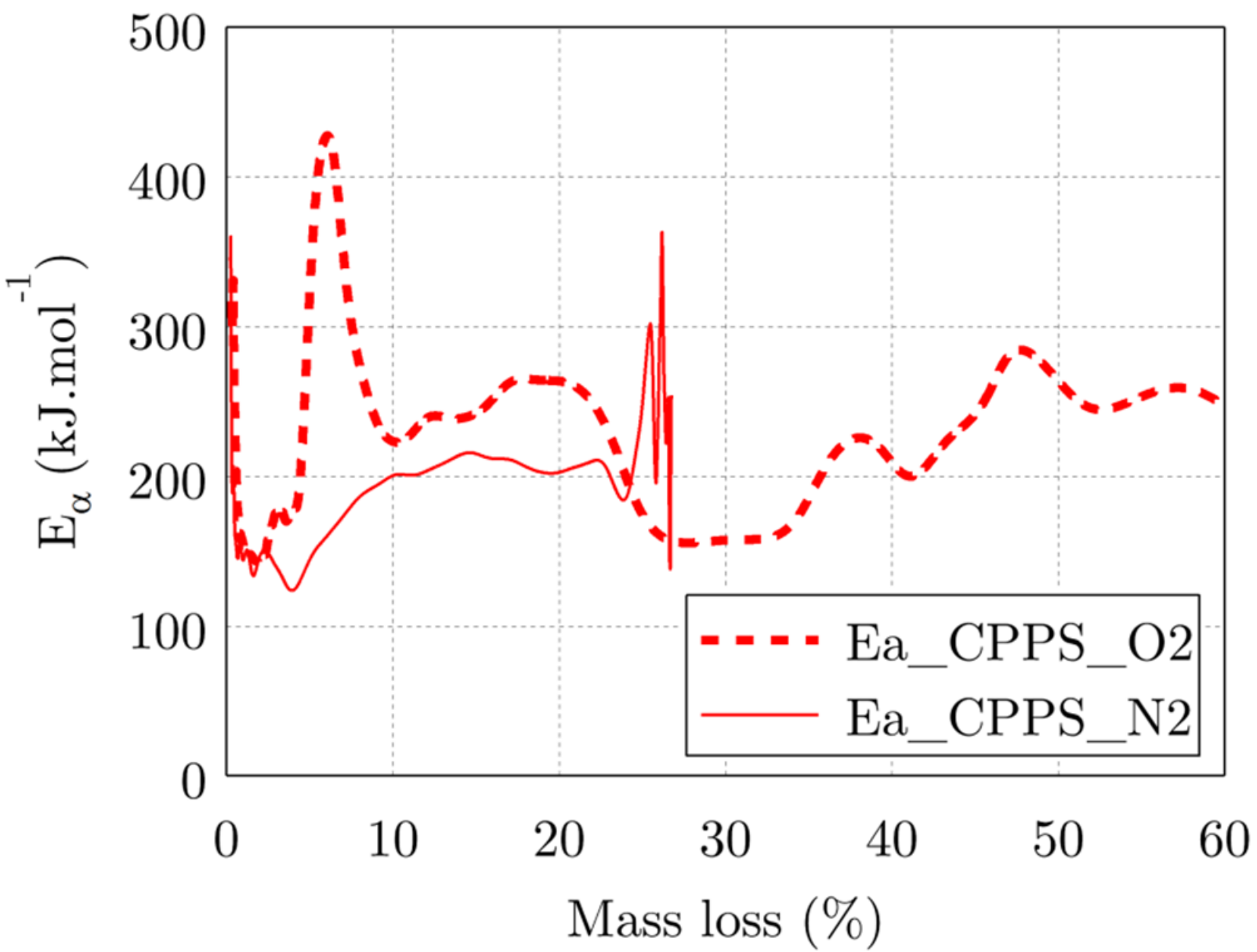


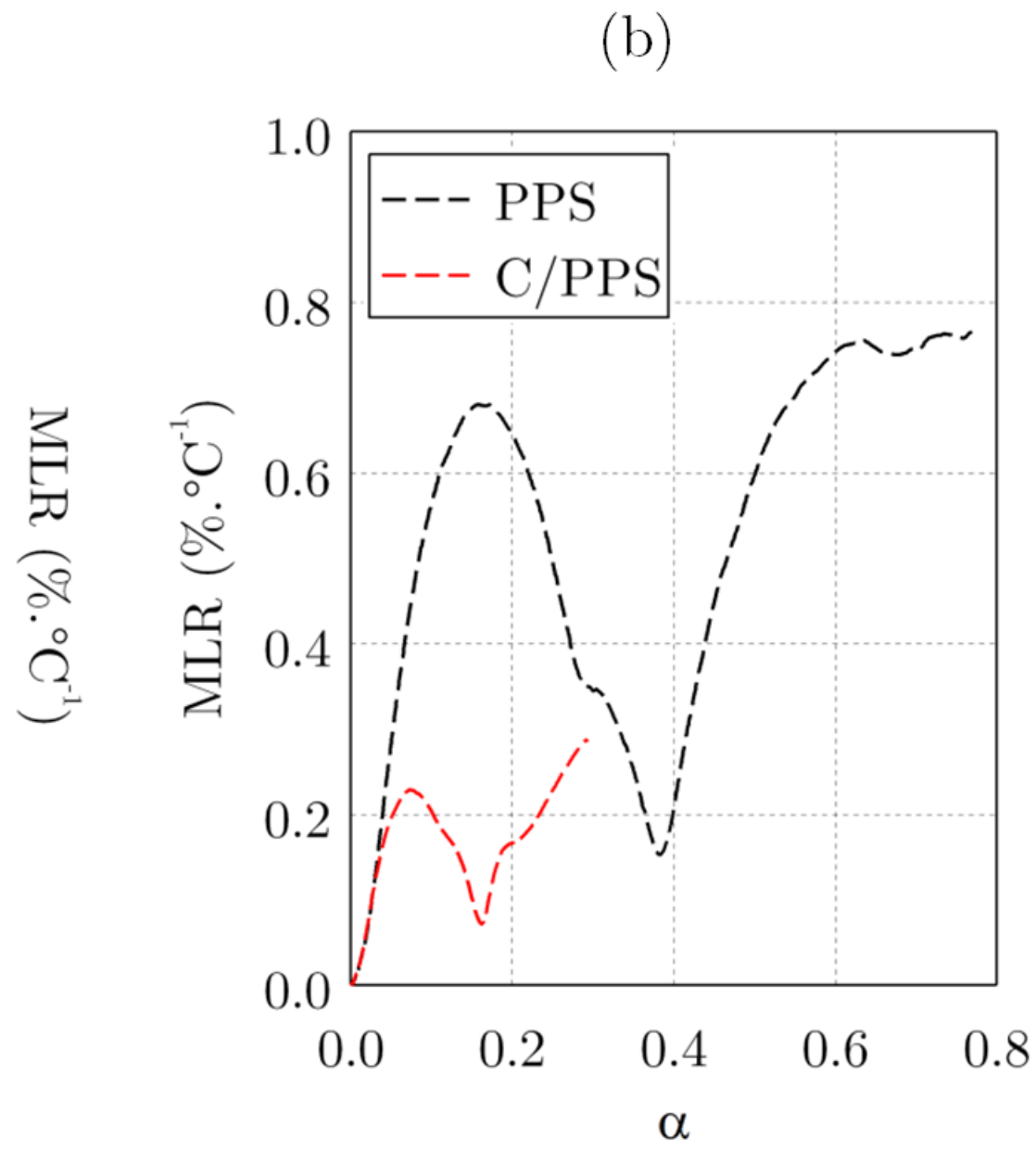
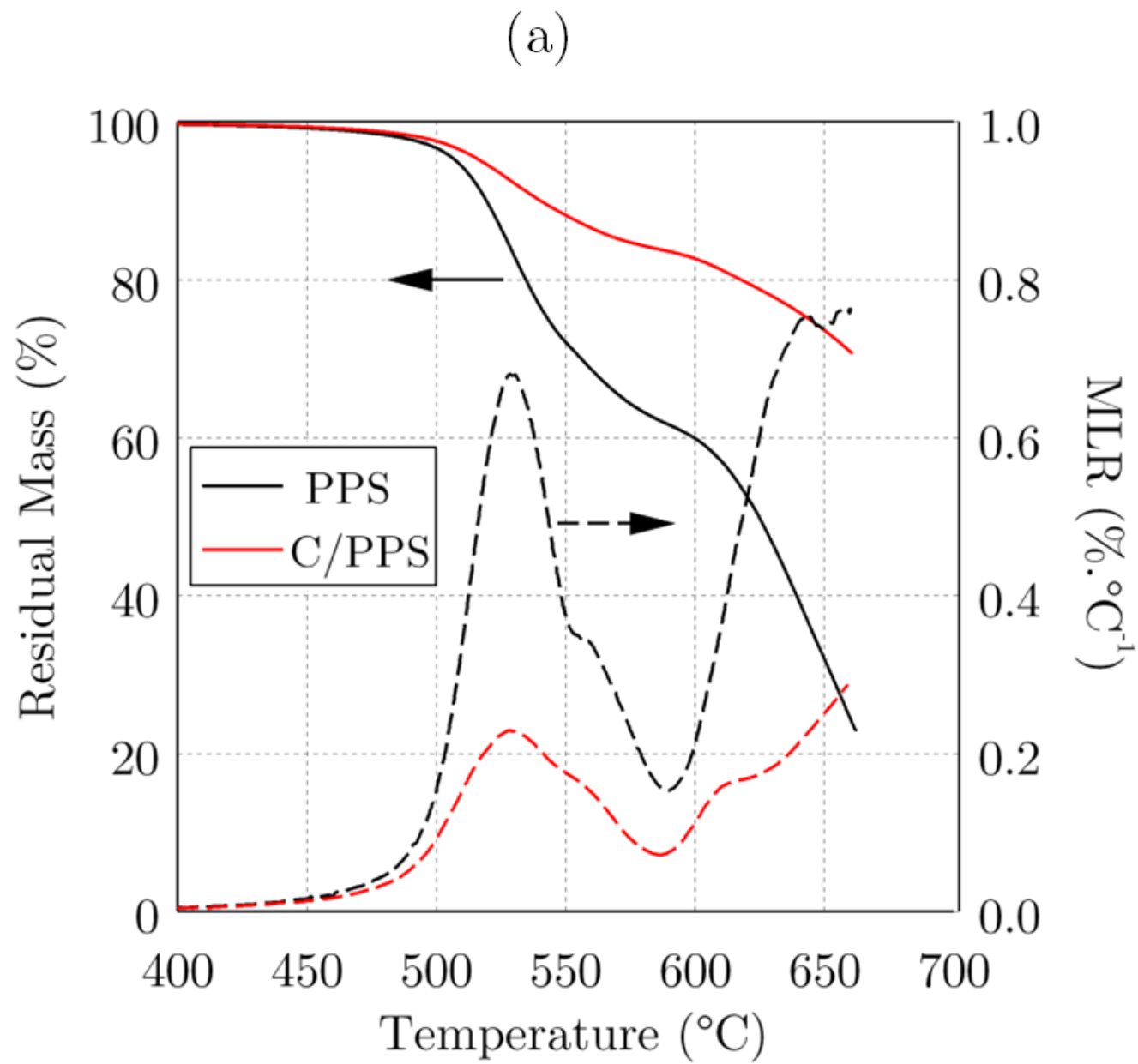
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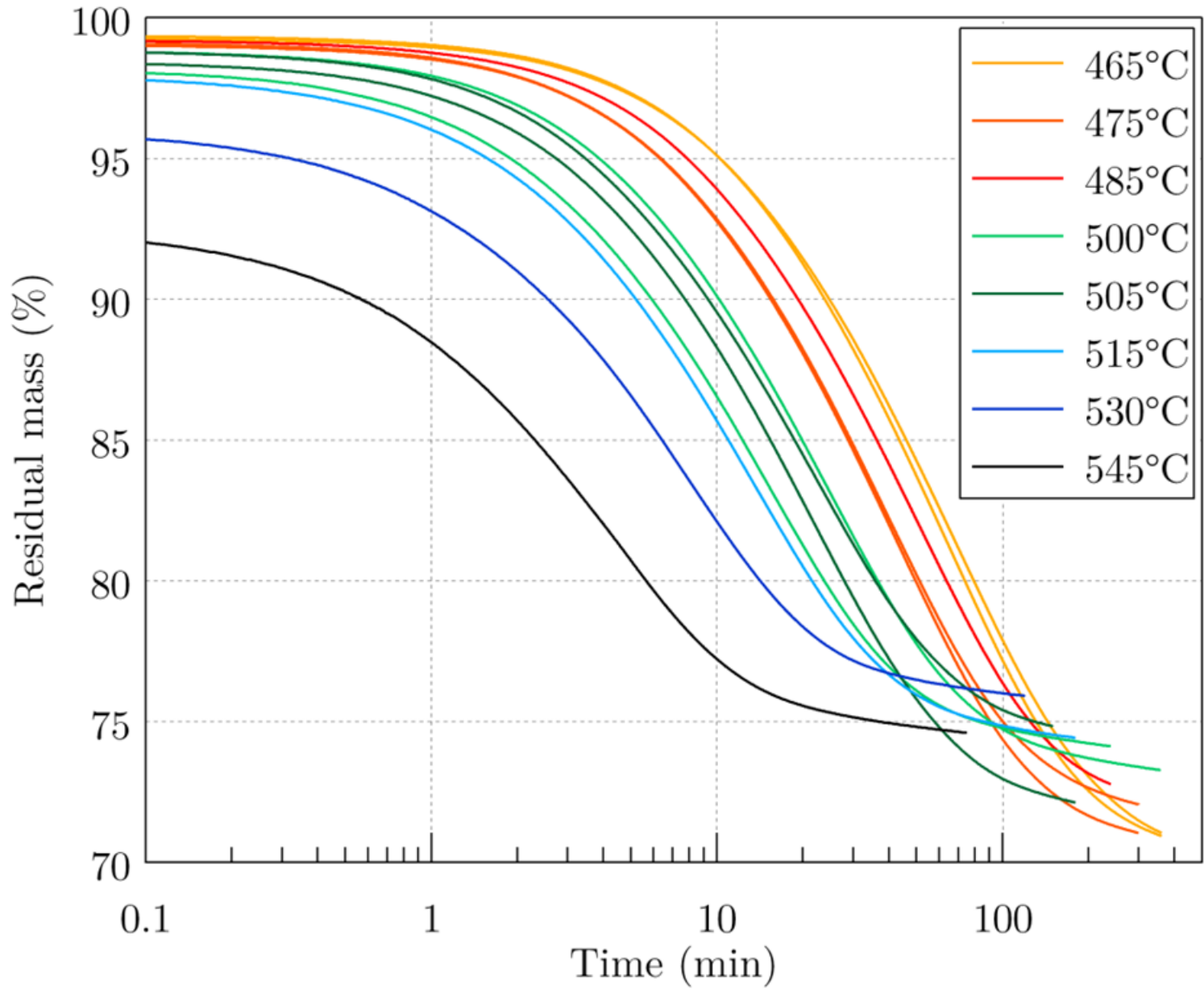


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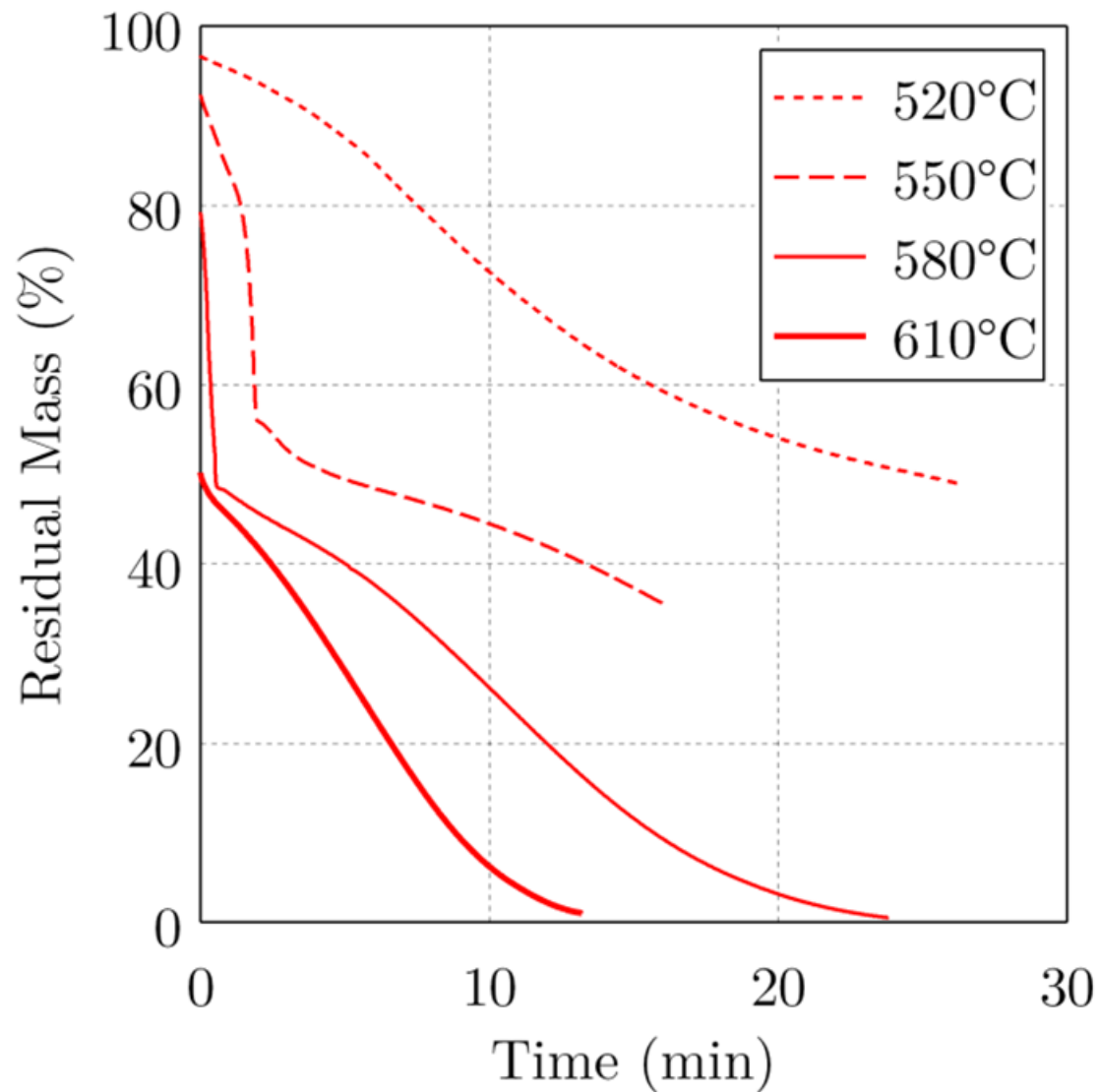




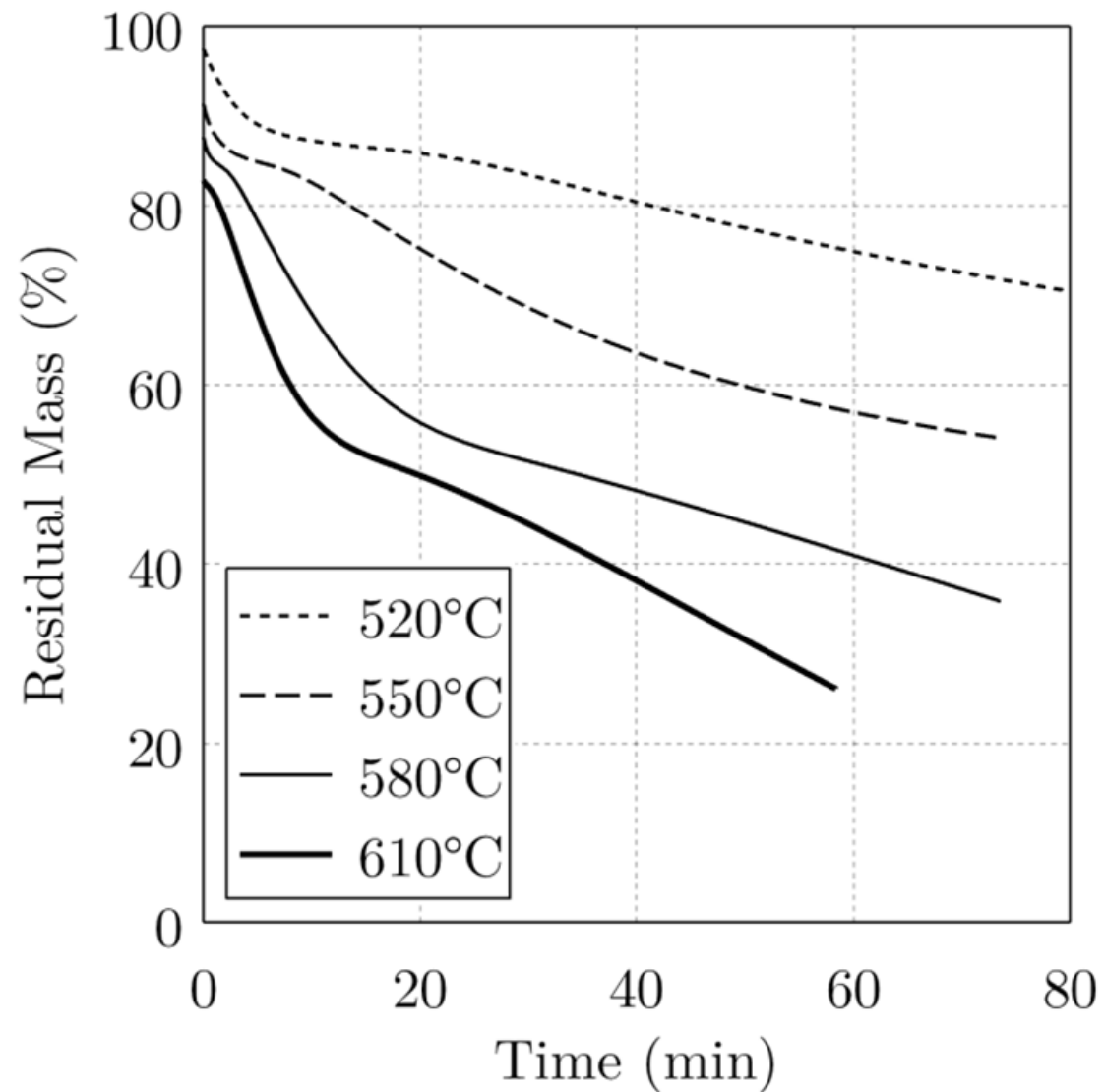




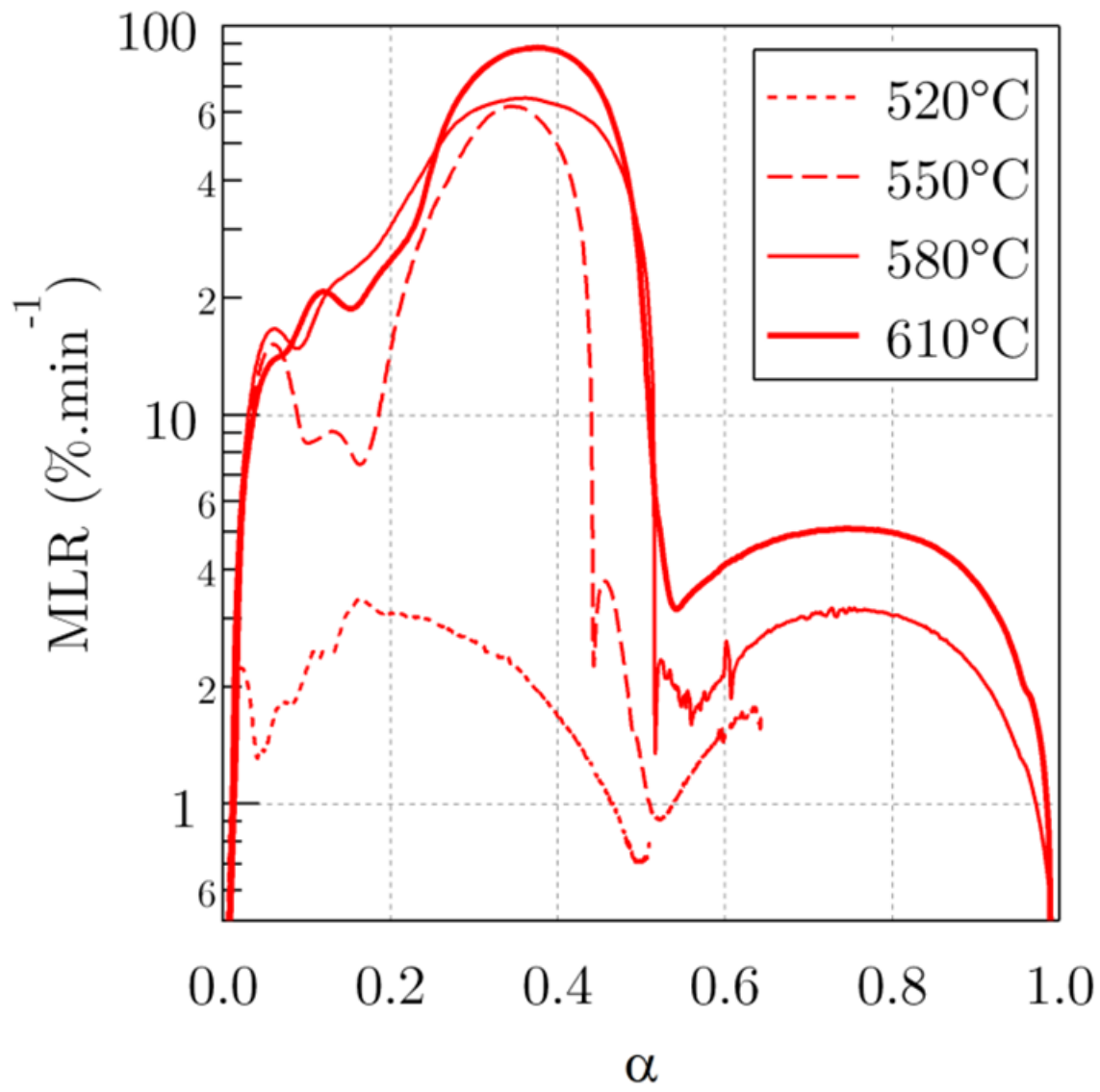
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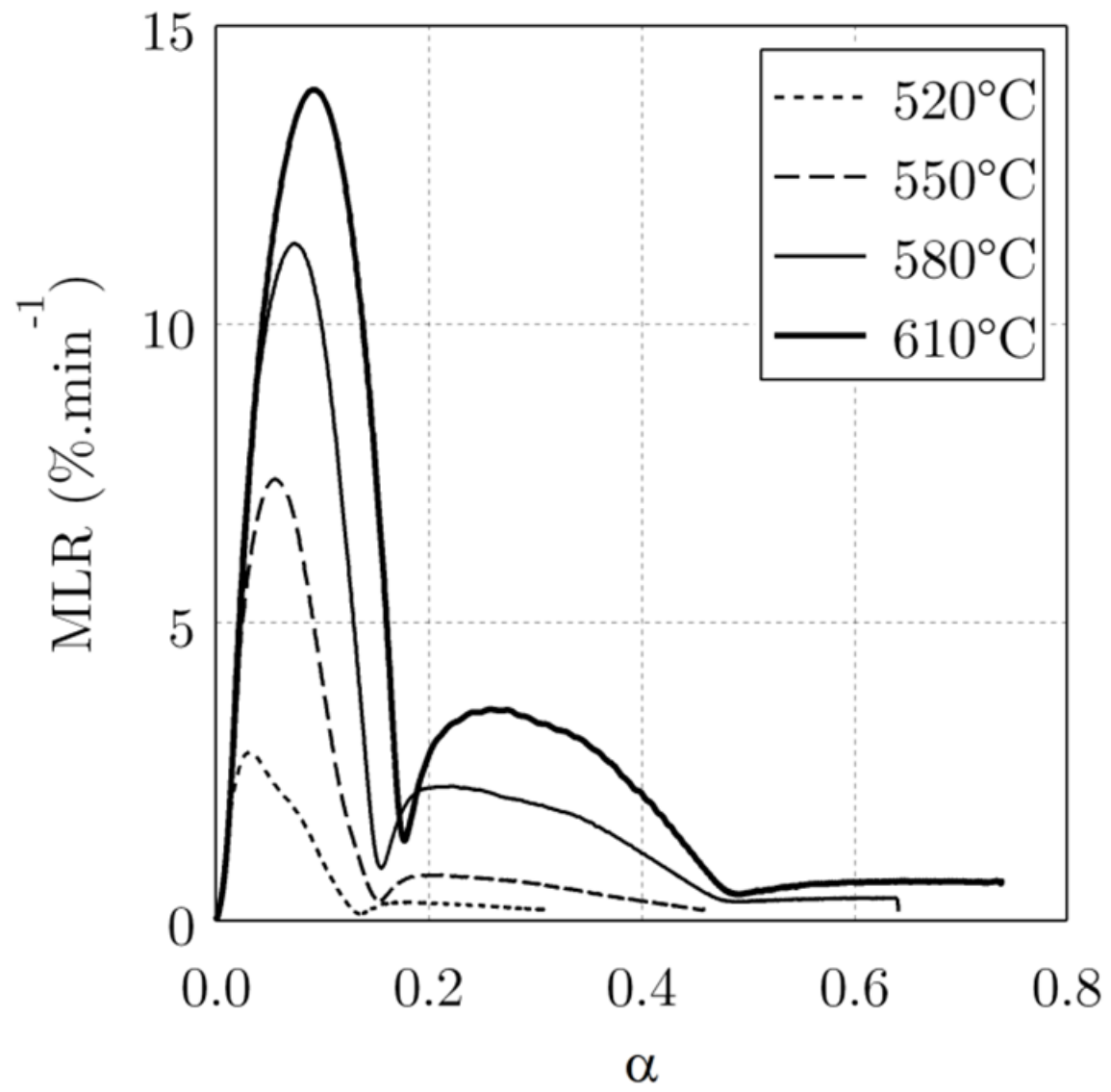
(b)



(a)



(b)



Tables

	N ₂	O ₂
Plain PPS resin	503°C	502°C
C/PPS composite	483°C	515°C

Table 1 - Temperature at the onset of decomposition of plain PPS and C/PPS composites at a heating rate 10°C/min

	N ₂	O ₂	Air
Plain PPS resin	523°C	530°C	508°C
C/PPS composite	525°C	526°C	517°C

Table 2 - Temperature at the onset of decomposition of plain PPS and C/PPS composites at a heating rate 20°C/min