STUDY ON THE RHEOLOGY AND TENSILE PROPERTY OF CCF300/PEEK COMPOSITES VIA POWDER IMPREGNATION METHOD

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ABSTRACT

In order to manufacture excellent CCF300/PEEK composites, a comparative experimental investigation about the rheology of two PEEK resins and tensile strength of CCF300 reinforced PEEK composites via powder impregnation method was investigated with different kinds of PEEK powders. Two kinds of PEEK with different melting flow rates (MFR) were employed to study on their rheology behavior and reveal the processing characteristics. The results showed that the fiber distribution have a high dependence on the mobility of molten resin, which follows a skewed distribution. High viscosity of PEEK leads to a high value of the function parameters the skewness coefficient Cs and kurtosis coefficient K. Furthermore, the tensile property of composites also has a high dependence on viscous flow of PEEK, and the tensile strength of a low-viscosity PEEK composites is 10% to 20% higher than the other one.

1 INTRODUCTION

With the advent of high performance thermoplastic polymers, structural applications for thermoplastic composites are increasing rapidly. Recently, the increasing usage of continuous fiber reinforced thermoplastic composites (CFRTP) as a bearing component is partially replacing the conventional thermoset composites. It is mainly due to some attracting properties such as the repeatable processing and recyclability [1-3], excellent impact toughness [4-6] and et al. High temperature resistance and impact toughness are the two most important technical requirements for practical applications of CFRTP, especially in the area of aerospace [7,8]. Carbon fiber reinforced PEEK (CF/PEEK) composites are an excellent candidate for manufacturing the components [9-11], which can be prepared by many ways, for example, powder impregnation [12,13], commingled yarns [14-16] or prepregs [17,18]. In these methods, powder impregnation process is undeniably an economical and convenient way to manufacture the thermoplastic composites[19].

However, the impregnation of high molten viscosity PEEK into carbon fibers is a great challenge. Cogswell et al. [20] reported that in order to achieve an excellent impregnation of molten thermoplastic resin into fiber bundles, the viscosity of molten thermoplastic resin should be less than 30 Pa·s[21-23], preferably between 1 and 10 Pa·s[24-27]. When the melt viscosity is more than 100 Pa·s, the impregnation of molten thermoplastic resin into fiber bundles will be very difficult[28-32]. Actually, the viscosity of PEEK melt is far more than 100 Pa·s[33,34]. So it is very important to find out the relationship between the viscosity of molten resins and tensile property of composites. It is worth noting that in allusion to different reinforcements and thermoplastic resins, for the determination and optimization of the processing parameters is an empirical and time-consuming process, so an efficient and accurate study is needed to obtain the relationship by a simple and veracious way, guiding the production.
2 EXPERIMENTAL

2.1 Raw Materials

Carbon fiber CCF300 (Weihai Tuozhan Fiber Co., Ltd.) was mainly made of unidirectional yarns consisting of 3000 filaments with diameter of about 7 μm each. Two kinds of PEEK with different MFR were produced from Changchun Jilin University Special Plastic Engineering Research Co., Ltd. (in powder form) and ICI (Victrex 450P), respectively. And each PEEK is numbered uniformly in turn, that is, PEEK1 and PEEK2. The glass transition (T_g) and the melting point (T_m) temperatures of PEEK are about 140 °C and 343 °C, respectively.

2.2 Measurement of Melt Flow Rate and mechanical properties of PEEK

Melt Flow Rate (MFR) measurements were performed on Melt Flow Indexer RZY-400. Testing weights included 2.160 kg, 3.605 kg, 5.000 kg, 7.925 kg and 10.000 kg and testing temperatures included 380 °C, 390 °C and 400 °C. A brief description of the procedure is as follows: the instrument including the removable die is maintained at the test temperature for 15 min. PEEK powders are charged into the barrel and then compacted. The piston is inserted into the barrel and the test weight is added on the top of the piston followed by a three-minute preheat period. The extrudates can be obtained, some of which need to be discarded if there are several visible bubbles. The MFR can be calculated according to ASTM D1238.

2.3 Preparation and Characterization of composites

CCF300/PEEK composites were manufactured by a two-step process. PEEK powders mentioned above were crushed to a size of about 100 microns. PEEK powders were coated on the double side of single layer CCF300 by a preheating process without pressure firstly. The weight ratio of CCF300 to PEEK was controlled at 2 to 3. The semi-impregnated sheets were stacked layer by layer and prepared in a vacuum press according to the designed process followed by furnace cooling for high crystallinity and low residual stress. Unidirectional composite laminates were obtained with the final thickness of about 2 mm. Decomposition of sizing agent on carbon fiber is not considered in this paper.

Theses composite laminates were cut into standard sizes for testing mechanical properties based on the corresponding ASTM standards. The stereomicroscope (LEICA DM4000) was utilized to analyze the internal defects, fiber volume contents, and failure mechanisms of composite specimens. Scanning electron microscope (SEM, 6010) was employed to illustrate the fracture morphology of composite specimens.

3 RESULTS AND DISCUSSION

3.1 Preparation and Characterization of composites

In order to manufacture CCF300/PEEK composites, it is necessary to analyze PEEK rheology behavior and reveal the processing characteristics by a comparative study. Two kinds of PEEK with different MFR were employed. PEEK1 presents higher MFR than the other PEEK, which indicates that PEEK1 has lower molten viscosity. The measured MFR value of PEEK1 obtained at 400 °C with 10.000 kg is 112 g/min. However, PEEK2 shows 4-6 times lower MFR than PEEK1 at 400 °C with 10.000 kg. With the reduction of temperature and pressure, their MFR present a bigger difference. The relationship between MFR and pressure is shown in Fig. 1. It can be observed that MFR versus Pressure profiles present a non-linear relationship. Polynomial fitting is adopted to expatiate the rule of MFR along with the change of pressure [35]. The MFR of PEEK1, PEEK2 at 400 °C from 2.160 kg to 10.000 kg increase by about 5 times and 8 times, respectively. It is obvious that MFR versus Pressure profiles of PEEK1 is relatively close to linear variation compared with the other PEEK. For PEEK with a high MFR such as PEEK2, increasing the processing pressure can make a great
contribution to decrease the viscosity. So pressure plays a key role in increasing viscous flow to improve processing performance.

MFR can indicate the viscous flow characteristic of PEEK, which is similar to the viscosity. The relationship between MFR and η has been reported by Saini and Shenoy [36].

\[ \eta = \frac{\tau}{\dot{\gamma}} = \frac{5 \times 10^4 \rho M}{M FR} \quad (1) \]

where \( \eta \) is the viscosity of the molten thermoplastic resin (Pa·s), \( \tau \) is the shear stress, \( \dot{\gamma} \) is the shear rate, \( \rho \) is the density of the thermoplastic resin (g/cm\(^3\)), \( M \) is the load applied on the molten thermoplastic resin (kg) and MFR is the melt flow rate (g/10min).

According to Arrhenius-Eyring Equation [37,38],

\[ \eta = A \exp\left(\frac{E}{RT}\right) \quad (2) \]

where \( E \) is the activation energy of viscous flow (J/mol), \( R \) is the ideal gas constant, 8.314 J/(mol·K), \( T \) is the temperature (K), and \( A \) is the frequency term. The premise of Arrhenius's empirical formula is that the activation energy \( E \) is regarded as the temperature independent constant.

Combining the equation (1) and (2), we can get

\[ M FR = \frac{5 \times 10^4 \rho M}{A} \exp\left(-\frac{E}{RT}\right) = \beta \times \exp\left(-\frac{E}{RT}\right) \quad (3) \]

Transforming into the logarithmic form, thus

\[ \ln\left[M FR^{-1}\right] = -\ln \beta + \frac{E}{RT} \quad (4) \]

Based on equation (4), the activation energy \( E \) can be calculated from the slope of ln [(MFR)\(^{-1}\)] versus \( T^{-1} \) plot [30]. The smaller the \( E \) is, the lower the energy required for the viscous flow of molten thermoplastic resin is. Activation energy, as the nature of PEEK, reveals the temperature sensitivity of its viscosity. Activation energies are obtained based on the linear fitting of ln [(MFR)\(^{-1}\)] versus \( T^{-1} \) seen in Fig. 3. These lines in Fig. 3 with similar slopes can be used to calculate the activation energy in each graph. Activation energies of PEEK are presented in Fig. 4. We can conclude that the MFR of these PEEK at a certain temperature and pressure have an opposite trend with the activation energy. The order of different PEEK with the highest activation energy to the lowest is PEEK3, PEEK2, PEEK4, and PEEK1, which has the same rule as temperature sensitivity of PEEK viscosity. As mentioned in the discussion of Fig. 2, PEEK1 has the lowest temperature sensitivity during
processing. Of course, it is obvious that PEEK1 has the lowest activation energy and highest MFR and presents a better flow performance.

3.2 Fiber distribution in optical images

Further research about the relationship between the impregnation status and the viscosity of PEEK resin carry on to analyze the tendency of fiber distribution in the composites.

To analyze the fiber distribution in a more accurate way, all the fiber spacings were count to explore the regularity in the flowing way shown in Fig. 2: a random 500x optical image was selected, the center of each fiber was marked, then we started from one fiber, connected its center to its near fibers' centers and repeated again and again until all the loops became closed, then the images are cut into many triangles. All the triangles were be adjusted to make as many triangles’ internal angle between 45 ° to 90 ° as possible, finally, all the fiber spacings were count and a skewed distribution curve was draw.

Fig. 2 fiber distribution statistical method

In order to analyze the skewed distribution curve, two significant parameters should be compared: the skewness coefficient $C_s$[39] and kurtosis coefficient $K$[40]. The skewness coefficient $C_s$ is identified as

$$C_s = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^3}{n\bar{x}^3C_v^3} \quad (4)$$

Where $x_i$ is one fiber spacing, $n$ is the number of fiber spacings, and $C_v$ is the standard deviation. In general, $C_v$ larger than 0 means that it is a positive partial function, most of data remain small, the lager $C_v$ is, the more concentrated the distribution is.

Kurtosis coefficient $K$ is identified as

$$K = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^4}{(n-1)s^4} \quad (5)$$

Where $x_i$ is one fiber spacing, $n$ is the number of fiber spacings, and $s$ is the variance. In general, $K$ larger than 3 means that the data is more concentrated than Gaussian distribution, which means that the high viscosity of resin has influenced the random distribution of fibers. The lager $K$ is, the more concentrated the distribution is.

The 500x optical image and the skewed distribution curve of PEEK1 and PEEK2 are shown in Fig. 3 and Fig. 4, and it is obvious that the fiber distribution of PEEK2 is more concentrated, for the viscosity of PEEK2 is much higher.
The comparative results of PEEK1 and PEEK2 are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fiber number</th>
<th>Fiber spacing number</th>
<th>$C_v$</th>
<th>$K$</th>
</tr>
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<tbody>
<tr>
<td>PEEK1</td>
<td>457</td>
<td>1306</td>
<td>0.82</td>
<td>7.4</td>
</tr>
<tr>
<td>PEEK2</td>
<td>513</td>
<td>1657</td>
<td>1.13</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Table 1: The comparative results of PEEK1 and PEEK2

It is obvious that the parameters of PEEK2’s image is higher than the other one, for the impregnation is less sufficient.

The schematic for fiber distribution process of resin impregnation is shown in Fig. 5. First of all, in the initial phase, the PEEK powder distribute among the fibers evenly via powder impregnation method and the fibers gather in tow; then, in the impregnation phase, the PEEK powders melt and fill the space among the fibers, and the fibers move outside against the resistance of the high-viscosity resin; finally, in the impregnation phase, the fibers distribution trend to achieve Gaussian distribution, higher viscosity the resin is, more concentrated the fibers will be.
3.3 tensile strength of composites

PEEK rheology behavior has a great effect on the impregnation of composites in a quite directly way, which need to be investigated further.

![Tensile Strength Graph](image)

**Fig. 6** The tensile strength of CCF300/PEEK1 and CCF300/PEEK2 composites

As shown in Fig. 6, the tensile strength of PEEK1 is between 10% and 20% higher than that of the other one in both 25°C and 70°C. It can be easily explained, for PEEK1 has a higher MFR and better flexural properties, but PEEK2 is just the opposite. However, as we can see in both optical images, both resin can impregnate the fibers sufficiently, there is nearly no void in the images, but the tensile strength has visible difference. It may be due to that the viscosity of resin influences the distribution of fibers, which play an important role on the mechanical property of composites. Obviously, it is noted that PEEK with a high MFR and a relatively excellent mechanical property is expected to display a great advantage as a matrix of composites. As for the preparation of CF/PEEK composites by our process, the low molten viscosity can be a key factor. As discussed above, PEEK1 is a better choice to prepare the CCF300/PEEK composites in the following research.

4 CONCLUSION

In summary, we have revealed a significant influence of PEEK rheology on the tensile property of composites. Besides, we obtain a complete understanding about the impregnation characteristics of molten PEEK into carbon fiber CCF300, the distribution characteristics of CCF300 and the mechanical performance of CCF300/PEEK. Fiber distribution have a high dependence on the mobility of molten resin, which follows a skewed distribution. High viscosity of PEEK leads to a high value of the function parameters the skewness coefficient Cs and kurtosis coefficient K. Furthermore, the tensile property of composites also has a high dependence on viscous flow of PEEK, and the tensile strength of a low-viscosity PEEK composites is 10% to 20% higher than the other one. The result shows that rheology plays a more significant role on the tensile property of composites because of its decisive effect on the impregnation states of laminated plates.

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