

Effect of interfacial crystalline growth on autohesion of PEEK

Lilian Martineau, France Chabert, Benjamin Boniface, Gérard Bernhart

▶ **To cite this version:**

Lilian Martineau, France Chabert, Benjamin Boniface, Gérard Bernhart. Effect of interfacial crystalline growth on autohesion of PEEK. International Journal of Adhesion and Adhesives, 2019, 89, pp.82-87. 10.1016/j.ijadhadh.2018.11.013 . hal-01949351

HAL Id: hal-01949351

https://imt-mines-albi.hal.science/hal-01949351

Submitted on 6 Mar 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of some Toulouse researchers and makes it freely available over the web where possible.

This is an author's version published in: http://oatao.univ-toulouse.fr/21733

Official URL: https://doi.org/10.1016/j.ijadhadh.2018.11.013

To cite this version:

Martineau, Lilian and Chabert, France and Boniface, Benjamin and Bernhart, Gérard Effect of interfacial crystalline growth on autohesion of PEEK. (2019) International Journal of Adhesion and Adhesives, 89. 82-87. ISSN 0143-7496

Any correspondence concerning this service should be sent to the repository administrator:

tech-oatao@listes-diff.inp-toulouse.fr

Effect of interfacial crystalline growth on autohesion of PEEK

L. Martineau[a,b], F. Chabert[c,*], B. Boniface[a], G. Bernhart[b]

[a] Université de Toulouse, CNRS, Mines Albi, INSA, UPS, ISAE-SUPAERO, ICA (Institut Clément Ader), Campus Jarlard, F-81013 Albi, France
[b] NIMITECH Innovation, LAUAK Group, 1 avenue des Victimes du 11 Juin 1944, F-65200 Bagnères de Bigorre, France
[c] Université de Toulouse, LGP-ENIT-INPT, F-65016 Tarbes, France

Keywords:
Autohesion
Crystallinity
Annealing
PEEK

A B S T R A C T

This work aims to clarify the role of the crystalline growth on the autohesion strength of amorphous PEEK below its melting temperature. The self-bonding strength versus temperature, pressure and time has been measured by lap shear test on 250-micron thick amorphous PEEK assembled at various conditions. The effect of the crystalline growth on the adhesion strength has been established at 155 °C, 200 °C and 250 °C. Autohesion is temperature dependent, whereas pressure at less than 1 MPa and time up to 3 h, have less impact on the adhesion strength. Nevertheless, the evolution of the crystalline morphology with time results in increasing the interfacial strength: a gain of 40% is noticed between 1 and 3 h at 250 °C to reach 0.9 MPa. The degree of crystallinity is higher at the interface than elsewhere in the material, the interface acting as nucleating agent. The evolution of the crystalline morphology at the interface with time shows the refinement of the primary lattice when the temperature is higher than or equal to the previous crystallization temperature, corresponding to the highest temperature seen by the polymeric material. The crystalline growth has an ambivalent effect on the autohesion of PEEK: it reduces the mobility of the macromolecular chains and thus their interdiffusion through the interface and at the same time, it is observed that the improvement of its crystal lattice reinforces the interfacial strength.

1. Introduction

To address our world's race towards sustainability, an increasing number of industrial products traditionally manufactured with thermoset polymers are shifting to high-performance thermoplastics, which show comparable mechanical properties and better chemical resistance. Processing and assembling high performance thermoplastics, highlights the lack of knowledge and *know-how* about the couple materials/processes. Particularly, PEEK (polyetheretherketone) is still a promising material because of its inertia to chemical reagents and heat resistance, high elastic modulus and durability in thermo-oxidative conditions. Even if it is unanimously conceded that its properties would authorize the replacement of metallic parts in some applications, processing and assembling PEEK is still a serious challenge that needs to be overcome, before a widespread utilization in the industry.

Self-bonding, also called auto-adhesion, autohesion or welding, is the bonding of two surfaces of an identical polymer [1]. Autohesion takes place at a temperature above the glass transition temperature (Tg) and below or above the melting temperature (T_m), without an adhesive. Autohesion is expected to be given off, in particular for medical, electronics and microfluidics applications, for which low environmental impact and reliability process are noteworthy characteristics.

This assembling process has been applied for years to join thermoplastics parts with a precise and strong adhesion [1]. Voyutskii [2] and Vasenin [3] studied in 1960s the autohesion mechanisms, based on the diffusion of macromolecules above Tg. Then, the theory of reptation exposed by De Gennes [4,5] and Brochard-Wyart [6] described the motion of polymeric chains and was successful in predicting the molecular weight dependency of the self-diffusion. From these theories, a number of attempts have been made in order to link the process parameters to the interfacial strength in welding processes. Among them, Wool's model [7], predicting the mechanical energy required to separate two welded polymeric parts as a function of time, pressure, temperature and molecular weight, appears to best fit the experimental data. The main parameters of autohesion process are temperature, pressure and time. Interdiffusion of macromolecules occurs when two polymer surfaces are brought into close contact, the interdiffusion becomes more likely when the temperature is higher than the polymer glass transition temperature and the interdiffusion accelerates as temperature increases. For amorphous thermoplastics, it has been demonstrated that interdiffusion takes place below the glass transition temperature [8], however, higher bonding strength is measured from Tg.

* Corresponding author.
E-mail addresses: lilian.martineau@mines-albi.fr (L. Martineau), france.chabert@enit.fr (F. Chabert), benjamin.boniface@nimitech.fr (B. Boniface), gerard.bernhart@mines-albi.fr (G. Bernhart).

For semi-crystalline polymers, it is commonly admitted that the effective bonding starts from melting temperature, the presence of crystalline zone prevents the macromolecules of the amorphous phase from moving to the neighborhood. However, some studies show that a physical bond is formed between two surfaces of amorphous PEEK at temperature below its melting temperature [9–13]. Rationally, Boiko noticed in 2001 that the crystallization hinders auto-adhesion phenomenon applied to PEEK [14]. Macromolecular chains included into crystalline structures or linked to them, that is to say, rigid amorphous phase, are tightened to each other's. Their limited mobility prevents interdiffusion of free chains, the free amorphous phase [13]. On the other hand, Cho and Kardos [12] in 1995 determined that amorphous PEEK films are self-bonded by crystalline growth after diffusion and entanglement of the polymer chains across the interface. When the crystallization takes place at the interface, the crystalline structure strengthens the adhesion between the two surfaces. They found that the crystalline growth rate is much higher at higher temperatures, leading to a higher bonding strength of PEEK [12].

Since, meaningful progress has been pointed out in 2016 by Awaja [13]. The chemical bonding mechanism between the two surfaces in contact may be promoted by the presence of reactive polar functional groups which enable the formation of strong chemical bonds, thus increasing the bonding strength. His work focuses on the effect of plasma surface treatment of PEEK in order to increase the bonding strength.

Nevertheless, the role of crystallinity growth over the interface, during the autohesion process is not clear. The crystallinity growth is suspected to be one of the major impacting factor into autohesion of bonded polymers. The evaluation of the rate, density and morphology of crystals at the interface will assist in achieving shorter bonding times and higher strength between the surfaces in contact.

Even though PEEK specimens contain the same amount of crystallinity, Cho and Kardos [12] showed that the resultant self-bonding strength is sensitively dependent on bonding history. Most of the crystallinity is produced by cold crystallization and the additional crystallization due to annealing effects is negligible. Some slight additional crystallization occurs at 200, 250 and 300 °C as time increases. They noticed that the higher the crystalline growth rate across the interface, the higher self-bonding strength. It is therefore important to control the crystallization during the autohesion process. If crystallization occurs first, chain diffusion and entanglement will be inhibited because only the amorphous regions of the polymer have chains with sufficient mobility. In the continuity of Cho and Kardos's study [12], our contribution aims to go further in the understanding of the crystalline growth at the interface for initially amorphous PEEK films.

This work bears out the idea of joining amorphous PEEK below its melting temperature. The self-bonding strength has been measured varying the process parameters: temperature, pressure and time. The interfacial adhesion strength is explained by the evaluation of the degree of crystallinity and the morphology of crystals at the interface, which is dependent on the process parameters.

2. Experimental

2.1. Materials

Thick amorphous PEEK films (250 µm) Aptiv™ 2000 were purchased; they are produced by Victrex. Films were wiped with ethanol and dried 24 h in an oven at 120 °C before using.

2.2. Methods

Film specimens of 30 × 10 mm^2 were superimposed to obtain assemblies with a contact surface of 10 × 10 mm^2. The autohesion was studied at an isothermal temperature between Tg and Tm, namely 155 °C, 200 °C and 250 °C. A fixed pressure of 0.1, 0.5 and 1 MPa was applied with a load (metallic part) of controlled mass for the preparation of bonded specimens placed in the oven.

2.3. Characterization

2.3.1. DSC

Isothermal crystallization was carried out by using a Netzsch DSC 200 F3 at 155, 156, 157, 158, 159 and 160 °C. The isothermal point was reached with a heating rate of 10 °C min^{-1}. The initial time of the analysis was taken right after the sample reaches the equilibrium at the crystallization temperature. For clearer results, the baseline was corrected as a straight line passing through the two limits of the exothermal peak obtained. Annealing treatments were applied, each composed of successive isothermal step of 30 min. The melting behavior was studied by scanning the resultant polymer with a heating rate of 10 °C min^{-1}.

2.3.2. X-ray diffraction

Crystalline rate and morphology were checked by wide angle X-ray scattering, using a Philips PW 1700 in reflection mode with CuK_α radiation. The degree of crystallinity was calculated by integrating the area of the narrow peaks on the halo region of the amorphous phase and then by converting this volume ratio into weight ratio. At least 3 measurements were considered for the calculation of an average degree of crystallinity.

2.3.3. Mechanical tests

Lap shear tests were carried out to quantify the adhesion strength with an electromechanical tensile testing machine Bose ElectroForce for a constant crosshead speed of 0.002 mm s^{-1} (0.0001 s^{-1}) at room temperature. The autohesion strength was calculated as the measured force at failure divided by the contact area. For each test condition, 5 samples were prepared to ensure repeatability and reproducibility. The pressure sensor used has an accuracy of 0.01 MPa.

3. Results and discussion

3.1. Kinetics of cold crystallization of PEEK

The crystallization rate is about one second at Tg + 20 °C [15,16], so only the range 150 °C to 160 °C has been selected to define the temperature insuring that the material stays amorphous during the experiments. DSC results for isothermal tests are shown in Fig. 1. The thermograms show an exothermic peak attributed to the cold crystallization. From this peak, the characteristic times of the crystallization could be deduced, they are reported in Table 1. The crystalline growth starts after 41 min at 155 °C and oppositely, the crystallization rate is much faster at higher temperatures. As observed by Blundell [15], the

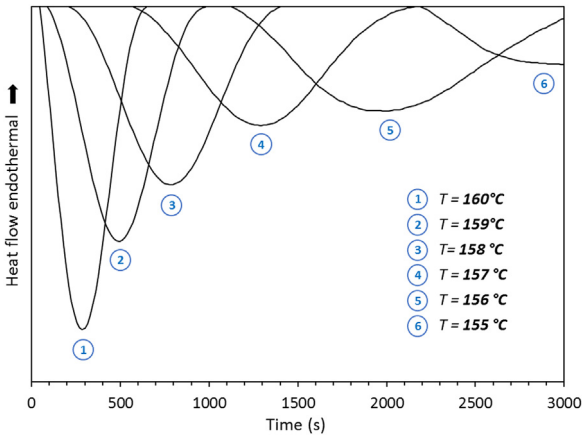


Fig. 1. Isothermal thermograms for amorphous PEEK at different temperatures.

Table 1
Initiation time (t_i,) time at the maximum of the peak (t_p) and time at the end of the crystallization (t_f) for amorphous PEEK during cold crystallization.

T(°C)	t_i (min)	t_p (min)	t_f (min)
155	41	51	165
156	18	36	76
157	11	24	41
158	6	16	28
159	3	10	20
160	1	7	14

kinetics of cold crystallization appears to be exponential with increasing temperature: a temperature difference of 5 °C lowers the initiation of 40 min to 1 min for the amorphous PEEK film.

3.2. Autohesion of PEEK

There is no adhesion without the application of a pressure enabling the two surfaces to come into close contact. For numerous polymers, a pressure of less than 1 MPa can be applied without changing the rupture stress since it does not induce any modification of the joint geometry and thus does not change the diffusion phenomenon [2,7,14].

The effect of the pressure applied during the welding process has been studied. Varying the pressure has a slight effect on the adhesion strength of amorphous PEEK. However, it is worth to notice that increasing the pressure results in an increase of self-bonding strength. As shown in Fig. 2, in this pressure range of less than 1 MPa, the tendency is undeniable for the bonding of two amorphous PEEK surfaces above the glass transition. The adhesion strength measured by lap shear test, increases of about 0.1 MPa when the pressure is raised from 0.1 MPa up to 1 MPa. In a study on polyisobutylene, Stacer and Schreuder-Stacer [17] observed an enhancement of the energy at break in this pressure range. They assume that this effect is due to an improvement in the contact surface and does not stem from a faster macromolecular diffusion. Indeed, upon pressure the material deforms because of viscoelasticity to cancel the roughness of the two surfaces. For the PEEK film they used (APTIV® 2000), an arithmetic average of the profile roughness (Ra) was measured at 0.56 µm [18]. This relatively high roughness could cause pressure dependence, supporting the Stacer and Schreuder-Stacer hypothesis. As the same films are used in our study, it is also assumed that creep of PEEK above Tg leads to enhance the intimate contact between the two surfaces. A dependence of the adhesion force with the contact time is observed on our assemblies: the rupture stress goes from 0.30 to 0.36 MPa with a difference of 2 h. Consistent results have been widely shown in the literature [7,8,12] notably for PEEK by Cho and Kardos. According to these studies [12], a power law with an

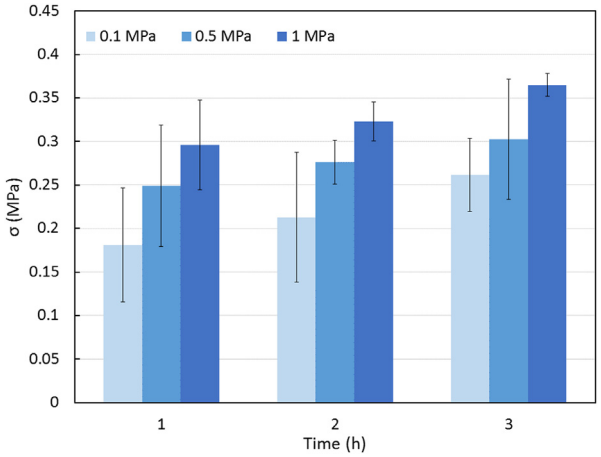


Fig. 2. Autohesion strength of PEEK at 200 °C with pressure.

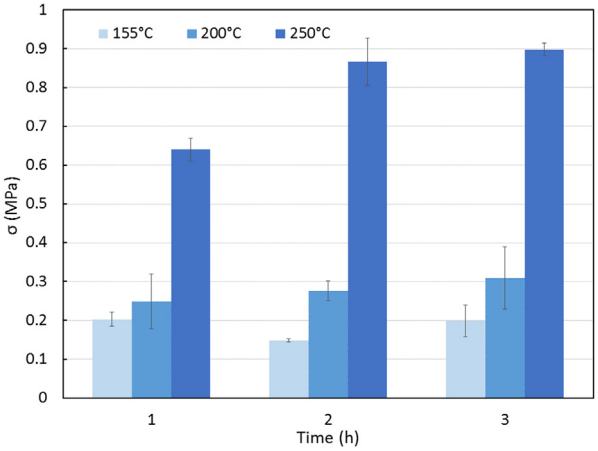


Fig. 3. Autohesion strength of PEEK between Tg and Tm at P = 0.5 MPa.

index of 1/4 corresponds to the Wool relation [19], the latter links the stress at break to the contact time. The effect of time has not been considered here beyond 3 h in order to remain realistic with manufacturing cycle time for thermoplastic materials.

The autohesion strength of the initially amorphous PEEK at various temperatures in the rubbery range, ie between Tg and Tm: 155 °C, 200 °C and 250 °C, is shown in Fig. 3. At 155 °C, corresponding to Tg + 5 °C, the fracture strength is 0.2 MPa, which appears to be relatively low. However, this temperature is worth being studied because the two PEEK surfaces in contact are purely amorphous for 41 minutes before the macromolecules self-arrange in ordered structures. At 200 °C and 250 °C, the crystallization is so fast that the samples undergo cold crystallization while reaching the temperature of the test. The autohesion of semi-crystalline polymers results from the competition of the mechanisms of diffusion of the chains through the interface and crystallization growth. At 155 °C, the diffusion of the chains would be possible before the crystallization prevents their mobility. For other temperatures, the crystallization kinetics being already of the order of the second at Tg + 20 °C, the material will inevitably begin to crystallize during the rise to the isotherm [15,16]. Nevertheless, there is a marked enhancement of the adhesion at 250 °C, which increases from 0.2 MPa at 155 °C to 0.9 MPa at 250 °C for a 3 h adhesion time. At 155 °C, the time has very poor influence on adhesion strength while at 250 °C, a gain of 40% is noticed between 1 and 3 h.

Autohesion of polymers is temperature dependent, the temperature affects the macromolecular chains diffusion kinetics and, in the case of semi-crystalline polymer, it has an effect on the crystalline growth. At slightly above Tg, chains would have enough mobility to move through the interface via diffusion. The coexistence of these two mechanisms, diffusion and crystallization, has effects on the autohesion strength, this has been shown by several authors [20,21]. A low temperature, considering a homogeneous environment, is associated with a slow diffusion and generates a nucleation at the interface, this one acts as a barrier which hinders the chains diffusion. Conversely, at higher temperature, the diffusion predominates over the crystallization and the adhesion strength is improved. In this case, Lo shows that the diffusion of polyethylene (PE) in isotactic polypropylene (iPP) interferes with the nucleation of the iPP at the interface which will prefer to nucleate further [21]. The role of crystallization on autohesion of PEEK is explained in the following part.

3.3. Analysis of contact surface of PEEK

Following the shear tests, the two fractured part of each assembly were analyzed to check their crystalline rate. The degree of crystallinity was measured on the former contact zone and outside the contact zone by X-ray diffraction. Since the material is not sufficiently dense, the

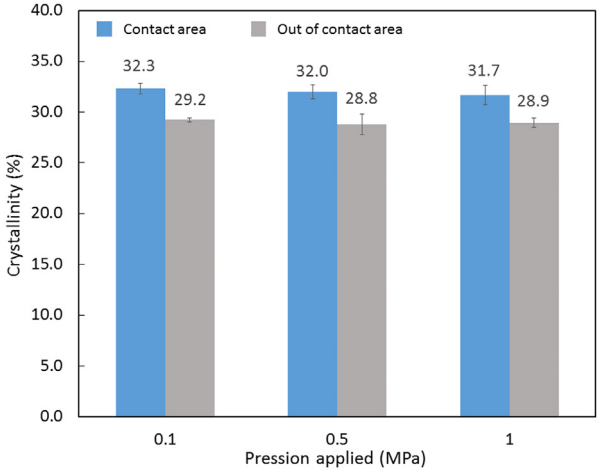


Fig. 4. Crystalline rate after adhesion for 2 h at 200 °C for various contact pressures.

beam passes through the sample, so the obtained rate is an average over the thickness (250 µm). A crystallinity difference of at least 2% is observed between the two locations for all autohesion conditions, the crystalline rate being higher in the former contact zone. This difference between the contact and non-contact areas is probably underestimated, the whole sample thickness being crossed over by XR beam.

The pressure applied to the adhesion zone could not be the reason of this rise since the pressure has no effect on the degree of crystallinity, as seen in Fig. 4. Moreover, the crystalline rate is similar over the entire sample for the application of the same conditions when a part of a raw film is subjected to a pressure range. The crystallinity deviation is similar for autohesion temperatures of 200 °C and 250 °C but appears to be slightly lower for 155 °C, as seen in Fig. 5.

The nucleation of PEEK taking place preferentially at the interface seems to be an hypothesis that could explain this difference of crystallinity. Schonhorn demonstrates the formation of a transcrystalline zone at the interface [22–24] when many semi-crystalline polymers such as polyethylene, polypropylene or polyamide 6,6 are joined by autohesion. The interface acts as a nucleating agent, leading locally to heterogeneous germination. Therefore, the nucleation would be favored in this region during cold crystallization. The nucleation at the interface is to the detriment of the adhesion since it hampers the chains interdiffusion. Another hypothesis could be the diffusion of short chains at the interface. Because of their greater mobility, the shortest chains could be able to move faster across the interface. Given that the crystallization of short chains is characterized by faster kinetics and higher crystallinity [25,26], the presence of these short chains at the interface could explain the highest crystalline rate measured in this region.

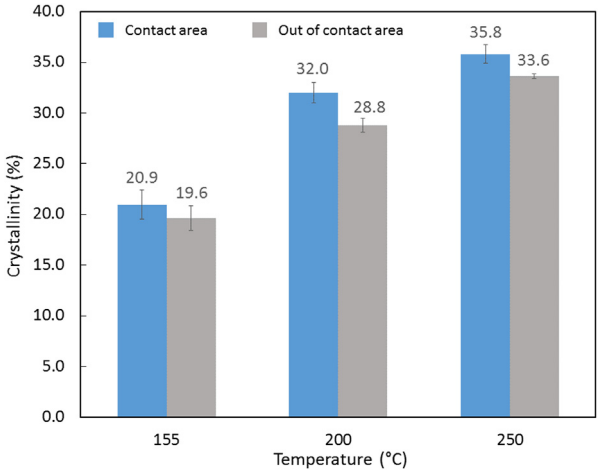


Fig. 5. Crystalline rate after adhesion for 2 h at a pressure of 0.5 MPa for various temperatures.

The crystallization conditions are identical for samples bonded at 200 °C and 250 °C since they both crystallize during heating ramp to reach the isotherm at about 160 °C. As a result, their nucleation sites are similar, supposed to be more numerous at the interface. However, considering the stress at break, the improvement of the autohesion thus occurs during the annealing stage. Until now, there is no certainty about the origin of the reinforcement, which could stem from the diffusion of chains of the free amorphous phase or from a modification of the crystalline phase. Based on an adhesion temperature of 250 °C, Cho and Kardos observed a crystallization developing through the interface by scanning electron microscopy [12]. Their images show only a few bonding points which is consistent with the low bonding strength they obtained. The evolution of the crystallinity during annealing is therefore the topic of the next part to clarify the role and the evolution of the crystalline morphology on the autohesion strength.

3.4. *Effect of annealing on the crystallinity of PEEK*

X-ray diffraction patters obtained from experiments at large angles on annealed PEEK are shown in Fig. 6. Before annealing, the samples were crystallized for 30 min at 160 °C so that the evolution of the measured crystallinity is, as far as possible, dependent on annealing and not on heating ramp to reach the isotherm. Each pattern correspond to a different isothermal treatment and same holding temperature, so that the thermal treatment undergone by the sample numbered 1 is 30 min at 160 °C and 2 h at 300 °C, the sample numbered 2 is 30 min at 160 °C and 2 h at 270 °C and so on for the others.

The position of the diffraction peaks does not change with the annealing temperature, which indicates the conservation of the orthorhombic structure. The width at half height will be discussed in the next part. The "weak" crystal lattice formed near the glass transition seems to be improved by annealing above 200 °C. The degree of crystallinity χ_c calculated from XRD pattern is shown in Table 2. The degree of crystallinity increases when the annealing temperature is shifted to higher temperature.

However, Buggy found much lower rates for similar annealing conditions and for the same analytical technique [27]. The discrepancy between their results and the ones presented hereby is due to the presence of carbon fibers in their study, assuming that the fibers decrease the crystalline rate. Indeed, Gao observed a significant decrease of crystallinity comparing carbon fiber/PEEK pre-impregnated and pure PEEK crystallized from the melt [28]. Other authors agree that DSC is not a reliable technique for PEEK because of the intrusive nature of the

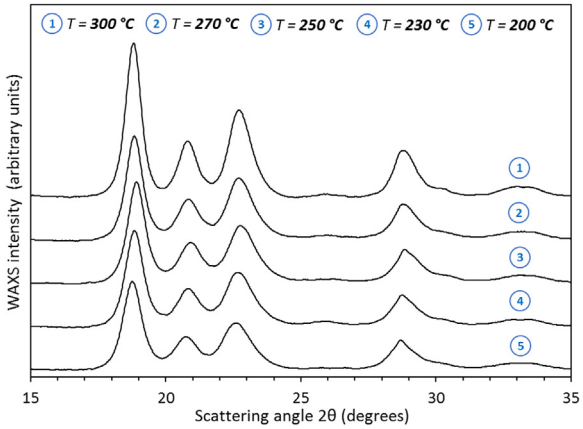


Fig. 6. XRD diffractograms for PEEK after 2 h annealing at various temperatures.

Table 2
Characteristic values from XRD in Fig. 6.

Annealing temperature (°C)	Diffraction angle (2θ) of the line (110) (°)	$\partial(2\theta)_{(110)}$ (°)	χ_c (%)
200	18.8	0.82	28.1
230	18.9	0.81	32.1
250	18.9	0.78	34.4
270	18.8	0.73	35.6
300	18.8	0.67	37.0

Table 3
Characteristic values from XRD after annealing at 250 °C for different annealing times.

Annealing time (h)	Diffraction angle (2θ) of the line (110) (°)	$\partial(2\theta)_{(110)}$ (°)	χ_c (%)
0.5	18.9	0.78	30.6
1	18.9	0.78	33.1
2	18.9	0.78	34.4
3	18.9	0.77	33.7

test: the crystallization is modified by the heat provided to the material during the test, which increases the uncertainty on the expression of the crystalline rate [16,29].

The effect of time on annealing seems to be more moderated than the effect of temperature, as shown in Table 3, where the crystalline rate increases slightly with time: a 3% increase between 30 min and 3 h. The degree of crystallinity as a function of the annealing conditions appear to follow the same evolution as the rupture stress presented in Fig. 3. If a link really exists between the degree of crystallinity and autohesion strength, it is not yet established how the crystallization generated during the annealing play a role on the interfacial behavior. For that, the crystal morphology is discussed in the next part.

The half-height width d(2θ) of the most intense diffraction peak (110) is inversely proportional to the average thickness of the crystalline lamellae [30]. In the patterns presented in Fig. 6, for the different annealing conditions, the increase of the crystallinity leads to a decrease in the width at half height as seen in Table 2 and Table 3. An improvement of the primary lamellae would therefore be running during the isothermal treatment. Using small-angle XRD analysis, Fougnies quantified the thickness of the crystalline lamellae of PEEK and he followed its evolution during anisothermal cold crystallization [26]. His results also seem to show a refinement of the crystal morphology with time after the formation of the main crystalline network.

This morphology appears to be different that the one established on a sample crystallized from the melt and then annealed. By thermal analysis, Ko and Woo [31] showed that annealing from the melt results in one melting peak for each annealing condition on the thermogram. According to them, each peak corresponds to a population of lamellae with their own thickness [31]. In order to clarify the relationship between the thermal history and the crystal morphology, two types of successive annealing were applied to our amorphous PEEK material. The first consists in successive isothermal step in descending order (Fig. 7) and the second in ascending order (Fig. 8). Holding time at the plateau is kept constant:30 min. In both cases and whatever the annealing conditions, the main melting peak varies only slightly and at least one minor fusion peak is present on the thermograms. These minor melting peaks could find two justifications: the reorganization of the primary lamellae during the DSC analysis or the apparition of a new population of lamellae due to annealing. Being confident in the study of Tardif [16], it seems that the minor peak closest to the main peak is the consequence of a reorganization.

In comparison with the multiple peaks observed for descending steps, the annealing for ascending steps does not lead to the apparition of a new minor peak, but the already existing one near 210 °C for the

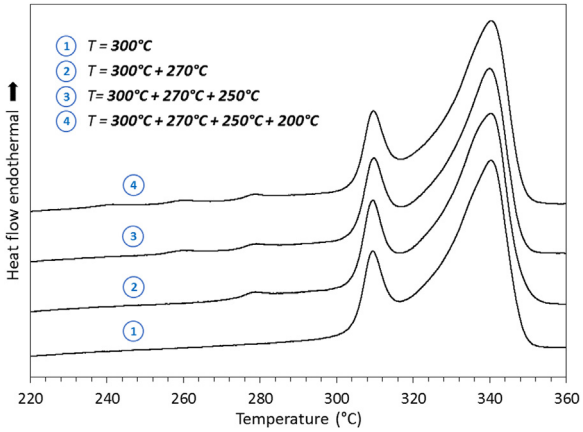


Fig. 7. DSC thermograms of melting peaks for different annealing conditions by descending steps.

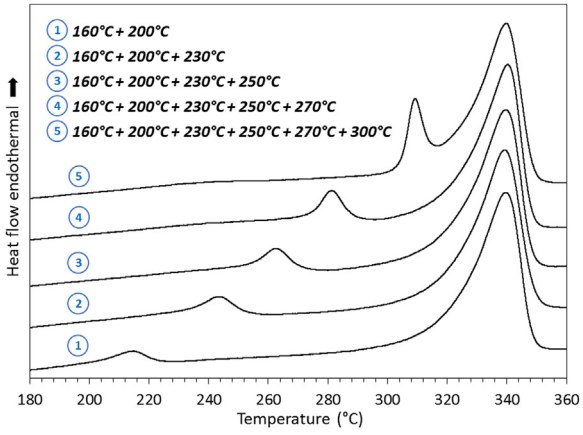


Fig. 8. DSC thermograms of melting peaks for different annealing conditions by ascending steps.

annealing conditions of 160 °C and 200 °C is shifted towards higher temperatures when the annealing is continued at higher temperatures. Considering the hypothesis of a reorganization during heating, this peak could be interpreted as an improvement of the primary crystal lattice when increasing the annealing temperature. Indeed, an imperfect crystal will be subject to the phenomenon of melting-recrystallization at lower temperature. This hypothesis is corroborated by the results previously obtained by X-ray diffraction. For the descending steps, the shape of the thermograms is similar to those obtained by Ko and Woo [31] with the apparition of one peak for each annealing condition. The origin of the minor melting peak present after an isotherm step at 300 °C can be explained by the phenomenon of reorganization. However, this phenomenon does not make it possible to explain the presence of the other peaks following the application of descending steps, the presence of different crystalline lattices is then assumed. The improvement of the primary crystals requires an annealing temperature higher than or equal to the previous crystallization temperature, corresponding to the highest temperature seen by the polymeric material.

From our results and the micrographic observations made by Cho and Kardos [12], we assume that the crystals at the contact zone would be able to improve through the interface and explain the increasing of the bonding strength.

Thus, the role of the crystallization is ambivalent: on one hand, the cold crystallization is promoted by the interface, thus creating a barrier for the diffusion of the chains. On the other hand, the improvement of the crystalline morphology seems to strengthen the adhesion force.

4. Conclusions

The autohesion strength versus temperature, pressure and time has been measured by lap shear test on 250-micron thick amorphous PEEK assembled at various conditions. An amorphized semi-crystalline tends inexorably towards its state of equilibrium, that is to say towards an ordered (crystallized) structure. The choice of the temperatures takes into account the initiation time of this reorganization to ensure that the cold crystallization does not appear during the first times of the experiments. The crystalline growth starts after 41 min at 155 °C and oppositely, the crystallization rate is about one second at 200 °C and 250 °C.

In the melted state, the adhesion between two surfaces stems from the interdiffusion of macromolecular chains. The self-adhesion of PEEK is possible in the rubbery state, but the mobility of the chains is strongly impacted by the crystalline zones: The latter rigidify the polymeric material, the mobility of macromolecules of the amorphous phase is reduced, the crystallinity prevents or greatly hinders long-range molecular mobility.

The autohesion of semi-crystalline polymers results from the competition of the mechanisms of diffusion of the chains through the interface and crystallization growth. At 155 °C, the diffusion of the chains would be possible before the crystallization prevents their mobility. At 200 °C and 250 °C, the crystallization is so fast that the material will inevitably begin to crystallize during the rise to the isotherm.

The pressure, at less than 1 MPa, has a slight effect on the bonding strength. Autohesion of polymers is temperature dependent, the temperature affects the macromolecular chains diffusion kinetics and, in the case of semi-crystalline polymer such as PEEK, it impacts the crystalline growth. The time is another impacting factor, even though the effect of time seems to be more moderated than the effect of temperature.

The highest bonding strength is obtained at 250 °C. For all studied temperatures, the strength increases with time. The degree of crystallinity on the former contact zone is always higher than outside the contact zone, which is explained by the fact that the nucleation of PEEK takes place preferentially at the interface.

In order to clarify the relationship between the thermal history and the crystal morphology, two types of successive annealing were applied by ascending and descending temperature steps. The crystalline morphology appears to be different for each heat treatment and different that the one observed on a sample crystallized from the melt and then annealed. Several peaks are noticed following the application of descending steps, which is explained by the presence of different crystalline lattices. The refinement of the primary crystals, requires an annealing temperature higher than or equal to the previous crystallization temperature, corresponding to the highest temperature seen by the polymeric material.

Crystalline growth across the interface may reinforce the interfacial strength between semi-crystalline polymers, however, this crystalline growth will only occur when interdiffusion precedes crystallization over the interface during autohesion. More investigation on the crystalline structure would be useful to go further in the understanding of the effect of crystalline growth on the bonding strength. For that, reflection high-energy electron diffraction would be a technique more appropriated to characterize only the first microns of the films instead of the whole thickness.

Acknowledgements

The authors would like to thank the company Nimitech Innovation for financial support through a Ph.D. funding.

References

[1] Wise R. Thermal welding of polymers. Cambridge, England: Woodhead Publishing /Elsevier; 1999.
[2] Voyutskii S. Autohesion and adhesion of high polymers. New York: Wiley; 1963.
[3] Vasenin R. Adhesion pressure in the diffusion theory of the adhesion of polymers. Polym Sci USSR 1962;3(4):608–15.
[4] Gennes PG De. Comptes Rendus De l'Académie des Sciences, Paris. B291. 1980. p. 219–21.
[5] Gennes PG De. Reptation of a polymer chain in a presence of fixed obstacles. J Chem Phys 1971;55(2):572–9.
[6] Brochart-Wyart F. Chapter kinetics of polymer-polymer interdiffusion. Fundamentals of Adhesion. New York and London: L.H.Lee / Plenum Press; 1991.
[7] Wool RP, Yuan BL, McGarel OJ. Welding of polymer interfaces. Polym Eng Sci 1989;29(19):1340–67.
[8] Boiko H, Prud'homme R. Strength development at the interface of amorphous polymers and their miscible blends, below the glass transition temperature. Macromolecules 1998;31(19):6620–6.
[9] Zhang S, Awaja F, James N, McKenzie D, Ruys A. Autohesion of plasma treated semi-crystalline PEEK: comparative study of argon, nitrogen and oxygen treatments. Colloids Surf A Physicochem 2010;374:88–95.
[10] Awaja SF. Self-bonding of PEEK for active medical implants applications. J Adhes Sci Technol 2015;29(15):1593–606.
[11] Awaja F. Autohesion of semi-crystalline PEEK near and under the glass transition temperature. Appl Surf Sci 2013;282:571–7.
[12] Cho B, Kardos J. Consolidation and self-bonding in Poly(ether ether ketone) (PEEK). J Appl Polym Sci 1995;56:1435–54.
[13] Awaja F. Autohesion of polymers. Polymer 2016;97:387–407.
[14] Boiko Y, Guerin G, Marikhin V, Prud'homme R. healing of interfaces of amorphous and semi-crystalline poly(ethylene terephtalate) in the vicinity. Polymer 2001;42:8695–702.
[15] Blundell D, Osborn B. The morphology of poly(aryl-ether-ether-ketone). Polymer 1983;24(8):953–8.
[16] Tardif X, Pignon B, Boyard N, Schmelzer J, Sobotka V, Delaunay D, Schick C. Experimental study of crystallization of polyetheretherketone (PEEK) over a large temperature range using a nano-calorimeter. Polym Test 2014;36:10–9.
[17] Stacer RG, Schreuder-Stacer HL. Time-dependent autohesion. Int J Fract 1989;39(1–3):201–16.
[18] Dreiser C, Bart H. Solvent interactions with polymeric heat transfer surfaces. J Mater Sci Eng 2013;3(9):591–600.
[19] Wool RP, O'Connor KM. Time dependence of crack healing. Polym Lett Ed 1982;20(13):7–16.
[20] Yuan B, Wool R. Strength development at incompatible semicrystalline polymer interfaces. Polym Eng Sci 1990;30(22):1454–64.
[21] Lo C, Laabs F, Narasimhan B. Interfacial adhesion mechanisms in incompatible semicrystalline polymer systems. J Polym Sci Part B Polym Phys 2004;42(14):2667–79.
[22] Schonhorn H, Ryan F. Effect of morphology in the surface region of polymers on adhesion and adhesive joint strength. J Polym Sci Part A-2 Polym Phys 1968;6(1):231–40.
[23] Schonhorn H, Ryan F. Effect of polymer surface morphology on adhesion and adhesive joint strength. II. FEP teflon and nylon. J Polym Sci Part A-2 Polym Phys 1969;6(7):105–11.
[24] Schonhorn H, Ryan FW, Hansen RH. Surface treatment of polypropylene for adhesive bonding. The J Adhes 1970;2(2):93–9.
[25] Yuan M, Galloway J, Hoffman R, Bhatt S. Influence of molecular weight on rheological, thermal, and mechanical properties of PEEK. Polym Eng Sci 2011;51(1):94–102.
[26] Fougnies C, Dosiere M, Koch M, Roovers J. Cold crystallization of narrow molecular weight fractions of PEEK. Macromolecules 1999;32(4):8133–8.
[27] Buggy M, Carew A. The effect of thermal ageing on carbon fibre-reinforced polyetherether-ketone (PEEK). J Mater Sci 1994;29:2255–9.
[28] Gao S, Kim J. Cooling rate influences in carbon fibre/PEEK composites. Part 1. Crystallinity and interface adhesion. Compos Part A: Appl Sci Manuf 2000;31(6):517–30.
[29] Sauer B. Temperature modulated DSC studies of melting and recrystallization in polymers exhibiting multiple endotherms. Polymer 2000:1099–108.
[30] Alexander L. X-ray diffraction methods in polymer science. New York: John Wiley and Sons; 1954.
[31] Ko T, Woo E. Changes and distribution of lamellae in the spherulites of poly (ether ether ketone) upon stepwise crystallization. Polymer 1996;37(7):1167–75.