# Study on the Compatibility of the Blend of Poly(aryl ether ether ketone) with Poly(aryl ether sulfone)

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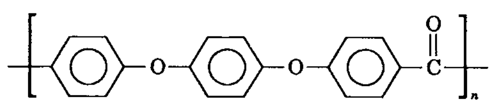
## Synopsis

Poly(aryl ether ether ketone) is found to be compatible with poly(aryl ether sulfone) at a blending temperature 310°C. There is a single glass transition temperature ($T_g$) for various compositions of the blend. The relationship of $T_g$ with composition obeys Gordon–Taylor's equation, where the adjustable parameter $k$ is 0.43. Thermodynamic interaction parameter $\chi_{12}$ is estimated to be −0.001 according to Nishi and Wang's melting point depression equation. When the processing temperature is above 350°C, phase separation takes place as shown by a double mechanical loss tangent relaxations in the range of 100–280°C.

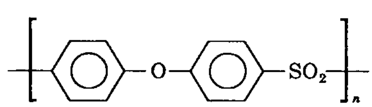
## INTRODUCTION

Poly(aryl ether ether ketone) (PEEK) with structure formula:



is a semicrystalline aromatic polymer. Its main application is in the area of high-performance composite materials. Because of its excellent thermal stability, good solvent resistance, and mechanical properties,[1] thermoplastic PEEK is an attractive alternative to the more conventional thermosetting resins used as matrix for most fiber composites. Unfortunately, this material has a relatively low glass transition temperature ($T_g$ = 145°C), resulting in one order decrease of modulus at elevated temperatures which limits its use in some applications.

On the other hand, poly(aryl ether sulfone) (PES) with structure formula



is an amorphous engineering thermoplastics.[2] It may be used as solvent castable amorphous matrix resins for high-performance graphite fiber-reinforced com-

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posites. It has a relatively high glass transition temperature ($T_g$ = 225°C), which remain its modulus at an elevated temperature.

In order to improve the properties of PEEK at a higher temperature, it is possible to blend PEEK and PES to elevate the $T_g$ of PEEK if they are compatible with each other. In this study, we present briefly the results on the compatibility of PEEK with PES.

## EXPERIMENTAL

### Materials

PEEK ($\eta_{iv}$ = 0.98, 25°C, in 98% conc. $H_2SO_4$) and PES ($\eta_{iv}$ = 0.38, 25°C, DMF) were prepared at our lab.[3,4]

Powder samples of the blend of PEEK and PES were prepared by solution mixing in diphenylsulfone, extracted with water and methyl alcohol and finally dried in a vacuum oven at 120°C.[5]

### Specimen Preparation

Films used in measurement were prepared by compression molding at 310°C and 350°C, respectively, with the thickness of 0.1 mm for differential scanning calorimeter (DSC) and 1 mm for dynamic mechanical analysis (DMA).

### DSC Measurements

Glass transition temperature ($T_g$) and melting temperature ($T_m$) of blend were measured with a Perkin-Elmer DSC-2C differential scanning calorimeter at a heating rate 10°C/min.

### Dynamic Mechanical Properties

Dynamic viscoelastic spectra of various samples were measured with a Rhevibron Model DDV-III apparatus at chuck distance 3 cm, with initial tension 10*g*, frequency for measurement 35 Hz, and heating rate 3°C/min.

## RESULTS AND DISCUSSION

Blend with various composition processed at 310°C shows only one composition-dependent glass transition temperature in DSC curve. The $T_g$ data for the blends as shown in Figure 1 can be described by the use of Gordon–Taylor's equation[7]:

$$T_g = [T_{g_1} + (kT_{g_2} - T_{g_1})w_2]/[1 - (1 - k)w_2]$$

$T_g$ is the glass transition temperature of blend, $T_{g_1}$ and $T_{g_2}$ are those of the component 1 and component 2 respectively, $w_2$ is the weight fraction of PEEK, $k$ is an adjustable parameter. The curve in Figure 1 is drawn using the Gordon–Taylor's equation with a $k$ value of 0.43. It reveals that PEEK is compatible with PES.[8] On the other hand, the $T_g$ of the blends of PEEK and polyetherimides (PEI) follows Fox's equation as presented last year by Harris and Robeson.[9]

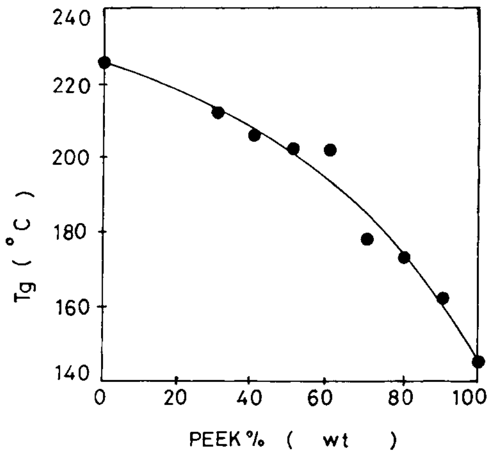


Fig. 1. $T_g$ vs. composition for PEEK/PES blend processed at 310°C. (●): measured; (—): calculated.

In that case,[10] $k = T_g(\text{PEEK})/T_g(\text{PEI}) = 0.85$, is higher than $k = 0.43$ for PEEK/PES blend. Hence, the $T_g$ of PEEK increase was more remarkable when it was blended with PES when comparing Figure 2 in this work with Harris and Robeson's recent results in PEEK/PEI blend. Therefore, PEEK/PES blend is a more effective and attractive system to improve the dynamic mechanical performance of PEEK at elevated temperatures.

PEEK/PES blend is crystalline/noncrystalline polymer/polymer blend. As many crystalline/noncrystalline blends, it is found that the melting temperature for the blends is lower than that for the crystalline component PEEK. Figure 3(a) shows the plot of melting temperature vs. composition for the blends. The melting point depression equation for compatible system developed by Nishi and Wang[6] as follows

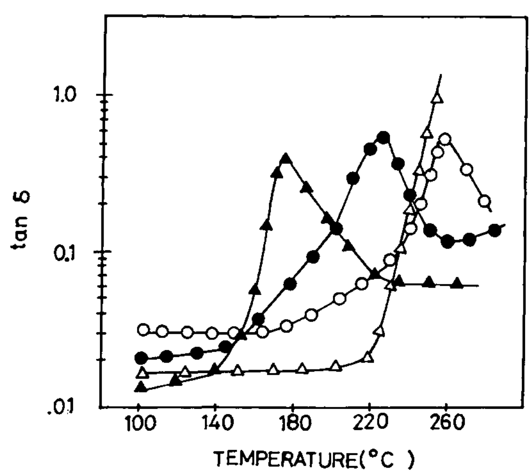


Fig. 2. Mechanical loss tangent relaxations of PEEK/PES blends processed at 310°C (PEEK% (▲): 100; (●): 50; (○): 40; (△): 0).

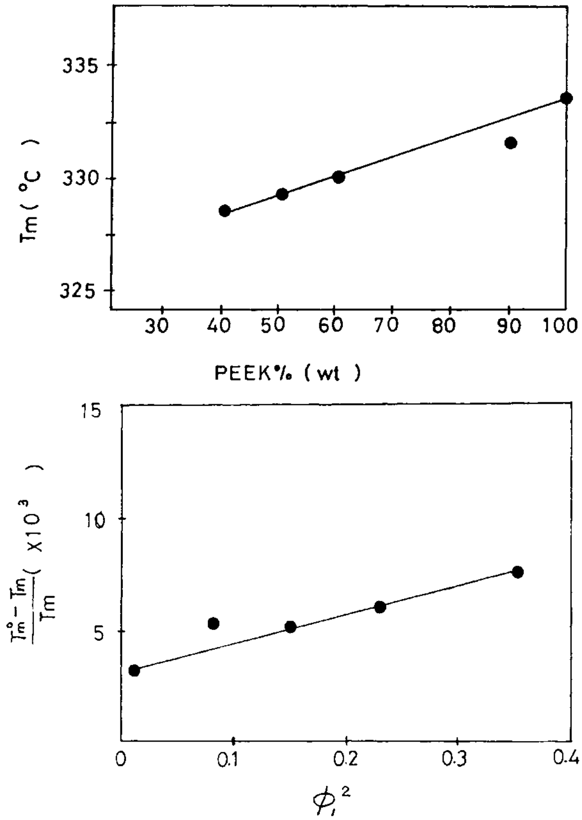


Fig. 3. (a) The melting point $T_m$ of PEEK/PES blends (directly measured by DSC). (b) Evaluation of interaction parameter from PEEK melting point depression.

$$\frac{T_m^\circ - T_m}{T_m} = -\frac{RV_2T_m^\circ}{V_1\Delta H_2}\chi_{12}\phi_1^2$$

where $T_m^\circ$ is the melting temperature of the neat crystalline component, $T_m$ is the observed melting temperature in the blend, $V_1$, $V_2$ are molar volume of each component, respectively, $\Delta H_2$ is the heat of fusion of the neat crystalline component, $\phi_1$ is the volume fraction of the amorphous component, and $\chi_{12}$ is the thermodynamic interaction parameter. From the slope of the line in Figure 3(b), we have the thermodynamic interaction parameter of PEEK with PES $\chi_{12} = S/A$, $S$: the slope, $A = -RV_2T_m^\circ/V_1\Delta H_2$. Here, $\chi_{12}$ is estimated to be $-0.001$. Values of $\chi_{12}$ are slightly lower than zero indicating that it has been favorable for mixing of PEEK with PES from thermodynamic point of view.

When the blend is processed at 350°C, it is found that there exists 2 glass transition temperatures for each blend as shown in Figure 4. It indicates that phase separation occurs in this case. Therefore it means that the phase diagram would reveal a low critical soluble temperature (LCST) behavior with the cloud point locate between 310°C and 350°C, when the fraction of PES is in the range from 70 to 30%.

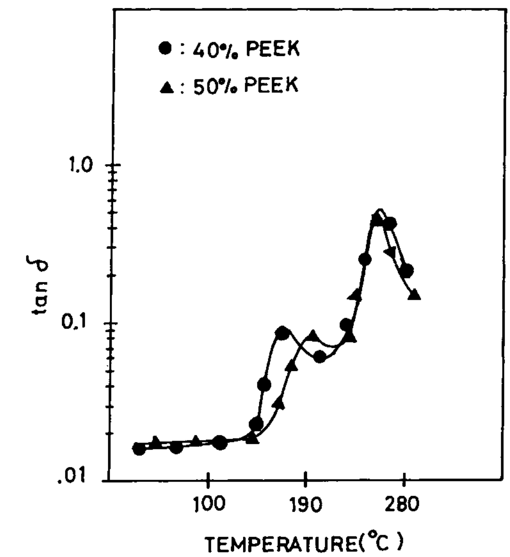


Fig. 4. Mechanical loss tangent relaxations of PEEK/PES blends processed at 350°C.

Figure 5 shows the temperature dependence of modulus $E'$ in the range of 100–280°C for the blends. The modulus of PEEK at temperature 150–180°C drops dramatically to an order of that at room temperature. After blending PEEK with proper composition PES and processed at the proper temperature, e.g., 310°C, the dynamic mechanical properties at elevated temperature of PEEK can be remarkably improved. For example, for the temperature, at which its modulus starts to drop are almost 60°C higher than that for neat PEEK because of the elevation of $T_g$. In a certain range of temperature (e.g., for 40% PEEK, the range is 180–220°C) the modulus $E'$ for blends is about 10 times of that for the neat PEEK. On the other hand, the dynamic mechanical properties at

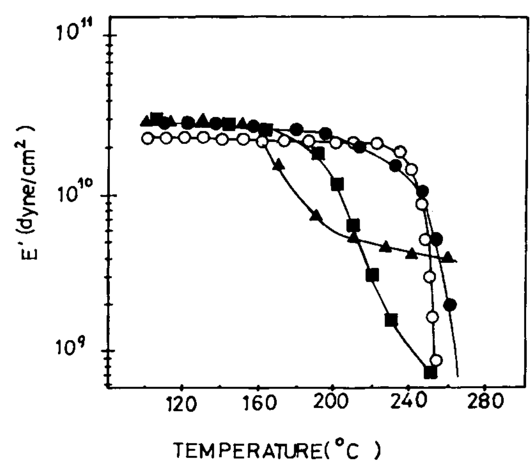


Fig. 5. Temperature dependence of modulus $E'$ for PEEK/PES blends processed at 310°C (PEEK% (▲): 100; (■): 50; (●): 40; (○): 0).

elevated temperature of PEEK/PES is much better compared with that of PEEK/PEI blend. Therefore, such kind of blend could be used as high-performance material at a higher temperature.

## CONCLUSIONS

Poly(aryl ether ether ketone) is compatible with poly(aryl ether sulfone) at a processing temperature 310°C. The variation of $T_g$ with composition obeys Gordon–Taylor's equation, where the adjustable parameter $k$ is 0.43.

Thermodynamic interaction parameter $\chi_{12}$ for PEEK/PES blend is −0.001. It indicates that the mixing of PEEK with PES is favorable from a thermodynamic point of view. However, when processing temperature is above 350°C, phase separation in PEEK/PES blends occurs. It means that LCST behavior exists in this system. And the cloud point locates between 310°C and 350°C in the phase diagram.

Compared with PEEK/PEI blend, PEEK/PES blend is more effective and potential system to improve the dynamic mechanical performance of PEEK at elevated temperatures.

Because of the elevated $T_g$ of the blend, the modulus $E'$ remarkable decreasing temperature is higher than that for PEEK. Thus, mixing PEEK with PES is an effective method to improve the dynamic mechanical performance of PEEK at higher temperature. The blend of PEEK with PES could be a more useful high performance material at elevated temperature than PEEK or PEEK/PEI blend.

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## References

1. T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose, and P. A. Staniland, *Polymer,* **22,** 1096 (1981).
2. T. E. Attwood, T. King, V. J. Leslie, and J. B. Rose, *Polymer,* **18,** 369 (1977).
3. Z. Wu, H. Yu, and H. Na, Chinese Patent CN85105138.
4. Z. Wu and Y. Zheng, Chinese Patent CN85107879.
5. Z. Wu, H. Yu, and Y. Zheng, Chinese Patent CN89100355.
6. T. Nishi and T. T. Wang, *Macromolecules,* **8,** 909 (1975).
7. M. Gordon and J. S. Taylor, *J. Appl. Chem.,* **2,** 1 (1952).
8. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer–Polymer Miscibility,* Academic, New York, 1979.
9. J. E. Harris and L. M. Robeson, *J. Appl. Polym. Sci.,* **35,** 1877 (1988).
10. J. R. Fried, in *Developments in Polymer Characterisation—4,* J. V. Dawkins, Ed., Applied Science Publishers Ltd., 1983.

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