Toward improvement of the properties of parts manufactured by FFF (Fused Filament Fabrication) through understanding the influence of temperature and rheological behaviour on the coalescence phenomenon

Shahriar Bakrani Balani, France Chabert, Valérie Nassiet, Arthur Cantarel, Christian Garnier

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Toward improvement of the properties of parts manufactured by FFF (Fused Filament Fabrication) through understanding the influence of temperature and rheological behaviour on the coalescence phenomenon

Bakrani Balani Shahriar[1,2, a)], Chabert France[1, b)], Nassiet Valerie[1, c)], Cantarel Arthur[2, d)], Garnier Christian[1, e)]

[1] LGP-ENIT-INPT, University of Toulouse, 47 Avenue d'Azereix, BP1629-65016 Tarbes Cedex, France
Web Page: http://www.enit.fr/
[2] Institut Clément Ader (ICA), CNRS UMR 5312, University of Toulouse, IUT of Tarbes, UPS, France
Web Page: http://www.institut-clement-ader.org/

a)Corresponding author: sbakrani@enit.fr
b) fchabert@enit.fr
c) vnassiet@enit.fr
d) arthur.cantarel@iut-tarbes.fr
e)cgarnier@enit.fr

Abstract. In this paper, the printing temperature ranges of PLA and PEEK, two semi-crystalline thermoplastics, have been investigated for the Fused Filament Fabrication (FFF) process. The printing range, comprised between the melting temperature and the degradation of each polymer, is 160°C to 190°C for PLA and 350°C to 390°C for PEEK. The complex viscosity has been measured for both polymers within the printing range. The kinetics of coalescence has been registered by measuring the bonding length between two filaments of the same polymer according to the temperature. At 167°C, the filaments of PLA reached the maximum value of bonding length. For PEEK, the filaments reached the maximum value of bonding length at 380°C. For the both materials, the final height of the filament is 80% of the initial diameter. The comparison of the obtained results with experimental study and predictive model shows a good agreement when the polymer is totally in fusion state.

INTRODUCTION

Additive Manufacturing (AM) has recently progressed in the industry, due to the versatility of applications and materials. Low environmental impact, capabilities of manufacturing complex shape parts and reduction of the mass of structures stemming from the possibility of new designs explain the upward trends of additive manufacturing. Fused Filament Fabrication (FFF) is one of the common processes for polymeric materials in industrial and domestic uses [1]. In this process, the part is manufactured by melting and deposing thermoplastic filament layer by layer .Nevertheless, the mechanical properties of the parts manufactured by FFF do not meet the requirements to be used as functional parts. Indeed, the low mechanical strength comes mostly from the lack of coalescence between deposed filaments. Furthermore, high deformation and weak dimensional accuracy is another source of defects.

It has been observed that these flaws are highly linked to the viscosity of the melted polymer [2]. On the other hand, the viscosity is highly influenced by the temperature and shear rate [3]. In order to improve the coalescence of two adjacent deposited filaments, it is necessary to decrease the viscosity during printing to facilitate the flow of the polymer and polymer chains [4]. However, it is observed that decreasing viscosity leads to harsh deformation on the printed parts. Hence, defining appropriate viscosity and consequently, shear rate and printing temperature are

necessary to obtain printed parts with the appropriate properties. In this work, the influence of the temperature on the coalescence phenomenon has been measured by monitoring the bonding length of two adjacent filaments. The experimental study has been carried out for two semi-crystalline polymers: PLA (Polylactic Acid) and PEEK (Polyetheretherketone). The experimental results have been compared to a predictive model.

MATERIAL AND METHODOLOGY

PLA is one of the most used polymers for rapid prototyping. PLA Premium White of 3 mm diameter provided by eMotion Tech company was used. Using a single screw extruder equipped with a 3 mm diameter die the PEEK filaments were home-made manufactured from PEEK 450G by Victrex Company. In order to eliminate the moisture in the polymer structure, the 'PLA' filaments were dried during 24h at 60°C in an oven. 'PEEK-450G filaments 'were dried during 24h at 140°C.

The samples for rheometric tests were manufactured using hot compression molding. The pellets were heated above their melting temperature, 160°C for PLA and 360°C for PEEK, under 70kN pressure and they were maintained at this temperature during 300 seconds. Then, the cooling step was carried out under the same pressure with a rate of 10°C.min^{-1}.

The rheological properties were determined with an A.R.E.S-LN2 rheometer from Rheometrics. The rheological tests have been done under air flow condition using the configuration of parallel-plate where the plates have diameter of 25 mm. All experiments were done in an oscillatory mode, in the viscoelastic linear domain, determined previously from strain sweep tests.

DSC (Differential Scanning Calorimetry) tests were performed with a Q200 – TA instrument under nitrogen flow. All experiments were carried out at 10°C.min^{-1} with the approximate sample mass of 10 mg. The glass transition, melting temperature, crystallization temperature, and kinetics of crystallization of both polymers were determined from DSC curve.

The evolution of the coalescence with time was measured experimentally. Two adjacent filaments were heated in a 200 cm^3 oven in order to minimize heat losses. Images were captured using a Photon Focus high-speed camera with a 35 mm diameter lens, with 1:1.4 magnifier scale. The exposure time was selected at 5000 ms. A thermocouple was placed in contact with the filaments in order to have an accurate control of the temperature and heating rate of the filaments. The temperature was recorded using a Graphtec-GL240 data logger. The high-speed camera was placed perpendicularly to the axis of the filament in order to record the bonding length of the adjacent filaments. At lowest temperatures, the sections of the filaments are initially circular. The more temperature increases, the more filament's shape will change.

Linking the dynamic (complex) viscosity to the shear viscosity was done by Cox-Merz relation [5][3]. Cox et al. noticed that the steady state shear viscosity at a given shear rate is equal to the dynamic viscosity at the same frequency in the linear domain, using empirical studies.

$$\eta(\dot{\gamma} = \omega) = |\eta^*|(\omega) \tag{1}$$

The schematic representation of the bonding mechanism during coalescence is represented in Figure 1.
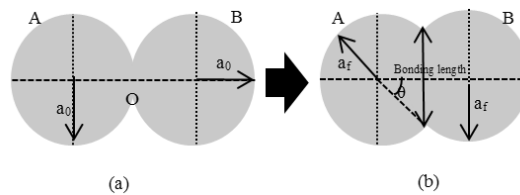
FIGURE 1: Schematic representation of the coalescence of two circles a) Initial state before coalescence   b) Filaments undergoing bonding by coalescence [4]

In order to compare the experimental results with theoretical models suitable for thermoplastics, the modified Frankel [2] bonding model was selected. This model has been originally developed for the sphere coalescence. Nevertheless, it has been applied to predict the filaments coalescence of an amorphous thermoplastic polymer, such

as ABS (acrylonitrile butadiene styrene) in the work of Bellehumeur in 2004[4]. To our knowledge, our work is the first time that, this model is applied to the filaments of semi-crystalline polymers.

$$\dot{\theta} = \frac{\Gamma}{\eta a_0} \frac{2^{\frac{-5}{3}} \sin\theta \cos\theta \, (2 - \cos\theta)^{\frac{1}{3}}}{(1 - \cos\theta)(1 + \cos\theta)^{\frac{1}{3}}} \qquad (2)$$

Where Γ is the surface tension, a_0 is the initial radius of the particle (in our case, the radius of the filament), η stands for viscosity, and θ indicates the angle between the intersecting line between the center and neck of the coalescence, as seen in Fig.1 and finally, θ' is the rate of angle evolution with time. The initial value of θ is zero.

Determining the surface tension is one of the key points in applying the predictive model. Whereas the surface tension of the rigid solids at the room temperature is relatively easy to determine, however because of high viscosity and high temperature no studies have been reported to measure the surface tension of thermoplastic in the melted state. As no data are available, the surface tension in the melted state was approximated by using Parachor approximation equation [6]. Thus, the surface tension was estimated at 0.022 N.m^{-1} for PLA at 160°C and at 0.015 N.m^{-1} for PEEK at 360°C.

RESULTS AND DISCUSSION

Figure 2 represents the results of DSC test are represented in. The curves represent the heating flux during heating and cooling cycles when the material undergoes the thermal transitions. For PLA, the glass transition is measured at 50°C, then during the first heating, an exothermic peak corresponds to the cold crystallization, occurring between 85°C and 110°C. After that, the melting peak appears between 140°C and 160°C. Above 160°C, the PLA is fully melted. In cooling phase, no crystallization is observed in the same range; probably due to the fact the kinetics of crystallization is slower than the temperature ramp of 10°C.min^{-1}. Only the glass transition appears at 50°C. On the second heating ramp, the glass transition is still at 50°C, whereas the cold crystallization range is a shift towards higher temperatures, it starts at 105°C up to 130°C. Then, the melting peak is narrower and also shifted to a higher temperature.

For the PEEK, glass transition is observed at 145°C. Contrary to the PLA, no cold crystallization is observed. The melting peak starts at 315 °C and it finishes at 355°C. Above 355°C, the polymer is fully melted. During the cooling step, the crystallization peak is observed between 300°C and 275°C. The glass transition takes place at 150°C for all tests. Keeping heating ramp constant for the second heating ramp, its melting peak is shifted to the higher temperature, between 325°C and 355°C. These results show that the thermomechanical history has an influence on the melting temperature. Moreover, the crystallization of PEEK is faster than those of PLA.

(a)   (b)
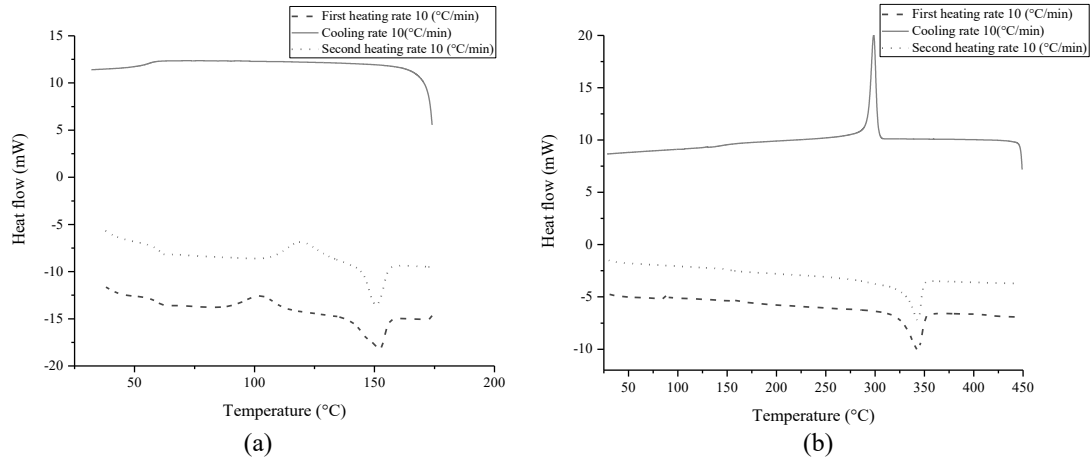
FIGURE 2: DSC curves determined at 10°C.min^{-1} a) PLA, b) PEEK

Based on DSC results, the temperature ranges were chosen for the rheometric tests to ensure fully melted state for both polymers. Figure 3 shows the complex viscosity versus angular frequency for PLA and PEEK.

(a) (b)
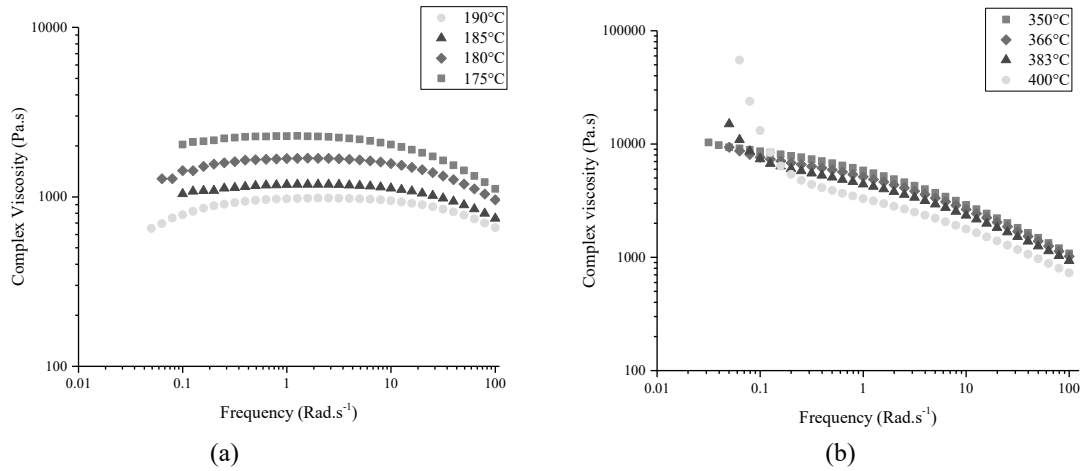
FIGURE 3: Isothermal complex viscosity versus angular frequency a) PLA, b) PEEK

As expected for melted polymers, PLA and PEEK demonstrate a shear-thinning behavior, with a Newtonian plateau for lowest frequencies. Additionally, for PLA, the viscosity drastically decreases when the temperature is increased. The complex viscosity for 1 rad.s^{-1} is 2279 Pa.s at 175°C, 1682 Pa.s at 180°C, 1181 Pa.s at 185°C, 974 Pa.s at 190°C. Still, for PLA, the curve can be divided into three parts from the highest to the lowest frequencies: the shear-thinning zone above 10 rad.s^{-1}, the Newtonian plateau between 1 and 10 rad.s^{-1} and the last one below 1 rad.s^{-1}, where the viscosity decreases. Indeed, the measurements at low frequencies last longer than the ones at high frequencies, meaning that the material stays longer at high temperature. This drop in viscosity is probably due to the polymeric chain breakage at a higher temperature [7]. These results show the sensibility of PLA at these temperatures.

In the case of PEEK, the complex viscosity for 1 rad.s^{-1} is 5841 Pa.s at 350°C, 5144 Pa.s at 366°C, 4413 Pa.s at 383°C and finally 3292 Pa.s at 400°C. At the highest angular frequencies, PEEK demonstrates the shear thinning behavior before exhibiting Newtonian plateau. Contrary to PLA behavior for the longest experiments, and for the small frequencies the viscosity increases drastically. Paradoxically to PLA, at the higher temperature the molecular chains of the polymer undergo the recombination of molecular bond degradation and chain branching [8].
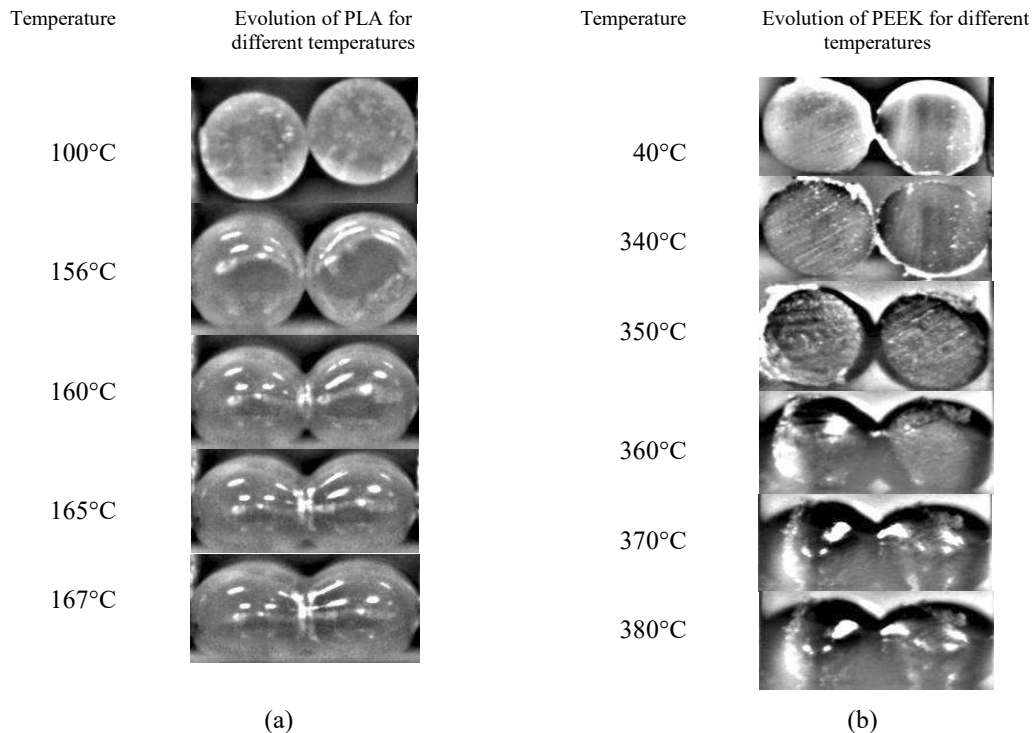
PLA is made of linear carboxylate ester moieties whereas PEEK is made of aromatic ether and ketone copolymers in 2/3 ratio. The heat resistance and mechanical strength of PEEK stem from the rigidity of the chemical structure. Indeed, the mobility of rigid chains (PEEK) is slower than those of linear chains (PLA), explaining the highest viscosity of PEEK.

The kinetics of coalescence of PLA and PEEK was recorded with a high-speed camera. The camera is set on the same axis of the filaments, thus only the cross sections are visible. A slow heating rate was applied to the filaments to get quasi-isothermal conditions and homogenous temperature distribution inside the samples. Thus, PLA was heated at 1.44°C.min^{-1} and PEEK at 1°C.min^{-1}. The evolution of the bonding length according to the different temperatures is represented in Figure 5. Observations for PLA show that there is no coalescence of adjacent filaments for temperature between glass transition and melting temperature. At 156°C, the filaments start to bond together. Comparing with DSC results, the polymer is not fully melted at this temperature. Increasing the temperature results in fastening the coalescence of the filaments. Meanwhile, upon the effect of gravity, the filaments subsided. And finally, at 167°C, the filaments of PLA reached the maximum value of bonding length.

Bonding of the PEEK filaments starts at 350°C. Again, comparing with DSC results, the polymer is not fully melted at this temperature. Like PLA, the filaments of PEEK undergo changes of shape due to gravity. At 380°C, the filaments of PEEK reached their maximum bonding length. At this temperature, the diameter of the filaments lost between 10% and 20% of the initial diameter.

In both cases, the coalescence starts when the polymer is not fully melted. The coalescence starts about 5°C before the end of the melting range(for PLA melting range is 140°C-160°C and for PEEK melting range is between 315°C and 355°C). Indeed, this result demonstrates that the mobility of polymeric chains is fast enough to ensure the interdiffusion of chains at the interface, even with a few remaining crystallites. Also, for PEEK, the bonding

temperature range is wider, 350°C to 380°C, compared to PLA, 156°C to 167°C. It is noticed that the kinetics of bonding is faster for PLA than for PEEK.

Temperature	Evolution of PLA for different temperatures	Temperature	Evolution of PEEK for different temperatures
100°C		40°C	
156°C		340°C	
160°C		350°C	
165°C		360°C	
167°C		370°C	
		380°C	

(a) (b)

FIGURE 4: Evolution of the coalescence of the filaments with temperature, a) PLA, b) PEEK

The experimental results have been compared to the modified Frankel [2] bonding model. For applying this model, the viscosity has been measured, as presented in Figure 3, the surface tension has been calculated. According to the predictive model, since the viscosity of PLA is lower than those of PEEK, the coalescence in PLA appears faster than PEEK.

(a) (b)
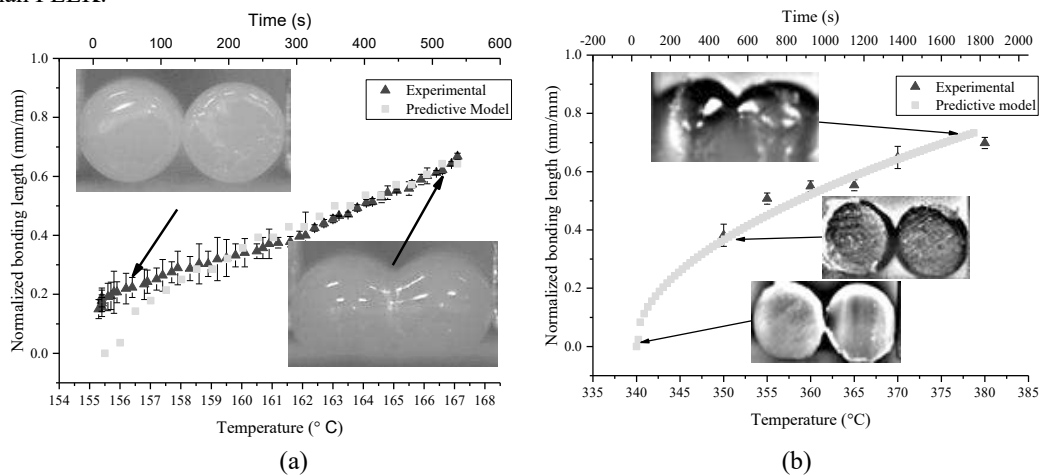
FIGURE 5: Evolution of coalescence of the filaments with temperature, a) PLA, b) PEEK

The comparison of predictive model and experimental study is presented in Figure 5. The bonding length of the polymers was determined by using predictive model and experimental study. For PLA, the agreement of model and experiments starts when the melting is completed at 160°C. For PEEK, due to the difficulties to carry experiments at high temperature, there is less experimental data. Nevertheless, once again, the model shows a good agreement with

the experimental data. For both polymers, it is clear that coalescence does not take place between glass transition and melting temperature. The crystalline phase in the polymer prevents the molecular chains to move in order to interdiffusion for the bonding. Accordingly, for semi-crystalline polymers, the coalescence takes place above the melting range.

CONCLUSION

The thermal transitions and rheometrical behaviour of PLA and PEEK have been thoroughly determined to clarify the relationship between these properties and the coalescence phenomenon during the FFF process. The PLA is fully melted from 160°C, PEEK is fully melted from 355°C. As seen by rheometry, the complex viscosity of PLA is much lower than those of PEEK in their respective melted state. Moreover, both are sensitive to thermal degradation. As a consequence, the fabrication range is limited to prevent their degradation. The studied polymers undergo different degradation mechanism, resulting in decreasing viscosity for PLA due to chain scission mechanism [7]. Contrary, the degradation mechanism of the PEEK by molecular recombination, leading to increasing the viscosity.

The experimental study of the coalescence phenomenon confirms that the viscosity highly influences the kinetics of interdiffusion of polymeric chains. This interdiffusion would impact the mechanical properties of the printed parts: if the interdiffusion is not done at most, the interlayer adherence will be weak, resulting in low fracture resistance of the parts. Indeed, the mechanical strength of printed parts stems from the interlayer adhesion. The latter is due to interdiffusion of polymeric chains in adjacent filaments. This interdiffusion is directly linked to the viscosity of the polymer.

The length of the bonding between two adjacent filaments has been registered with time and temperature. These results have been compared to a predictive model: the results demonstrate a good agreement from the melting temperature. Indeed, the coalescence starts when the polymer is completely in the melted state. This means that the crystalline phase prevents the mobility of polymeric chains, that is to say, the coalescence of adjacent polymers is not possible. Before melting, a difference between the predicting model and the experimental results is observed. Increasing the temperature results in decreasing the viscosity and thus, rising the mobility of polymeric chains, which facilitates the coalescence of the filaments. Another main parameter influencing the coalescence of the polymers is the surface tension. The latter has been determined from a predicting model. However, determining the real surface tension by experiments for the melted polymers above 200°C is a key issue This work is a step towards the optimization of the printing parameters to achieve high-speed manufacturing, low porosity and high fracture resistance of printed parts.

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