Nonisothermal Crystallization Kinetics and Its Effect on the Mechanical Properties Mechanical of Carbon Fiber/Polyphenylene Sulfide Composites

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ABSTRACT- The degree of crystallization of semi-crystalline thermoplastics is an important factor in determining the final properties of the structure of composite materials. This article studied the non-isothermal crystallization kinetics of carbon fiber (CF) reinforced polyphenylene sulfide (PPS) composites by differential scanning calorimetry (DSC) with various cooling rates from 10 k/min to 70 k/min. The MoZhiShen method was applied to the analysis of the nonisothermal crystallization of the composites. Moreover, the effects of the crystallization behavior of CF/PPS composites on their mechanical properties were also investigated. It was found that the MoZhiShen method can effectively be applied to study the nonisothermal crystallization kinetics of CF/PPS composites. The result indicated that the crystallization peak gradually became strengthened in intensity, and crystallization decreased with increasing the cooling rate. Moreover, the increase in the cooling rate during composite fabrication was found to decrease the flexural properties of the composite, but the energy absorption and the impact strength were significantly increased by 15.1%.

المستخلصـ تعتبر درجة تبلور اللدائن الحرارية شبه المتبلورة عاملاً مهمًا في تحديد الخصائص النهائية للمواد المركبة الإنشائية. هذه الورقة درست حركية التبلور غير المتساوي الحرارة لمركبات كبريتيد البولي فينايلين المقوى بألياف الكربون (PPS) عن طريق قياس المسعرات التفاضلية (DSC) بمعدلات تبريد مختلفة من 10 ك / دقيقة إلى 70 ك / دقيقة. تم تطبيق طريقة MoZhiShen لتحليل التبلور غير الحراري للمركبات. علاوة على ذلك ، تم دراسة تأثير سلوك التبلور لمركبات PPS / CF على خواصها الميكانيكية. وجد أن طريقة MoZhiShen يمكن تطبيقها بشكل فعال لدراسة حركية التبلور غير الحرارية لمركبات PPS / CF حيث أشارت النتيجة إلى أن قمة التبلور تزداد تدريجياً في الشدة وأن التبلور ينخفض مع زيادة معدل التبريد. علاوة على ذلك ، فقد وجد أن الزيادة في معدل التبريد أثناء التصنيع المركب تقلل من خصائص الانحناء للمركب ، ولكن امتصاص الطاقة وقوة التأثير زادت بشكل كبير بنسبة 15.1%.

INTRODUCTION

Polyphenylene sulfide (PPS) is a semi-crystalline, high-performance thermoplastic engineering plastic that possesses chemical resistance, and high mechanical and thermal properties, rendering it to be the alternative of choice for metals and thermosets [1-3]. Due mainly to its low melt viscosity (~200 Pa.s), the PPS thermoplastic polymer can be molded with high filler or reinforcement contents [4,5].

PPS is usually reinforced with various fillers such as glass fiber (GF) and carbon fiber (CF) for high-performance applications, including aerospace, electronics, and automotive [6-8]. The mechanical properties of such composite material depend not only on the interface between fiber and matrix but also depend on the crystalline structure and the degree of crystallinity of the polymer, which is strongly affected by the processing conditions and fabric structure [9].

Therefore, studying the relationship between the crystallinity of the polymer in composites and the mechanical properties is an important issue.

The crystallization kinetics of PPS-based composites have been studied extensively under isothermal conditions [1,10].

The first correlation between the properties and the structure of neat PPS and PPS-glass fiber composite was reported by *Brady, et al*. The semi-crystalline structure of the polymer was investigated using X-ray diffraction and it was found a maximum degree of crystallinity of about 60 percent after annealing at 204°C [11]. *AUER. C et al*. Investigated the isothermal crystallization of pure PPS and CF/PPS composite. The results showed that the storage temperature and time of the PPS melt play an important role in crystallization kinetics [12].

Most industrial processes are conducted under nonisothermal conditions and successful process development involving semi-crystalline polymers requires knowledge of the nonisothermal crystallization and melting processes and their kinetics to obtain a good performance of products [13]. In processing semi-crystalline thermoplastic polymers, cooling occurs from the melt in a nonisothermal crystallization process; this leads to a change in overall morphology which influences the polymer properties.

Therefore, there is a need to understand the nonisothermal crystallization process for resultant optimal properties in the industrial end product. The nonisothermal melt crystallization kinetics of CF reinforced PPS composite has not been investigated in detail, so far. In this study, nonisothermal crystallization kinetics of CF/PPS composites were investigated under different cooling rate.

The MoZhiShen method is used to study the nonisothermal crystallization kinetics of CF/PPS composites. Moreover, the effects of the cooling rate on the mechanical properties of composites were also investigated.

MATERIALS AND METHODS
Materials
The carbon fabric, 3K-T300-5HS, with a density is 1.27 g/cm³ used in this study was supplied by China Jiangsu Yixing Company. The PPS resin films were produced by China Sichuan drying keji high-tech material company.

Methods
Preparation of CF/PPS composite
First, CF and PPS films were cut into 15mm x 10mm sheets. The laminates were prepared by hot compression of alternating layers of 8 plies of CF and 18 PPS films as shown in Figure 1.

The processing took place in several steps. Firstly, the material was heated from room temperature (~25 °C) up to 320 °C, held at this temperature for 5 min under 0.5 MPa of pressure, then a pressure of 1 MPa was applied for 10 min, followed by held for 5 min under 2.1 MPa of pressure. Finally, different cooling rates of 10 k/min, 30 k/min, 50 k/min, and 70 k/min were applied to the mold until room temperature to vary the final degree of crystallization.
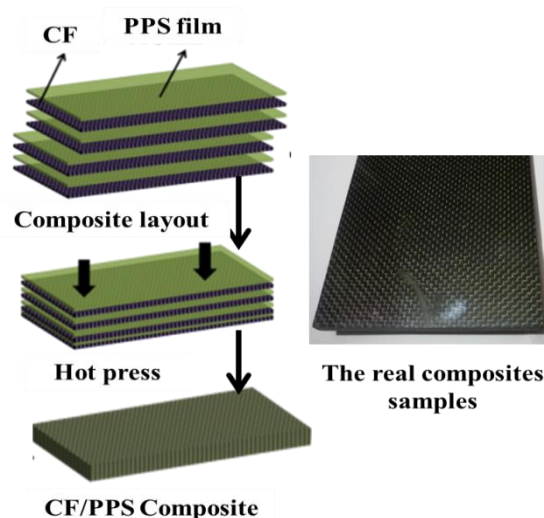

Figure 1: Preparation of CF/PPS composite.

Differential scanning calorimetric (DSC) measurements
Nonisothermal crystallization of prepared composites was measured using DSC2910 modulation type differential scanning calorimetric apparatus (MDSC, TA instrument companies in the United States). Samples of 8 ~ 10 mg were analyzed under nitrogen at a heating

rate of 20˚C/min from room temperature (25 °C) up to 320 °C.

The sample was kept for 3 min at this temperature to eliminate the heat history before cooling. Then, the melt was cooled at selected constant cooling rates of 10 k/min, 30 k/min, 50 k/min, and 70 k/min to remain consistent with the experimental data. Subsequently, all the prepared samples were heated from 50 to 350 ˚C at a rate of 20˚C/min under a nitrogen atmosphere.

The exothermal flow curves as a function of temperature were recorded to analyze the nonisothermal crystallization process. The following equation was used to calculate the degree of crystallinity:

$$Xc = \frac{\triangle Hc + \triangle H_f}{(1 - W_f)\triangle H_{fo}} \qquad (1)$$

Where: X_C is the degree of crystallinity, $\triangle H_f$ is the enthalpy of fusion at melting temperature, $\triangle H_c$ enthalpy of crystallization obtained during the DSC heating process, $\triangle H_{fo}$ is the melting heat of 100% crystalline PPS (80J/g), w_f is the weight fraction of carbon fiber in composite materials [14].

Mechanical properties measurements

Flexural properties of composites specimens were carried out according to ASTMD7264, using a Single edge notched bending specimen (2mm×13mm×78mm), using an Instron universal testing machine (American English strang Instrang company) at a test speed of 1.0mm/min and a span-to-thickness ratio of five. The notch impact tests were carried out by a Pendulum impact tester (Italian CEAST RESIL IMPACTOR). The specimen (55x10x10mm) was tested by a cantilever beam test at 5J. Five measurements were conducted and averaged for the final result.

Nonisothermal crystallization kinetics theory

The Avrami equation is mostly applied to characterize the isothermal crystallization kinetics [15]. The specific form of the Avrami equation is as follows:

$$1 - X(t) = \exp(-Zt^n) \qquad (2)$$

Take logarithm on both sides of the equation to get the following formula:

$$\lg[-\ln(1 - X(t)] = \lg tZ + n \lg t \qquad (3)$$

In the equation, Z is the crystallization rate constant (including nucleation and growth); n is the Avrami exponent which is relative to the mechanism of nucleation and dimension of growth; X (t) is relative crystallinity at time t.

Because the physical meaning of the Avrami index n is not clear, thus, the Avrami crystallization kinetics theory is not suitable for nonisothermal crystallization processes which are closer to industrial production.

Due to the Avrami equation cannot effective to describe the nonisothermal crystallization process, the posterity continuously improves the existing theory, and getting a series of theories can effectively describe the nonisothermal crystallization process, for example, improved Avrami equation of Jeziorny, Classic Ozawa equation, and MoZhiShen method. The MoZhiShen method is a new method that not only overcomes the drawback of the Ozawa method often appears nonlinear but also overcomes the

Avrami method. The most popular analysis of non-isothermal crystallization data utilizes the Ozawa equation, which was derived based on the Evans theory, this equation considered the influence of cooling rate Φ. Ozawa equation has extended the Avrami theory to the nonisothermal process from the crystallization nucleation and growth of the polymer, assuming that the amorphous polymer is heated or cooled at a constant rate.

$$\lg\ [-\ln\ (1 - X(T)] = \lg K(T) - m \lg \Phi \qquad (4)$$

Where: X (T) is the relative crystallinity at a temperature of T, m is the Ozawa exponent which depends on the dimensions of crystal growth, Φ is the heating or cooling rate, K(T) is the crystallization rate constant, and is related to

factors such as nucleation mode, and nucleation rate. By studying the nonisothermal crystallization process at different cooling rates, from log[-ln(1-Xt)] vs. log Φ plots at a given temperature, a straight line should be obtained, and values of m and K(T) can be found out by the slope and the intercept, respectively.

However, the Ozawa analysis is inappropriate to describe the kinetics of the nonisothermal crystallization behavior of certain polymer systems. Since the crystallization rate depends upon the cooling rate (Φ), Jeziorny suggested that the non-isothermal crystallization rate (Z) should be corrected by the cooling rate (Φ) to obtain the corresponding corrected rate constant (Zc) [16].

$$lgZ_c = \frac{lgz}{\Phi} \qquad (5)$$

The non-isothermal crystallization kinetic rate constant, Zc, increases substantially with the cooling rate, indicating faster crystallization. To understand the crystallization behavior, a new method established to describe the nonisothermal crystallization process by Mo's group has been used. Mo equation is based on combining the Ozawa and Avrami equations, and is defined with the following equation [17]:

$$\lg \Phi = \lg F(T) - a \lg t \qquad (6)$$

In the equation, Φ is standing for heating or cooling rate; F (T) = [K (T)/Z]$^{1/m}$, its physical meaning is the rate of cooling or heating value when a certain relative crystallinity is reached in a unit time for a system. F(T) can be used as the parameters of the characterization of polymer crystallization speed, its unit is K/min^{a-1}, a=n/m, n for the apparent Avrami index in the process of nonisothermal crystallization, m for Ozawa index; t is one point of time during the crystallization, it has the following relationship with temperature:

$$t = |T - T_0| / \Phi \qquad (7)$$

RESULTS AND DISCUSSION
Nonisothermal crystallization behavior of CF/PPS composites
The physical and mechanical properties of semi-crystalline polymer materials are largely dependent on the different processing conditions and the different crystal structures and crystal morphology.
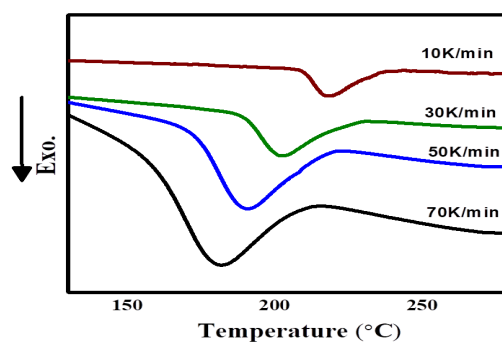
Figure 2: DSC curves of CF/PPS under different cooling rate

Figure 2 shows the DSC curves of heat flow as a function of temperature at different cooling rates of 10 °C/min, 30 °C/min, 50 °C/min, and 70 °C/min for PPS composites.

When the cooling rate increased, the exothermic peaks were become broader and shifted to a lower temperature, which indicated that the lower the cooling rates provide the better the crystal effect. Because under the lower cooling rate, PPS crystallization was maintained for a longer time at a higher temperature; the time was sufficient for the nucleation and crystal growth so that it could crystallize in a higher and narrower range of temperatures.

In contrast, when the cooling rate was too fast, there may not be enough time for nucleation and the crystal formation, so the crystallization peak becomes wider. The initial crystallization temperature and a crystallization peak temperature of the PEEK composite decreased with the increase of the cooling rate (Table 1).

$Φ$ is cooling rate; T_0 is initial crystallization temperature; T_c is crystallization peak temperature; T_f is crystallization termination temperature; $t_{1/2}$ is half crystallization time; $ΔH_c$

is crystallization enthalpy change.When the cooling rate is fast, the melted polymer had lower molecular mobility and the arrangement of PPS molecular chains is not complete.

The relative crystallinity X (T) was determined from the area under the exothermic peak of nonisothermal crystallization in the DSC thermo-gram at a temperature (T) divided by the total area under the exotherm during the cooling process.

TABLE 1: CHARACTERISTIC PARAMETERS OF CF/PPS UNDER DIFFERENT COOLING RATES

Samples	Φ/(K/min)	T_0(℃)	T_c(℃)	T_f(℃)	$t_{1/2}$ (min)	ΔH_c(J/g)
CF/PPS	10	239.2	219.3	206.2	1.42	26.81
	30	230.7	202.6	183.0	0.73	22.35
	50	224.2	190.9	161.3	0.62	18.29
	70	214.9	181.9	151.3	0.47	15.30

Figure 3 shows the plots of relative crystallinity as a function of temperature for the nonisothermal melt crystallization kinetics process of, CF/PPS composites at different cooling rates.
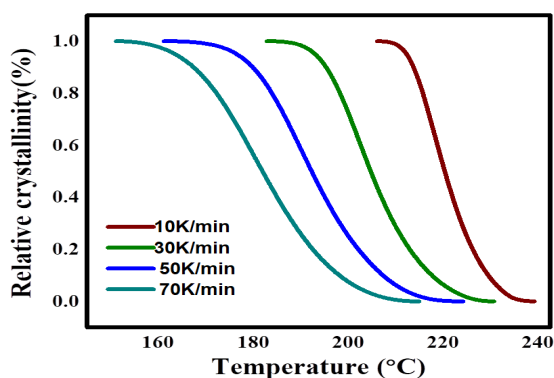

Figure 3: The relationship between the relative crystallinity of CF/PPS under different cooling rates and the temperature

The result showed that as the temperature decreased the curves of relative crystallinity X (T) as function temperature exhibited a sigmoid shape, suggesting that the crystallization rate was slow at the early and the last stage, on the contrary, the main segment of the curve features a higher slope indicating a faster reaction.

When the cooling rate was low, CF/PPS composites began to crystallize at a higher temperature. However, as the cooling rate increases, the crystallization temperature of CF/PPS composites decreases, indicating that crystallization has already begun at a low cooling rate.

To get the kinetic information based on the time, the crystallization temperature needs to be transformed to the relative crystallinity as a function of time (t). As shown in Figure 4, all curves showed an approximately sigmoidal shape at various cooling rates due to the spherulite impingement in the later stage of crystallization.
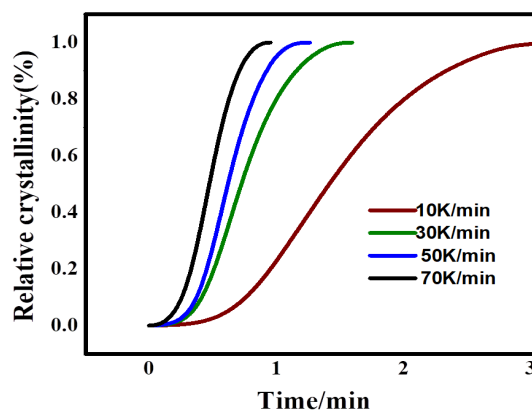

Figure 4: The relationship between the relative crystallinity of CF/PPS under different cooling rates and the time

With the increases in cooling rate, the crystallization time becomes shorter, which suggests that the polymer will not have enough time to crystallize and this causes smaller crystals with more defects. The results indicate that the crystallization temperature is an important influencing factor for estimating the crystallization time of PEEK and its composites, which should be attributed to the spherulite growth rate.

Avrami equation was initially applied to isothermal crystallization, later on; many reports of nonisothermal crystallization kinetics used it too. The plots of log [-ln(1 -Xt)] against logt for CF/PPS composites are shown in Figure 5.
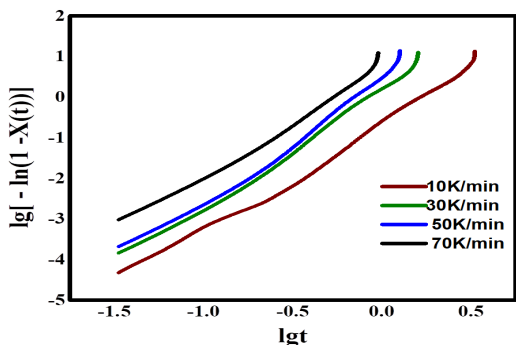

Figure 6: Avrami plots of CF/PPS composites

Each plot is composed of two parts, showing a linear part in a primary stage, which refers to the primary crystallization and the secondary stage deviates from linearity slightly indicating the impingement of spherulite in the later stage (referred to as the secondary crystallization stage). The values of n and Zc are listed in Table 2. It is well known that the parameter Zc describes the crystallization rate of the polymer molecules. The values of Zc for all samples increase with the increasing of cooling rate. Usually, a higher Zc value means a faster crystallization rate of the matrix [18].

TABLE 2: AVRAMI AND JEZIOMY PARAMETERS FOR NONISOTHERMAL CRYSTALLIZATION.

Samples	Φ/(K/min)	n	lgZ	lgZ_c	Z_c
CF/PPS	10	3.3	-0.58	-0.058	0.875
	30	3.2	0.18	0.006	1.014
	50	3.1	0.48	0.010	1.023
	70	3.1	0.82	0.012	1.028

As shown in Figure 6, all the plots show a good linear relationship between log b and log t. The quality of the linear fit is high (R2 > 0.99). R2 reflects the fitting degree of the fitting curve and the observation point, which proves that the Ozawa Avrami equation is a suitable choice for modeling the kinetics of nonisothermal crystallization behavior of PEEK matrices and their composites.
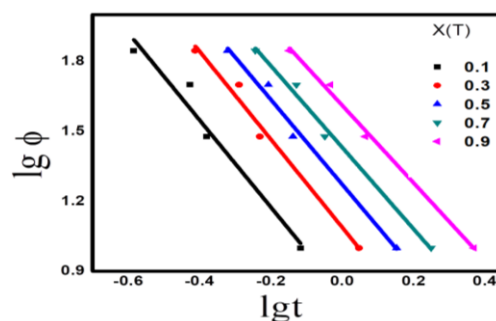

Figure 6: Avrami-Ozawa plots for samples of CF/PPS composites with different cooling rates.

As listed in Table 3, the value of F (T) increased with the increasing relative crystallinity, suggesting that the required cooling rate should be higher to achieve the same degree of crystallinity at unit crystallization time, which indeed indicated that the crystallization occurred at lower rates.

TABLE 3: NONISOTHERMAL CRYSTALLIZATION KINETICS PARAMETERS (F (T) AND A) BASED ON AVRAMI- OZAWA EQUATION.

| Samples	X(t)(%)	a	F(T)	R^2
CFF/PPS	10	1.87	6.3	0.950
	30	1.89	12.2	0.975
	50	1.82	18.7	0.982
	70	1.75	26.9	0.993
	90	1.66	40.7	0.991

Effect of cooling rate on the mechanical behavior of CF/PPS

Figure 7 A shows that different cooling rates affect the flexural properties of CF/PPS composites laminated. It is observed that the flexural strength and flexural modulus of composite laminate decreased with the increase of the cooling rate.

Flexural strength reduced from 613 MPa to 569 MPa and flexural modulus decreased from 70 GPa to 65.4 GPa. These changes occurred because the crystallization of the PPS matrix was decreased due to the high cooling rate and, as a result, the slips in the crystal blocks could induce more easily owing to the increased amorphous areas.

As shown in Figure 7 B, with the increase in

cooling rate, the notched impact strength increased from 63.0 KJ/m^2 and 72.5.0 KJ/m^2, increasing by 15.1%. As the cooling rate increased, the increase in ductility of the composite increased the deformation of the composite and the time of the maximum impact load, which indicates that the impact load was well dispersed.
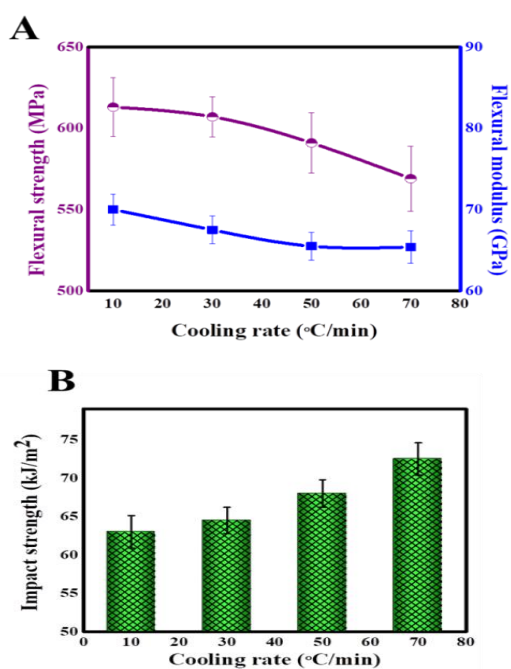
Figure 7: Effects of different cooling rates on (A) Flexural properties and (B) impact properties of CF/PPS composite

CONCLUSIONS

This article mainly discusses the nonisothermal crystallization kinetics of CF/PPS composite materials and crystallization behavior of CF/PPS under different cooling rates and its effect on the mechanical performance of composite materials. A differential scanning calorimeter (DSC) was used to study the nonisothermal crystallization behavior of CF/PPS.

From the Avrami kinetic parameters, the crystallization rate constant Zc increases with increasing cooling rate, and F(T) values increase with the increase of relative crystallinity, which suggests that to achieve high relative crystallinity of melted PPS need to select the high cooling rate. The effect of the cooling rate

on the mechanical properties of CF/PPS was also investigated.

Thermoplastic composites fabricated using high cooling rates reduced the crystallinity of the matrix. As a result, the flexural strength of the composite decreased by 7.2%, and the flexural modulus decreased by 7%. However, the high cooling rate increased the total absorbed energy by 15%. Therefore, the results of this study can be applied to composite-material-design scenarios in which the flexural properties are somewhat reduced, but high impact strength is required.

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