Infrared Spectroscopic and Thermal Investigations of a New Miscible Blend System Composed of 3,4′-Oxydianiline Derived Polyisophthalamide and 4,4′-Oxydianiline/3,3′,4,4′-Biphenyltetracarboxylic Dianhydride Based Polyimide

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ABSTRACT: A new high-performance, miscible polymer blend based on the aramid derived from 3,4′-oxydianiline and isophthaloyl chloride with the polyimide obtained from 4,4′-oxydianiline and 3,3′,4,4′-biphenyltetracarboxylic dianhydride has been prepared. The blends exhibited miscibility over entire composition range as evidenced by single glass transition at a temperature in between those of the component polymers. Unusual composition-dependent upward frequency shifts by $60 \, cm^{-1}$ in the N–H stretching band of the aramid due to dissociation of hydrogen bonding were observed, indicating enthalpy increase in the blend system. The results could be explained by the contribution of the Coleman-Painter's disorientational entropy change as well as possible side reactions.

KEY WORDS Aramid / Polyimide / Polymer Blend / Miscibility / Thermal Behavior / Infrared Spectroscopy /

In these years, high performance polymer blends have attracted much interest particularly from the technical viewpoint, and a number of such blend systems have appeared in the literature.[1-11] Earlier reports in this area have dealt with the molecular composites such as those comprising poly(*p*-phenylene benzobisthiazole)/poly(2,5(6)-benzimidazole) system[12] and poly(*p*-phenyleneterephthalamide)/nylon-6 system.[13] The concept of the molecular composite is the dispersion of a rigid-rod polymer in a flexible-coil polymer matrix at a molecular level. Fundamentally, a successful formation of the molecular composite involves the freezing of metastable homogeneous state which is attributed to low molecular mobility of the rigid-rod species. This concept seems attractive, because most polymer–polymer pairs are immiscible particularly when the rigidity of the polymer main chains largely differs.[14] However, the molecular composite system results in self-alignment of the rigid chains forming microfibrils,[13] and the ideal mixing at the molecular level was hard to be attained.[13]

In the field of polymer blends, specific intermolecular interactions such as hydrogen bonding are utilized to enhance the miscibility of the component polymers.[15-20] Introduction of an intermolecular interaction to the molecular composites is explored by Coleman and Painter for poly(γ-glutamate)/poly(vinyl phenol) system.[21] This system was shown to be thermodynamically stable, in spite of the different rigidity of the constituents.[21]

Recently, Karasz and his group reported that the metastable homogeneous mixing at the molecular level could be achieved for the

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polybenzimidazole/polyimide systems through a conventional solution blending.[22–28] In these systems, the homogeneity is thought to be attributed to the intermolecular hydrogen bonding between the N–H groups of the polybenzimidazole and the C=O groups of the polyimides, as well as to the low molecular mobility of the polybenzimidazole. We have also found that an aramid/poly(ether sulfone) system formed an apparently miscible film by solution casting.[29]

From these results, we hypothesized that an aramid and a polyimide derived from a similar diamine component might be made into a compatible blend film. This was really the case, and we anticipated that the aramid/polyimide system could form hydrogen bonding through the N–H groups of the aramid. Contrary to our expectation, the fact was that the hydrogen bonding was actually weakened by blending, nevertheless the blend system was miscible.

In this paper, we report the miscibility of the aramid/polyimide system and discuss the mechanism for the miscibility.

EXPERIMENTAL

Materials
Aramid 34I with the structure:
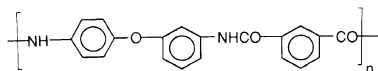
was synthesized from 3,4′-oxydianiline and isophthaloyl chloride by a conventional low temperature solution polycondensation method, as described elsewhere.[29] The inherent viscosity of the aramid in N-methyl-2-pyrrolidone was $1.4 \, dl \, g^{-1}$, measured at a concentration of $0.5 \, g \, dl^{-1}$ at $30°C$.

Polyimide UR with the structure:
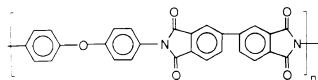
was obtained by chemical imidization of the polyamic acid, derived from 4,4′-oxydianiline and 3,3′,4,4′-biphenyltetracarboxylic dianhydride. The synthetic procedure is as follows. A 200 ml round-bottom three-necked flask equipped with a mechanical stirrer was charged with 3.00 g (15.0 mmol) of 4,4′-oxydianiline and 100 ml of N-methyl-2-pyrrolidone (NMP) under a slow stream of nitrogen. To the solution was added 4.41 g (15.0 mmol) of 3,3′,4,4′-biphenyltetracarboxylic dianhydride all at once, and the mixture was stirred for 12 h at room temperature. The viscous solution formed was poured into methanol to precipitate the polyamic acid. The polyamic acid isolated was washed with toluene, and then refluxed in 100 ml of a mixture of pyridine and acetic anhydride (90 : 10 by volume) for 12 h. The resulting polyimide flakes changed color to deep yellow. They were collected, washed in methanol, and dried at 100°C for 12 h under vacuum. The polyimide was further purified by reprecipitation from p-chlorophenol with methanol. The inherent viscosity of the polyimide in o-chlorophenol was $0.97 \, dl \, g^{-1}$, measured at a concentration of $0.5 \, g \, dl^{-1}$ at 30°C. The complete formation of imide by chemical cyclization are carefully checked by means of IR. The IR spectrum (film) exhibited characteristic imide absorptions at 1775, 1717, 1377, and $739 \, cm^{-1}$ with no amide and carboxylic absorptions.

o-Chlorophenol (OCP) and p-chlorophenol (PCP) were used as purchased.

Sample Preparation
The aramid, the polyimide, and the solvent (PCP/OCP = 50/50 by volume) were mixed at a polymer concentration of 10% (weight/volume), and the mixture was stirred overnight at room temperature to obtain a clear solution. The solution was cast onto a glass plate and the solvent was evaporated under vacuum at 50°C for 1 h. The film was dried at 100°C for 12 h and 240°C for 12 h under vacuum, and then peeled off. To remove a last

trace of the solvent, the film was washed by refluxing in methanol for 12 h, and dried again under vacuum at 100°C for 12 h and at 300°C for 12 h. Transparent films were obtained for all the compositions.

Annealing of Samples

Annealing of the blend film was carried out under vacuum at 330°C for 12 h.

Measurements

IR spectra were recorded for specimens coated on silicon wafers on a JASCO FT/IR-5000 spectrophotometer at a resolution of $2 \, cm^{-1}$ at room temperature and at 330°C. Differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TG) were carried out with Shimadzu DT-40 series thermal analyzers. The heating rates employed were $20°C \, min^{-1}$ for DSC and DTA, and $10°C \, min^{-1}$ for TG. Dynamic thermomechanical analysis (DMA) was performed with a Toyoseiki Reolograph-Solid in tensile mode at a frequency of 10 Hz at a heating rate of $2°C \, min^{-1}$ in air. Wide angle X-ray diffraction profiles were obtained for the film specimens on a Rigaku Denki XG X-ray diffraction apparatus using nickel-filtered CuKα radiation (35 kV, 20 mA).

RESULTS

Component Polymers

Both aramid 34I and polyimide UR were soluble in phenolic solvents such as PCP or a mixture of PCP and OCP. This enabled solution blending of the component polymers. In addition, both polymers, even after annealing at 330°C for 24 h, were shown to be amorphous by means of X-ray diffractometry. The DTA and TG thermograms exhibited that the aramid and the polyimide began to decompose in air at around 400°C and 450°C, respectively (curves A and B in Figure 1). Since the component polymers were enough stable at 330°C, where the miscibility was
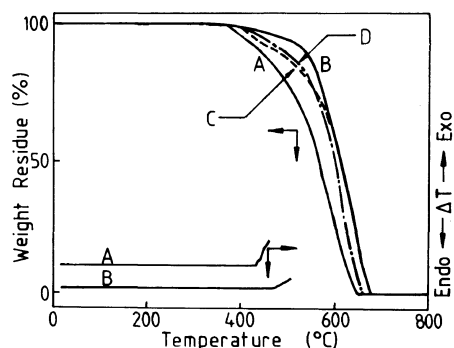

Figure 1. DTA and TG curves in air for (A) the aramid, (B) the polyimide, (C) the as-prepared aramid/polyimide 50/50 blend, and (D) the annealed blend.

examined, the annealing of neat polymer films at 330°C caused little change of the properties.

Thermal Behavior

Figure 1 also shows the TG thermograms of the aramid/polyimide 50/50 (wt/wt) blend film before and after annealing at 330°C for 12 h. Absence of the weight loss before the onset of the decomposition temperature around 400°C evidenced the thorough removal of the solvent from the as-prepared blend film. The as-prepared specimen showed two step weight loss comprising decomposition of the aramid and the polyimide. In the thermogram of the annealed specimen, the first stage decomposition based on the aramid was suppressed.

Figures 2 and 3 show the DSC scan and loss modulus E'' traces by DMA, respectively, of the polymer blends. Double glass transition temperatures (T_g's) close to those of the constituent polymers were detected for the aramid/polyimide 50/50 blend (curve C in both Figures 2 and 3). Again double T_g's were observed for all blend compositions, as shown in Figure 4, indicating that the as-prepared blend films had phase-separated structure.

The as-prepared blend films were annealed under vacuum at 330°C, well above the glass transition temperature of the aramid, for 12 h in order to allow the blend system to approach
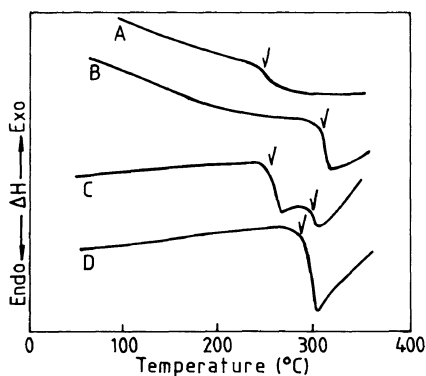
Figure 2. DSC thermograms of the neat polymers and the blend. See Legend for Figure 1.
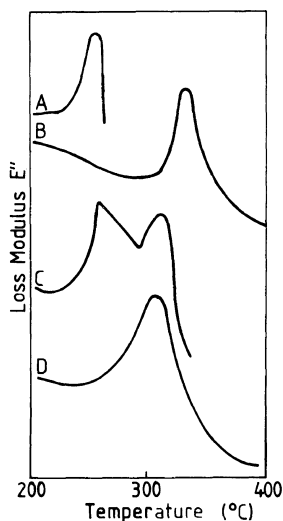
Figure 3. Loss modulus traces of the neat polymers and the blends by DMA. See Legend for Figure 1.

Figure 4. Composition dependence of (A.p.$_1$) the upper T_g of the as-prepared blends, (A.p.$_2$) the lower T_g of the as-prepared blends, and (Ann.) the annealed blend. Gordon–Taylor equation with $k = 2.5$ is shown by the solid line.

the equilibrium state. The DSC and DMA data of the annealed blend films were shown in Figures 2—4. By both analyses, single T_g intermediate between those of the component polymers was detected (curve D in both Figures 2 and 3), and the T_g varied monotonically with the composition (Figure 4). These results indicated that phase mixing had occurred during the annealing and the annealed blend films had single phase nature. The IR spectra of the blend films were changed in the N–H stretching region, because
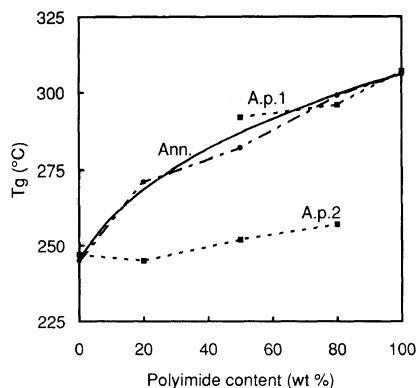
of the hydrogen bonding rearrangement accompanied by the phase mixing.[20, 21]

The composition dependence of the T_g is fitted well the Gordon–Taylor equation[30]:

$$T_g = (T_{gA} W_A + k T_{gB} W_B)/(W_A + k W_B)$$

with the k value of 2.5, where T_{gA} (246°C) and T_{gB} (306°C) are the T_g's of the aramid and the polyimide, respectively, and W_A and W_B are the volume fractions of the respective polymers. The k value of 2.5, which is much larger than unity, indicates that the T_g's of the blends are higher than the mean value of those of the neat polymers.

Then, we continued annealing of the blend films for additional 24 h at 330°C, and confirmed that the thermal properties and IR spectra of the annealed blend films did not change any more. Table I summarizes the T_g's and IR wavenumbers for the N–H and the C=O stretching bands of the neat polymers and the blends before and after annealing.

IR Spectroscopic Study

The variation of IR spectra at the N–H and C=O stretching band reflects the hydrogen bonding condition of amide groups,[20,31] and the hydrogen bond formation generally shifts

Table I. Thermal and IR-spectroscopic properties of the blend films

Aramid/Polyimide composition	As-prepared film			Annealed film		
	$T_g{}^a$	Wavenumbers[c]		$T_g{}^a$	Wavenumbers[c]	
		cm^{-1}			cm^{-1}	
wt/wt	°C	Amide	Imide	°C	Amide	Imide
100/0	247	3304	—	245	3320	—
		1657	—		1661	—
80/20	245	3306	1775	271	3330	1775
		1659	1719		1677	1719
50/50	252	3310	1775	282	3350	1775
	292	1655	1719		1673	1717
20/80	257	3312	1775	299	3374	1775
	296	1685	1721		1685	1717
0/100	307	—	1775	306	—	1775
	—	—	1721		—	1717

^{a} Measured at a heating rate of 20°C min^{-1} by DSC.
^{b} Temperature of 5% weight loss, measured at a heating rate of 10°C min^{-1} by TG.
^{c} Recorded by IR spectrophotometer at room temperature.

to lower frequency of the IR absorptions due to the N–H and C=O stretching modes.[20,31] This is an important source of information, since hydrogen bonding is a strong intermolecular interaction and should affect the miscibility.[20] In the present aramid/polyimide blend system, upward frequency shifts of the maximum peak positions by 60 cm^{-1} and 24 cm^{-1} of the N–H and C=O stretching absorptions, respectively, had occurred on blending (Table I). This result seems strange, since this implies dissociation of hydrogen bonding between amide groups and hence the increase in enthalpy on mixing, which seems to be unfavorable to miscibility.[32]

In order to confirm the dissociation of hydrogen bonding in the polymer blends, the IR spectra of the blend films were recorded at the annealing temperature of 330°C (Figure 5). Then, curve fitting of the N–H stretching region was carried out to separate into the components due to the free and hydrogen-bonded species. Figure 6 shows the results of band separation of the N–H stretching region for the neat aramid film and the aramid/
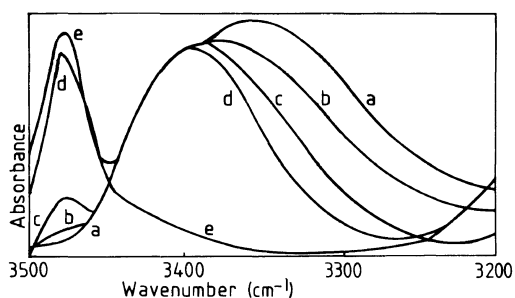

Figure 5. IR spectra of the annealed blend films recorded at 330°C for (a) the aramid, (b) the aramid/polyimide 80/20 blend, (c) the 50/50 blend, (d) the 20/80 blend, and (e) the polyimide.

polyimide 50/50 blend film, both of which were annealed at 330°C for 12 h. The synthesized spectra consisting of a sum of three Lorentzian curves fitted for the observed spectra, though some disagreement was seen on the skirt of the curves which might be affected by neighboring absorptions. The Lorentzian curves used for the peak separation are listed in Table II.

In the case of the neat aramid, possible species are $>$N–H:O=C$<$ (amide), $>$N–H:O$<$,

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Figure 7. Composition dependence of IR optical density of the species observed at the N–H stretching band: (1) peak No.1 in Table II, (2) peak No.2, and (3) peak No.3.
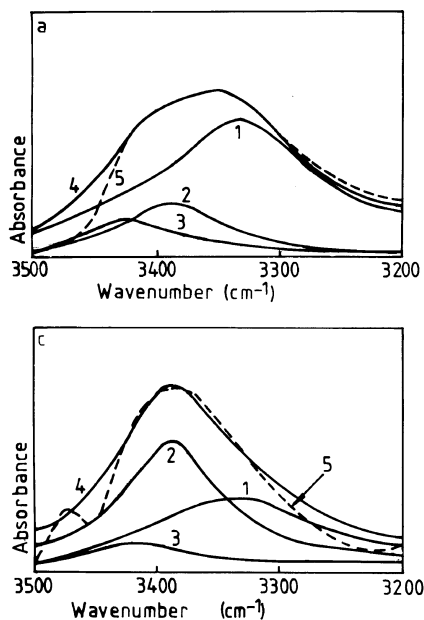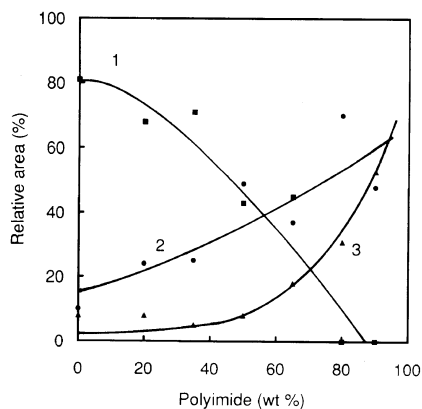
Figure 6. Peak separation results at the N–H stretching band, recorded at 330°C, of (a) the neat aramid and (c) the aramid/polyimide 50/50 blend. The samples were annealed at 330°C for 12 h: (1) peak No.1 in Table II, (2) peak No.2, (3) peak No.3, (4) total of (1)+(2)+(3), and (5) observed peak.

Table II. Lorenzian peaks employed for the peak deviation of N–H stretching band

No.	Assignment	Wavenumber at the center cm^{-1}	Half width cm^{-1}
1	$>$N–H:O$=$C$<$ (amide)	3336	152
2	$>$N–H:O$<$[a]	3390	88
3	$>$N–H (free)	3420	75

[a] Possibly includes $>$N–H:O$=$C$<$ (imide).

and $>$N–H (free). Naturally each curve employed in Figure 6 is assigned to one of the three species. The peak No. 3 in Table II (curve 3 in Figure 6), which possesses the highest frequency, is apparently assigned to $>$N–H (free). The fraction of the species $>$N–H:O$=$C$<$ (amide) should reduce with blending of the polyimide by dilution of amide C$=$O groups. Consequently we assigned peak

No. 1 (curve 1 in Figure 6) to $>$N–H:O$=$C$<$ (amide), whose relative area markedly decreased with polyimide content. At last, peak No. 2 (curve c in Figure 6) was assigned to $>$N–H:O$<$. The peak around 3480 cm^{-1} in Figure 6c (curve 5) is assigned to the overtone of N–H stretching mode of imide groups. The IR spectra of the blend films showed no appearance of other peaks. These results indicate that imide groups do not form hydrogen bonds at that temperature, or that this type of peak is fully overlapped to that of the species $>$N–H:O$=$C$<$.

The relative area of the component peaks *versus* blend compositions of the annealed blends is shown in Figure 7 and Table III. The main alteration by blending is breaking of the self-association between amide groups [the species $>$N–H:O$=$C$<$ (amide)]. Obviously the increase in the species $>$N–H:O$<$ [possibly including $>$N–H:O$=$C$<$ (imide)] and in the free N–H accompanied with the dissociation of hydrogen bonding. The dissociation of hydrogen bonding directly evidences the molecular mixing of the component polymers, while the single T_g observed might just indicate the mixing of component polymers at a larger scale including ten or more segments. We should keep in mind that the molecular

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absorption coefficient of each species can be several times different, as Coleman *et al.* pointed out,[20] and that the relative area would not be propotional to the number of the species.[20] With this reason, we just qualitatively treated these data.

The assignments give us another information on hydrogen bonding. In general, the formation of stronger hydrogen bonding results in larger value of downward frequency shift for a same kind of protic group.[20,31] Hence the N–H groups are shown to associate with amide $C=O$ groups more strongly than with ether groups and imide $C=O$ groups. This is consistent with the little change of the wavenumbers corresponding to the imide $C=O$ stretching bands recorded at room temperature (Table I).

The peak separation of amide $C=O$ stretching band was not performed, since the peak is overlapped to the imide $C=O$ stretching band and seems to be complex.

DISCUSSION

The spontaneous phase mixing usually means the thermodynamic miscibility at the annealing temperature of 330°C. On the other hand, the IR spectroscopic study revealed the large endothermic contribution of hydrogen bonding for the mixing enthalpy. Since the hydrogen bonding is the strongest kind of intermolecular interaction, the above result directly indicates the endothermic heat of mixing of this system. This seems contradict to the polymer miscibility.

One can suppose that some chemical reactions between the aramid and the polyimide occurs, resulting in the compatibilization of the blend. However, it is unlikely to assume reactions among amide, imide, and ether groups. The only possibility is some reactions between the amide and/or imide functions and the terminal amino groups of the aramid and/or the polyimide. The reaction products, some kinds of block copolymers, can affect

the morphology to some extent, but might not significantly change the miscibility. Moreover, the amount of the "compatibilizer" would be small, and the block length of the polyimide unit is as large as the degree of polymerization of polyimide. We therefore believe that this compatibilization effect relative to any chemical reactions is insufficient to cause such a dramatic phase mixing accompanying large unfavorable endothermic contribution.

Coleman and Painter claimed that non-combinatorial entropy change involves in the strongly associating polymer blends, and that the favorable contribution of the entropy can overcome the unfavorable enthalpy increase accompanied by the dissociation of the hydrogen bonding.[20,33] They supposed that the miscibility of poly(vinylphenol)/poly(*n*-butyl methacrylate) blends stemmed from this disorientational entropy gain.[20,33] We believe that the "disorientational entropy" relating to the rearrangement of hydrogen bonding of the aramid mainly caused the miscibility.

This non-combinatorial entropy mechanism of miscibility also explains the phase separation observed in the as-prepared blend films. In general, the free energy of mixing increases with decrease in temperature for the systems possessing endothermic heat of mixing. Hence, the miscibility of such a system should be reduced by lowering the temperature.[20] Thus, the present system can be immiscible at the temprature the films were dried (around 50—100°C), in spite of the miscibility at 330°C.

CONCLUSION

The miscibility of the aramid/polyimide blend system was investigated. The phase-separated as-prepared blends became homogeneous after the annealing at 330°C. This spontaneous homogenization indicates that the system is miscible at the annealing temperature, and also implies the existence of the

upper critical solution temperature below the annealing temperature. Simultaneously, the dissociation of the hydrogen bonding between the aramid molecules was shown to occur during the annealing. We believe these behavior could be explained by the residual mixing entropy associated with the rearrangement of the hydrogen bonding, rather than possible side reactions.

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