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Miscibility of fluoro-containing polyimide blends

Tai-Shung Chung*
Department of Chemical Engineering, National University of Singapore, 10 Kent Ridge Crescent, Republic of Singapore 119260

and E. Ronald Kafchinski
Hoechst Celanese, Research Division, 86 Morris Avenue, Summit, NJ 07961, USA
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Experimental results confirm the general rules for miscible polyimide pairs containing the hexafluoroisopropylidene group if (1) the dianhydride composition is the same in each pair and (2) the diamine is changed from the 3,3′ (*meta*-substituted) 6F-diamine to the 4,4′ (*para*-substituted) 6F-diamine. These rules are also applicable to end-capped polyimide pairs. This conclusion is supported with the calculations of χ values based on the Flory–Huggins theory. We also discover two interesting polyimide alloys: 6FDA–PMDA–3,3′-6F-diamine/6FDA–PMDA–4,4′-6F-diamine forms fully miscible blends, while 6FDA–3,3′-6F-diamine/BTDA–4,4′-6F-diamine forms partially miscible blends (6FDA = hexafluorodianhydride, PMDA = pyromellitic dianhydride, BTDA = benzophenonetetracarboxylic dianhydride). These surprising results confirm that the rigidity, bond angle, space and the length of the dianhydride can significantly affect the molecular packing and miscibility tendency of polyimide blends. Copyright © 1996 Elsevier Science Ltd.

(Keywords: fluoropolyimides; blend miscibility; glass transition temperature)

INTRODUCTION

Because of their high inherent thermal stability and low dielectric properties, fluoro-containing aromatic polyimides have been identified as having excellent potential for use in electronic devices, aerospace composites, and aircraft wire and cable coatings. A variety of these polymers have been synthesized, and their composite properties have been reported by NASA[1–3] and others[4–7]. Polymer blends of amides with imides or of imides with other conventional polymers have also received attention. For example, MacKnight and Karasz and their coworkers[5–7], Jaffe[8] and coworkers[9] have reviewed and investigated polyimide blends as well as polybenzimidazole/polyimide (PBI/PI) blends. Some of the polyimides contain fluoro-containing aromatic repeat units. Yokota *et al.*[10] reported their work on rigid-rod polyimide blends. Yoon *et al.*[11] have analysed 'molecular composite' films made from rigid and flexible polyimides, and Liang *et al.*[12] reported thermal and rheological properties of miscible poly(ether sulfone) and polyimide blends.

In the last decade, a series of hexafluoroisopropylidene-group-containing polyimides have been synthesized by researchers at Hoechst Celanese Corporation[13,14]; this has provided us with an opportunity to investigate the miscibility of closely related polyimides. Chung *et al.*[15] have discovered the miscibility criteria for fluoropolyimides with one another using the Flory–Huggins theory. They found that hexafluoroisopropylidene-group-containing polyimides were miscible with each other if (1) the dianhydride composition was the same in each pair and (2) the diamine was changed from the 3,3′ (*meta*-substituted) 6F-diamine to the 4,4′ (*para*-substituted) 6F-diamine. These miscibility criteria worked well for seven pairs of polyimides containing the hexafluoroisopropylidene group. In this report, we intend to extend this general rule to another pair of polyimides containing the hexafluoroisopropylidene group and also investigate other complicated systems.

EXPERIMENTS

Material syntheses

Two pairs of new hexafluoroisopropylidene-group-containing polyimides are synthesized using solution polycondensation reactions in *N*-methylpyrrolidone (NMP) at room temperature and then chemically imidized using acetic anhydride and β-picoline. The first pair are end-capped 50%/50% 6FDA/3,3′-6F-diamine and end-capped 50%/50% 6FDA/4,4′-6F-diamine polyimides; and the second pair are polyimides made from 25%/25%/50% 6FDA/PMDA/4,4′-6F-diamine and 25%/25%/50% 6FDA/PMDA/3,3′-6F-diamine. All percentages used in this paper are in molar ratio. A detailed description of the polymerization steps for hexafluoroisopropylidene-group-containing polyimides was given in our previous report and elsewhere[13–15].

All other hexafluoroisopropylidene-group-containing polyimides used in this study were the same as those in

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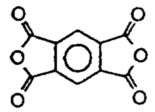
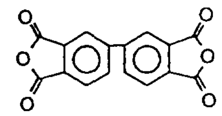
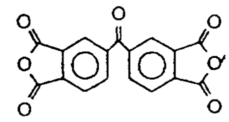
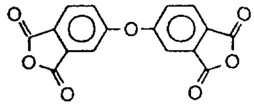
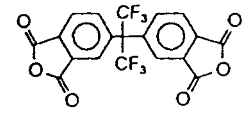
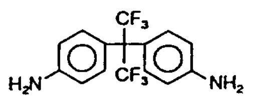
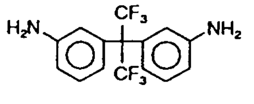
* To whom correspondence should be addressed

Table 1 Chemical structures of monomers for 6F-containing polyimides

Dianhydrides	
PMDA	
BPDA	
BTDA	
ODPA	
6FDA	
Diamines	
4,4′-6F-diamine	
3,3′-6F-diamine	

PMDA = pyromellitic dianhydride
BPDA = biphenyltetracarboxylic dianhydride
BTDA = benzophenonetetracarboxylic dianhydride
ODPA = oxydiphthalic anhydride
6FDA = hexafluorodianhydride

the previous study[15]. *Table 1* describes all monomer structures and *Table 2* shows their chemical compositions. Their glass transition temperatures are summarized in *Table 3*. A Perkin-Elmer DSC was used to determine these T_g values at a heating rate of 20°C $\min^{-1}$. All T_g were measured at the second heating unless specified otherwise. 6FC1P and 6FC1M are the new pair of 6F polyimides.

Blending

All polyimide alloys were solution blended at a 50/50 weight ratio by co-dissolving the polymer pairs in a common solvent, such as methylene chloride ($MeCl_2$) or a mixture of $MeCl_2$ and HFIP (hexafluoroisopropanol), co-precipitation in methanol and then drying overnight under vacuum at 100°C. *Table 4* describes all new alloy systems for further study and comparison.

Table 2 Compositions of 6F-containing polyimides

	Composition		
Polymer	Dianhydride	Diamine	Molar ratio[a]
6F1P	6FDA	4,4′-6F-diamine	50/50
6F2P	BPDA	4,4′-6F-diamine	50/50
6F3P	BTDA	4,4′-6F-diamine	50/50
6F4P	OPDA	4,4′-6F-diamine	50/50
6FC1P	PMDA + 6FDA	4,4′-6F-diamine	25/25/50
6FC2P	PMDA + BPDA	4,4′-6F-diamine	25/25/50
6FC3P	PMDA + BTDA	4,4′-6F-diamine	25/25/50
6FC4P	PMDA + OPDA	4,4′-6F-diamine	25/25/50
6FD5P	OPDA + 6FDA	4,4′-6F-diamine	25/25/50
6F1M	6FDA	3,3′-6F-diamine	50/50
6F2M	BPDA	3,3′-6F-diamine	50/50
6F3M	BTDA	3,3′-6F-diamine	50/50
6F4M	OPDA	3,3′-6F-diamine	50/50
6FC1M	PMDA + 6FDA	4,4′-6F-diamine	25/25/50
6FC2M	PMDA + BPDA	3,3′-6F-diamine	25/25/50
6FC3M	PMDA + BTDA	3,3′-6F-diamine	25/25/50
6FC4M	PMDA + OPDA	3,3′-6F-diamine	25/25/50

[a] Dianhydrides/diamine ratio

Table 3 The T_g values of 6F polyimides

Polymer	T_g (°C)	Polymer	T_g (°C)
6F1M	250.5	6F1P	318.5
6F2M	267.0	6F2P	343.0
6F3M	239.0	6F3P	304.0
6F4M	224.5	6F4P	305.0
6FC1M	270.9	6FC1P	354.0
6FC2M	280.0	6FC2P	375.0
6FC3M	261.0	6FC3P	349.5
6FC4M	233.0	6FC4P	347.0

Table 4 Blends of 6F polyimides

Blend system	Composition
Alloy system 1	6FC1M/6FC1P and previous seven pairs
Alloy system 2	6F1M/6F1P end-capped 6F1M/end-capped 6F1P
Alloy system 3	6F1M/6F2P, 6F1M/6F3P and 6F1M/6F4P
Alloy system 4	6F1M/6FC2P 6F1M/6FC4P

Calculation of parameters for the Flory–Huggins theory

The calculations of solubility parameter δ, interaction parameter χ and critical interaction parameter χ_{cr} for the Flory–Huggins theory of polymer solutions have been given in our previous paper[15]. For simplicity of calculations, we assumed that the densities of these polymers were the same as that of 6FIP, which was $1.47\,g\,cm^{-3}$, and we specifically used Hoy's table to calculate and predict the molar attraction constant for each chemical group[15–18]. The unit for the interaction parameter χ is $cal\,cm^{-3}$.

Fox equation

The Fox equation has been used to predict the T_g of a miscible blend defined as follows[15–18]:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where W_1 and W_2 are the weight fractions of each component, and T_{g1} and T_{g2} are the corresponding glass transition temperatures in kelvins.

RESULTS

System 1: 6FC1P/6FC1M and previous seven pairs

Table 5 gives the χ value for the new pair of 6F polyimides, 6FC1P/6FC1M, and also compares it to the previous seven pairs of 6F polyimide blends with a ranking. As discussed in the previous articles, a low calculated χ implies that the effect on the solubility parameter of changing from the *meta*-substituted 6F-diamine to the *para*-substituted 6F-diamine is very small. A high calculated χ may indicate that, when mixing two polymers which both have the same dianhydride rigid and flexible monomers in their repeat units, homogeneity on the molecular level is relatively difficult to achieve.

Although the rigidity (inflexibility) of the dianhydrides for both *meta*- and *para*-substituted 6F-diamine polyimides follows the order[15]:

$$\text{PMDA} > \text{BPDA} > \text{6FDA} > \text{BTDA} > \text{OPDA}$$

6F1M/6F1P blends have the lowest calculated χ. This indicates that 6F polymides made from 3,3′- or 4,4′-6F-diamine and 6FDA have the strongest interaction and the highest tendency to form miscible blends. This probably derives from the fact that they already have a hexafluoroisopropylidene group in their diamine part, leading to strong fluoro interaction. Based on molecular modelling for 6F1M, the bond angles of $-C(CF_3)_2-$ in 6F-diamine and dianhydride moieties are 106.74° and 109.2°, respectively, while those for 6F1P are 111.38° and 109.2°, respectively. The chain length between $-C(CF_3)_2-$ and a phenyl group in a diamine moiety for 6F1M is 1.51 Å, while for 6F1P it is 1.5 Å. Owing to these similarities in bond angle and length, the molecular-level packing for 6F1M/6F1P alloys is facilitated and this pair is the most stable identified in this study.

The strong molecular interaction in 6F1M/6F1P alloys seems to stay quite well for the new pair, 6FC1M/6FC1P. (The difference between 6F1M/6F1P and 6FC1M/6FC1P is the replacement of 50% 6FDA by PMDA.) As a result, its χ value ranks the third lowest in these eight pairs of polyimides. However, 6F3P/6F3M still ranks the second lowest in this series because the chain length (1.48 Å) of –CO– units in BTDA is closer to that (1.5 Å) of $-CF_3)_2-$. The χ value increase from 6F1M/6F1P blends to 6FC1M/6FC1P blends is greater than either that from 6F3P/6F3M to 6FC3P/6FC3M or that from 6F4P/6F4M to 6FC4P/6FC4M. This clearly indicates that PMDA causes more molecular-level structure changes in 6F1M/6F1P alloys than in other alloys.

Based on Krause's analysis and table[16], 6FC1M/6FC1P blends should be miscible because the χ value is smaller than χ_{cr}, which is about 0.01. *Table 6* proves our prediction and demonstrates that there is only one T_g for each blend at a 50/50 blend ratio. *Table 7* summarizes the measured T_g values for 6FC1M/6FC1P at various blend ratios, and *Figure 1* illustrates their T_g values as a function of 6FC1M composition. These data reconfirm

Table 5 Calculation of interaction parameters χ

Polymer blend (50/50)	χ	Order[a]
6F1M/6F1P	0.00297	1
6F2M/6F2P	0.00546	8
6F3M/6F3P	0.00405	2
6F4M/6F4P	0.00421	4
6FC1M/6FC1P	0.00414	3
6FC2M/6FC2P	0.00518	7
6FC3M/6FC3P	0.00494	5
6FC4M/6FC4P	0.00504	6

[a] Based on χ values: the lower the χ, the lower the order

Table 6 The T_g values of 6F/6F polyimide blends (50%/50%) for system 1

Polymer blend	T_{g1}/T_{g2}[a] (°C)	T_g of 50/50[b] (°C)	Fox eq.[c] (°C)	Temp. diff.[d] (°C)	Order[e]
6F1M/6F1P	250.5/318.5	275.0	282.4	7.4	1
6F2M/6F2P	267.0/343.0	279.3	302.5	23.1	5
6F3M/6F3P	239.0/304.0	252.8	269.6	16.7	3
6F4M/6F4P	224.5/305.0	242.7	261.7	19.0	4
6FC1M/6FC1P	270.9/354.0	295.0	309.5	14.5	2
6FC2M/6FC2P	280.0/375.0	295.5	323.7	28.2	7
6FC3M/6FC3P	261.0/349.5	273.4	301.8	28.5	8
6FC4M/6FC4P	233.0/347.0	258.4	284.2	25.8	6

[a] T_g of individual polymers in a blend
[b] Measured T_g of a blend
[c] Calculated T_g from the Fox equation
[d] Difference between the measured T_g and the calculated
[e] Based on temp. diff.

Table 7 The T_{gs} values of 6FC1M/6FC1P polyimide blends (system 1)

Composition ratio				
6FC1M (%)	6FC1P (%)	T_g (°C)	T_g (°C) from Fox eq.	T_g difference (°C)
0	100	354.00	354.00	0.00
25	75	313.00	330.96	−17.96
50	50	296.00	309.56	−13.56
75	25	278.00	289.62	−11.62
100	0	271.00	271.00	0.00

that, as long as the dianhydride is the same in the composition, the change of 6F-diamine from 3,3′- to 4,4′- does not alter solubility significantly, and the pairs are miscible. The T_g deviations between the measured T_g data and assumed T_g expectation values, as calculated from the Fox equation[17,19], closely follow the order of the predicted χ values. The slight disagreement between the ordering of T_g and χ may arise from a number of factors: (1) densities for all polyimides were assumed constant in our calculations; (2) we neglected the effect of the variation of the degree of polymerization on the χ_{cr} value; and (3) the Fox equation may not be fully applicable for these random copolymers, as discussed in MacKnight *et al.*[17].

Based on trends of the calculated χ and the T_g deviations defined above, we may conclude that the strength of the molecular interaction resulting in miscibility among these pairs follows the order:

$$\text{6F1M/6F1P} \gg \text{6F3M/6F3P} = \text{6FC1M/6FC1P}$$

$$> \text{6FC3M/6FC3P} \geqslant \text{6F4M/6F4P} > \text{6F2M/6F2P}$$

$$\geqslant \text{6FC4M/6FC4P} \gg \text{6FC2M/6FC2P}$$

System 2: end-capped 6F1M and end-capped 6F1P

Tables 8 and *9* summarize the T_g values of these blends and *Figures 2* and *3* illustrate their T_g values as a function of 6F1M composition. Similar to non-end-capped 6F1M/6F1P blends, end-capped 6F1M and end-capped 6F1P appear to be miscible in all compositions. The agreement between the measured T_g and the calculated T_g using the Fox equation is reasonably good. The magnitude of the T_g differences between the measured and the calculated values is almost the same for the end-capped pair and the non-end-capped pair. However, the end-capped pair has a positive deviation from the calculated results using the Fox equation. The positive

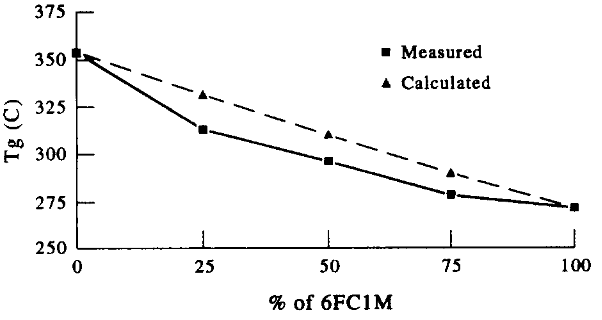


Figure 1 The T_g values of 6FC1M/6FC1P blends (system 1)

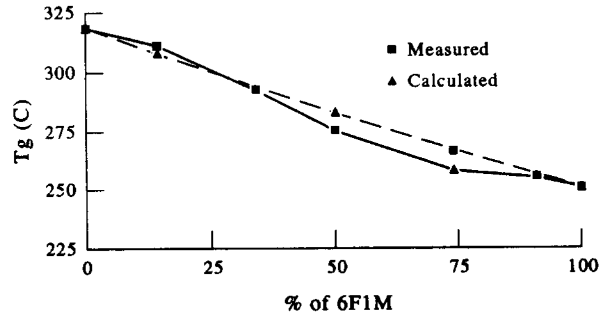


Figure 2 The T_g values of 6F1M/6F1P blends (system 2)

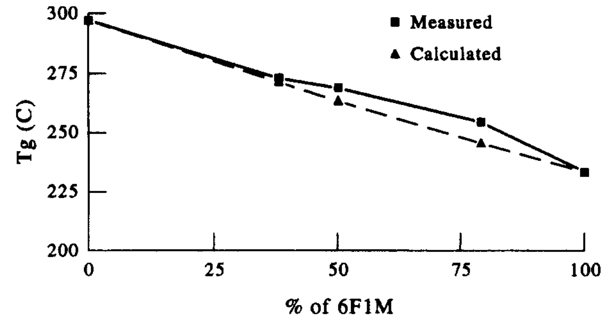


Figure 3 The T_g values of end-capped 6F1M/end-capped 6F1P blends (system 2)

Table 8 The T_g values of 6F1M/6F1P polyimide blends (system 2)

Composition ratio				
6FC1M (%)	6F1P (%)	T_g (°C)	T_g (°C) from Fox eq.	T_g difference (°C)
0	100	318.50	318.50	0.00
14.3	85.7	311.00	307.71	3.29
34	66	292.00	293.48	−1.48
50	50	275.00	282.43	−7.43
74	26	257.50	266.63	−9.13
91	9	254.50	255.97	−1.47
100	0	250.50	250.50	0.00

Table 9 The T_g values of end-capped 6F1M/end-capped 6F1P polyimide blends (system 2)

Composition ratio				
End-capped 6F1M (%)	End-capped 6F1P (%)	T_g (°C)	T_g(°C) from Fox eq.	T_g difference (°C)
0	100	297.00	297.00	0.00
38	62	273.00	271.30	1.70
50	50	269.00	263.66	5.34
79	21	254.50	246.05	8.45
100	0	234.00	234.00	0.00

deviation phenomenon has been reported by Zhuang *et al.*[20] and Kwei[21] for other polymer systems. They claimed that these high T_g values were due to the effect of strong hydrogen-bonding interactions. This explanation may also be applicable to our case because the hydrogen-bonding interaction is stronger in an end-capped pair than in a non-end-capped pair.

Therefore, we may conclude that the strength of the molecular interaction resulting in miscibility among these pairs follows the order:

$$\begin{aligned}&\text{end-capped 6F1M/end-capped 6F1P} = \text{6F1M/6F1P}\\ &\gg \text{6F3M/6F3P} = \text{6FC1M/6FC1P} > \text{6FC3M/6FC3P}\\ &\geqslant \text{6F4M/6F4P} > \text{6F2M/6F2P} \geqslant \text{6FC4M/6FC4P}\\ &\qquad\qquad\qquad\qquad \gg \text{6FC2M/6FC2P}\end{aligned}$$

System 3: 6F1M/6F2P, 6F1M/6F3P and 6F1M/6F4P

Since 6F1M/6F1P has the strongest interaction and the lowest calculated χ, what happens if 6F1P is replaced by either 6F2P, 6F3P or 6F4P? *Table 10* summarizes the results. 6F1M/6F3P has a better molecular interaction compared to those of 6FM/6F2P and 6F1M/6F4P. This interesting phenomenon is also due to the fact that BTDA-containing 6F polyimide blends have similar chain lengths and, therefore, have a greater tendency for molecular packing than pairs containing ODPA or BPDA. However, 6F1M and 6F3P blends are not miscible in all compositions. *Table 11* summarizes our results and indicates that 30/70 6F1M/6F3P is not miscible.

Table 10 The T_g values of 6F polyimide blends (50%/50%) for system 3

Polymer blend	T_{g1}/T_{g2}[a] (°C)	T_g of 50/50[b] (°C)
6F1M/6F1P	250.5/318.5	275.0
6F1M/6F2P	250.5/343.0	2 × T_g
6F1M/6F3P	250.5/304.0	261.0
6F1M/6F4P	250.5/305.0	2 × T_g in the 1st scan 1 × T_g in the 2nd scan

[a] T_g of individual polymers in a blend
[b] Measured T_g of a blend

System 4: 6F1M/6FC2P and 6F1M/6FC4P

Based on our previous experience on the rigidity (infexibility) and chain lengths of the dianhydrides, we thought that both 6F1M/6FC2P and 6F1M/6FC4P alloys should not be miscible. D.s.c. scans give us a surprising result. 6F1M/6FC2P is not miscible, while 6F1M/6FC4P is fully miscible. *Table 12* summarizes the experimental results and the predicted T_g values using the Fox equation. This unexpected miscibility between 6F1M and 6FC4P is clearly due to the incorporation of PMDA in 6FC4P. PMDA has extremely rigid and short chain lengths, which makes the molecular conformation of 6FC4P more suitable for molecular packing with 6FlM molecules than that of 6F4P. However, a more fundamental study is needed to explain this interesting result.

CONCLUSIONS

Experimental results reconfirm the previous general rules that polyimide pairs containing the hexafluoroisopropylidene group are miscible with each other if (1) the dianhydride composition is the same in each pair and (2) the diamine is changed from the 3,3′ (*meta*-substituted) 6F-diamine to the 4,4′ (*para*-substituted) 6F-diamine. End-capped polyimide pairs also follow these rules. These results are consistent with calculation based on the Flory–Huggins theory.

This study also reports that 6FDA–PMDA–3,3′-6F-diamine/6FDA–PMDA–4,4′-6F-diamine forms fully miscible blends, while 6FDA-3,3′-6F-diamine/BTDA-4,4′-6F-diamine forms partially miscible blends.

Table 11 The T_g values of 6F1M/6F3P polyimide blends (system 3)

Composition ratio				
6F1M (%)	6F3P (%)	T_g (°C)	T_g (°C) from Fox eq.	T_g difference (°C)
0	100	318.50	318.50	0.00
18.3	81.7	298.50	304.77	−6.27
30.4	69.6	264, 293.5	296.03	
50	50	261.00	282.43	−21.43
67.5	32.5	258.00	270.82	−12.82
87	13	253.00	258.44	−5.44
100	0	250.50	250.50	0.00

Table 12 The T_g values of 6F1M/6FC4P polyimide blends (system 4)

Composition ratio				
6F1M (%)	6FC4P (%)	T_g (°C)	T_g (°C) from Fox eq.	T_g difference (°C)
0	100	347.50	347.50	0.00
18.1	81.9	314.50	327.37	−12.87
39.6	60.4	291.00	305.08	−14.08
50	50	282.00	294.89	−12.89
72.3	27.7	265.00	274.19	−9.19
86.7	13.3	260.00	261.62	−1.62
100	0	250.50	250.50	0.00

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