A new solvent for poly(ether ether ketone)

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(Received 17 March 1992)

A new solvent, 4-chlorophenol, has been used to dissolve poly(ether ether ketone), PEEK, over an extended concentration range. Some properties of the solution were measured and possible effects of the solvent on PEEK were investigated.

(Keywords: PEEK; 4-chlorophenol; solvent; solution properties)

Introduction

Exceptional solvent resistance is one of the important properties of crystalline poly(ether ether ketone), PEEK, as a high performance polymer and as an attractive thermoplastic matrix for advanced composites[1,2]. At room temperature, PEEK has been described as insoluble in all common solvents[1] except for some strong acids such as 98% sulphuric acid[3] and hydrofluoric acid[4]. At temperatures approaching the melting point, it has been found that PEEK can be dissolved in high-boiling point esters[5] and diphenyl sulphone[3,5]. Crystallization of PEEK from a solution of 1-chloronaphthalene and benzophenone at elevated temperatures has also been reported[6,7]. Dichloroacetic acid (heated to ~150°C) has been used to prepare blends of PEEK and poly(ether ketone)[8].

In studies of the solution properties of PEEK, concentrated sulphuric acid has been most widely used in viscometric, light scattering and g.p.c. measurements[3,9,10]. However, significant sulphonation of the phenyl groups strongly influences the solution behaviour of PEEK[9,10]. Although correlations have been made for the chemical changes, these results seem to be useful only for the determination of PEEK molecular weights. Viscosity and g.p.c. measurements of PEEK in a phenol/1,2,4-trichlorobenzene solvent mixture have also been reported[10,11] but this is a more laborious process than for sulphuric acid due to the high operating temperature.

Except for the strong acids, the reported[12] solubilities of PEEK in many of these solvents were quite low, generally ranging from 0.001 to 0.1 (w/v). So far, available data on the solution properties of PEEK, other than for molecular weight determination, have been very limited. This is probably due to the absence of suitable solvents which not only dissolve PEEK without causing chemical modification of the polymer, but can also be used at ambient temperatures. Recently, in an attempt to fractionate PEEK samples to study molecular weight effects on PEEK crystallization, we found that 4-chlorophenol may be used as a good solvent for PEEK. In this communication, some solution properties of this system are reported.

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0032-3861/92/204432-03

Experimental

Materials. PEEK powder containing no additives (ICI grade 450P) was used. The 4-chlorophenol used was CP grade (99.0% pure) with a melting temperature of >41°C and a boiling temperature of ≅220°C. 4-Chlorophenol is miscible with a number of alcohols and ethers. In order to eliminate errors due to vaporization during the cloud point titration, 1-butanol was used as the precipitant. All solvents were filtered through a fritted glass funnel prior to use.

Solution property measurements. 4-Chlorophenol solutions of PEEK were obtained by dissolving the polymer samples directly into the solvent with stirring and heating. Cloud point titrations were carried out following the major procedures described by Elias[13] with the bath temperature controlled to better than ±0.1°C. The start of precipitation was determined visually with the aid of a light beam; and the results were found to be reproducible. For freezing point determination, PEEK solution was sealed in a capillary tube (care was taken to avoid burning of the sample), refrigerated to allow solidification, and then heated slowly to melting.

Results and discussion

PEEK can be dissolved up to as much as 20–25% (w/v) in 4-chlorophenol, while heating was usually needed to speed up the dissolution, especially for higher polymer concentrations. The high solubility of PEEK in this solvent makes it suitable for solution processing techniques such as casting, coating and impregnating, over a varied concentration range. On a laboratory scale, we have recently succeeded in making unidirectional impregnated tapes containing 50 wt% continuous carbon fibres using a 20% solution.

When a clear solution was cooled down, precipitation of PEEK occurred. *Figure 1* shows the incipient precipitation temperatures of the solutions as a function of concentration. A linear relation can be seen up to a concentration of 16%. In practice, a solution of a few per cent can be handled at ambient temperature without any visible precipitate. The results of freezing point measurements are given in *Table 1*. The data showed that the dissolution of PEEK depressed the freezing point of the solvent. However, the measured freezing points are all higher than the incipient precipitation temperatures

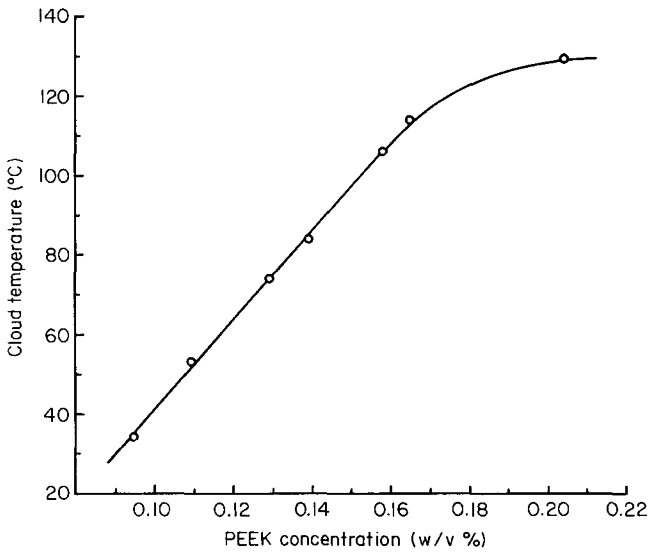

Figure 1 Cloud temperatures of PEEK/4-chlorophenol solution at different concentrations

Table 1 Freezing points of the PEEK/4-chlorophenol solution

Concentration ($g\,ml^{-1}$) × 100	Freezing point (°C)
Pure 4-chlorophenol	42–43
0.554	38–39
0.830	30–31
1.660	24–25

that would be predicted from the extrapolated line in *Figure 1* to the corresponding concentration. Since the temperature change in the two methods started from opposite directions to pass through the freezing point (43°C) of pure solvent (i.e. in the cloud point measurement temperature was changed from high to low, while the freezing point measurement changed from low to high), supercooling may be one of the reasons for this difference. Further detailed studies, however, are necessary before a more specific explanation can be given.

The cloud point method may be used to determine the θ temperature of polymer solutions, where the inverse precipitation temperatures are plotted against the logarithmic volume fraction of the polymer to obtain an extrapolated value of the θ temperature[13]. A plot of the data from *Figure 1* also gave a straight line, but yielded an unreasonable θ temperature because of the much higher concentrations used in this study than that required by the method (<1%). Using 4-chlorophenol as a solvent for PEEK makes it possible to determine the θ conditions and other solution properties of PEEK.

Cloud composition titrations have been carried out to optimize the fractionation conditions. The solution concentration used was 1.28% which was within the range generally chosen for polymer fractionation. *Figure 2* is a plot of incipient precipitation *versus* the relative volume of 1-butanol/4-chlorophenol. Using this working curve, the fractionation of PEEK has been carried out at 30°C to obtain meaningful results. Our preliminary results showed that phase diagrams could be worked out using this ternary system if careful measurements were performed.

The solution viscosity of PEEK in 4-chlorophenol was determined and compared with that obtained in 98% sulphuric acid (both at 25°C). The value for the intrinsic viscosity obtained in 4-chlorophenol was higher than that in sulphuric acid for the same PEEK sample. Thus, to use the new solvent in molecular weight measurements, the values of k and α in a Mark–Houwink equation should be determined.

Another important aspect concerning the new solvent is that chemical modification should not occur when dissolving PEEK in 4-chlorophenol. *FT*i.r. spectra of PEEK samples before and after dissolution were studied. The two i.r. spectra were essentially the same without any obvious new bands. In the sulphonation of PEEK, substitution was found to occur exclusively in the phenol rings which are surrounded by two ether linkages[10,14]. Attention was, therefore, paid mainly to the aromatic C–C skeletal vibration at 1490 cm^{-1} and the out-of-plane C–H bending (1,4-disubstitution) at 840 cm^{-1}. In the spectrum recorded from the sample treated with 4-chlorophenol, no evidence was found either for splitting of the 1490 cm^{-1} band, which is indicative of trisubstitution on the aromatic rings[15], or for any new band at $\sim$865 cm^{-1}, which is characteristic of the out-of-plane C–H bending of an isolated aromatic hydrogen in a 1,2,4-trisubstituted phenol ring[15,16]. These results suggest that chemical reaction between PEEK molecules and the solvent is unlikely to occur. In addition, PEEK samples precipitated from the solution were also used in crystallization studies. No unusual changes were found in the glass transition temperature, melting temperature, crystallinity and spherulitic morphology of the PEEK samples. The four characteristic peaks at $2\theta = 18.9$, 20.9, 22.8 and 28.9°, found in the wide-angle X-ray diffraction pattern, corresponding to 1 1 0, 1 1 1, 2 0 0 and 2 1 1 reflections, respectively, were in good agreement with melt crystallized PEEK samples[17], indicating no change in the crystal structure. It is known that chemical modification of the polymer main chain significantly affects the thermal transition temperatures and crystallization behaviour of a crystalline polymer, such as found for sulphonated PEEK[14,18]. Based on the above experimental results, it is believed that 4-chlorophenol does not react with PEEK and can be used as a solvent for the polymer.

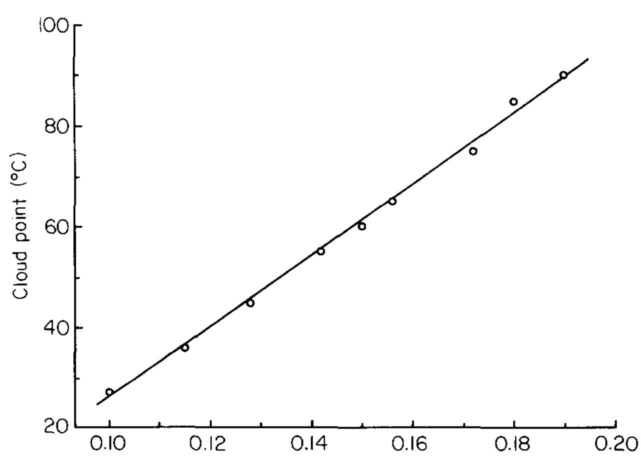

Figure 2 Cloud points determined at 40°C for the PEEK/4-chlorophenol/1-butanol ternary system

Conclusions

In conclusion, 4-chlorophenol can be used as a good solvent for PEEK and the solution can be handled at ambient or moderate temperature. A number of experiments have shown that there is no evidence of chemical reaction between PEEK and the solvent. This provides a suitable solvent for measuring the solution properties of PEEK as well as for use in solution processing techniques such as casting, blending and impregnating.

Acknowledgements

Financial support by the National Natural Science Foundation of China and the State Educational Commission of China is gratefully acknowledged.

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