Chapter 1. Introdution

1-1. Polymer: high molecular weight

$$\overline{M}_n$$
 = number average molecular weight () \overline{M}_w = weight average molecular weight () \overline{M}_v = viscosity average molecular weight (

polymer

$$\overline{M}_{w}$$
 >10,000

ex) · polyethylene (PE)

$$\begin{array}{c|c}
H & H \\
\hline
C & C \\
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· polypropylene (PP)

$$\begin{array}{c|c} CH_2 H \\ \hline -C-C \\ \hline -C-H \\ \end{array}$$
 repeating unit=42g/mol

· polystyrene (PS)

$$\begin{array}{c|c} H & H \\ \hline \begin{array}{c} C \\ C \\ \end{array} \\ H \end{array} \qquad \begin{array}{c} \text{repeating unit=104g/mol} \end{array}$$

1 -2. Classification of polymers

1-3. Structure

- i) Thermoplastic(가) 가 flow가 ex) PS, PE, PP, Nylon, PET etc
- - ex) epoxy , phenol , polyester etc

1 - 4. Grade

i) Commodity plastic (plastics) ex) PS, PE, PP, PVC

- a) easy processibility
- b) soft
- c) excellent electrical resistance
- d) stable in low temp, not in boiling water
- e) low price

ii) Engineering plastics

ex) Nylon, PET, Polycarbonate (PC), PBT, Poly (oxy methylene) (POM),

Polyacetal, Polypropylene oxide + PS → Noryl(blend).

- a) good heat stability
- b) good impact strength
- c) good mechanical properties
- d) price is 2 or 3 times higher than commodity plastics

iii) Specialty polymers

ex) poly (ether ether ketone) (PEEK), polyimide, liquid crystalline polymer

(LCP), polysulfone, etc.

- a) high temp. stability, $T_g > 100$ °C
- b) high modulus
- c) high price

· PEEK

$$\left\{ \begin{array}{c} -0 \\ -0 \end{array} \right\}_{n}$$

trade name : Victrex PEEK, by ICI Tg = 143-150 C, Tm = 334-340 C

· Polyimide

$$\begin{bmatrix}
R - N & C \\
C & R'
\end{bmatrix}_{r}$$

· Polyimide 2080

$$\begin{bmatrix}
N & O & O & O \\
C & C & C & C
\end{bmatrix}$$

$$\begin{bmatrix}
N & C & C & C
\end{bmatrix}$$

$$\begin{bmatrix}
N & C & C & C
\end{bmatrix}$$

$$\begin{bmatrix}
N & C & C
\end{bmatrix}$$

Where R is
$$-CH_2$$
— (20%) or CH_3 (80%) Tg = 305 C

· Polyimide (PI)

upper service

temp.

$$_{\circ C}$$
 $\left[N \right]_{CO}^{CO} N - R = 1$

· Polyamide -imide (PAI)

$$\begin{bmatrix}
NH & CO & N - CO \\
CO & N - CO
\end{bmatrix}$$

· Polyetherimide (PET) – ultem

$$\alpha \equiv \frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_{P}, \left(K^{-1} \right)$$
 : thermal expansion coeff.

$$\beta = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{P}, (K^{-1})$$
 : the linear expansion coeff.

Thermal Properties of Melt-Blended Poly(ether ether ketone) and Poly(ether imide)

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ABSTRACT: The thermal properties of blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) prepared by screw extrusion were investigated by differential scanning calorimetry. From the thermal analysis of amorphous PEEK-PEI blends which were obtained by quenching in liquid nitrogen, a single glass transition temperature (T_g) and negative excess heat capacities of mixing were observed with the blend composition. These results indicate that there is a favorable interaction between the PEEK and PEI in the blends and that there is miscibility between the two components. From the Lu and Weiss equation and a modified equation from this work, the polymer–polymer interaction parameter (χ_{12}) of the amorphous PEEK-PEI blends was calculated and found to range from -0.058 to -0.196 for the extruded blends with the compositions. The χ_{12} values calculated from this work appear to be lower than the χ_{12} values calculated from the Lu and Weiss equation. The χ_{12} values calculated from the χ_{12} was expected by John Wiley & Sons, Inc. J Appl Polym Sci 72: 733–739, 1999

Key words: poly(ether ether ketone); poly(ether imide); blend; glass transition temperature; polymer-polymer interaction parameter

INTRODUCTION

The blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) are known to be miscible in an amorphous state. $^{1-6}$ Recently, many researchers have investigated the mechanism and the morphology of PEEK crystallization in PEEK–PEI blends. $^{1-4}$ Crevecoeur and Groeninckx studied the crystallization behavior of PEEK in PEEK–PEI blends using thermal analysis and small-angle X-ray scattering. They reported that the glass transition temperature (T_g) of the amorphous samples of the PEEK–PEI blends varies nearly as predicted by the Fox equa-

tion. In semicrystalline samples, because the amorphous phase is enriched in PEI, the glass transition temperature increases. Therefore, the PEEK component in the blends crystallizes as it does in pure PEEK, with the PEI segregating to the amorphous phase. From the SAXS measurements, Crevecoeur and Groeninckx concluded that, within the spherulites, PEI is primarily rejected between bundles of lamellae.

Recently, we showed that the blends of PEEK and PEI are miscible in the amorphous state and partially miscible in the semicrystalline state.³ Also, the rigid amorphous fraction for the semicrystalline PEEK-PEI blends was calculated and found to be 0.117-0.358 with a cooling rate using differential scanning calorimetry (DSC).³

Hsiao and Sauer⁶ investigated the interaction between PEEK and PEI using the melting-point depression method. They reported that the poly-

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Blends of a thermotropic liquid crystalline polymer and some flexible chain polymers and the determination of the polymer-polymer interaction parameter of the two polymers

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Summary

Blends of a thermotropic liquid crystalline polymer (LCP) with poly(ether imide) (PEI), poly(ether ether ketone) (PEEK), polysulfone (PSF) and polyarylsulfone (PAS) prepared by screw extrusion have been investigated by differential scanning calorimeter and dynamic mechanical thermal analysis. From the measured glass transition temperature (T_g) and specific heat increment (ΔC_p) at the T_g , it appears that the LCP dissolves more in the PEI- and PEEK-rich phases than does the PEI and PEEK in the LCP-rich phase. From the DSC study of PSF-LCP and PAS-LCP blends, the T_e(PSF) and T_e(PAS) of each blends are almost constant with blend composition. Therefore, it is concluded that PSF and PAS are immiscible with LCP. The polymer-polymer interaction parameter (χ_{12}) and the degree of disorder (y/x₁) of LCP have been investigated using the Flory lattice theory in which the anisotropy of LCP is considered. The χ_{12} values have been calculated from the $T_{\rm g}$ data and found to be 0.181 ± 0.004 at 593 K for the PEI-LCP blends and 0.069 ± 0.006 at 623 K for the PEEK-LCP blends. Using the previously presented method, the χ_{12} and y/x_1 in partially miscible systems have been determined.

Introduction

The blends of a flexible chain polymer with a thermotropic liquid crystalline polymer (LCP) have been of great interest in recent year (1-15). Some investigators(4,13) have used the thermal properties such as glass transition temperature (Tg) and specific heat increment (ΔC_p) at T_g to investigate the polymer-polymer compatibility between a thermotropic LCP and a flexible chain polymer by differential scanning calorimetry (DSC). The polymer blends which have been reported have contained polycarbonate (PC) (1-5), poly(ether imide) (PEI) (6-9), poly(ether ether ketone) (10-13), and polysulfone (PSF) (14,15).

Friedlich and coworkers (4) have reported that a thermotropic LCP is partially miscible with polycarbonate (PC). Bafna and coworkers (9) have studied the blends of a thermotropic LCP and poly(ether imide) (PEI) using thermal analysis and scanning electron microscopy (SEM). They have reported that PEI is partially miscible with the themotropic LCP. Acierno and Naddeo (12) have reported that a thermotropic LCP is miscible with PEEK by using thermal analysis. Bretas and Baird (13) have reported that a

^{*} Corresponding author

- i) thermotropic LCD , 가 crystal-to-nematic transition
 - ex) Hoechst -celanese Vectra A900:

$$\begin{array}{c|c}
 & O \\
 & C \\
 & C \\
 & O \\
 & C \\
 & O \\$$

(hydroxy benzoic acid) 73 mol%

6 -hydroxy -2 -naphthoic -acid 27mol%

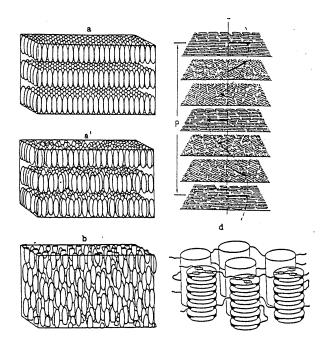
Du Pont, Eastman Kodak Amoco

ii) Iyotropic LCP -

ex) Du -pont Kevlar

$$\begin{bmatrix}
NH & -NHC & -NHC & -C \\
-NHC & -NHC & -NHC & -NHC & -NHC
\end{bmatrix}$$

high modulus fiber (10⁶kg/cm²)



- a. ordered smectic
- a'. unordered smectic
- b. nematic
- c. cholesteric
- d. discotic

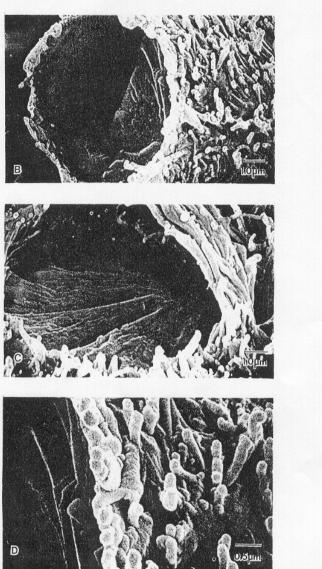


Fig. 5.96 A glass fiber reinforced LCP composite is shown to have interesting morphology. A polished thin section is shown in polarized light (A) (color section) to exhibit a fine domain texture with some orientation of the polymer on the glass surfaces. SEI fracture views (B-D) show the tenacious adhesion of the LCP to the fibers. Fibrillar structures are oriented paralled to the fiber surface and submicrometer sized domains are observed (D).

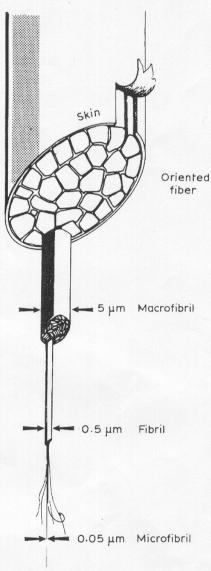


Fig. 5.97 The structures observed in uniaxially oriented LCP fibers, ribbons and films can be summarized by this structural model. The model defines the nature of the fibrillar textures into three categories based upon size: macrofibrils, fibrils and microfibrils. In each case the sizes of structures have been determined from complementary microscopy techniques. (From Sawyer and Jaffe [353]; reproduced with permission.)

Ref., L.C Sawyer and D.T. Grubb,
"Polymer Microscopy", Chapman and Hall
(1989).