Effect of Novel Lubricant GPSL on Crystallization Behavior of PEEK Resin

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Poly(aryl ether ketone)s (PAEKs) are one of the most important classes of high performance engineering thermoplastics, and have found extensive applications in the aviation, automotive, and electric industries owing to their excellent thermal stability, mechanical properties and good chemical resistance[1]. High melting temperature and high melt viscosity are characteristic of PAEKs, however are also the primary drawbacks associated with processing these materials [2]. To obtain different properties of PAEKs for various applications and improve processing characteristic, researchers have done a lot of work [3-7]. In this paper, a novel high temperature lubricant (GPSL) were used in poly (ether ether ketone) (PEEK) resin to improve processing characteristic and crystallinity of PEEK resin. Ones can find that the torque of extruder screw decrease observably with increase of GPSL, and the velocity of crystallization of PEEK resin increase because of adding of the lubricant GPSL. The novel lubricant GPSL maybe is an effective modifying agent for processing of PEEK.

Effect of lubricant GPSL on torque of screw

The compounding formula and experiment data of PEEK/GPSL and PEEK/CF/GPSL are listed in table 1.

Table 1 The compounding formula and processing temperature of samples

Sample	PEEK c(wt%)	GPSL (wt%)	CF[a] (wt%)	Speed of screw	Speed of feeder	Torque of screw
1	100	0	0	80	120	88
2	99	1	0	80	120	62
3	80	0	20	90	140	90
4	79	1	20	90	140	63
5	97	3	0	80	120	58
6	77	3	20	90	140	52

Barrel	1	2	3	4	5	6	7	8	Head
Temp. (℃)	280	330	350	365	365	365	360	350	330

a: CF is abbreviation of carbon fiber.

In order to exhibit the change of torque with lubricant GPSL further clearly, the change of

torque to content of GPSL is showed in Figure 1.

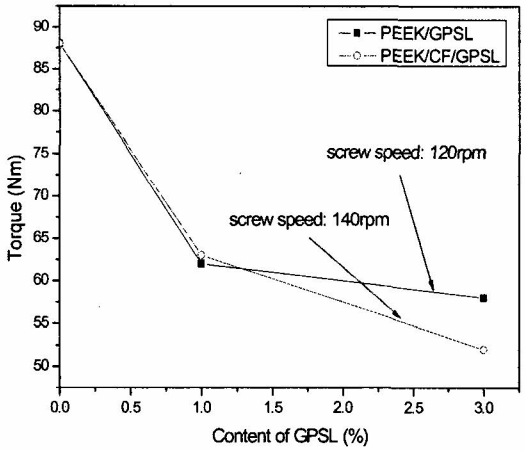

Fig. 1 The effect of lubricant (GPSL) on torque of screw

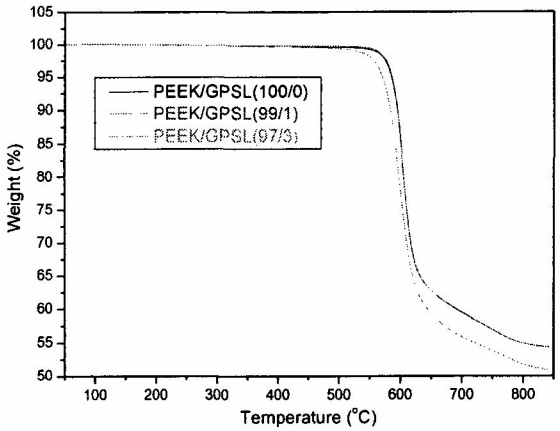

Fig. 2 TGA curves of PEEK resin and PEEK/GPSL in nitrogen

The results of Table 1 and Figure 1 show that the torque of extruder screw can be reduced by little lubricant GPSL (only 1% wt). So GPSL is an efficient lubricant for processing of PEEK resin.

Effect of lubricant GPSL on the stability of PEEK resin

Generally, lubricants perhaps affect the stability of polymers. A comparison of TGA curves was given in Figure 2. The 5.0% weight loss temperatures (T_d) of the PEEK and PEEK/GPSL were determined by thermo gravimetric analysis given in Table 2. Sample 2 and sample5 showed the T_d (585.6℃ and 570.1℃), sample 2 is almost same as PEEK(585.2 ℃) resin, and sample 5 is little lower than that of PEEK (585.2℃). This indicates the novel lubricant GPSL almost don't affect the stability of PEEK resin in the given dosage of GPSL.

Table 2 The 5.0% weight loss temperature (T_d) of PEEK and PEEK/GPSL

Sample	T_d (5.0%) (℃)
PEEK/GPSL (100/0) (sample 1)	585.2
PEEK/GPSL (99/1) (sample 2)	585.7
PEEK/GPSL (97/3) (sample 5)	570.1

Crystallization behavior and Isothermal crystallization kinetics of PEEK/GPSL and PEEK/CF/GPSL

Because there is nanometer SiO_2 in lubricant GPSL, the crystallization behavior of PEEK will be changed by adding GPSL in PEEK resin. We study the crystallization of PEEK/GPSL and PEEK/CF /GPSL. Figure 3 shows the curves of isothermal crystallization time of PEEK/GPSL, PEEK/CF/GPSL at 298℃. It indicates that the crystallization speed of PEEK/GPSL, PEEK/CF/GPSL were improved by adding GPSL but decreased by CF.

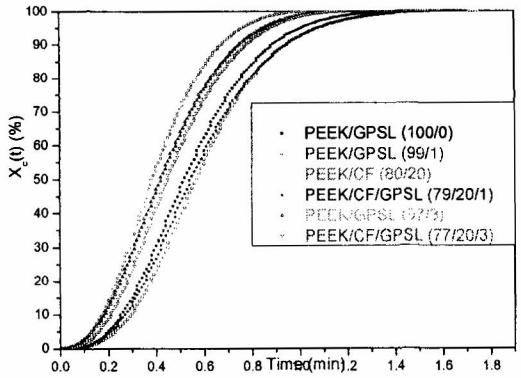

Fig. 3 The isothermal crystallization curve of relitive crystallinity of PEEK/GPSL and PEEK/CF/GPSL vs time at 298 °C

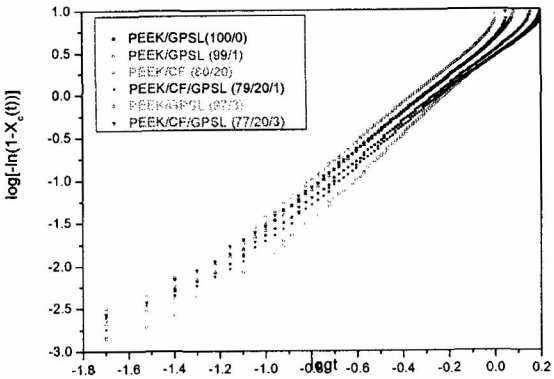

Fig. 4 Plot of log(-ln(1-Xc(t))) vs. Logt for PEEK/GPS at 298 °C

The isothermal crystallization kinetics of PEEK/GPSL and PEEK/CF /GPSL was studied at 298°C. The result was analyzed by means of the Avrami equation:[8]

$$1\text{-}X_t = \exp - kt^n \qquad (1)$$

Equation (1) is often written in the logarithmic form:

$$\ln(1 - X_t) = -kt^n \qquad (2)$$

Where k is the rate constant of crystallization and n is the Avrami exponent, which can be related to the type of nucleation and the geometry of crystal growth. Plots of lg[-ln $(1\text{-}X_t)$] vs lg$t$ for PEEK/GPSL and PEEK/CF /GPSL are shown in Figure 4. The curve of sample 2 sample 5 and sample 6 showed one stage, and the curve of sample 1, sample 3 and sample 4 contains two stages: a primary stage, and a secondary stage. From the intercept and slop of the linear part, the values of k and n were calculated, respectively. The t_{max}, the time to reach the maximum rate of heat flow, and $t_{1/2}$, the half time of crystallization, can be calculated using the follow equations:

$$t_{\max} = [(n - 1)/nk]^{1/n} \qquad (3)$$

$$t_{1/2} = (\ln 2/k)^{1/n} \qquad (4)$$

The values of n and k, as well as $t_{\max\ cal}$ ($t_{\max\ exp}$), $t_{1/2cal}$ ($t_{1/2exp}$) and $\tau_{1/2exp}$ ($\tau_{1/2cal}$) are listed in Table 3. The Avrami exponent n, is in a range from 2.12 to 2.58, and almost independent on lubricant GPSL and carbon fiber (CF). The values of the kinetic rate constant k are influenced by adding lubricant GPSL and CF. For the given composition, k increase by adding GPSL and decrease by adding CF, while the crystallization rate constant of PEEK with GPSL was always higher than that of pure PEEK and PEEK/CF. This implies that as a nucleation agent, GPSL may promote the crystallization process of PEEK, but not affect the crystallization mechanism. From Table 3, it is clear that the time to reach the maximum rate of heat flow and the half time of the crystallization decrease because of adding GPSL, and the time to reach the maximum rate of heat flow and the half time of the crystallization of PEEK with CF are lower than those of without CF, as well as the fact that there is not much difference between the values calculated with eqs. (3) and (4) and those experimentally measured. The agreement in values $t_{\max\ cal}$ ($t_{\max\ exp}$), $t_{1/2cal}$ ($t_{1/2exp}$) and $\tau_{1/2exp}$ ($\tau_{1/2cal}$) suggests that the Avrami equation works well in describing the crystallization process of PEEK/GPSL

and PEEK/CF/GPSL.

Table 2 Avrami Parameter n, k, $t_{1/2exp}$, $t_{1/2cal}$, $t_{max\ cal}$, $t_{max\ exp}$, $\tau_{1/2exp}$ and $\tau_{1/2cal}$

PEEK/CF/GPSL (w/w/w)	n	k (1/min)	$t_{1/2exp}$ (min)	$t_{1/2cal}$ (min)	$t_{max\ exp}$ (min)	$t_{max\ cal}$ (min)	$\tau_{1/2exp}$ (1/min)	$\tau_{1/2cal}$ (1/min)
100/0/0	2.55	3.13	0.47	0.55	0.43	0.53	2.13	1.82
99/0/1	2.25	5.77	0.37	0.39	0.33	0.35	2.70	2.56
80/20/0	2.58	2.45	0.53	0.61	0.53	0.58	1.89	1.64
79/20/1	2.51	2.59	0.50	0.59	0.48	0.56	2.00	1.69
97/0/3	2.12	4.38	0.42	0.42	0.36	0.37	2.38	2.38
77/20/3	2.42	4.47	0.42	0.46	0.37	0.43	2.38	2.17

A small amount of GPSL can decrease torque of screw for processing PEEK resin, namely the novel lubricant GPSL can improve processing characteristic of PEEK resin, at the same as can promote the crystallization process of PEEK, but not change the nucleation and growing mechanisms.

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