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# 不均一系 폴리벤지미다졸/폴리이미드 블렌드

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# Immiscible Polybenzimidazole/Polyimides Blends

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요 약 : Poly(2,2(*m*-phenylene)-5,5′-bibenzimidazole) (PBI)와 두 폴리이미드(PI) 6F-3,3′-ODA와 6F-$DDSO_2$ 블렌드에 대한 DSC와 Fourier-Transform Infrared (FTIR) 分光學的 側面이 硏究되었다. 6F-3,3′-ODA는 2,2′-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoro propane과 4-aminophenyl ether로 製造되며, 6F-$DDSO_2$는 2,2′-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3,-hexafluoro propane과 4-aminophenyl sulfone으로 부터 製造되었다. PBI/6F-3,3′-ODA와 PBI/6F-$DDSO_2$ 블렌드들은 不均一하다 ; 그 證據로는 光學的으로 不透明한 形態이며, DSC에서 두 單重合體들에 相應되는 두개의 유리轉移 溫度를 갖고, 그리고 FTIR 스팩트럼에서 PBI의 N−H와 PI의 C=O에 相應하는 피이크들에서 顯著한 周波數 變化가 없는 것이다. 이 블렌드系들에서의 不均一性은 두 폴리이미드들에 있는 벌크한 $-CF_3$기의 空間障碍를 根據로 設明될 수 있다. 두 블렌드系들에서의 結果는 均一系에서 觀察된 以前의 硏究結果들과 比較된다 ; 즉 不均一性에 대한 化學的 相互作用들의 可能한 役割이 檢討되었다.

**Abstract** : DSC and Fourier-Transform Infrared(FTIR) spectroscopic studies in blends of poly(2,2(*m*-phenylene)-5,5′-bibenzimidazole) (PBI) with two polyimides, 6F-3,3′-ODA and 6F-$DDSO_2$, are presented. 6F-3,3′-ODA is formed from 2,2′-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3,-hexafluoro propane and 4-aminophenyl ether while 6F-$DDSO_2$ is formed from 2,2′-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3,-hexafluoro-propane and 4-aminophenyl sulfone. The PBI/6F-3,3′-ODA and PBI/6F-$DDSO_2$ blends are immiscible ; the evidence is in the form of optically opaque films, two distinct $T_g$'s corresponding to that of the two homopolymers in DSC and no significant frequency shifts in the peaks corresponding to the N−H in PBI and the C=O in polyimides in FTIR spectra. The immiscibility of the present blend systems may be rationalized on the basis of steric hindrance of the bulky-$CF_3$ group present in two polyimides. The results in both systems are compared with those observed in previous miscible systems ; the possible role of chemical interactions for immiscibility is discussed.

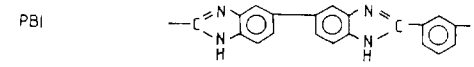
## INTRODUCTION

During the past few years, miscible aromatic polybenzimidazole(PBI) with aromatic polyimide (PI) blend systems have been studied in solid state using thermal and spectroscopic techniques.[1~8] The existence of specific interactions between two homopolymers has been demonstrated by observing optically clear transparent films, single composition-dependent $T_g$, tan $\delta$ dynamic mechanical relaxation peaks associated with these $T_g$'s and FTIR frequency shifts of the functional groups upon blending. The observations suggest that specific intermolecular interactions are necessary for blend system to be miscible. The common features displayed in thermal studies are positive deviations from the weighted-average $T_g$ ($T_{g\ mid\ point}$) value and the existence of a minima and a maxima in $\Delta C_p$($C_p$ difference between glassy and rubbery region) and in $\Delta T_g$($T_g - T_{g\ onset}$), respectively, as a function of composition. The blend systems showed enhanced thermal stability and improved weight retention upon addition of PBI into PI. In FTIR results, an S-shaped curve was obtained when the frequency shift in the peak maximum of the N−H group in PBI was plotted as a function of PI concentration ; a similar behavior was shown for the frequency shift of the carbonyl band in PI as a function of PBI concentration. Moreover, the peak width at half-height of the carbonyl band in PI versus the blend composition also produced S-shaped curve.

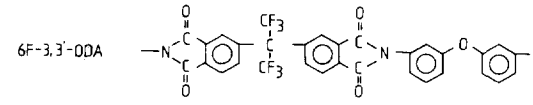
From studies of temperature dependent FTIR spectra in PBI/PI (Ultem 1000 and XU 218) blends,[2,8] a hydrogen bonding type of interaction between the N−H and the carbonyl is suggested. This does not rule out the possibility of the simultaneous presence of other interactions such as (a) $\pi$-complexation between the imidazole and imide rings or (b) charge-transfer complexation between the benzimidazole and phthalimide ring, in PBI and PI, respectively. We have been interested in two points in PBI/PI blends. First, if the miscibility of PBI/PI blends are universal and the second, if they are not, what is the nature for them to be.

In this paper, we present the results of DSC thermal and FTIR spectroscopic studies in blends of PBI with two polyimides. The chemical structures of PBI, 6F-3,3′-ODA and 6F-$DDSO_2$ are as follows ;

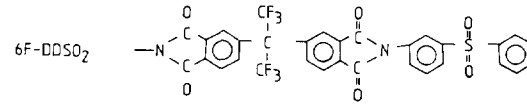
PBI



6F-3,3'-ODA



6F-$DDSO_2$



Thermal and FTIR spectroscopic studies of both systems show no analogous behavior to the previous systems.[3,4]

## EXPERIMENTAL

The physical properties of PBI used in this study have been described elsewhere.[1~8] 6F-3,3′-ODA and 6F-$DDSO_2$ were obtained from NASA Langley Laboratory, Virginia. The molecular weight of the polymers are not known. Both the polyimides were dissolved in warm dimethylacetamide (DMAc) for several hours and filtrated for fractionation. Blends of PBI with two polyimides were film cast onto petri dishes from a 0.5%(w/w) DMAc solution. 60~100$\mu$m thick films for DSC and 1~5$\mu$m films for FTIR experiments were prepared and washed in warm distilled water for few days. For better removal of moisture or DMAc, the films were dried in vacuo at 180℃ for a few days and stored in a desiccator until used. DSC experiments were performed using a Perkin-Elmer DSC-7 Differential Scanning Calorimeter equipped with 7500 Professional Computer and the scans were performed under nitrogen at a heating rate of 20℃/min.

FTIR spectra were obtained on an IBM IR/30 FTIR spectrometer ; 30 scans at a resolution of

$2cm^{-1}$ were signal-averaged. The films were sufficiently thin to be within the absorbance range where the Beer-Lambert law is obeyed.[9]

## RESULTS AND DISCUSSION

### DSC Thermal Study

The two PI homopolymers were heated to 350℃, 400℃ and 450℃, held for 5 min at each temperature and rescanned from 30℃ to 450℃ after quench cooling from the ambient temperature to room temperature. The $T_g$'s, $\Delta T_g$'s and $\Delta C_p$'s of the two polyimides and of PBI are listed in Table 1 ; the values are averages of at least five different measurements because of slightly scattered data. The $T_g$ increased between the first and the second scans and remained constant for the additional scans ; this is presumably believed to be the loss of solvent. The pure polyimides appear to be thermally stable at least up to 450℃.

Sample films in various blend compositions were opaque indicating that these blends are not miscible. Fig. 1 shows a typical DSC thermogram obtained from a 50/50 wt% PBI/6F-3,3′-ODA blend. The thermal conditions of the samples in DSC are scanning from room temperature to 450℃(or to ambient temperature, if any is described), annealing for 5 min at 450℃, quench cooling to room temperature and reheating it to 450℃. The scan rate is 20℃/min under atmospheric nitrogen purge.

Curves A and B are the first and the second scans in DSC, respectively ; the second scan was performed after holding the sample for 5 minutes at 450℃ following the first scan. Distinct $T_g$'s are observed in curve A at 214℃ and 410℃ ;the former corresponds to that of 6F-3,3′-ODA, and the latter corresponds to that of PBI. The Tg's are approximately 30℃ and 10℃ lower than that of PI and PBI, respectively. This may result from residual moisture, volatiles and/or solvent effects. $T_g$'s corresponding to those of the pure homopolymers are clearly shown in curve B, describing

**Table 1.** Thermal Properties of the Homopolymers

| | $T_g$(℃)[(a)] | $\Delta T_g$(℃) | $\Delta C_p$(J/°K) |
|---|---|---|---|
| PBI | 422 | 5 | 0.15 |
| 6F-3,3′-ODA | 245 | 5 | 0.22 |
| 6F-DDSO2 | 280 | 5 | 0.22 |

[(a)] Tg's are obtained from the second DSC scan.

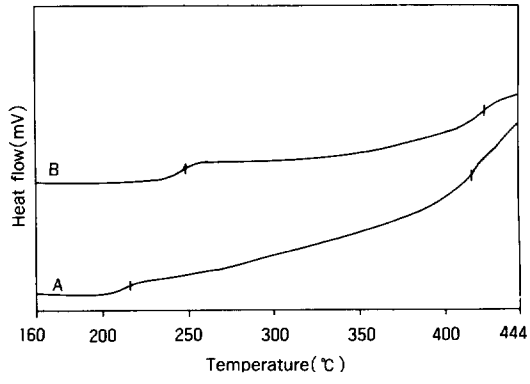



**Fig. 1.** DSC thermogram of a 50/50 wt% PBI/6F-3,3′-ODA blend at a heating rate of 20℃/min. A, the first scan ; B, the second scan.

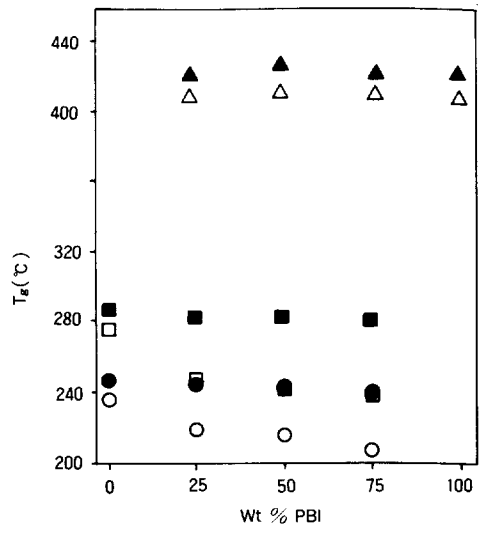



**Fig. 2.** $T_g$'s of PBI/6F-3,3′-ODA and PBI/6F-$DDSO_2$ blends as a function of blend composition(open symbol, first scan ; solid symbol, second scan) : circle, 6F-3,3′-ODA-rich phase ; square, 6F-$DDSO_2$-rich phase ; triangle, PBI-rich phase.

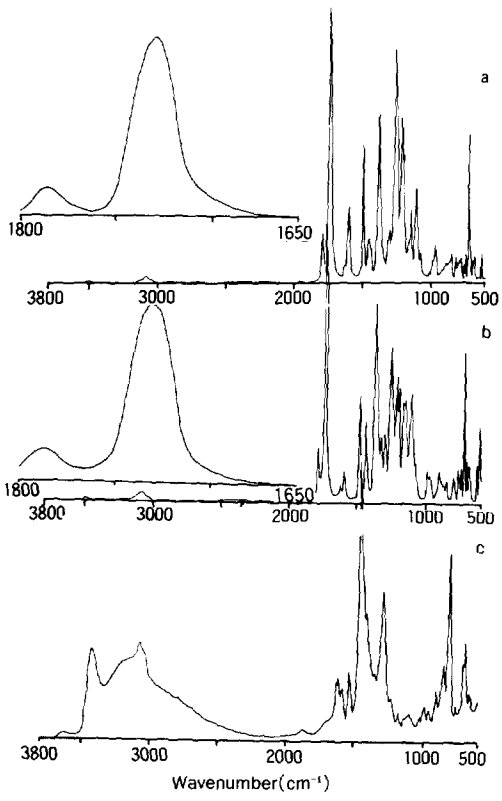



**Fig. 3.** FTIR spectra of PBI(a), 6F-3,3′-ODA polyimide(b) and 6F-DDSO$_2$ polyimide(c) in the 500 to 3800cm$^{-1}$ region at room temperature.

a two-phase regime. In the PBI/6F-DDSO$_2$ blend system, the DSC scan shows $T_g$'s at 282℃ and 424℃ for the second scan corresponding to PI and PBI, respectively; it repeatedly indicates a two-phase system. $T_g$'s as a function of blend compositions are shown in Fig. 2 for both PI blend systems.

**FTIR Study**

The FTIR spectroscopic studies were conducted at room temperature. Fig. 3a, 3b and 3c show the FTIR spectra of 6F-DDSO$_2$(PI), 6F-3,3′-ODA(PI) and PBI, respectively. Each spectrum of PI homopolymers includes a magnified region, which is the carbonyl group absorption band in 1800~1650cm$^{-1}$. The aromatic C−H peak occurs at 3077cm$^{-1}$ and the carbonyl stretching band occurs near 1786cm$^{-1}$ and 1732cm$^{-1}$. In previous systems in PBI/PEI

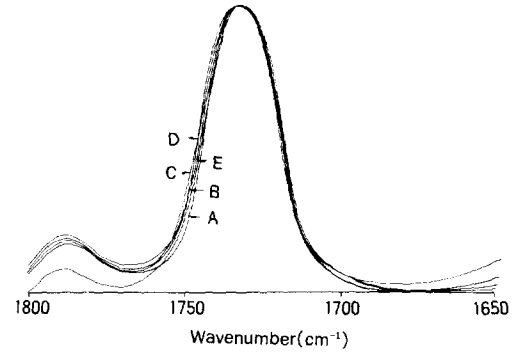



**Fig. 4.** Representative FTIR spectra, in 1650cm$^{-1}$ ~1800cm$^{-1}$ region, of pure 6F-3,3′-ODA(A) and PBI/6F-3,3′-ODA blends containg 20, 50, 70 and 90 wt% PBI(B through E, respectively).

Ultem 1000 and in PBI/PI XU 218,[2,4,7,8] the analogous bands of each homopolymer occur near 3063 cm$^{-1}$ for the aromatic C−H and near 1780cm$^{-1}$ and 1726cm$^{-1}$ for the carbonyl groups. The shift to higher frequency for the both groups may indicate a weaker association in the present system, which implies that the relative strength of the aromatic C−H and the carbonyl bands are weakened because of the steric hinderance of the bulky-$CF_3$ in 6F-3,3′-ODA and in 6F-DDSO$_2$.

Fig. 4 shows the FTIR spectra in 1650cm$^{-1}$~1800cm$^{-1}$ region of pure 6F-3,3′-ODA and four blends of PBI/6F-3,3′-ODA containing 20, 50, 70 and 90 wt% of PBI. In contrast to observations in the PBI/Ultem 1000 and the PBI/XU 218 blend systems, where similar experiments produced significant frequency shifts and band broadening in the well defined carbonyl peak, the present system yields a rather no broadening and no frequency shifts in the carbonyl band. The behavior of remaining a constant position and shape of the carbonyl band, regardless of the presence of up to 90 wt% PBI, indicates an immiscible blend system. A similar behavior is observed in PBI/6F-DDSO$_2$ blend system. Moreover the peak width at half-height of the carbonyl band in both the PBI/6F-3,3′-ODA and PBI/6F-DDSO$_2$ remains constant; the peak widths as a function of blend composition are shown

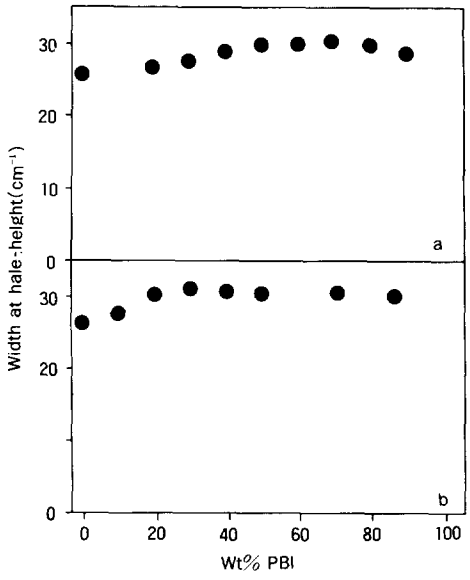



**Fig. 5.** The peak width at half-hight of the carbonyl band as a function of blend composition : (a), PBI/6F-3,3'-ODA ; (b), PBI/6F-$DDSO_2$.

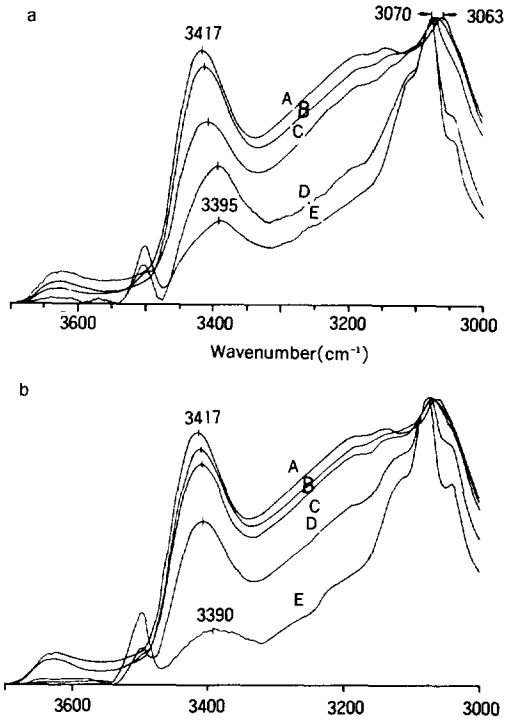



**Fig. 6.** (a) Representative FTIR spectra, in 3000 $cm^{-1}$ ~3700 $cm^{-1}$ region, of PBI/6F-3,3'-ODA blends containing : (A) 0, (B) 30, (C) 50, (D) 80, and (E) 90 wt% 6F-3,3'-ODA. (b) Representative FTIR spectra, in the 3000 $cm^{-1}$ to 3700 $cm^{-1}$ region, of PBI/6F-$DDSO_2$ blends containing : (A) 0, (B) 30, (C) 50, (D) 70, and (E) 90 wt% 6F-$DDSO_2$.

in Fig. 5. A corresponding plot for the miscible PBI/XU 218 or PBI/Ultem 1000 systems produced an S-shaped curve.[2,4,7]

In Fig. 6a and 6b, which show the FTIR spectra in 3000$cm^{-1}$~3700$cm^{-1}$ region corresponding to the N−H bands in PBI/6F-3,3'-ODA and in PBI/6F-$DDSO_2$, respectively, three features are noteworthy : (1) The location of the N−H peak maximum, which is originated near 3417$cm^{-1}$ is shifted to 3390$cm^{-1}$ at 90 wt% of 6F-3,3-ODA and to 3385$cm^{-1}$ at 90 wt% of 6F-$DDSO_2$. (2) The aromatic C−H band, which is originated at 3063$cm^{-1}$ for pure PBI is shifted to 3076$cm^{-1}$ at 100 wt% of 6F-3,3'-ODA and 100 wt% of 6F-$DDSO_2$. (3) The N−H peak broadens as the 6F-3,3'-ODA or 6F-$DDSO_2$ content increases. From the first observation, the 25~30$cm^{-1}$ shift to lower frequency and a slight band broadening of the N−H peak may be suggested as a result of a partial mixing in microscopic phase indicating that this system has some interactions between the two homopolymers. Any specific interaction between N−H and ether oxygen or between N−H and sulfone is not rule out, however it is not possible to detect the relationship at this moment. However the apparent opaque films, the results of thermal study, and the lack of frequency shifts in the carbonyl band are insufficient to reflect intermolecular interactions between the two. The second observation, as mentioned before, may be a result of steric hindrance from the bulky $-CF_3$. Since $-CF_3$ has a strong electron withdrawing tendency, the C−H group on the phenyl ring may be influenced ; as a result, the C−H band is shifted toward a higher frequency indicating, in general, a weakly associated aromatic ring. The carbonyl band observed at 1786$cm^{-1}$ and 1732$cm^{-1}$ in both 6F-3,3'-ODA and 6F-$DDSO_2$ may likewise be affected by the $-CF_3$ group. This

differs from the Ultem 1000 and XU 218 cases where the carbonyl is located at 1780cm$^{-1}$ and 1726cm$^{-1}$. The third observation may be rationalized as a consequence of distribution of hydrogen bonds which originally existed between the N−H and the carbonyl groups and which is alterd by the $-CF_3$ or as a consequence of altered charge transfer complexation in $-CF_3$ ; the N−H peak is thus broadened.

In comparison to the systems we have studied earlier,[2,4] the $-CF_3$ group serves as a spacer between two phthalimide rings in present system. This is believed to be a major factor in preventing specific intermolecular interactions such as hydrogen bonding with PBI, thereby inducing immiscibility. Coleman et al. in their FTIR studies on polymer blends involving the carbonyl group noted that chain-chain interactions between two homopolymers can be detected by the presence of frequency shifts and band broadening.[10] The absence of band broadening and frequency shifts of the carbonyl band in the present system can thus be rationalized as indicating phase separation or a two phase regime caused by the steric effects.

In the miscible phenoxy-poly(vinyl methyl ether) blend, the evidence has been obtained in the form of a frequency shift for an intermolecular interaction involving the phenoxy hydrogen. However in the immiscible poly(vinyl ethyl ether)-poly(vinyl isobutyl ether) blend system, no such frequency shift is observed.[11]

The smaller ratio of hydrogen to carbon in the repeat unit of the chain in 6F-3,3′-ODA and 6F-DDSO$_2$ compared with that in Ultem 1000 or XU 218 may affect the balance in the electron distribution. The chemical structure of polyimides is thus believed to be important factor governing miscibility/immiscibility relationship with PBI.

## CONCLUSION

The blend systems of PBI/6F-3,3′-ODA and PBI/6F-DDSO$_2$ were studied using DSC and FTIR spectroscopy and found to be immiscible based on the presence of opaque films, two composition-independent $T_g$'s and an absence of frequency shifts and of band broadening in the carbonyl peak upon blending. In contrast, 25cm$^{-1}$ frequency shifts in N−H peak, which are smaller than the shifts(55cm$^{-1}$) in PBI/Ultem 1000 and PBI/XU 218 blend are indicative the possibility of other interactions than hydrogen bonding, such as charge transfer complexations. The $-CF_3$ group, because of its electronegativity, may be suggested to alter the electron distribution in the polymer chain causing weaker interactions. The chemical structures of various polyimides may be important factors governing miscible blend systems with PBI.

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