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Abstract

The present work focuses on the thermomechanical behaviour of thermoplastic-based composite materials subjected to the combined action of a mechanical loading in tension and homogeneous temperature conditions. The investigations on the relationship between local temperature resulting from the local atmosphere and the mass losses are essential in understanding the influence of fire on the thermo-mechanical behaviours of polymers and polymer matrix composites. Regardless the testing atmosphere, the decomposition onset temperature is about 500°C. From isothermal tensile tests conducted at temperatures ranging from ambient to 520°C, it appears that the retention of the axial stiffness of quasi-isotropic carbon fibers reinforced polyphenylene sulfide (PPS) laminates is relatively high (about 70% of its initial value) beyond the decomposition temperature. At the same time, the ultimate strength dramatically decreases (about 25% of its initial value). The obtained results also show that melting is instrumental to rule the tensile behavior of quasi-isotropic C/PPS laminates. Conversely, matrix melting significantly influences the damage mechanisms within the laminate. Finally, for testing temperatures close to the onset decomposition temperature, porosities appear and grow within the laminates, ultimately contributing to the degradation of the mechanical properties.

Keywords: thermoplastic; thermal decomposition; high temperature; mechanical behavior, damage

1. Introduction

The study of fire resistance aims at understanding and characterizing how and for how long the composite material can bear a mechanical loading when it is subjected to heat fluxes resulting in temperature differences through-the-thickness. Most Polymer Matrix Composite (PMC) materials usually cannot bear significant mechanical loading at temperature higher than 200-250°C. High-performance thermoplastic-based (TP) composites (e.g. PEEK, PPS, PEI…) are promising materials for structural applications in aeronautics as they are resistant to impact. They have a good damage tolerance as well as they have a very good retention of their mechanical properties under fire conditions. Among the most common PMCs used in load-bearing aircraft structures, Carbon/epoxy (thermosetting) composites are flammable and readily decompose when exposed to heat and fire. The literature dealing with the fire behavior of composite materials focuses mainly on thermosetting-based composites [1] and rarely on thermoplastic-based composites [2][3].

1.1 Thermal decomposition of PMCs

To better understand the changes in the thermal and mechanical behaviors of polymer-based composites under fire exposure the first step usually is to investigate the influence of thermal heat fluxes, hence temperature, resulting from a fire. Such heat fluxes lead to significant temperature gradients within composite structures. From thermal analyses it is therefore possible to study the decomposition mechanisms as well as their kinetics under different testing conditions (heating rate, isothermal and anisothermal, inert or oxidizing atmosphere). The decomposition mechanisms are closely associated with the chemical nature of the polymer [4]. These analyses are extremely useful for determining the primary steps of the decomposition: T_d=$T_{5\%}$ refers to pyrolysis or decomposition onset and corresponds to the temperature at which 5% of the polymer mass has decomposed; T_{max} refers to the maximum peak of decomposition rate. Such analyses can also be considered for studying the thermal decomposition kinetics. From a general standpoint, the influence of temperature on PMCs properties can be investigated considering two temperature ranges: (i) $T < T_d$ and (ii) $T > T_d$.

When $T < T_d$, the first consequence of a temperature increase is the thermal expansion of the specimen [1]. High temperature gradients and the difference in thermal expansion coefficients of the fiber and of the matrix may result in incompatibilities of deformations, leading to the appearance of matrix cracks that contribute to slowing down thermal conduction. The changes in matrix state (glass transition, melting) require energy input which can result in a slowing of the temperature increase by surface or within the sample [5]. These transformations lead to matrix softening and can promote material damage such as porosities which will induce matrix cracks, inter and intra-laminar, leading to delamination. Ancillary mechanisms, such as the formation of water vapour in matrices with high water recovery, can also damage the material via the formation and growth of porosities.

When $T > T_d$, temperature is high enough to induce thermal decomposition and damage within the material is then the most important [1]. Different chemical transformations of the material occur according to the mechanisms described in [6]. The issue of fire resistance of polymer matrices with poor temperature resistance is not widely addressed in the literature: most studies primarily focus on matrices with medium (epoxy, polyester, vinylester) or high (phenolic, PPS, PEEK) char yield [4].

1.2 Thermomechanical coupling at high temperature in PMCs

The influence of high temperatures on both the mechanical properties and the thermomechanical behaviour of PMCs can be considered up to T_d. In thermally stable PMCs, changes in mechanical properties with temperature can be considered reversible up to matrix decomposition [1]. In the case of a fire scenario it is necessary to consider the changes within the laminates occurring at T_d (see section 1.1). In addition, the study of the thermomechanical coupling in PMCs requires specific technical means. Such an issue has been widely addressed in the literature. As for most of the studies dealing with high temperature exposure [7], a weak coupling between thermal transfers and mechanics is postulated for our analyses. It means that the thermal state of a given point influences its mechanical behavior but a variation in its mechanical state leaves its temperature unchanged. Weak coupling refers to the influence of temperature on mechanical behaviour but not the influence of mechanical behaviour on thermal one. This section is focused on the

tensile behaviour under homogeneous and isothermal temperature conditions. Figure 1 shows the typical influence of temperature on the mechanical properties of PMCs under isothermal conditions (i.e. constant and uniform temperature within the material). Among the classical mechanical properties which are significantly degraded by a temperature increase, the Young's modulus, shear modulus and compressive strength are the most common ones. T_{cr} represents the critical temperature from which the properties start decreasing, T_g the glass transition temperature and T_m the melting temperature. To understand the behaviour of PMCs under critical service conditions, e.g. fire, it is necessary to determine the residual properties at temperatures higher than T_d.

For temperature testing conditions higher than T_d, polymer matrix decomposition may lead to a high activity of porosity formation and growth in the laminates, which severely degrades their mechanical properties and behaviour [8]. From monotonic tensile tests conducted on different types of orthotropic woven fabric laminates (glass/vinyl ester, glass/polyester and glass/polypropylene) up to 400°C (e.g. lower than T_d), there is significant tensile strength retention at high temperatures due to the mechanical load borne by the 0° fibers [9]. To the authors' best knowledge; there are very few studies in the literature dealing with the mechanical behaviour under fire conditions [9-10]. Gibson et al. showed that the same mechanism appeared to control the failure in tension and compression (associated with the matrix melting) in TP-based composites (glass fibre reinforced PP laminates). In the case of creep loadings, the evolution of the creep stress at failure as a function of exposure time has been studied in composite materials with TP [9-10] and thermosetting (TS) [11] matrices. These studies highlight that damage mechanisms significantly depend on the applied creep stress as well as the testing temperature.

1.3 Objectives of the study

Before studying the coupling between thermal and mechanical behaviours in TP-based composites laminates, it is necessary to determine the characteristic temperatures (T_g, T_m, T_d). Thus TGA tests were carried out under anisothermal conditions and different atmospheres (inert or oxidizing) to investigate the

104 influence of temperature on the thermal decomposition of C/PPS composite and its constitutive materials.
105 From the knowledge of the characteristic temperatures, it is therefore possible to conduct mechanical tests
106 (monotonic tension and tensile creep) under isothermal conditions to specifically address the issue of
107 thermomechanical coupling within carbon fibers reinforced PPS laminates for testing temperatures ranging
108 from ambient temperature to temperatures higher than T_d.
109
110 **2. Material and methods**
111 **2.1 Materials and specimens**
112 The studied composite materials are carbon fabric reinforced laminates consisting of a semi-crystalline
113 high-performance PPS supplied by the Ticona company. The woven-ply prepreg, supplied by SOFICAR,
114 consists of 5-harness satin weave carbon fiber fabrics (T300 3K 5HS) whose weight fraction is 58%. The
115 prepreg plates are hot pressed according to a quasi-isotropic [(0,90)/(±45)/(0,90)/(±45)/(0,90)/(±45)/(0,90)]
116 stacking sequence. The glass transition temperature of the material is T_g=98°C and its melting temperature
117 T_m=280°C, as measured by DSC [12]. The degree of crystallinity of PPS matrix is close to 30% and the
118 initial porosity ratio is very small (less than 2%).
119
120 **2.2 Experimental set-up**
121 **2.2.1 Thermogravimetric Analysis (TGA)**
122 To carry out these experiments a thermo-gravimetric analyzer TA Instruments Discovery is used. Thermal
123 decomposition is characterized under three atmospheres: nitrogen, air and dioxygen. The gas flow rate is
124 set at 20 mL.min^{-1}.The extent of decomposition is characterized by a degree of progress in the reaction
125 defined by the following expression [13]:
126 $$\alpha = \frac{m_i - m}{m_i - m_f} \quad (1)$$
127 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.
128 When the analysis is carried out in an inert atmosphere, α corresponds to the degree of pyrolysis and its

129 value reaches 1 for a fully completed pyrolysis. Under oxidizing atmosphere, it corresponds to the degree
130 of decomposition and its value is 1 when the entire solid residue is completely gasified.

131 The thermal decomposition of studied materials (Plain PPS resin and C/PPS composite) has been
132 conducted using anisothermal heating at 10°C/min from room temperature to 700°C. These experiences are
133 supposed to be representative of the increase in material temperature during the transient phase of its
134 thermal response. However they are not suitable for clearly identifying the involved chemical mechanisms.
135 These analyses were conducted on samples whose initial mass is about 8mg.
136

137 **2.2.2 Porosities rate via density measurements**

138 The density of solids can be determined using the buoyancy method. The density is determined using
139 Archimedes' Principle. The upward buoyant force exerted on a body immersed in a fluid is equal to the
140 weight of the fluid the body displaces. Density determination using the buoyancy method is based on the
141 following formula [14]:

142 $$\rho = \rho_{fl} * \frac{w_a}{(w_a - w_{fl})} \quad (2)$$

143 Where ρ is the density of sample, ρ_{fl} is the density of buoyancy liquid, w_a is the weight of sample in air and
144 w_{fl} is the weight of sample in liquid. The density is determined by means of a densitometry balance
145 Sartorius Secura whose accuracy is 1mg.
146 Finally, the porosity rate or void fraction is therefore defined from the density of sample as follows:

147 $$P = 1 - \frac{\rho}{\rho_0} \quad (3)$$

148 Where ρ_0 is the density of the sample referred to as-received.
149 Specimens whose dimensions are 25*25*2.2mm where subjected to isothermal temperature conditions
150 (465-500-530°C) for different exposure times (5-10-20-30-40-60 min) in a primary vacuum furnace to
151 evaluate the changes in the residual mass associated with thermal decomposition. Specimens are put into
152 the furnace once the temperature is stabilized.

2.2.3 Tensile mechanical testing under isothermal conditions

The tensile mechanical behaviour under isothermal conditions is investigated using a uniaxial servo-hydraulic machine MTS, equipped with hydraulic grips and a load cell with a 100kN capacity. Stable and homogeneous temperature conditions are applied by means of a tube furnace composed of 3 zones, which is positioned between the grips of the machine. High temperature testing conditions (e.g. temperatures close to or higher than polymer matrix decomposition temperature) usually requires samples with a specific geometry because temperatures are sometimes beyond the range of testing ovens. In the present case, the dimensions of the tube furnace make it necessary to use specimens with a gage length of 20cm long (Fig. 2). The tensile mechanical properties were determined according to the European standards EN 6035 [15]. The axial modulus (E_x) and ultimate strength (σ^u) were calculated from the following definitions:

$$E_x = \frac{\Delta F}{S.\Delta\varepsilon_x} \quad \text{and} \quad \sigma^u = \frac{F^u}{S} \tag{1}$$

Where ΔF is the difference in the tensile loads at $(\varepsilon_x)_2 = 0.25\%$ and $(\varepsilon_x)_1 = 0.05\%$,

S is the specimen cross section,

$\Delta\varepsilon_x = (\varepsilon_x)_2 - (\varepsilon_x)_1$ is the difference in the axial strains obtained from the cross machine displacement,

F^u is the maximum force borne by the specimen at failure.

Estimation of the axial stiffness under different isothermal conditions

The evolution of the axial stiffness E_x with temperature was measured from the following experimental protocol:

- Heating to a temperature T1 at 50°C/min,
- Two minutes at T1 (to ensure the temperature homogeneity through-the-thickness),
- Mechanical loading (50 MPa) then unloading at 0 MPa,
- Measurement of axial stiffness during unloading (the low viscosity of the matrix can cause the extensometer to slip during loading),

The testing temperatures range from ambient temperature to 520°C.

Tensile response to failure under different isothermal conditions

The monotonic tensile behavior at failure was investigated under different isothermal conditions. As for stiffness measurements, the specimens are heated to 50°C/min and then maintained at the test temperature for 2 minutes to ensure homogeneity of the temperature through-the-thickness. The tensile test is conducted in cross machine displacement-controlled mode at a rate of 2 mm.min-1. The ultimate tensile strength and tensile behaviour have been studied for temperatures representative of four different material states:

- 220°C: rubbery state of the PPS matrix between Tg (Glass transition) and Tm (Melting),
- 270°C: slightly melted material,
- 320°C: completely melted material,
- 470°C: slightly decomposed material.

Tensile creep behavior under isothermal conditions

Finally, creep tests were performed on quasi-isotropic C/PPS specimens according to the following experimental protocol:

- Tensile mechanical loading (loading time = 10 seconds)
- Temperature increase from room temperature to 320°C at a rate of 25°C.min-1. This temperature is selected because the failure behaviour at this temperature has been characterized in the case of monotonic tensile tests.
- Both mechanical loading and temperature level (320°C) are maintained.

It has been chosen to apply the mechanical force first and then the temperature increase because it corresponds to the succession of solicitations an in-service material would have to face in the event of fire. At the laboratory scale, a mechanically loaded sample is suddenly subjected to a heat flux applied by means of a tube furnace. The creep levels tested vary between 8 and 31% of the ultimate strength σ_u at ambient temperature). These stress levels are chosen such as to analyze the tensile behavior for tensile loadings lower and higher than the onset of necking.

3. Results and discussion

3.1 TGA tests

Before considering mechanical testing under different isothermal conditions, it is utmost important to investigate the thermal decomposition of plain PPS matrix and C/PPS laminates by means of TGA tests under anisothermal conditions and different atmospheres (inert and oxidizing), with a particular attention paid to the determination of decomposition temperature [16-17]. An inert atmosphere is representative of what specimens undergoes at core with respect to what specimens experience in an oxidizing atmosphere at the outer surface.

Under dioxygen, the thermal decomposition of PPS begins at 502°C, approximately the same temperature as under an inert atmosphere (see Table 1). The curve representing the Mass Loss Rate (MLR) of plain PPS resin as a function of temperature $MLR = f(T)$ is characterized by 3 peaks (see Figure 3). The first peak corresponds to a mass loss of about 15%. Thus it may be associated with the first pyrolysis mechanism, depolymerization (Figure 4b). Following this reasoning, the second peak, which extends to $\boldsymbol{\Delta m = 37\%}$, may be associated with the second pyrolysis mechanism. Even before the pyrolysis ends a new mechanism starts and may be associated with the simultaneous oxidation of PPS matrix and the pyrolysis residue as it extends until the entire initial material is carbonated (Figure 4a). The maximum oxidation rate is virtually 3 times higher than the pyrolysis rate.

The decomposition of carbon fibre-reinforced composites under oxidizing atmosphere is faster than the one of other fibers-reinforced composites (e.g. glass fibers), because carbon fibres are sensitive to oxidation phenomena just like polymeric matrices. For practical reasons decomposition under air has been little studied, as the oxidation phenomena are mainly characterized with TGA analyses under dioxygen. In C/PPS, thermal decomposition under air begins at 517°C compared to 483 and 515°C under N_2 and O_2 respectively (see Table 1). Thus the mechanisms of crosslinking and improvement of thermal resistance observed under O_2 do not appear to occur under air. Oxidation appears to start faster under O_2 simply because there are more reactive species and the atmosphere is more oxidizing.

Similar observations have already been made by Ma et al. in the study of the decomposition of C/PPS under air [18]. When heated in an oxidizing atmosphere at temperatures higher than its melting temperature, PPS can crosslink like a thermosetting polymer thus having a higher thermal stability. If the delay in the onset of decomposition is only observed in C/PPS composite, this suggests that these phenomena are promoted by the presence of fibres. As for plain PPS resin pyrolysis and char oxidation overlap in the C/PPS. Nevertheless the fact that the second peak of MLR ends with a mass loss of 43% equivalent to the matrix mass in the composite, it tends to indicate that oxidation of char and fibres occurs separately and not simultaneously (Figure 4).

Under air, the thermal decomposition of PPS begins at 508°C. For the same heating rate, decomposition begins at 503°C and 502°C respectively under N_2 and O_2 (see Table 1). Pyrolysis results in a mass loss of 39%, which is lower than that observed under inert atmosphere (Figure 5a), which is consistent with the observations made in the case of a PEEK resin by Patel et al [19-20]. As under dioxygen, oxidation begins before the pyrolysis ends. Nevertheless the appearance of the characteristic peak of pyrolysis on the MLR curve $MLR = f(T)$ indicates that pyrolysis is almost completed when oxidation begins under air (Figure 5b) while it did not even reach its maximum rate when this transition occurs under O_2.

3.2 Determination of porosities rate as a function of the degree of decomposition

C/PPS laminates specimens undergo different degrees of thermal decomposition when they are subjected to isothermal conditions for different exposure times in a primary vacuum furnace (oxidizing atmosphere). Three temperature levels (465-500-530°C) and 6 exposure times (5-10-20-30-40-60 min) were considered to induce changes in the residual mass associated with thermal decomposition. From the evaluation of the residual mass it is therefore possible to assess the changes in the degree of decomposition vs time according to Eq. (1), as well as the porosity rate vs time with Eq. (2) and (3). Figure 6a represents the evolution of specimens' residual mass as a function of the exposure time at given temperatures. The initial decrease in the residual mass is all the more significant than the testing temperature is elevated. As a consequence, the degree of decomposition ranges from 50 to 80% after a 5 minutes exposure (Fig. 6b). The

255 transient stage lasts about 10 minutes before the mass loss and the degree of decomposition reach a
256 stationary state (Fig. 6). During the transient stage, the higher the test temperature, the higher the thermal
257 decomposition rate is contrary to what is observed during the stationary stage. After a 40 minutes exposure,
258 all the curves representing the degree of decomposition vs time converge, suggesting that regardless the
259 testing temperatures, the differences in the thermal decomposition kinetics ultimately result in the same
260 degree of decomposition. Finally, figure 7 represents the porosity rate as a function of the degree of
261 decomposition for the different testing temperatures. It appears that all the experimental points virtually
262 follow the same evolution to reach a plateau corresponding to about 35% of porosities within the
263 specimens. From these curves, one can assume that the porosities rate is very well correlated with the
264 degree of decomposition. The knowledge of the porosities rate is important as porosities within the
265 laminates are stress concentrators contributing to the degradation of the mechanical properties.
266

267 **3.3 Tensile mechanical testing under isothermal conditions: monotonic loading**
268
269 **3.3.1 Evolution of axial stiffness with temperature**

270 The evolution of the axial stiffness under different isothermal conditions is shown in Figure 8. The material
271 initially loses 14% of its axial stiffness when testing temperature becomes higher than the glass transition
272 temperature of the PPS matrix (about 98°C, see section 2.1). This decrease may be attributed to the
273 decrease in the shear modulus of the ±45° plies during softening of the matrix (-67% at Tg [21]). Above the
274 glass transition temperature, the axial stiffness of the laminate decreases gradually up to 220°C. This
275 phenomenon is associated with the decrease in shear strength of the PPS matrix and the fibre-matrix
276 interface as the viscosity of the matrix increases.
277 There is a significant drop in axial stiffness for a temperature taken between 220 and 270°C. This can be
278 linked to the melting of the matrix (T_m=280°C, see section 2.1) and the significant degradation of the fiber-
279 matrix interface. Indeed, according to the results of DSC [12], the melting occurs between 220 and 295°C
280 (even if the shape of the melting peak suggests that most of the crystalline zones are destroyed around
281 280°C). After melting, the ±45° plies no longer play a mechanical role because their behaviour is driven by

282 the matrix. Beyond that temperature, the material has a residual stiffness equal to 58% which comes solely
283 from the contribution of 0/90° oriented plies. The latter initially bear 73% of the load (according to
284 laminate theory), the decrease in their stiffness after melting can be estimated at 19%. These observations
285 are in agreement with the results obtained by Mahieux el al. on a C/PPS laminate [22]. Thus, the stiffness
286 reductions of constitutive elements considered individually do not explain the decrease with temperature
287 observed in the C/PPS composite laminates. The PPS has a stiffness 100 times lower than that of the
288 carbon fibres, which virtually retain their initial stiffness at this temperature level. The decrease in the
289 stiffness of the 0/90° plies may result from other damage mechanisms such as the appearance of transverse
290 cracks at the interface between strands and matrix. These mechanisms are suspected to take place mainly at
291 the overlap areas of the longitudinal and transverse strands as a consequence of the stress concentration
292 induced by longitudinal strands (mechanically loaded) on the transverse strands (Fig. 9), as well as
293 metadelamination.
294 Above the melting temperature, the axial stiffness no longer changes, at least until 520°C (maximum
295 temperature studied). When the ±45° plies have lost all rigidity after PPS melting, the axial stiffness of the
296 material is mainly due to the stiffness carbon fibres parallel to the loading direction, which is virtually
297 unchanged up to 1000-1400°C (depending on the fibres) in an inert atmosphere [23]. Then the longitudinal
298 stiffness of the composite is assumed to be virtually unchanged up to these temperatures, unless fibres
299 undergo oxidation. However these assumptions cannot be confirmed here because the behaviour of C/PPS
300 could not be characterized for temperatures higher than 520°C due to the ignition of pyrolysis gases into
301 the tube furnace.
302
303 **3.3.2 Tensile response to failure under different isothermal conditions**
304 Figure 10 shows the influence of different isothermal conditions on the tensile response of quasi-isotropic
305 C/PPS laminates whose mechanical behavior is fibre-dominated. The ultimate tensile strength dramatically
306 decreases (about 25% of its initial value – see Table 2) between room temperature to 470°C (lower than the
307 onset decomposition temperature). At 220°C, the material exhibits a quasi-linear behaviour with a bending

308 at around 180 MPa (referred to as knee point in the literature [24]) characteristic of matrix cracking, which
309 occurs most frequently in overlapping areas of strands (Figure 9a). The catastrophic failure is driven by the
310 0° fibres whose elongation at failure is significantly lower than the PPS matrix one. The observation of
311 specimens surfaces show a womb type failure surface resulting from the poor adhesion of the fibre-matrix
312 interface, which is often observed in composites with thermoplastic matrices. This poor adhesion is
313 promoted by the high temperatures and low viscosity of the matrix (Fig. 11).
314 At 270°C, the behaviour remains generally elastic-fragile, with a noticeable inflection around 25 MPa. This
315 non-linearity is associated with the localized crushing of the strands in the overlap area, which first results
316 in: (i) deformation localization in resin-rich areas and (ii), only then, in matrix cracking. On the front and
317 rear faces of the specimens, the surface crack densities is more important than at 220°C (Fig. 9b). The
318 ultimate stress is between 2 and 3 times lower than at 220°C and the elongation at failure is about 20%
319 lower, which means that damage can also be explained by the higher density of inter- and intra-laminar
320 cracks than at 220°C (Fig. 12).
321 For temperatures higher than T_m, significant changes in the mechanical response are observed. Before
322 melting, the fibres of the same strand are held by the matrix and elongate evenly within the strand. After
323 melting, the cohesion of the strand is no longer insured by the matrix, allowing significant transverse
324 contraction of the fibres and a more significant elongation. Thus, for stresses higher than 70 MPa, the
325 elongation of the 0° strands is accompanied by the generalization of the necking along the 0° direction.
326 This necking ultimately results in a generalized necking of the 90° oriented plies, which greatly increases
327 the bending force at the crimp (where the warp strands undulate over the weft strands) and leads to the
328 misalignment of the strands (Fig. 13a).
329 Beyond a certain elongation, the generalization of necking is such that the transverse strands are strongly
330 crushed by the longitudinal strands. Such crushing leads to significant out-of-plane displacements resulting
331 in surface bending effects and extensive delamination (Fig. 14). In ±45° plies, the fusion of the matrix is
332 accompanied by a reorientation of the strands in the direction of solicitation. They then undergo a shear
333 stress at the level of their overlapping areas. The space between the strands decreases until they enter the

334 contact, causing the rotation to be blocked and their transverse contraction to begin [25]. The transition
335 between the two phenomena (reorientation and compaction) is characterized as follows by a "shear
336 locking" angle. When the specimen is elongated, the compaction increases and results in the stiffening of
337 rotation of ±45° plies leading to the increase in laminates axial stiffness.
338 For temperatures higher than T_m, the actual failure of the specimens could not be observed. Indeed, the
339 necking of 0°strands extends along the 0° direction until it reaches the area of the specimen taken in the
340 machine grips. Necking generalization is associated with an elongation of approximately 40% and a
341 significant reduction (about 25%) in their initial diameter (Fig. 13b). Tensile tests suggest that both
342 deformation and damage mechanisms significantly change in C/PPS laminates subjected to monotonic
343 loading at temperatures higher than PPS matrix melting temperature. However, creep loadings are more
344 representative of the critical service conditions met by mechanically loaded composite parts exposed to a
345 fire scenario. From the tensile failure behaviour of C/PPS laminates investigated in this section, significant
346 changes in the monotonic thermomechanical behaviors are observed at temperatures higher than T_m. In
347 quasi-isotropic C/PPS laminates whose mechanical behaviour is driven by 0° plies, the rate-dependent
348 behaviour is very limited at temperatures lower than T_m [26], but it is expected to be much more important
349 at temperatures higher than T_m.
350

351 **3.3.3 Tensile mechanical testing under isothermal conditions: creep loading**

352 The evolution of time to failure as a function of tensile creep stress is shown in Figure 15. The time to
353 failure corresponds to the time elapsed since the application of mechanical loading. The time to failure
354 significantly decreases as creep stress increases. As a result, three specific failure mechanisms have been
355 identified in C/PPS laminates under creep loading depending on the applied creep stress:

356 • For a creep stress higher than $0.25\sigma_u$, the failure occurs even before the material reaches its
357 melting temperature. On the one hand, the failure therefore results from the decrease in the
358 mechanical strength of the ±45° plies (related to matrix softening and degradation of the
359 fiber/matrix interface). On the other hand, it is associated with the appearance of transverse cracks

and meta-delamination in 0/90° oriented plies (Fig. 9a and 12a). The failure mechanism is similar to that observed in figure 11, i.e. a transverse break of the fibres at 0°.

- For intermediate creep stresses ($0.11\sigma_u \leq \sigma_{creep} \leq 0.15\sigma_u$), failure occurs at the beginning of the creep test or in some cases shortly before the material has reaches 320°C. Thus, the failure can be associated with matrix melting and damage mechanisms similar to those observed during tensile tests at 320°C. The creep stress is then approximately equivalent to the one for which necking starts at 320°C (Fig. 10). The creep stress being higher than the stress levels where necking occurs in monotonous tensile tests, the deformation mechanisms that occur at that time (elongation of the longitudinal strands and crushing of transverse strands in 0/90° plies, reorientation of ±45° plies) will be initiated and developed within a few seconds, resulting in a deformation of the specimen without reaching ultimate failure, in agreement with the mechanisms observed during monotonous tension (Fig. 13b).
- For a stress lower than 60 MPa, there is an increase in the elongation of the specimen as temperature increases, but once 320°C is reached, the deformation no longer evolves. Indeed, despite matrix melting, the applied stress is too low to initiate necking.

4. Conclusion

In the literature, there are very few studies dealing with the mechanical behaviour of thermoplastic matrix composite materials beyond matrix melting temperature T_m. Through the results and discussion proposed in the present work, melting and thermal decomposition are instrumental to rule the tensile behavior of quasi-isotropic C/PPS laminates. Between the ambient temperature and T_m, the laminates axial stiffness decreases with increasing temperature, mainly due to the loss of stiffness of the ±45°oriented plies and the degradation of the fibre-matrix interface. Beyond T_m, the axial stiffness no longer changes, as long as no oxidation takes place. Conversely, matrix melting significantly influences the damage mechanisms within the laminate. The bonding of carbon fibres within the strands is no longer ensured, and the 0° strands experience necking resulting in a much higher elongation than the one observed before matrix melting.

This elongation comes along with other phenomena such as the reorientation of the ±45° plies and the crushing of transverse strands that are not observed before melting. Finally, for testing temperatures close to the onset decomposition temperature, porosities appear and grow within the laminates. The porosities rate is very well correlated with the degree of decomposition. The knowledge of porosities rate is utmost important as they are stress concentrators contributing to the degradation of the mechanical properties.

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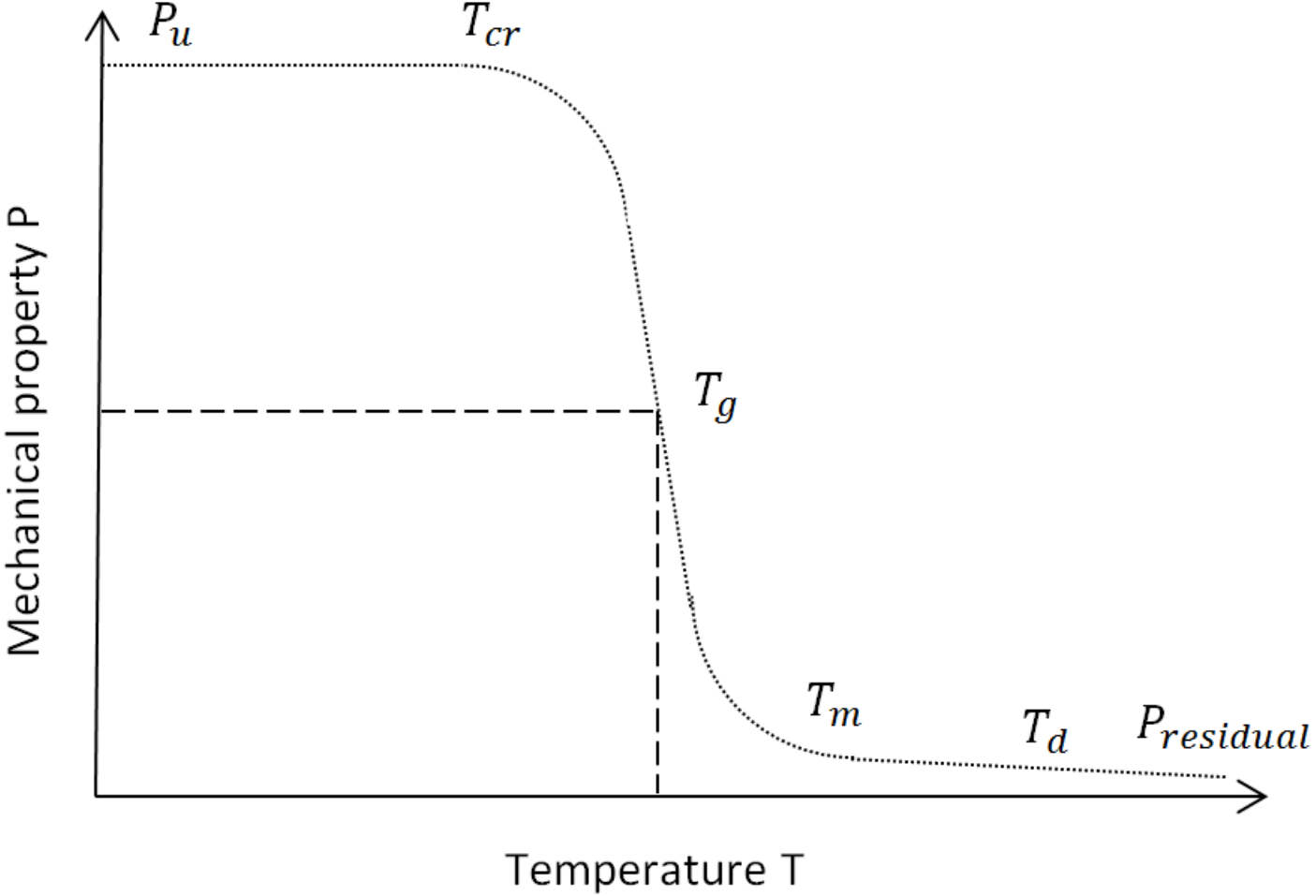
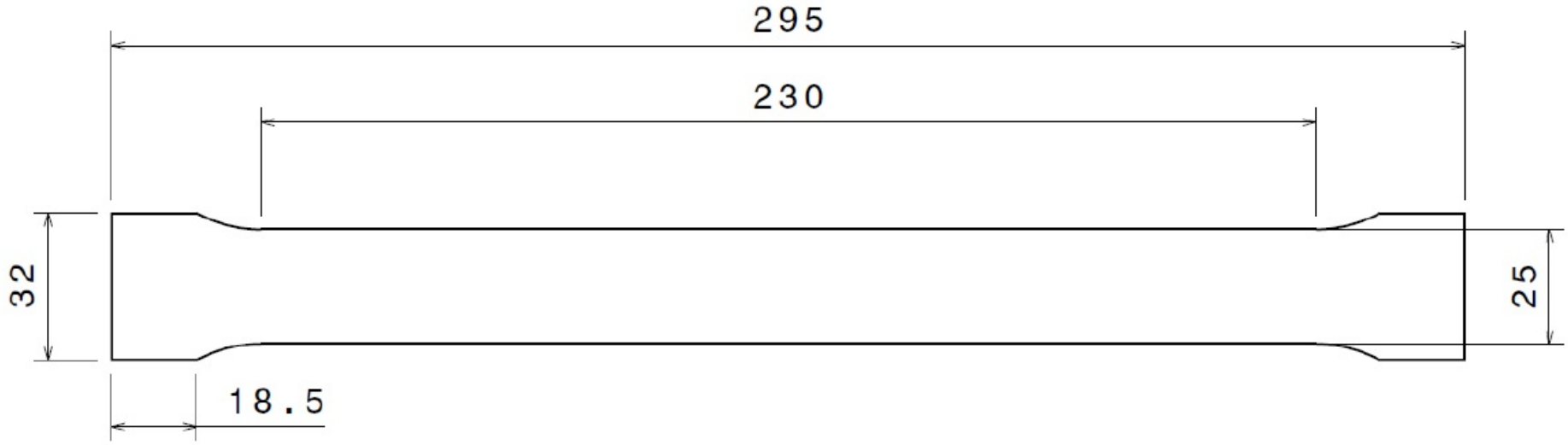
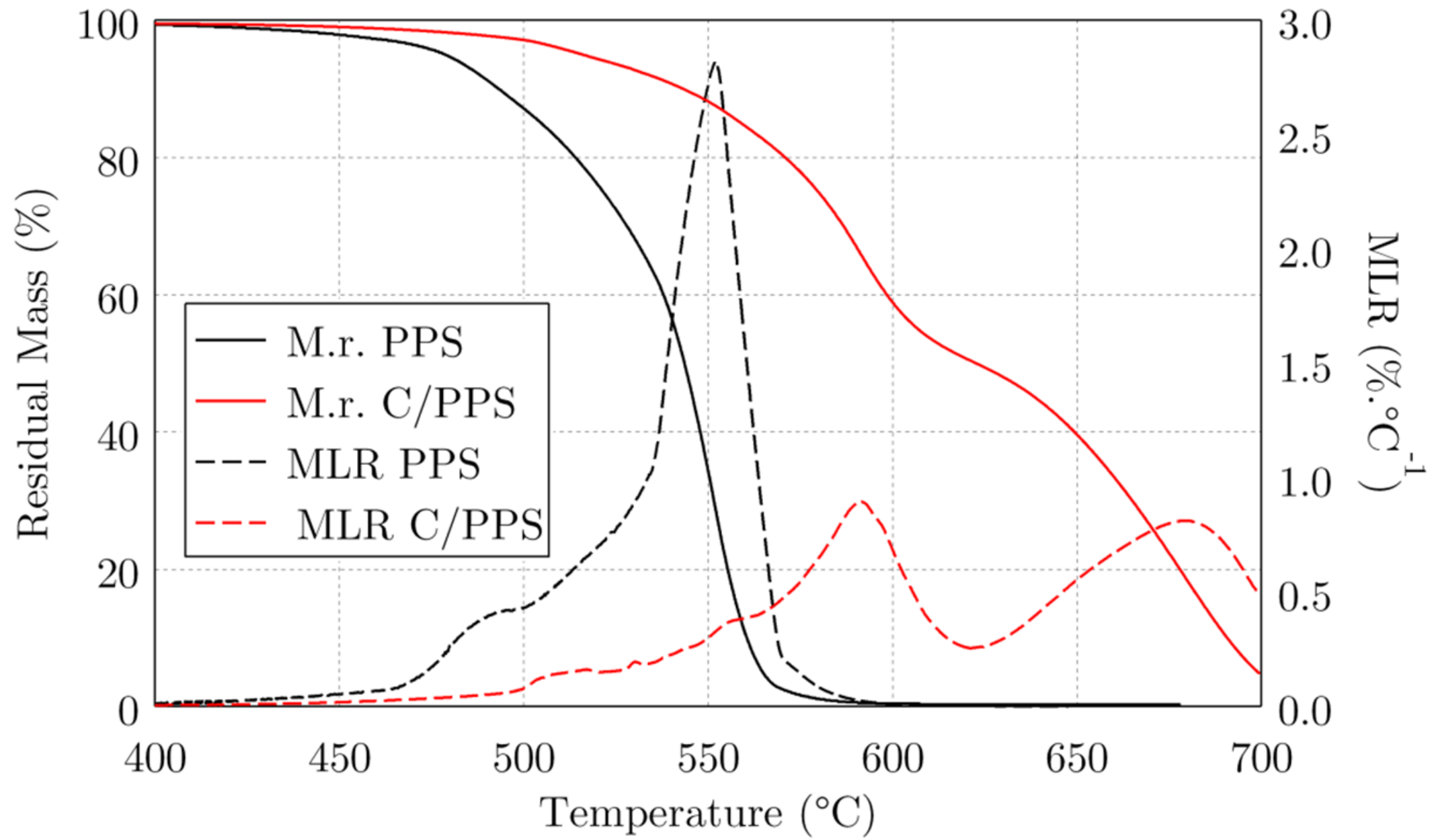
456 behavior of woven-ply PPS thermoplastic laminates at temperatures higher than glass transition
457 temperature. Composites Part A: Applied Science and Manufacturing 2013; 49: 165-178.
458
459

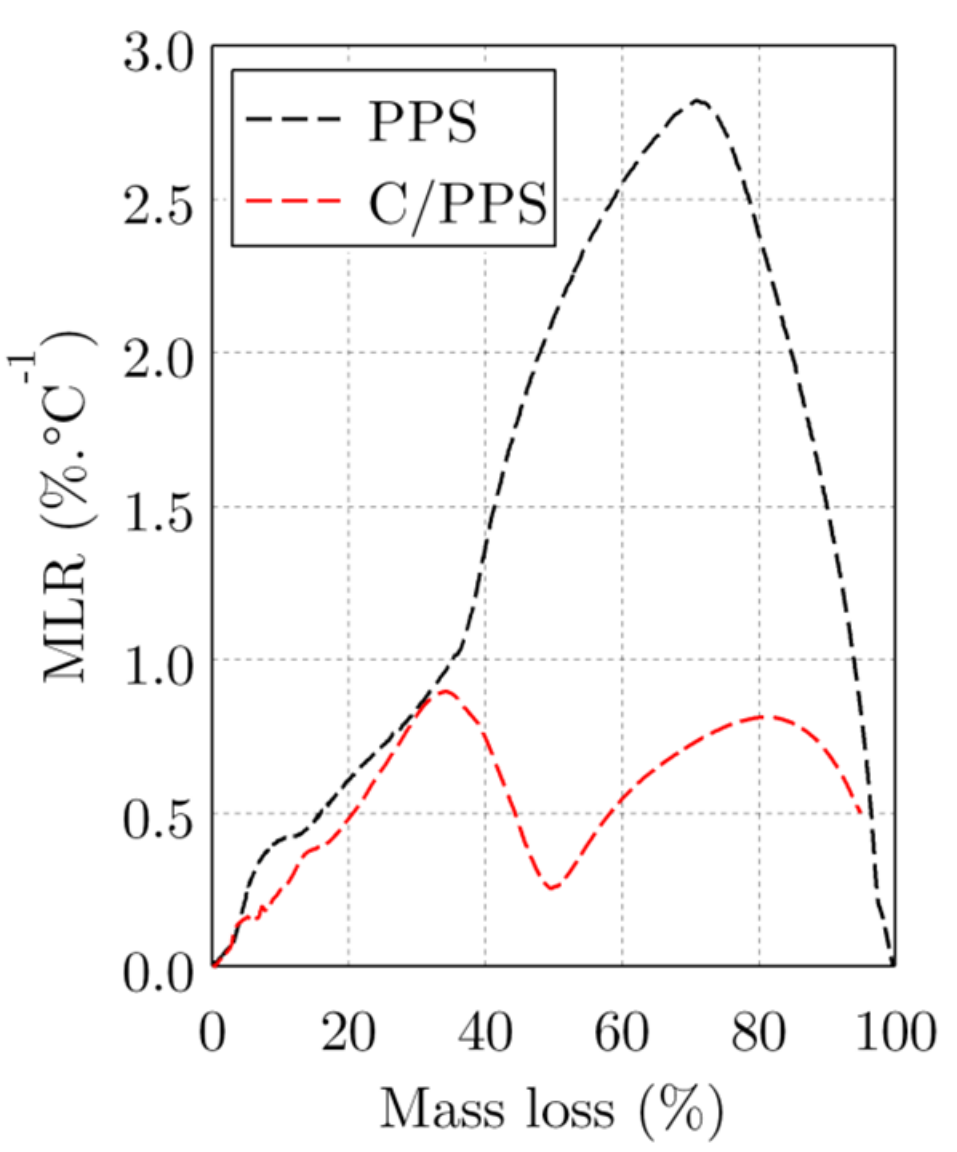
460 **List of figure**

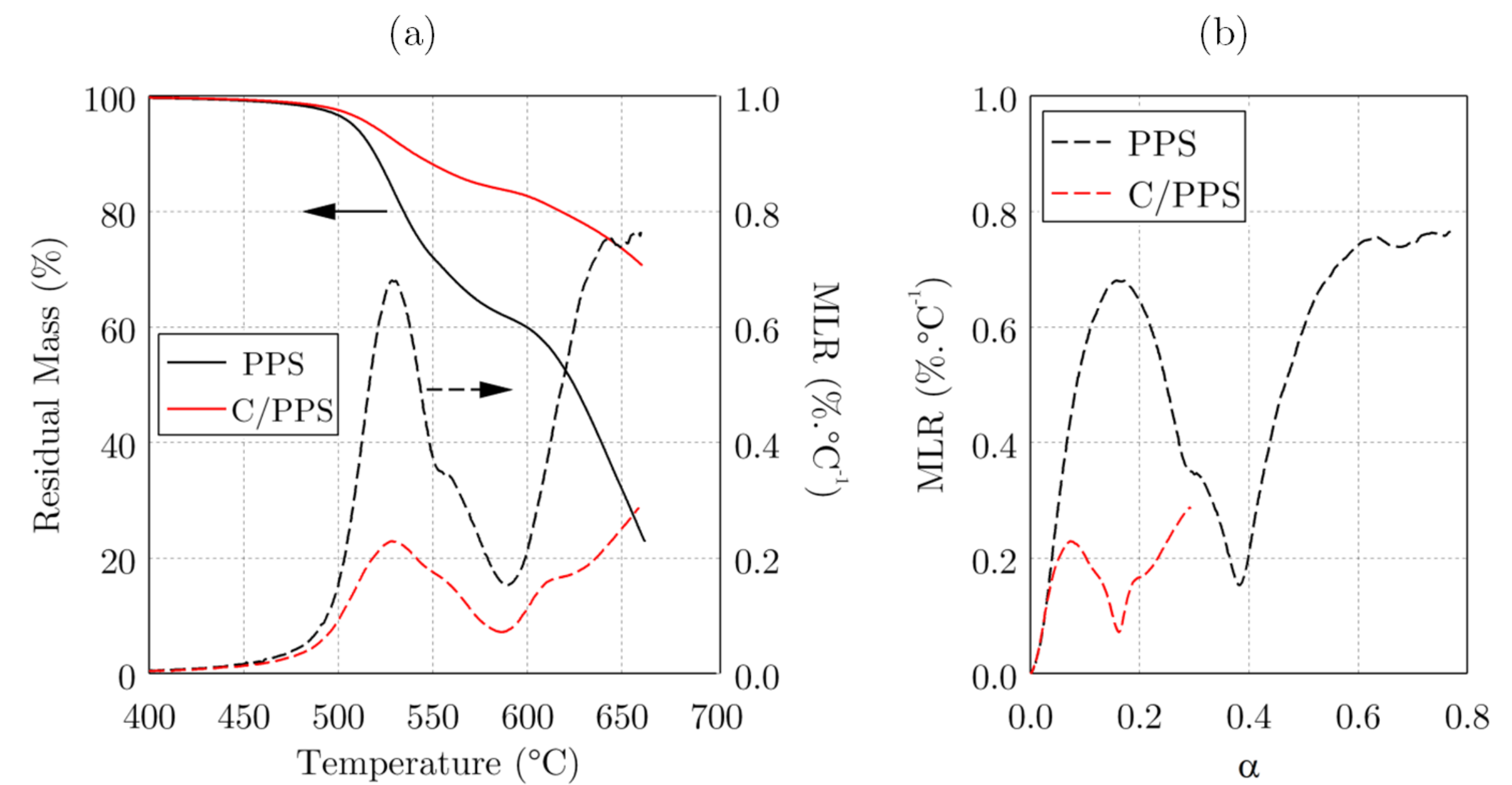
483


P_u
T_{cr}
T_g
T_m
T_d
$P_{residual}$
Mechanical property P
Temperature T

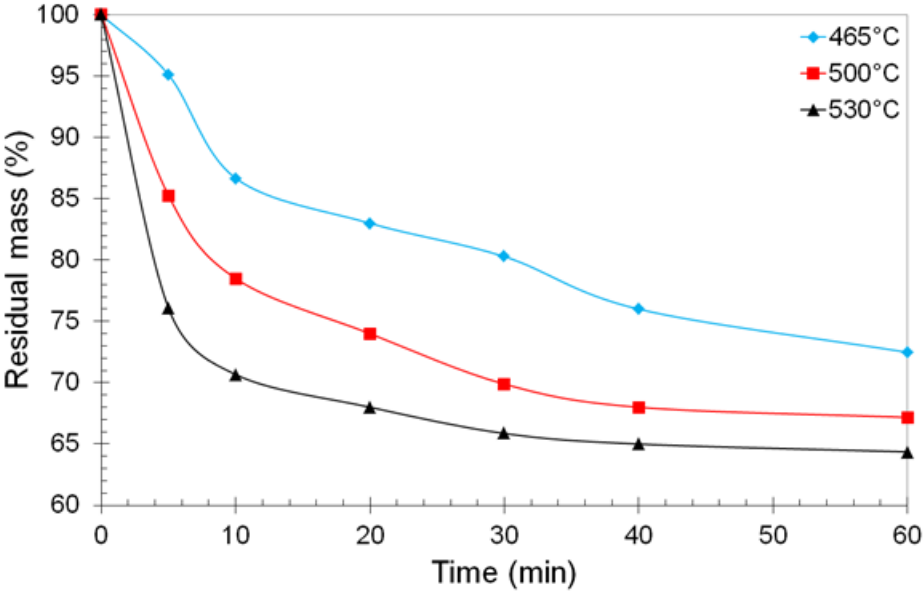

295
230
32
25
18.5


Residual Mass (%)
MLR (%.°C^{-1})
Temperature (°C)
M.r. PPS
M.r. C/PPS
MLR PPS
MLR C/PPS
100
80
60
40
20
0
3.0
2.5
2.0
1.5
1.0
0.5
0.0
400
450
500
550
600
650
700

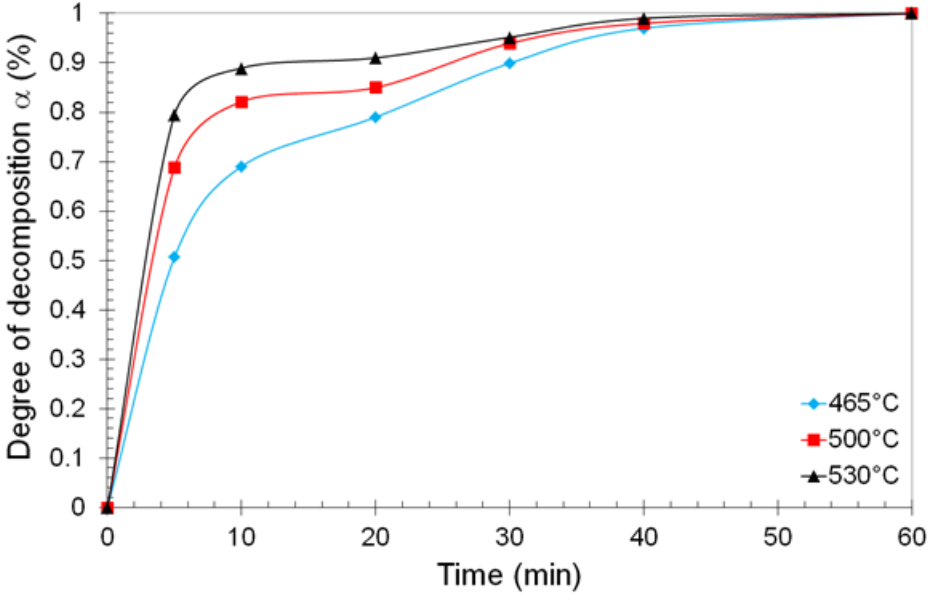

PPS
C/PPS
MLR (%.°C-1)
Mass loss (%)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
20
40
60
80
100

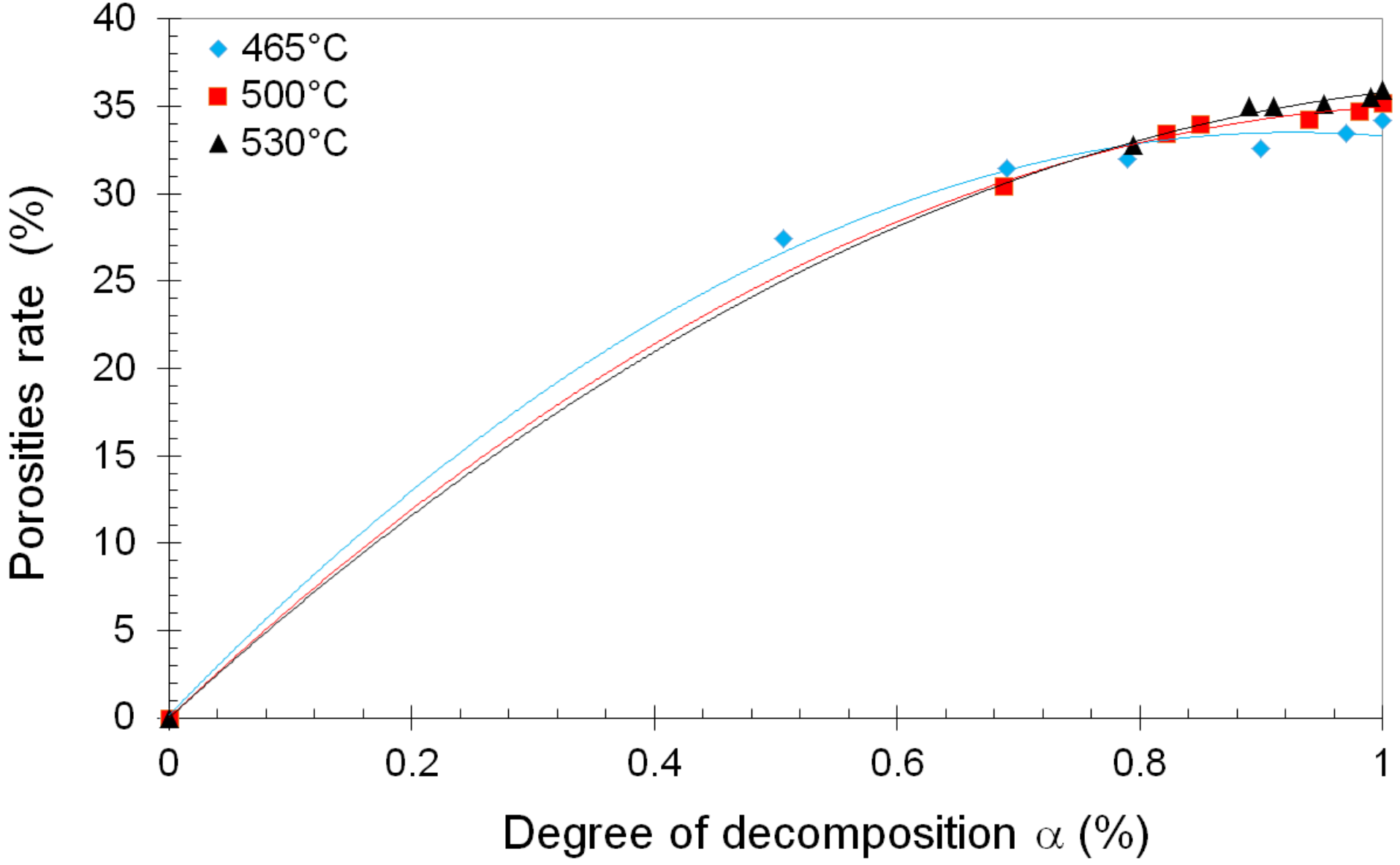

(a)
(b)
Residual Mass (%)
MLR (%.°C-1)
Temperature (°C)
PPS
C/PPS
MLR (%.°C-1)
α
0
20
40
60
80
100
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
650
700
0.0
0.2
0.4
0.6
0.8

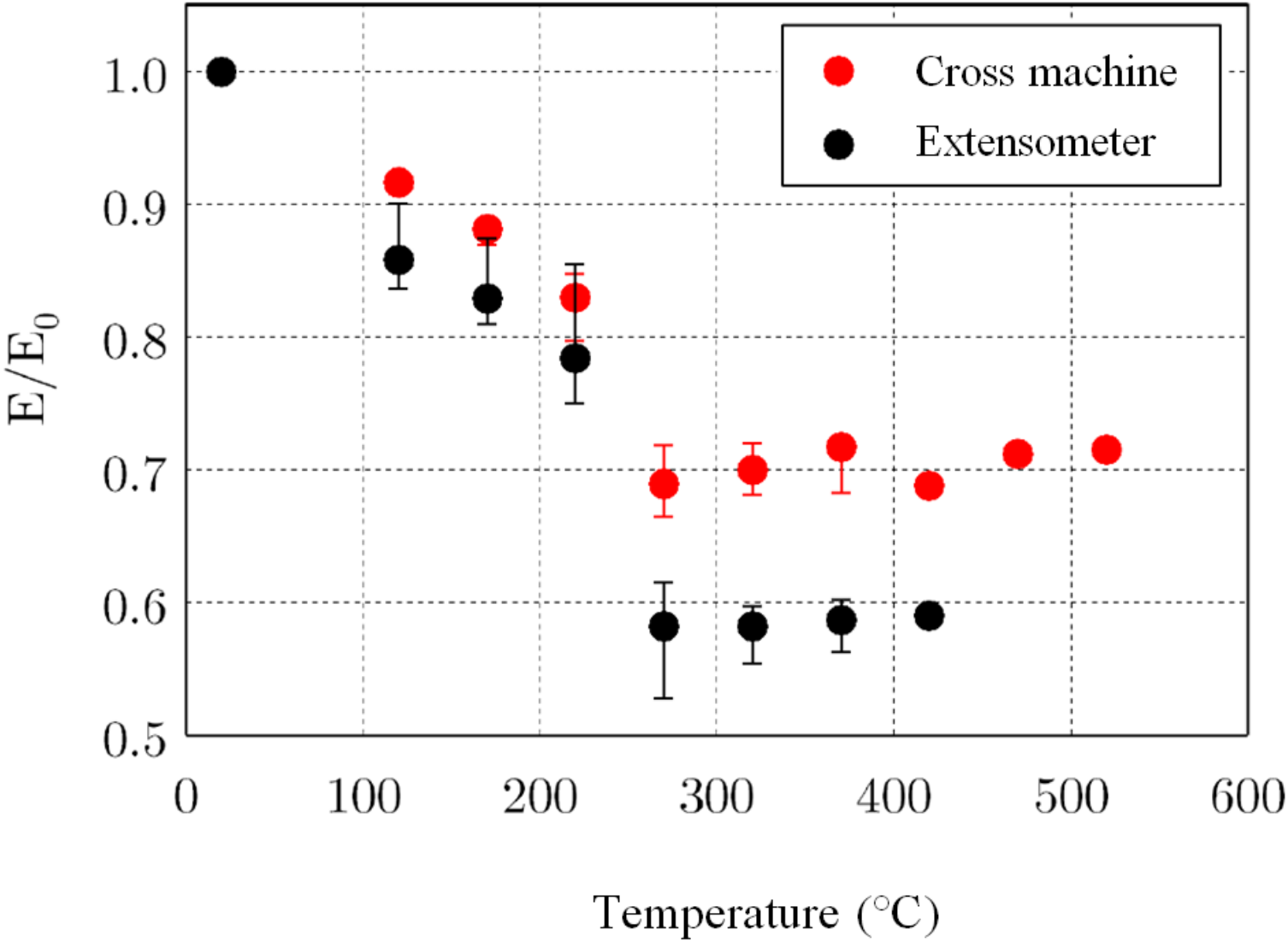
(a)

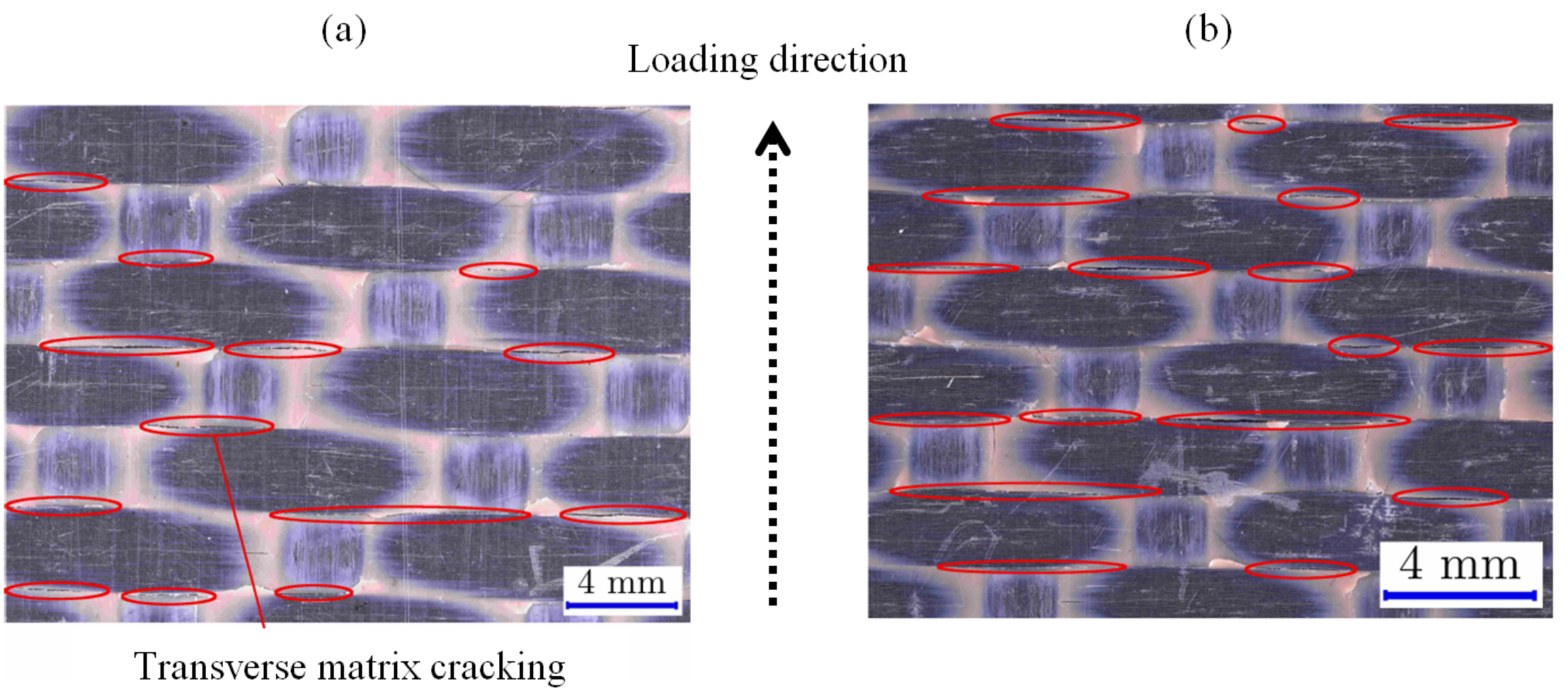

Residual mass (%)
Time (min)
465°C
500°C
530°C

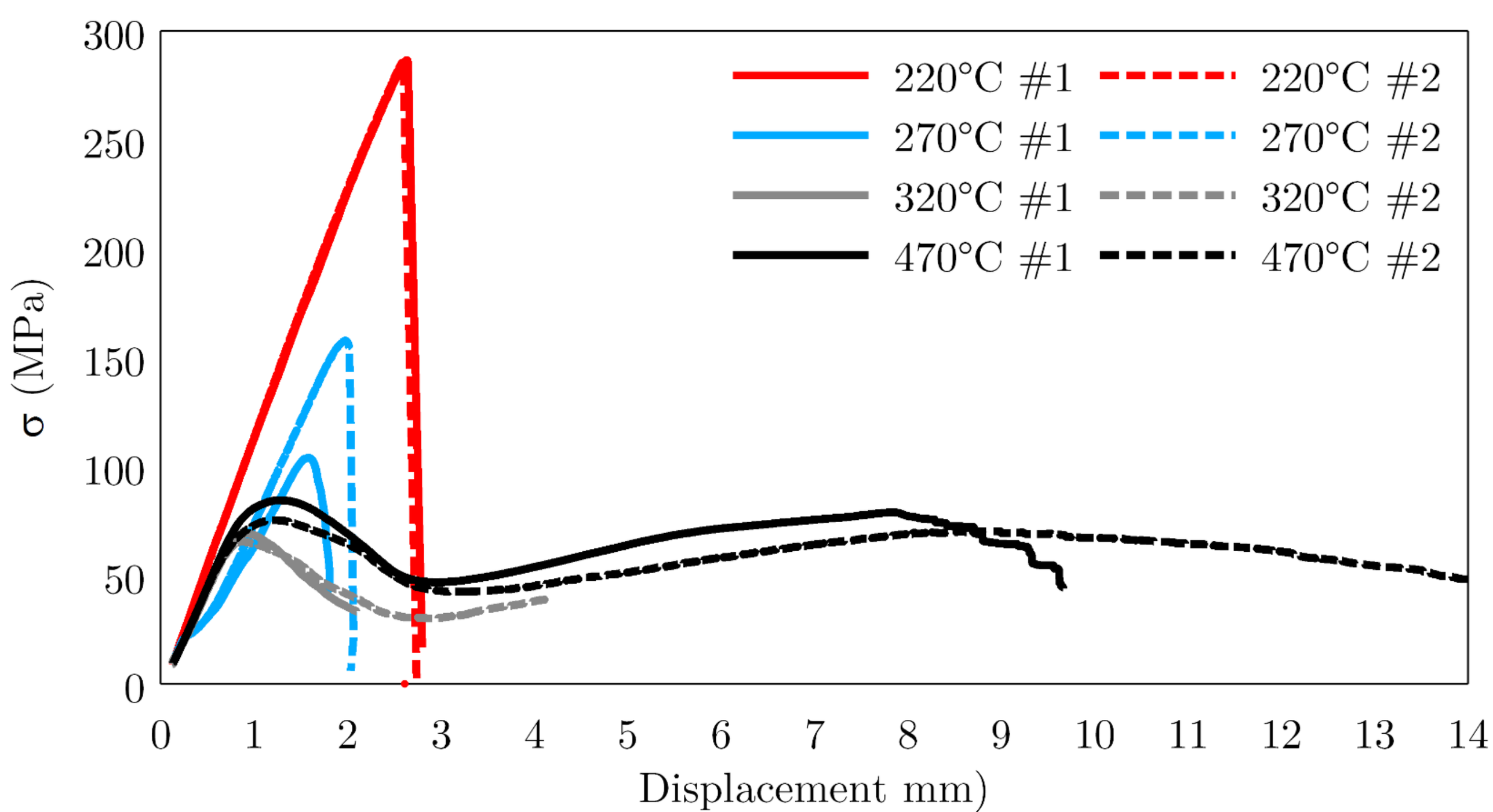
(b)

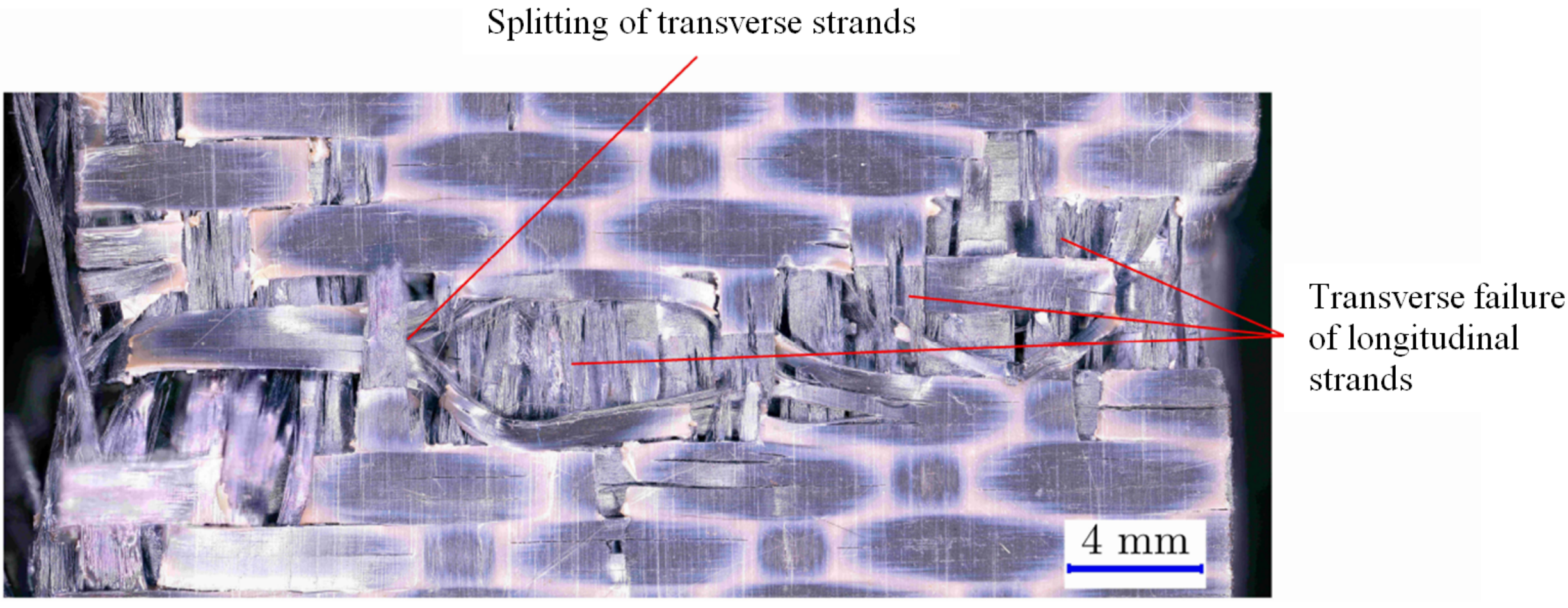

Degree of decomposition α (%)
Time (min)
465°C
500°C
530°C

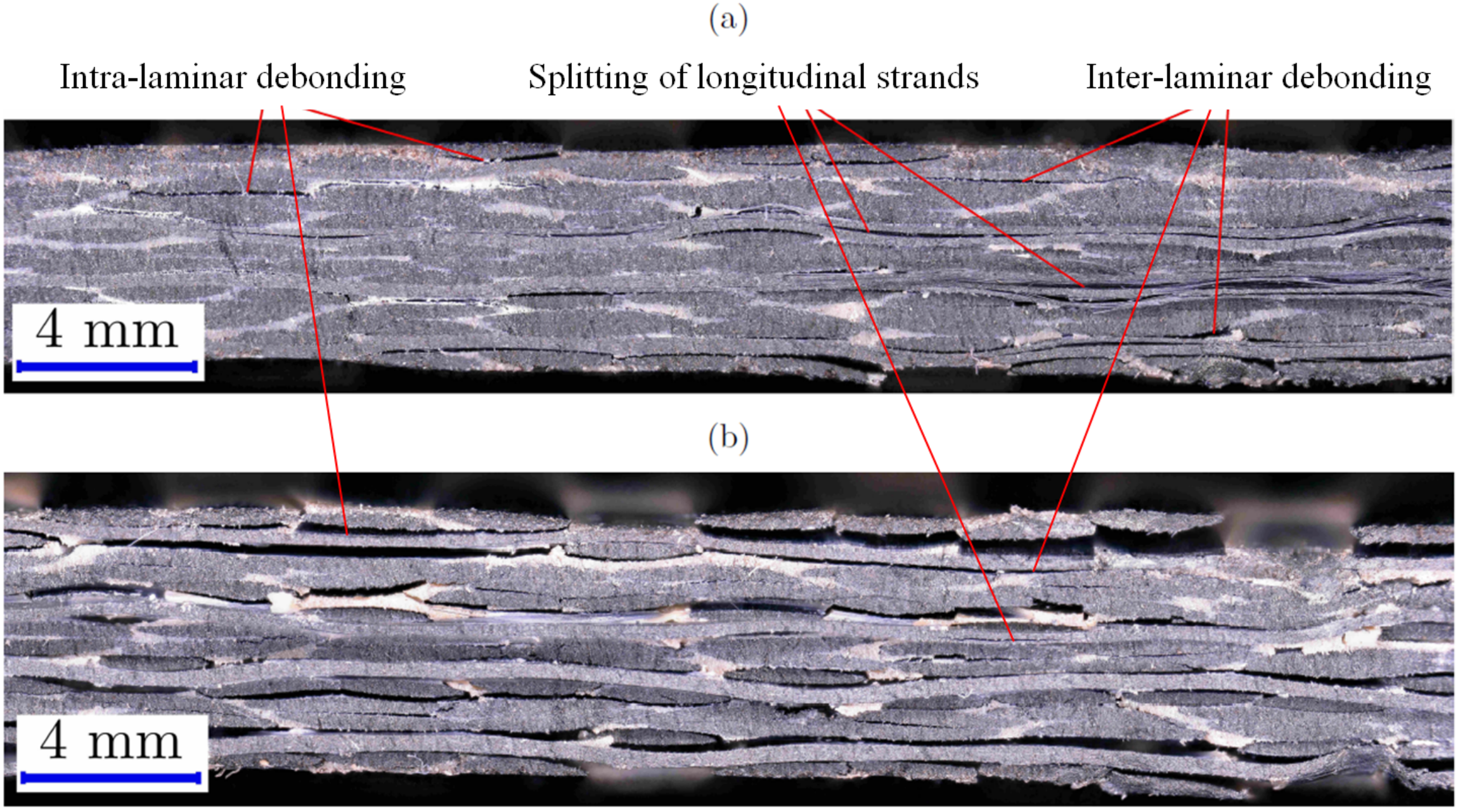

465°C
500°C
530°C
Porosities rate (%)
Degree of decomposition α (%)
0
5
10
15
20
25
30
35
40
0
0.2
0.4
0.6
0.8
1


Cross machine
Extensometer
1.0
0.9
0.8
0.7
0.6
0.5
E/E0
0
100
200
300
400
500
600
Temperature (°C)

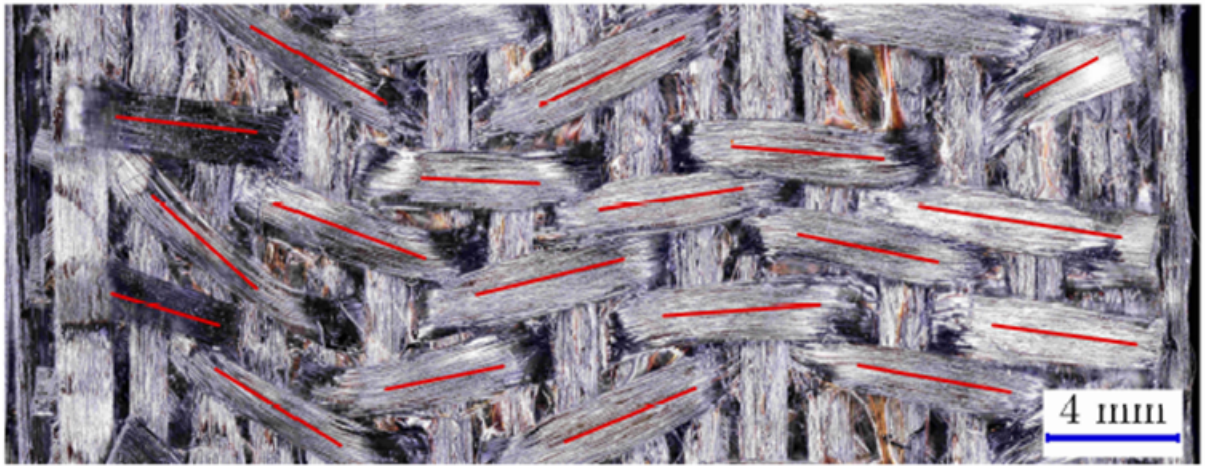

(a)
Loading direction
(b)
4 mm
4 mm
Transverse matrix cracking


300
250
200
150
100
50
0
σ (MPa)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Displacement mm)
220°C #1
220°C #2
270°C #1
270°C #2
320°C #1
320°C #2
470°C #1
470°C #2


Splitting of transverse strands
Transverse failure of longitudinal strands
4 mm

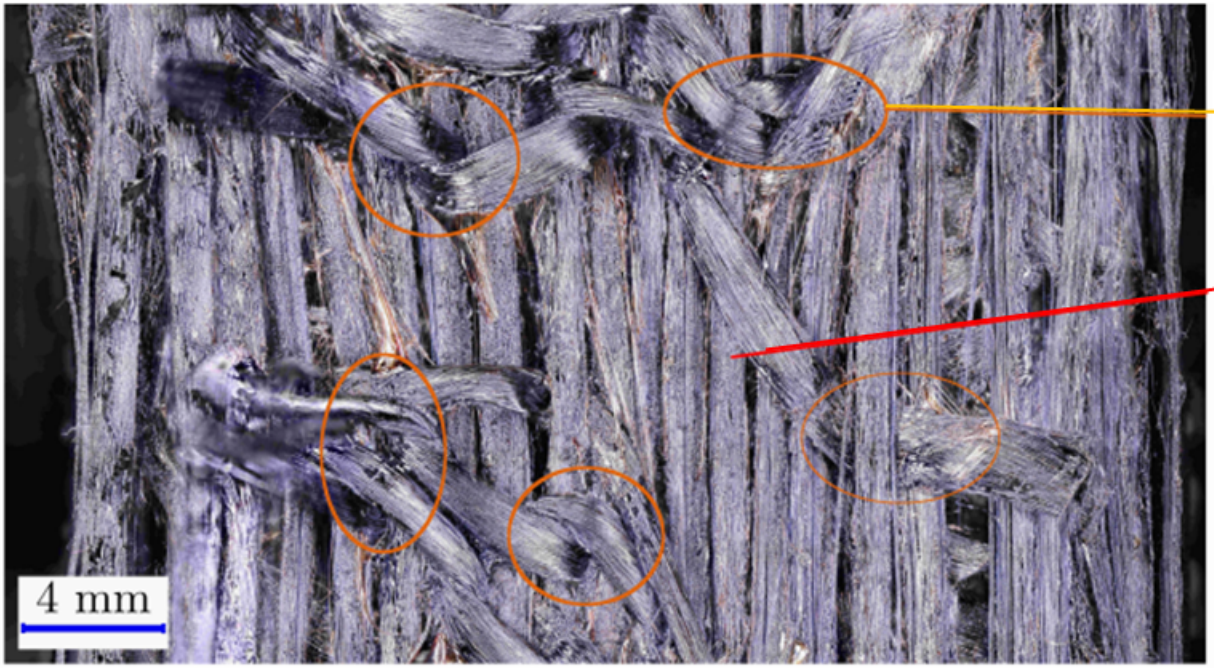

(a)
Intra-laminar debonding
Splitting of longitudinal strands
Inter-laminar debonding
4 mm
(b)
4 mm

(a)



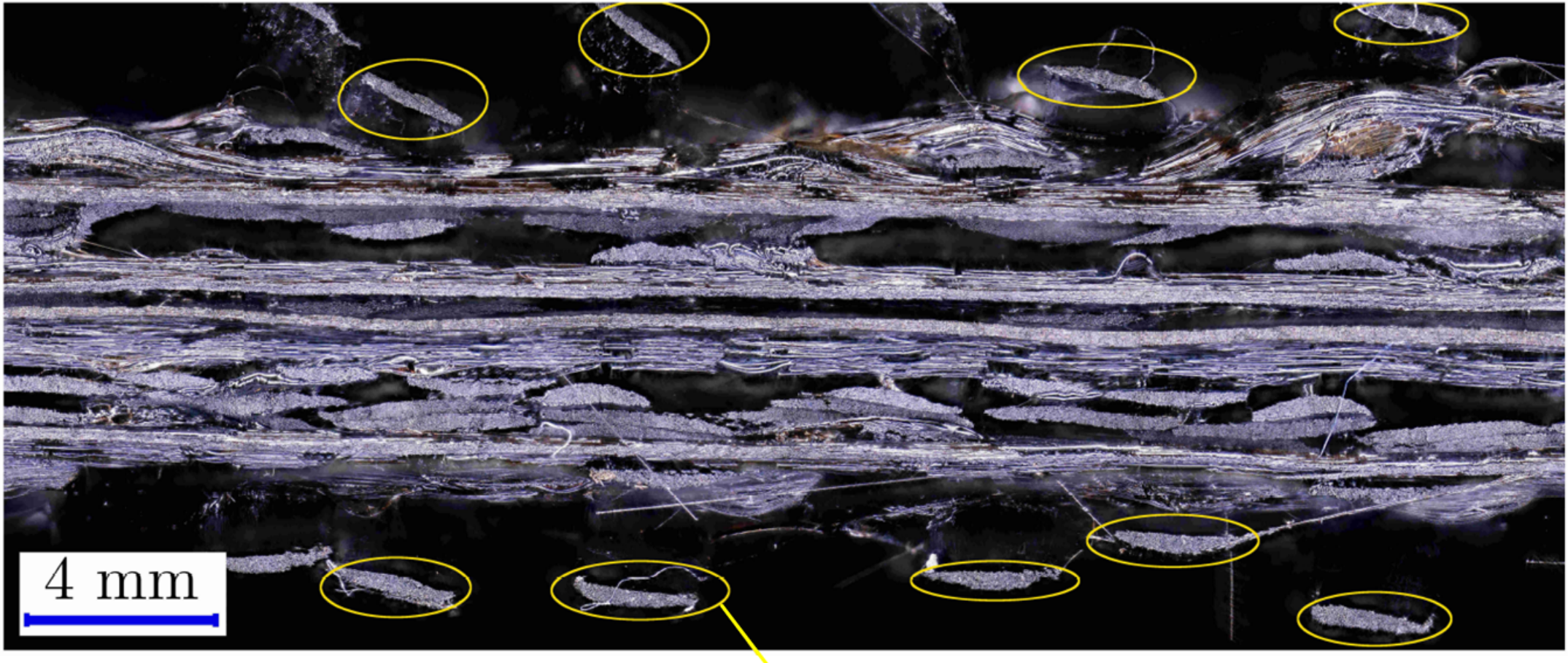
Disalignment of transverse strands

(b)

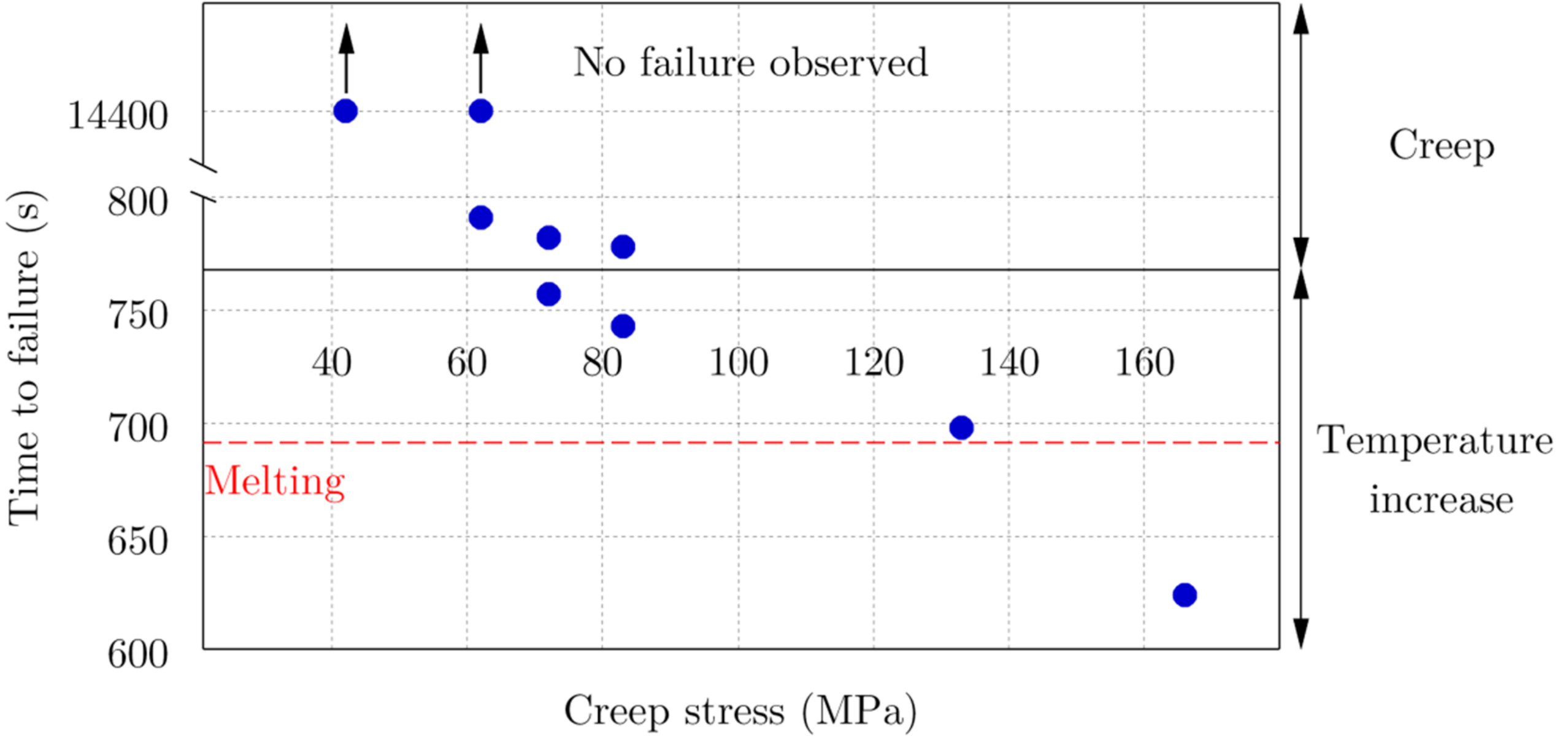


Crushing of transverse strands

Generalized necking of 0° strands



Delamination and bending of the transverse strands on the external plies


No failure observed
14400
800
750
700
650
600
40
60
80
100
120
140
160
Melting
Time to failure (s)
Creep stress (MPa)
Creep
Temperature
increase

Tables

	N_2	O_2	Air
Plain PPS resin	503°C	502°C	508°C
C/PPS composite	483°C	515°C	517°C

Table 1 - Temperature at the onset of decomposition of plain PPS and C/PPS composites under different atmospheres

	RT	220°C	270°C	320°C	470°C
$\boldsymbol{\sigma_u}$ $(\boldsymbol{MPa})$	514±8	286±1	131±38	68±3	80±6

Table 2 – Evolution of the ultimate tensile strength with temperature