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### ► To cite this version:

Théo Baumard, Arthur Lévy, Elissa El Rassy, Nicolas Boyard, Steven Le Corre, et al.. Development of a coupled diffusion-crystallization-degradation model during welding of paek thermoplastics. 23rd International Conference on Composite Materials (ICCM23), Jul 2023, Belfast, United Kingdom. hal-04208128

**HAL Id: hal-04208128**

**<https://hal.science/hal-04208128>**

Submitted on 15 Sep 2023

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# DEVELOPMENT OF A COUPLED DIFFUSION-CRYSTALLIZATION-DEGRADATION MODEL DURING WELDING OF PAEK THERMOPLASTICS

T. Baumard<sup>1\*</sup>, A. Levy<sup>1</sup>, E. El Rassy<sup>1</sup>, N. Boyard<sup>1</sup>, S. Le Corre<sup>1</sup>, J.L. Bailleul<sup>1</sup>, J. Bikard<sup>2</sup> and L. Trouillet-Fonti<sup>2</sup>

<sup>1</sup> Nantes Université, CNRS, Laboratoire de thermique et énergie de Nantes, LTeN, UMR 6607, F-44000 Nantes, France

<sup>2</sup> Solvay R&I, 69190 Saint Fons, France

\* Corresponding author (theo.baumard@univ-nantes.fr)

**Keywords:** Adhesion, Thermoplastic composites, Crystallization, Degradation

## ABSTRACT

The influence of crystallization and degradation on diffusion in PEEK is investigated experimentally in this work. The evolution of reptation time during degradation at temperatures above the melting point is evaluated from creep-recovery tests. Fast scanning calorimetry is used to quantify the evolution of crystallization kinetics with degradation, while the impact of crystallization on diffusion is described using literature data. A coupled model is proposed, based on a multiplicative decoupling of the effects of crystallization and degradation, and can be used to derive process diagrams to predict the degree of healing from a given temperature cycle.

## 1 INTRODUCTION

Welding of thermoplastic composites allows for the manufacturing of large structural parts without fasteners, which presents a clear advantage in the aerospace industry. During welding, the molten thermoplastic molecular chains can diffuse across the interface to form new entanglements. This diffusion process is classically described according to the reptation theory [1] as follows, where  $D_H$  is the degree of healing and  $t_w$  the welding time required to reach the maximum mechanical strength of the interface.

$$\frac{d(D_H^4)}{dt} = \frac{1}{t_w} \quad (1)$$

In the case of PAEK composites, recent experimental work [2] has shown a strong influence of crystallinity development on adhesion, as the formation of crystals restricts the mobility of molecular chains.

Polymer degradation, which in the case of PAEK occurs in the same temperature range as processing, is also detrimental to the weld strength. In this context, this work presents the development of an adhesion model taking into account the thermal history (degradation and crystallinity) of the material before welding, based on experimental characterization of rheological behavior, crystallization and degradation kinetics.

## 2 MATERIALS AND METHODS

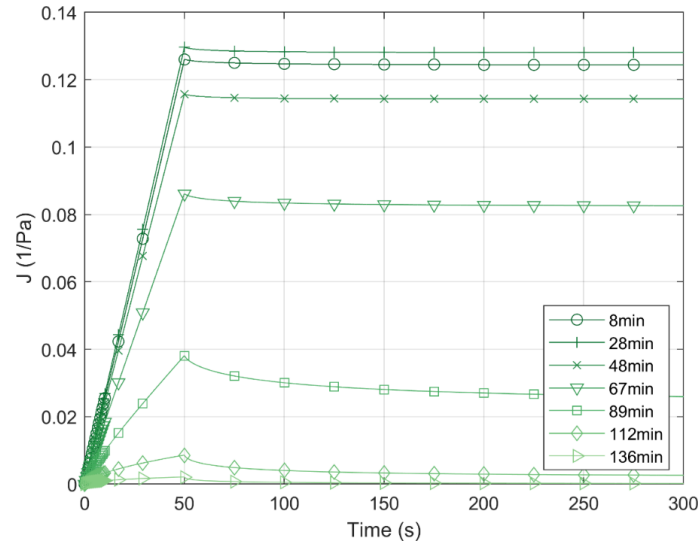
### 2 Materials and methods

The material used for this study is a low viscosity poly(ether-ether-ketone) (PEEK) grade supplied by Solvay.

#### 2.1 Rheometry

Rheological tests have been performed at temperatures between 360°C and 400°C using a Haake

Mars rheometer with plate-plate geometry. Initial tests have shown that the terminal regime is not accessible with frequency sweep tests down to 10-1 rad/s. Consequently, successive creep-relaxation tests have been used to determine the long relaxation times (equivalent to  $t_w$ ) as a function of the dwell time during isothermal degradation. The results of these successive tests is shown in Figure 1 for various degradation times at 380°C. The material behaves initially as a viscous fluid ; as the degradation times increases, crosslinking leads to a more viscoelastic behavior with noticeable recovery.



**Figure 1 - Creep-relaxation tests at 380°C**

The relaxation times are evaluated directly from the creep recovery tests using the Cox-Merz equation (2).

$$\tau_w = J_e^0 \eta \quad (2)$$

A marked increase of the relaxation time is observed with degradation, from 0.3s in the virgin material to approximately 100s after 20min at 400°C under air, because of the crosslinking of the polymer which restricts the movement of the macromolecules [3]. As expected from the literature, higher test temperatures lead to faster degradation kinetics. The relaxation time also increases faster for tests conducted under air compared to nitrogen.

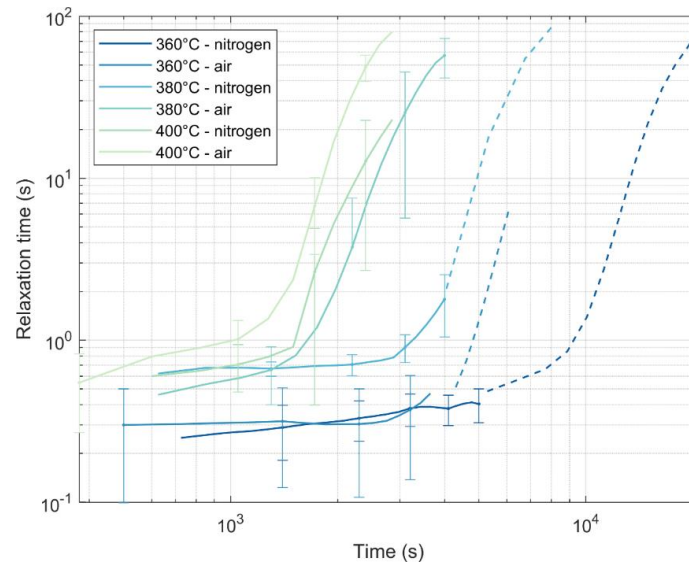


Figure 2 : Evolution of relaxation time with degradation

## 2.1 Fast scanning calorimetry

The crystallization kinetics of the polymer has been studied using fast scanning calorimetry (FSC). The high heating and cooling rates achievable (up to 5000K/s) allows decoupling of crystallization and degradation at high temperatures. A stepwise method presented in previous work [5] is used to characterize the isothermal crystallization kinetics of the material between 160°C and 320°C. The analysis is repeated after the material has been subjected to isothermal degradation at 400°C for various times.

The results are presented in Figure 3, which shows time-temperature-transformation (TTT) diagrams as a function of the dwell time at 400°C. It is evident from this graph that degradation affects the ability of the material to crystallize as crosslinking limits the mobility of the molecular chains : the TTT diagrams appear to be shifted towards the longer times.

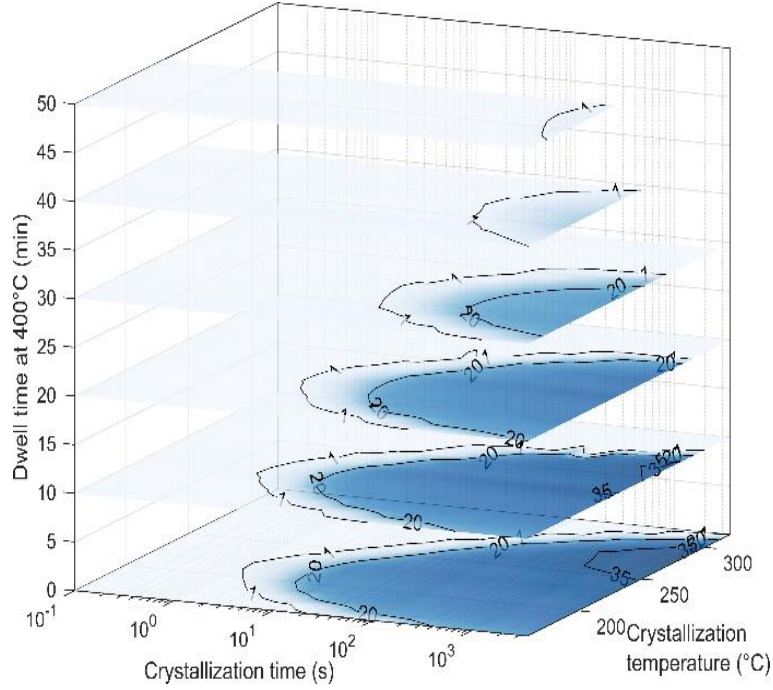


Figure 3 : TTT diagram as a function of degradation time at 400°C

### 3 MODELLING

The experimental work has highlighted the impact of degradation on both molecular diffusion and crystallization kinetics. A multiplicative coupling between the effects of crystallization and degradation on welding time is assumed, via the use of shift factors, such that:

$$t_w = f(T) \times g_1(\alpha(\gamma)) \times g_2(\gamma) \quad (3)$$

With  $\alpha$  the crystallinity,  $\gamma$  a dimensionless parameter related to degradation,  $f$  an Arrhenius based function describing the temperature dependence of rheological properties, and  $g_1$  and  $g_2$  shift factors describing the couplings with crystallization and degradation respectively.

#### 3.1 Diffusion-crystallization coupling

The crystallization kinetics is described with a modified Nakamura model to take into account secondary crystallization from lamellar thickening. The shape of the shift factor  $g_1$  is obtained from literature [5] with an exponential increase of the welding time with  $\alpha$ .

#### 3.2 Degradation kinetics

The main degradation mechanism of PEEK at high temperature under an oxidative atmosphere is branching, which affects chain diffusion and thus both the ability to crystallize and mobility through the interface. The influence of degradation on the welding time is described with a double exponential form [3] with parameters identified from the experimental rheological tests.

$$g_2 = \exp \left( \left( A_0 \exp \left( \frac{-E_a^c}{RT} \right) \right) \times t^B \right) \quad (4)$$

The modelled evolution of relaxation time as a function of degradation time at different temperatures

is presented in Figure 4. A good agreement between the experimental measurements and the model is observed with the exception of long degradation times where the model appears to overpredict the relaxation time. This is due to limitations in the experimental determination of the reptation time from the rheology tests : as the material degrades, longer recovery times should have been used to ensure full recovery. As a consequence, the relaxation times computed with the Cox-Merz relation are lower than reality for the highly crosslinked material.

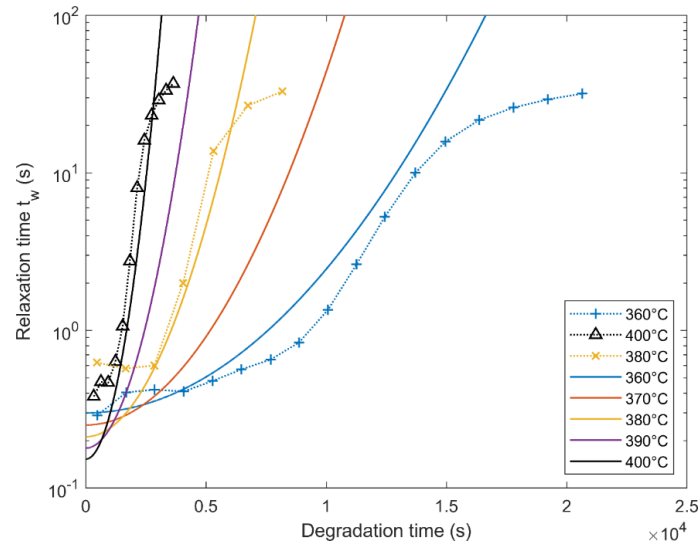


Figure 4 : Modelled diffusion-degradation coupling

In addition, the dependence of crystallization on degradation is taken into account through the evolution of the Nakamura parameter  $K_{Nak}$ .

## 4 PROCESS DIAGRAMS

The model developed can be used to generate process diagrams that allow for the prediction of welding quality as a function of the temperature cycle used. As an example, Figure 5 presents the process diagram corresponding to isothermal welding of the virgin (non-degraded) material in the following conditions :

- Melting at 380°C
- Ballistic cooling to the isothermal weld temperature
- Hold time before contact of 10s
- Contact & isothermal welding.

We can observe that for isothermal welding temperatures above 280°C, the welding time is unaffected by crystallization as the hold time is not sufficient for the material to start crystallizing : i.e. the chain diffusion through the interface and crystallization are decoupled. For temperatures between 260°C and 160°C, chain diffusion at the interface and crystallization are coupled, and the advancement of crystallization leads to a much slower diffusion kinetics with maximal adhesion attained approximately 100s after contact (compared to ~1s in the uncoupled case).

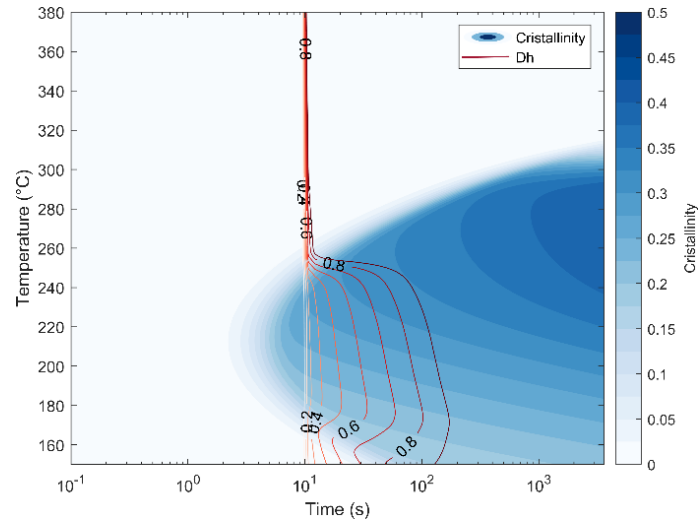


Figure 5 : Predicted evolution of Dh and cristallinity for isothermal welding after 10s hold time

## 5 CONCLUSIONS & PERSPECTIVES

Rheometry and FSC have been used to characterize the influence of degradation and crystallization on macromolecular diffusion of PEEK. A multiplicative coupling based model has been proposed to describe the change in welding time due to chain branching and crystallization, and would allow for a more accurate simulation of welding processes for PAEK. Experimental validation of this model, using an in-house welding apparatus is under way.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge Solvay for funding this study and providing the materials used.

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