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Note

Effect of a polyaryletherketone-bearing bulky substituent on the non-isothermal crystallization kinetics of polyphenylene sulfide

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Abstract

The non-isothermal crystallization kinetics of polyphenylene sulfide (PPS) and its blends with polyaryletherketone-bearing phthalidylidene group (PEK-C) was investigated by differential scanning calorimetry. The experimental data were evaluated quantitatively. It was found that the blend of PPS incorporating 10 wt% PEK-C has the maximum crystallizability. The mechanism involved in the effect of PEK-C on PPS crystallization behaviour is proposed.

1. Introduction

Polyphenylene sulfide (PPS) is a high-performance semicrystalline thermoplastic polymer that has excellent chemical resistance, good thermal stability, good mechanical properties and inherent flame resistance. However, its brittle nature places restrictions on its industrial application. One of the most effective and conventional methods to remedy this defect lies in blending [1–4].

Polyaryletherketone-bearing phthalidylidene group (PEK-C, systematic name: poly(phthalidylidene-1,4-pheyleneoxy-1,4-pheylenecarbonyl-1,4-pheyleneoxy-1,4-pheylene)) is a newly synthesized member of the polyetherketone family, and exhibits mechanical properties at room temperature similar to those of polyetheretherketone (PEEK). Nevertheless this polymer is amorphous and shows a higher T_g (493 K), better

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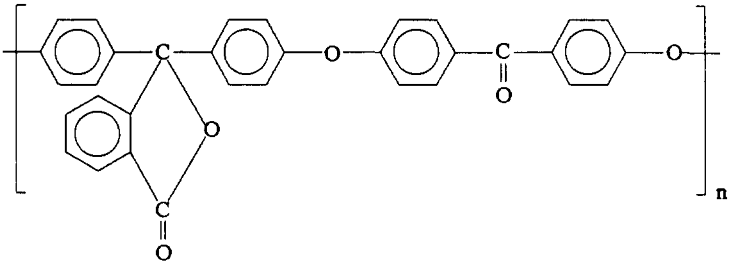
solubility in certain solvents, and is more economical in cost compared to PEEK [5, 6]. The chemical structure of PEK-C is



It has received considerable attention in the advanced composite field and has been recognized as possessing potential application in separation membranes, due to its large phthalidylidene side-group in the chain [6, 7]. In order to improve the toughness of PPS, PEK-C was selected as the blending component in our project. The mechanical property measurements on the blending systems (PPS/PEK-C) revealed that PPS could be rather ductile, e.g. the unnotched Charpy impact strength of the blend of 90 wt% PPS and 10 wt% PEK-C is 21 times that of neat PPS [8].

As with any semicrystalline polymer, the mechanical property and compatible extent of PPS/PEK-C blends (crystalline/amorphous blends) might be strongly dependent upon the crystallization behavior of PPS. An investigation of the effect of PEK-C on the crystallization of PPS in these blends is of both theoretical and practical interest. However, due to the fact that the non-isothermal crystallization process of a polymer is similar to real moulding conditions, a non-isothermal experiment is complementary to an isothermal study for understanding the crystallization behavior of polymers [9].

The present paper reports the non-isothermal crystallization kinetics study on PPS and PPS/PEK-C blends, aimed at providing useful information as an aid to research on the toughening mechanism of PPS/PEK-C blends as well as obtaining knowledge of the mutual interaction of PPS and PEK-C in the blends.

2. Experimental

Powdered PPS with a melt viscosity of 181 Pa and powdered PEK-C with a reduced viscosity of 1.1 ml g^{-1}, were kindly supplied by the Sichuan University and the Xuzhou Engineering Plastics Co. of China, respectively. In order to coincide as far as possible with the sample preparation employed in the mechanical property measurements, the samples for non-isothermal crystallization measurement were made by mixing PPS and PEK-C in powder form. The composition of the blends were 90, 75 and 60% PPS by weight, with the balance being PEK-C. A Perkin-Elmer DSC-2C differential scanning calorimeter was used. Under nitrogen flow, samples were heated to 603 K at 20 K min^{-1}, kept there for 5 min, and then cooled at selected rates, namely 10, 20 and 40 K min^{-1}. The crystallization thermograms were recorded simultaneously.

3. Results and discussion

Although the non-isothermal crystallization kinetics of PPS has been the subject of a few works [9, 10], no related information about PPS blended with high-performance thermoplastics is available. By examining the dependence of the crystallization exothermic peak temperature T_{max} on the cooling rate, dT/dt, it is found that with increasing dT/dt, T_{max} decreases linearly for every sample, i.e. a rise in supercooling is unfavorable to PPS crystallization. In addition, the values of T_{max} of different blend compositions at the same cooling rate differ from each other. Neat PPS and PPS/PEK-C(90/10) blend have the highest and almost the same T_{max}. T_{max} of PPS/PEK-C(60/40) blend is the lowest, while PPS/PEK-C(75/25) has moderate T_{max}. Thus, the non-isothermal crystallization of PPS in the blends is composition-dependent.

In order to evaluate quantitatively the non-isothermal crystallization kinetics of PPS, the method developed by Jeziorny [11] was used, which considers the non-isothermal crystallization of a polymer as a combination of a series of discontinuous isothemal crystallizations, and suggests that it could be characterized by a rate constant Z_c.

$$\log Z_c = \frac{\log Z_t}{dT/dt} \tag{1}$$

where Z_t is the Avrami kinetic constant. In addition, the crystallization is supposed to follow first-order kinetics [12]

$$\frac{dX}{dt} = (1 - X)K(T) \tag{2}$$

where X is the normalized crystallinity after time t and $K(T)$ a temperature-dependent rate constant. On the assumption that the curve of rate constant against temperature resembles a Gaussian function in shape, the "kinetic crystallizability" G, which characterizes the degree of crystallization obtained over the crystallization range $T_m \sim T_g$ with unit cooling rate, can be calculated from

$$G = \int_{T_g}^{T_m} K(T)\,dT = \sqrt{\frac{\pi}{\ln 2}}\,\frac{D}{2}\,K_{max} \tag{3}$$

where K_{max} is the maximum rate constant corresponding to the crystallization exothermic peak, D is the half-width of the crystallization curve, T_m is the melting temperature and T_g is the glass transition temperature. With regard to the non-isothermal feature of the investigation, the final form of the kinetic crystallizability G_c is corrected as follows

$$G_c = \frac{G}{dT/dt} \tag{4}$$

According to the above-mentioned theory and the well-known Avrami equation, the parameters characterizing non-isothermal crystallization kinetics of neat PPS and the PPS component in blends were obtained and are listed in Table 1. Considering that the kinetic crystallizability acts as a measure of the crystallizability of various polymers

Table 1
Some parameters of non-isothermal crystallization kinetics of PPS

Composition of PPS/PEK-C blends	Cooling rate $dT/dt/(\mathrm{K\,min^{-1}})$	Avrami exponent n	Rate constant $Z_c/\mathrm{min}^{1-n}\,\mathrm{K}^{-1}$	Kinetic crystallizability G_c
100/0	10	1.84	1.02	0.90
	20	1.95	1.05	1.38
	40	2.10	1.05	1.07
90/10	10	2.01	1.01	1.53
	20	1.81	1.08	1.69
	40	1.78	1.06	1.50
75/25	10	1.94	0.99	1.49
	20	1.80	1.05	1.35
	40	1.70	1.05	1.32
60/40	10	1.96	0.90	1.26
	20	2.11	1.01	1.11
	40	2.20	1.03	1.01

during non-isothermal crystallization, and the higher the G_c the higher the degree of crystallinity at the same cooling rate [9], the difference in G_c of the materials shown in Table 1 demonstrates the effect of PEK-C on the non-isothermal crystallization of PPS. It can be seen that by incorporation of PEK-C, the values of G_c change non-monotonically with the blend composition: G_c increases to pass through a maximum and then decreases with increasing PEK-C content. In fact, as was found in the isothermal crystallization kinetics study of PPS/PEK-C blends [13], PEK-C can lower the crystalline surface free energy of PPS and promote the crystallization of PPS; however, PEK-C can also be obstructive to PPS crystallization and decrease the overall crystallization rate of PPS. Therefore, it can be deduced that under non-isothermal conditions, the nucleation and obstruction effect of PEK-C on PPS should still be responsible for the non-linear dependence of G_c on blend composition shown in Table 1, i.e. on the one hand, PEK-C phase serves as nuclei leading to a rise in the crystallizability of PPS; on the other, because the amorphous PEK-C is foreign matter, its presence increases the system viscosity and hinders the crystallizable PPS chains from diffusing towards the nuclei, resulting in a decrease in the crystallizability of PPS. These are two contradictory effects and their combined result depends to a large extent on the blend composition. In the case of a lower PEK-C fraction, the nucleation effect plays the deciding role, and in the case of a higher PEK-C fraction, the obstruction effect predominates. At a certain blend ratio, e.g. PPS/PEK-C(90/10), they reach an equilibrium and a maximum crystallizability is found.

With respect to the rate constant Z_c, see Table 1, its dependence on blend composition at every cooling rate is similar to that of G_c, i.e. Z_c is controlled by the same mechanisms as discussed above.

The Avrami exponent n is plotted as a function of cooling rate dT/dt in Fig. 1. It can be seen that the values of n vary from 1.7 to 2.2. Due to the fact that n is linear with dT/dt, the Avrami exponent n at zero cooling rate can be estimated through extrapola-

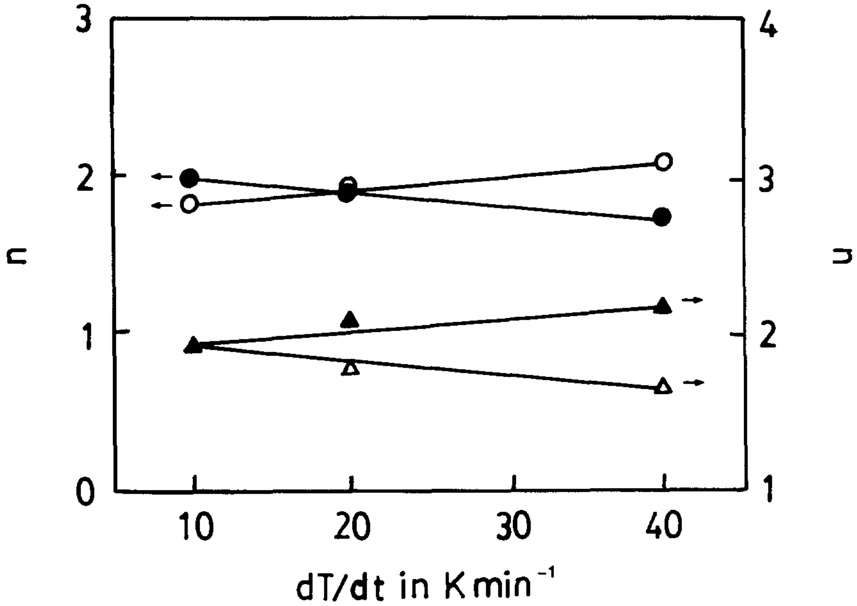


Fig. 1. Plots of the Avrami exponent *n* versus cooling rate d*T*/d*t*: ○, neat PPS; ●, PPS/PEK-C(90/10); △, PPS/PEK-C(75/25); ▲, PPS/PEK-C(60/40).

tion in the ragne 1.8–2.1, which coincides with the result obtained under isothermal conditions [13, 14]. In addition, it should be noted that in the case of neat PPS and PPS/PEK-C(60/40) blend, *n* increases with increasing cooling rate, but decreases with increasing cooling rate in the case of PPS/PEK-C(90/10) and PPS/PEK-C(75/25) blends. It seems that different nucleation processes might be involved. For the time being, the occurrence of such a phenomenon cannot be explained in a rational way. Further experiments will be necessary to acquire a deeper understanding of the micro-mechanism.

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