Rheological Properties in Blends of Poly(aryl ether ether ketone) and Liquid Crystalline Poly(aryl ether ketone)

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ABSTRACT: Rheological properties of the blends of poly(aryl ether ether ketone) (PEEK) with liquid crystalline poly(aryl ether ketone) containing substituted 3-trifluoromethylbenzene side group (F-PAEK), prepared by solution precipitation, have been investigated by rheometer. Dynamic rheological behaviors of the blends under the oscillatory shear mode are strongly dependent on blend composition. For PEEK-rich blends, the systems show flow curves similar to those of the pure PEEK, i.e., dynamic storage modulus G′ is larger than dynamic loss modulus G″, showing the feature of elastic fluid. For F-PAEK-rich systems, the rheological behavior of the blends has a resemblance to pure F-PAEK, i.e., G″ is greater than G′, showing the characteristic of viscous fluid. When the PEEK content is in the range of 50–70%, the blends exhibit an unusual rheological behavior, which is the result of phase inversion between the two components. Moreover, as a whole, the complex viscosity values of the blends are between those of two pure polymers and decrease with increasing F-PAEK content. However, at 50% weight fraction of PEEK, the viscosity-composition curves exhibit a local maximum, which may be mainly attributed to the phase separation of two components at such a composition. The changes of G′ and G″ with composition show a trend similar to that of complex viscosity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4040–4044, 2006

Key words: poly(aryl ether ketone); liquid crystalline poly(aryl ether ketone); blends; rheology

INTRODUCTION

Poly(aryl ether ketone)s (PAEKs) are one of the most well-known series of high temperature, high performance semicrystalline aromatic thermoplastics, and have been widely used in various fields because of their excellent mechanical properties, good electrical properties, thermal stability, and chemical and radiation resistance.[1–5] However, high melting points and high melt viscosities are the primary drawbacks to limit the processing and application of these materials. Because of the lower cost involved relative to synthesizing new polymers, it is expected to improve the processability of PAEKs via physical blends. Provided that they are blended with the common polymers, there will certainly be a rapid reduction in mechanical properties of PAEKs. Compared with the conventional polymers, the thermotropic liquid crystalline polymers (TLCP) possess the unique structural properties, such as the rigid rod nature of TLCP molecules, molecule anisotropy, and low viscosity.[6–9] By blending with TLCP, which can act as processing aids to reduce blend viscosity and reinforcing agents, both improvements of processing property and reinforcement of

mechanical strength of poly(aryl ether ether ketone) (PEEK) can be achieved. A series of thermotropic aromatic liquid crystalline polyesters are currently being used in the composites or blends with PAEKs to improve the processing and performance of these materials.[10–15] However, because of the poor miscibility and unmatched melting temperatures of two components, it is difficult to acquire the ideal blend system.

Recently, based on introduction of substituted side-groups (such as chloro, p-phenyl, t-butyl, methoxy, etc.) and biphenyl mesogenic units into the PAEK backbones, a series of thermotropic liquid crystalline poly(aryl ether ketone)s (LC-PAEKs) have been successfully designed and synthesized,[16–22] especially a batch production of liquid crystalline PAEK containing substituted 3-trifluoromethylbenzene side group (F-PAEK) with better thermal stability.[23–25] This provides us the possibility to investigate the properties of the PAEK/F-PAEK blends. Furthermore, F-PAEK and PAEKs have similar chain structure, preferable miscibility and matchable melting temperatures, showing great promise for improved processing of the blends. Therefore, it is of great interest to study the thermal behavior and rheological properties of F-PAEK/PAEK blends for practical applications.

In this article, the dynamic rheological measurements under the oscillatory shear mode are carried out for the PEEK/F-PAEK blends in an attempt to investigate the interplay of rheological properties with com-
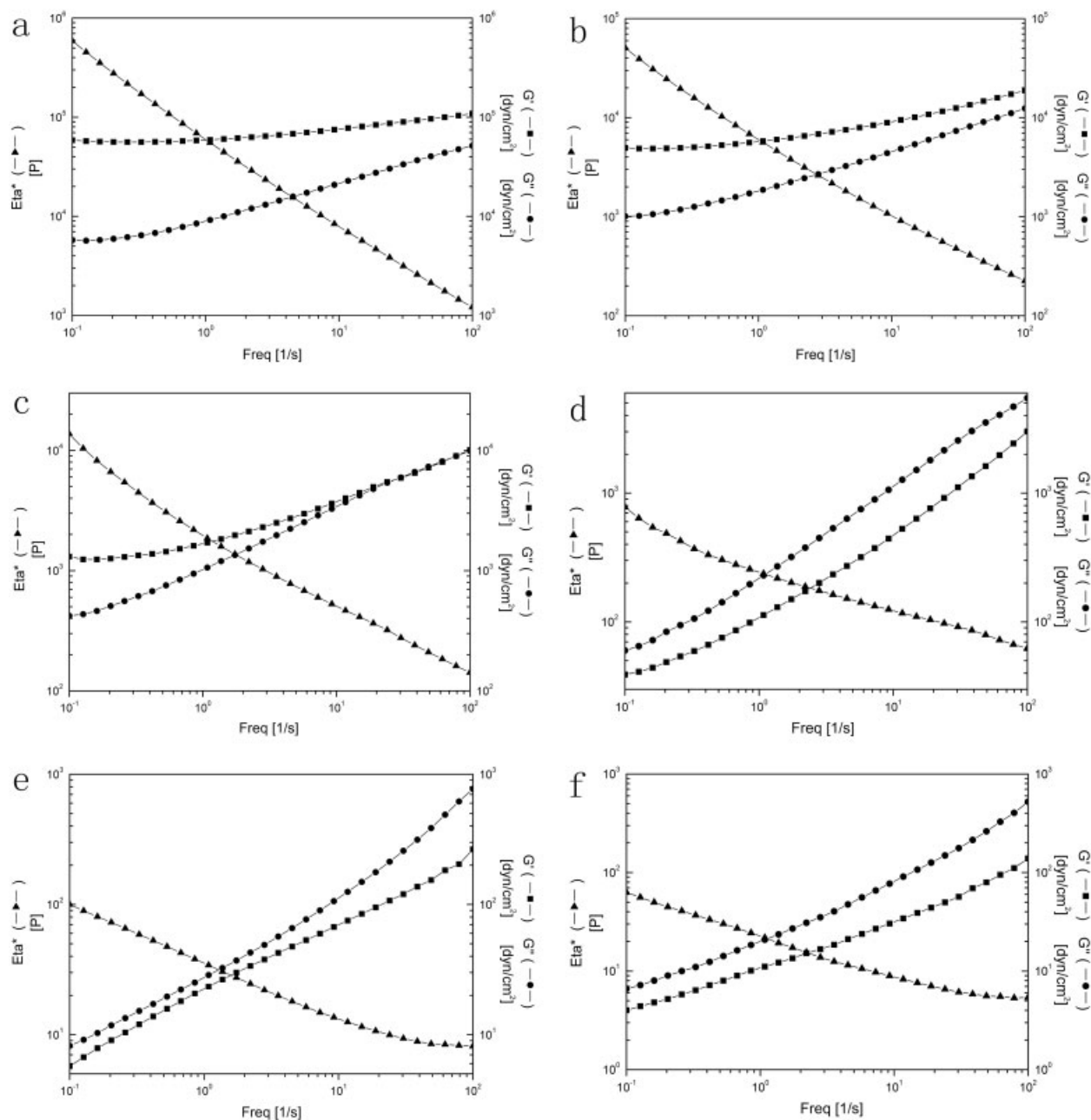
Figure 1 Plots of η^*, G', and G'' as a function of frequency for PEEK/F-PAEK blends at 380°C: (a) 100/0, (b) 80/20, (c) 70/30, (d) 50/50, (e) 30/70, (f) 0/100.

position, interactions between the two components, and phase inversion in the blends.

EXPERIMENTAL

Materials

The PEEK used in this work was a commercial product, with a number average molecular weight of 22,000 and a polydispersity index (M_w/M_n) of 2.8. The F-PAEK with a substituted side group of 3-trifluoromethylbenzene was synthesized by a nucleophilic substitution reaction based on 2-(3'-trifluoromethyl)

phenyl-hydroquinone (FH), 4,4'-biphenol (BP), and 4,4'-difluorobenzophenone (DF). The number average molecular weight was about 6800 and the polydispersity index was 1.5. The chemical structure of the polymer chain is indicated below.

Samples preparation

The samples of PEEK/F-PAEK blends with different weight compositions were prepared by means of solution precipitation. The mixtures of PEEK and F-PAEK were first dissolved in hot pentafluorophenol and the

solution was then precipitated with methanol in a volume ratio of 1:7. The precipitate was dried in a vacuum oven at 140°C for over 24 h to remove the residual solvent, and then pressed into wafers of 15 mm diameter and 1 mm thick for rheological measurements.

Measurements

Rheological measurements of the blends were carried out using a Physica MCR 300 rheometer operating in the parallel plate mode under a protective nitrogen atmosphere. The dynamic rheological experiments were measured under the oscillatory shear flow, i.e., conducting dynamic frequency sweep test in the range of 0.1–100 rad/s on the blends at preset temperatures. The curves of dynamic storage modulus and dynamic loss modulus versus oscillatory frequency at fixed temperature (380°C) were plotted, and the complex viscosity was hereby achieved. The values of the complex viscosity η^* could be calculated with the following equation:

$$|\eta^*| = \sqrt{\left[\frac{G'}{\omega}\right]^2 + \left[\frac{G''}{\omega}\right]^2}$$ (1)

RESULTS AND DISCUSSION

Taking 30FH/70BP/100DF (F-PAEK) as an example, the dynamic rheological experiments are carried out for the PEEK/F-PAEK blends with the whole compositions. The plots of dynamic storage modulus G', dynamic loss modulus G'', and complex viscosity η^* versus oscillatory frequency are prepared by conducting dynamic frequency sweep test (ω = 0.1–100 rad/s) on the blends at the temperature of 380°C, as shown in Figures 1(a)–1(f).

Figure 1(a) shows the flow curve of neat PEEK at 380°C. Complex viscosity of PEEK decreases as the oscillatory frequency increases, while dynamic storage modulus G' and dynamic loss modulus G'' increase with frequency, G' being greater than G'' in the whole frequency range studied, showing the dominance of elasticity in the melt. Figure 1(f) shows the flow curve of pure F-PAEK at 380°C. Complex viscosity of F-PAEK decreases with increasing oscillatory frequency, behaving the shear thinning behavior. The log–log plot of complex viscosity and frequency exhibits a straight line, in agreement with the exponential model: $\eta^* = k\lambda^{n-1}$. G' and G'' of F-PAEK increase with the frequency, G'' being greater than G' within the frequency range investigated, showing the dominance of viscosity in the melt.

As it is well known, the rheological properties of blends in the molten state are dominated by the matrix phase.[26,27] At higher PEEK content (W$_{PEEK}$≥ 80%), the blends show flow curves similar to those of the pure PEEK [see Fig. 1(b)], while at low PEEK percentage
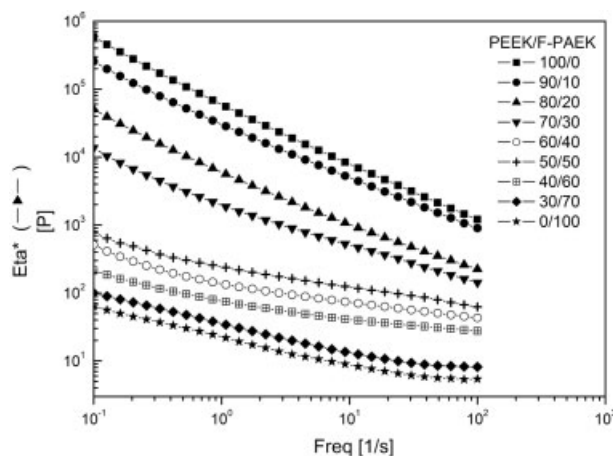

Figure 2 Plots of complex viscosity as a function of frequency for different compositions of PEEK/F-PAEK blends at 380°C.

(W$_{PEEK}$≤ 0%) the rheological behavior of the blends has a resemblance to pure F-PAEK [see Fig. 1(e)], which is an indication of that the dynamic rheological behavior of the above-mentioned blends is mainly dominated by continuous phase.

Only at the intermediate concentration range of PEEK (%≤W$_{PEEK}$≤%), the PEEK/F-PAEK blends behave an unusual rheological behavior. With 70% of PEEK, G' and G'' are almost equal each other at high frequency region, although G' is still greater than G'' at low frequency region [Fig. 1(c)]. When the content of PEEK decreases to 50%, G'' is higher than G' over the whole frequency range [Fig. 1 (d)]. The above unusual rheological behavior indicates that, with decreasing PEEK content, the melt blends transform from the elastic fluid into the viscous fluid in relation to phase inversion between the two components.

It is known that the viscoelastic behavior of polymers is thought to arise from the influence of molecular weight or entanglements of the macromolecules.[28] As mentioned above, the pure PEEK mainly exhibits a typical elastic characteristic (G' > G'') within the frequency range investigated because of its higher molecular weight and resultant entanglements. However, for liquid crystalline polymer F-PAEK, the relatively lower molecular weight and higher chain rigidity result in its viscous characteristic (G'' > G').[29] For the PEEK/F-PAEK blends, the addition of F-PAEK not only increases the chain rigidity of the blend system, but also prevents the PEEK molecular chains from entanglement, which, unambiguously, results in the change of rheological behavior of the blend, i.e., from elastic to viscous. This is the main reason of the above abnormal rheological behavior of the blends with 70–50% PEEK.
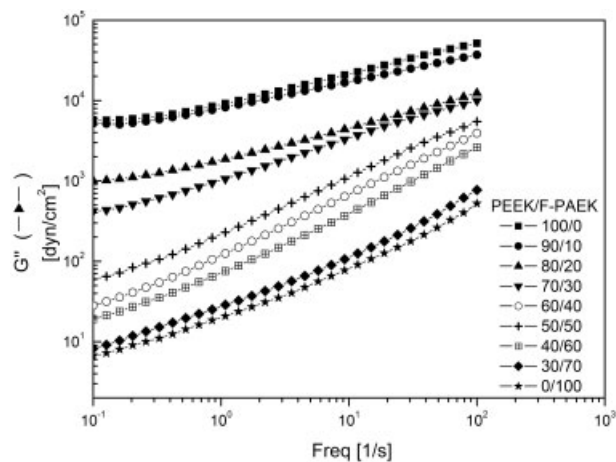
To clearly show the composition dependence of dynamic rheological behavior of the blends, plots of η^*, G', and G'' as a function of frequency for different compositions of PEEK/F-PAEK blends are prepared using the data from Figure 1, as shown in Figures 2, 3,
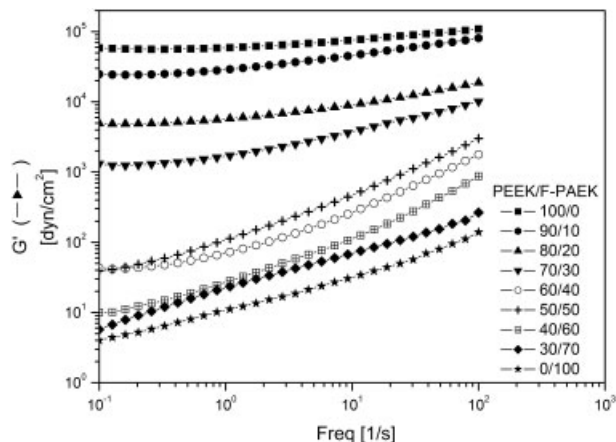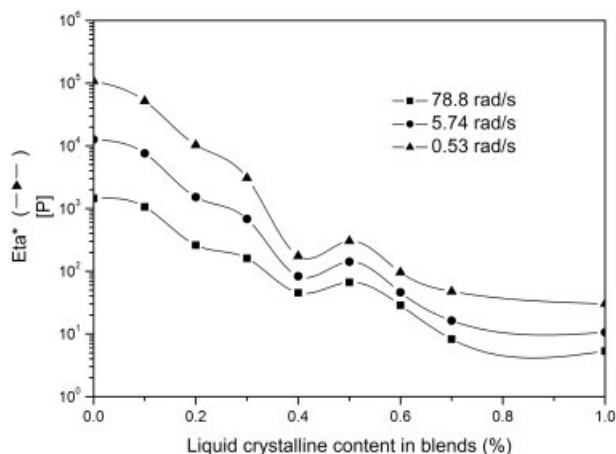
Figure 3 Plots of dynamic storage modulus as a function of frequency for different compositions of PEEK/F-PAEK blends at 380°C.

Figure 5 Plots of complex viscosity as a function of blend composition for PEEK/F-PAEK blends at various frequencies.

and 4, respectively. In the molten state, η^*, G', and G'' of PEEK are much higher than those of F-PAEK. As a whole, η^*, G', and G'' of the PEEK/F-PAEK blends are between those of two pure components and gradually decrease as the F-PAEK content increases. Only the blend with 50% of PEEK shows an unusual behavior, i.e., its η^*, G', and G'' are higher than those of the 60/40 PEEK/F-PAEK blend.

Figure 5 shows plots of η^* as a function of blend composition for PEEK/F-PAEK blends at fixed frequencies (78.8, 5.74, 0.53 rad/s). Complex viscosity of the blend rapidly decreases with increasing amount of F-PAEK at first. The following increase in the F-PAEK content results in the rise of complex viscosity and it ultimately attains a maximum at 50% F-PAEK content. Upon further addition of F-PAEK, the blend viscosity shows a slight decrease again. Figures 6 and 7 show plots of G' and G'' as a function of blend composition for PEEK/F-PAEK blends at fixed frequencies (78.8,
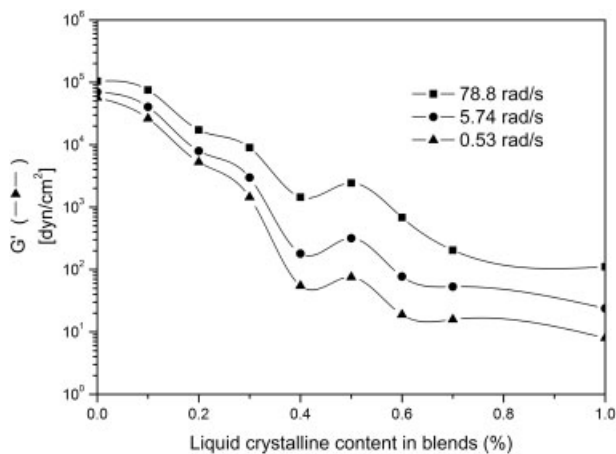
5.74, 0.53 rad/s), respectively. Variation of the storage modulus (G') or loss modulus (G'') versus composition curve shows a trend similar to that observed for complex viscosity, i.e., the G' or G'' of the blends does not decrease monotonically as the F-PAEK content increases, but exhibits a local maximum at 50% weight fraction of F-PAEK.

To sum up, it is found that the rheological behavior of the PEEK/F-PAEK blends in the melt state is strongly dependent on the blend composition, miscibility between two components and phase inversion. In the blends with PEEK as the predominant component ($W_{PEEK} \geq 80\%$), it seems reasonable that PEEK, as the matrix phase, dominate the rheological properties of the blends. In this case, because of the better miscibility between the two components, low molecular weight F-PAEK, can act as the plasticizing agent to improve the rheological properties of the blends by a sharp reduction of complex viscosity of the blends.

Figure 4 Plots of dynamic loss modulus as a function of frequency for different compositions of PEEK/F-PAEK blends at 380°C.

Figure 6 Plots of dynamic storage modulus as a function of blend composition for PEEK/F-PAEK blends at various frequencies.
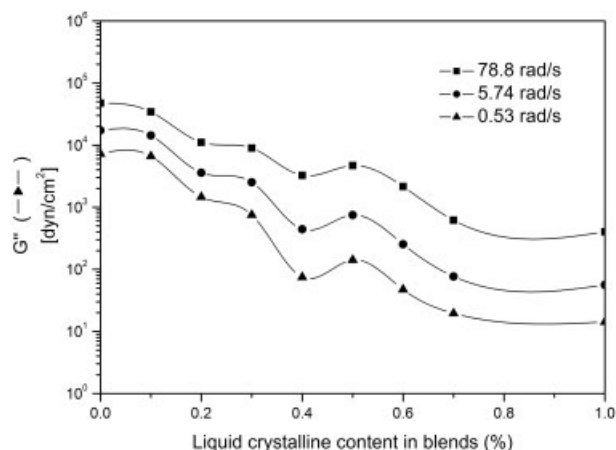
Figure 7   Plots of dynamic loss modulus as a function of blend composition for PEEK/F-PAEK blends at various frequencies.

This significant decrease in the viscosity is expected to improve the processability of PEEK. The blends with PEEK content in the range of 50–70% ($50\% \leq W_{PEEK} \leq 70\%$) exhibit an unusual rheological behavior, implying that a phase inversion occurs in the blends between two components. When the PEEK content decreases to 50%, because of the serious phase separation, the significant increase of plasticity of separated PEEK phase results in ascending of η^*, G', and G'' in the blend instead of descending and reaching a maximum at such a composition. With further reduction of PEEK ($W_{PEEK} < 50\%$), the shape of flow curves of the blends is very similar to that of neat F-PAEK. Meanwhile, high molecular weight PEEK, dispersing in low molecular weight F-PAEK matrix, is difficult to be miscible with F-PAEK. Therefore, η^*, G', and G'' of the melt blends are slightly affected by the composition.

CONCLUSIONS

Dynamic rheological behaviors of the blends under the oscillatory shear mode are strongly dependent on blend composition, miscibility between two components, and phase inversion. The rheological behavior of the blends is mainly dominated by the matrix phase. At higher PEEK content, the blends show flow curves similar to those of the pure PEEK, while at low PEEK percentage, the rheological behavior of the blends has a resemblance to pure F-PAEK. However, at the concentration range of 50–70% of PEEK, the blends behave an abnormal rheological behavior in relation to phase inversion between two components. Moreover, the complex viscosity, storage, and loss moduli of the blends do not decrease monotonically as the F-PAEK content increases, but exhibit a local maximum at 50% weight fraction of PEEK, ascribing to the phase separation of two components at such a composition.

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