

Properties of Fluorinated Polyimides

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This paper reports on two fluorinated polyimides synthesized using a fluorinated diamine, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB). One polyimide, synthesized with TFDB and 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane (6FDA), has a low dielectric constant, high optical transparency, and a low refractive index. The other, synthesized with TFDB and pyromellitic dianhydride (PMDA), has a low coefficient of thermal expansion (CTE). Because the two polyimides are synthesized using the same diamine, we can easily prepare a polymer blend of these two polyimides and synthesize their copolymer. The physical properties, such as the CTE, of the polymer blend or copolymer can be controlled by changing the 6FDA/TFDB polyimide or the 6FDA content, respectively.

1. Introduction

Polyimides have been extensively applied to microelectronic devices [1,2] because of their thermal stability. Interlayer dielectrics use low-dielectric-constant polyimides to achieve a high signal-propagation speed [3]. Low-thermal-expansion polyimides are also needed because they are used with low-thermal-expansion substrates such as silicon or silicon dioxide [4]. Optical applications demand precise control of the optical transparency and refractive index. St. Clair et al. [5,6] reported nearly colorless polyimide films.

We have been investigating the synthesis and characterization of fluorinated polyimides. We have already reported a new series of polyimides containing fluorinated alkoxy groups [7], and two new fluorinated polyimides made from a fluorinated diamine, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) [8]. One polyimide, synthesized with TFDB and 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA), has a low dielectric constant, high optical transparency, and a low refractive index. The other, synthesized with TFDB and pyromellitic dianhydride (PMDA), has a low thermal expansion coefficient.

To match the coefficient of thermal expansion (CTE) with that of substrates, we prepared polyimide blends of PMDA/TFDB and 6FDA/TFDB. Then, we copolymerized 6FDA, PMDA and TFDB. This paper describes the properties of the fluorinated polyimide blends and copolymers.

2. Methods

Preparation of Polyimide Blends: 6FDA was dissolved in N,N-dimethylacetamide (DMAc) to give a colorless solution. TFDB was added to the solution with vigorous stirring. The solution became viscous. This solution was 6FDA/TFDB poly(amic acid). PMDA/TFDB poly(amic acid) solution was prepared in the same manner, but with PMDA instead of 6FDA. These two poly(amic acid) solutions were mixed. Then the mixture of poly(amic acid)s was spin-cast onto silicon wafers and converted into polyimides by heating.

Copolyimide Preparation: The fluorinated copoly(amic acid)s were synthesized with TFDB and a mixture of 6FDA and PMDA in DMAc. Then the poly(amic acid)s were spin-cast onto silicon wafers and converted into copolyimides by heating.

Measurements: The refractive indexes were measured by Abbe's method with an Atago 4T-Type refractometer. The measurement temperature was 20°C and the light was sodium D line light with a wavelength of 589.3 nm.

The stress-strain behavior was observed with an Instron Universal Testing Instrument Model 1122 at room temperature. The viscoelastic properties were measured with a Rheometrics Dynamic Spectrometer.

The CTEs were measured with a Sinku-Riko TMA-7000 thermomechanical analyzer. The measurements were carried out three times during elongation with a heating rate of 5°C/min under a nitrogen

atmosphere at a load of 3 g. After the first measurement (first run), the sample was cooled gradually to 25°C in a nitrogen atmosphere. Then the second measurement (second run) was made. The sample was cooled again between the second and third run. The CTE values were taken to be the mean over the range 50-300°C.

3. Results and Discussion

Gel Fraction: 6FDA/TFDB polyimide dissolved in polar solvents such as DMAc or acetone [8]. This implies that there are no crosslinks in the 6FDA/TFDB polyimide. Namely, the imidization of poly(amic acid) was due not to intermolecular reactions but to intramolecular reactions. On the other hand, PMDA/TFDB polyimide cannot be dissolved in a common solvent because of its rigid structure and high cohesion. Therefore, acetone extraction of the (6FDA/TFDB)/(PMDA/TFDB) blend specimen was carried out while refluxing for 24 h.

Figure 1 shows how the gel fraction of the blend depends on composition. The broken line shows PMDA/TFDB polyimide fraction in the blend. The gel fraction of the blend increases with increasing PMDA/TFDB content. The gel fraction is much larger than the PMDA/TFDB content when

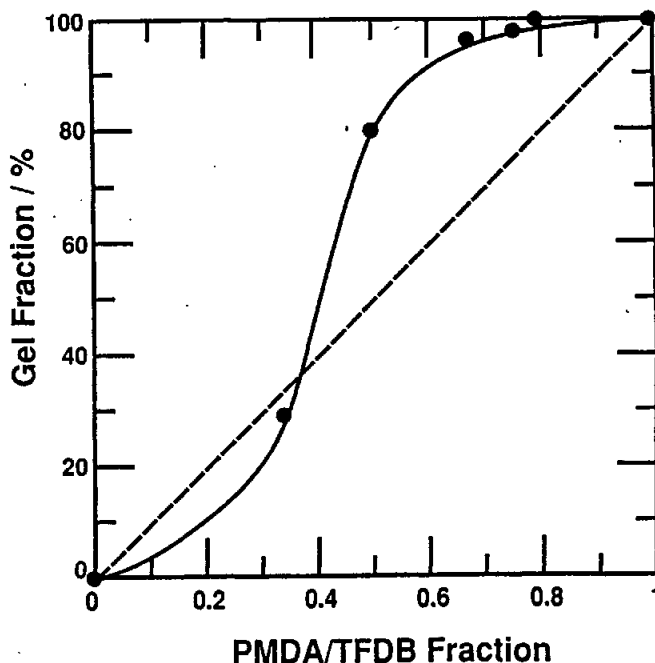


Figure 1. Dependence of the gel fraction of polyimide blends on the composition.

the PMDA/TFDB content is above 0.5. Then the gel fraction is nearly 1 where the PMDA/TFDB content is beyond 0.7. This implies that the 6FDA/TFDB polyimide chain in the blend specimen cannot dissolve because it is anchored to the PMDA/TFDB polyimide. In other words, the 6FDA/TFDB polyimide chain may be entangled in the PMDA/TFDB polyimide matrix due to their good miscibility, similar to interpenetrating polymer networks. On the other hand, the gel fraction is smaller than the PMDA/TFDB content when the PMDA/TFDB content is below 0.4. The solution extracted from the blend specimen whose PMDA/TFDB content was 0.33 was turbid, like an emulsion. We hypothesize that 6FDA/TFDB-polyimide-rich solution can dissolve in PMDA/TFDB polyimide.

Stress-Strain Behavior: Figure 2 shows stress-strain the behavior of the blend. All the specimens have a yield point. The yield strength increases with increasing PMDA/TFDB content. The elongation at the break point of a blended specimen is larger than that of either homopolyimide. The maximum elongation at the break point is observed for a 1/1 composition. The sliding between 6FDA/TFDB and PMDA/TFDB polyimide chains may increase the elongation at the break point.

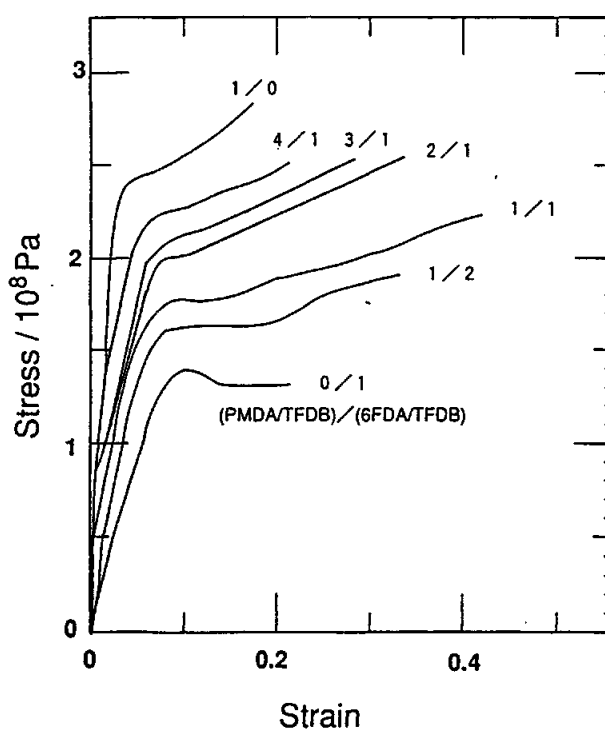


Figure 2. Stress-strain behavior of polyimide blends.

Viscoelastic Properties: The temperature dependence of the viscoelastic properties of the (6FDA/TFDB)/(PMDA/TFDB) polyimide blends and homopolyimides is shown in Figure 3. The storage modulus E' curve for 6FDA/TFDB polyimide falls at 300°C and reaches a rubbery plateau at 400°C. Differential scanning calorimetry (DSC) measurements gave a glass transition temperature of 335°C [8]. Thus, this mechanical relaxation is due to the glass transition. The E' curve for PMDA/TFDB falls at 350°C and reaches a rubbery plateau at 450°C. The drop in E' and $\tan \delta$ for PMDA/TFDB are smaller than those for 6FDA/TFDB. This implies that the relaxation of PMDA/TFDB due to the glass transition is smaller than that of 6FDA/TFDB. The PMDA/TFDB polyimide relaxed at a higher temperature than 6FDA/TFDB. We assume that the PMDA/TFDB polyimide chain is restricted in its movement because of the tight chain packing in the film.

Each E' curve for the (6FDA/TFDB)/(PMDA/TFDB) blends falls in one step. The drop temperature in the E' curve increased with increasing PMDA/TFDB content. There is a single peak in the $\tan \delta$ curve for each blend. The peak strength of each blend is smaller than that of 6FDA/TFDB or PMDA/TFDB homopolyimide. This implies that there is not phase separation but a homogeneous mixing phase in the blend film due to good compatibility.

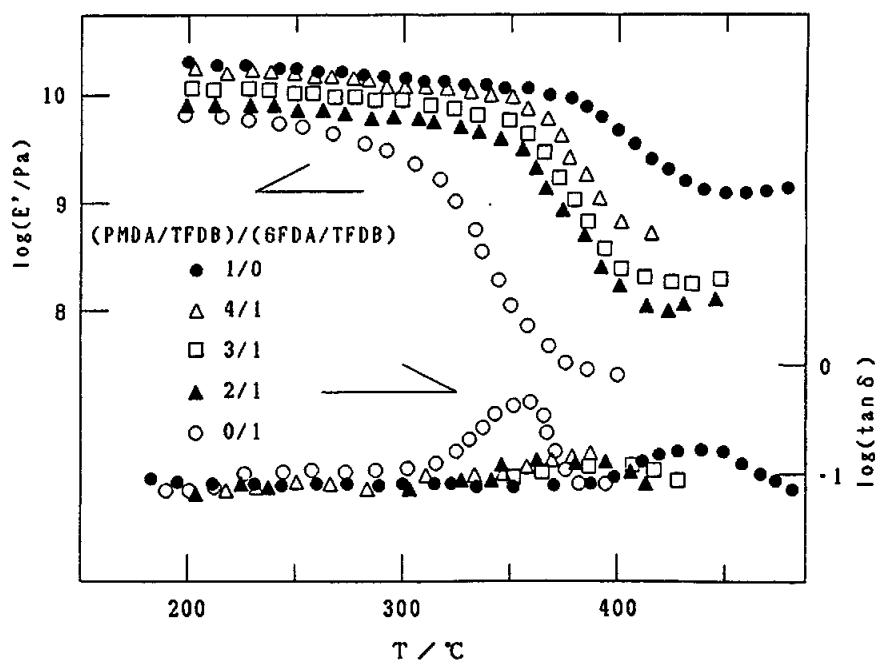


Figure 3. Temperature dependence of viscoelastic properties of polyimide blends.

Thermal Expansion: Figure 4 shows the CTE in the first and second run for the (6FDA/TFDB)/(PMDA/TFDB) polyimide blends and their homopolyimides against the PMDA/TFDB content. In the first run, the CTE ranged from 3×10^{-6} for pure PMDA/TFDB to $4.8 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ for pure 6FDA/TFDB. In the second run, the CTE varied from -5×10^{-6} to $8.2 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$. The CTE in the third run were the same as those in the second run. The difference between the first run and the second run may be due to the thermal strain which induced during thermal imidization. The thermal strain can be released by heat treatment such as annealing. Thus, the thermal strain in the polyimide specimens might be released during the first run. Therefore, the polyimide blend film whose CTE coincides with the CTE of the substrate has no thermal strain. In this experiment, we used a silicon wafer as a substrate. Thus, the polyimide blend that has the same CTE in the first run as the CTE of silicon should have the same CTE in the second run.

Figure 5 shows the dependence on composition of the CTE in the second run for the (6FDA/TFDB)/(PMDA/TFDB) polyimide blends, 6FDA/PMDA/TFDB copolyimides and their homopolyimides. The CTE for copolyimides and the polyimide blends increased from -5×10^{-6} to $8.2 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ with increasing 6FDA content. For the same composition, the CTE

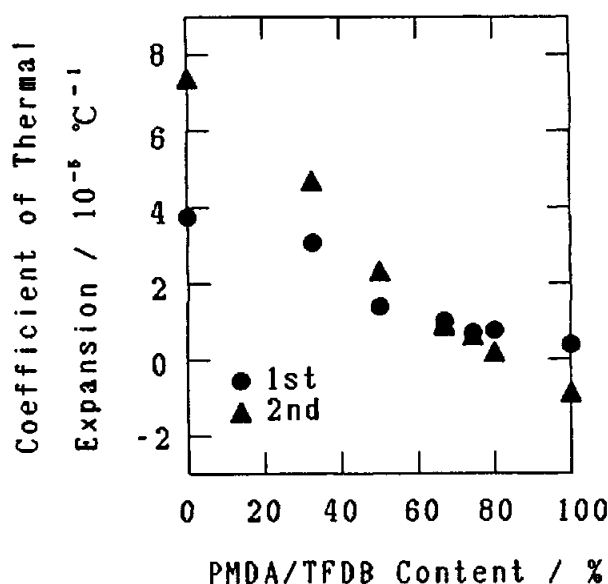


Figure 4. Coefficient of thermal expansion in the 1st and 2nd run for the polyimide blends.

of the copolyimide is larger than that of the polyimide blend. The CTE curve for the polyimide blends is sigmoidal. This implies that the 6FDA fraction in the copolyimide is mixed with the PMDA fraction, which is not case for the polyimide blends.

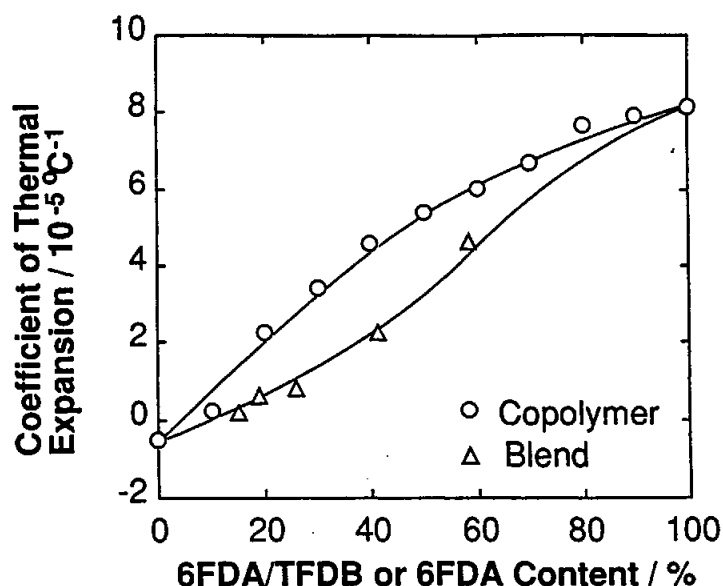


Figure 5. Coefficient of thermal expansion for the polyimide blends and copolymers.

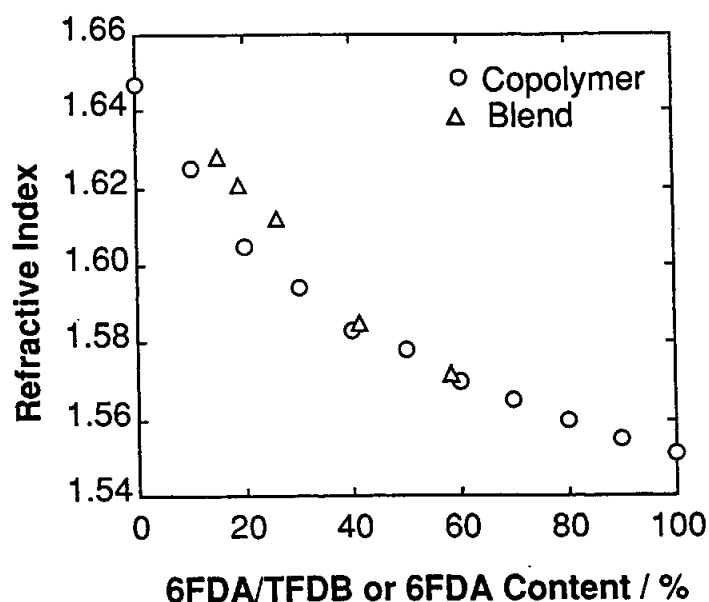


Figure 6. Refractive index of copolyimide.

Refractive Index: Figure 6 shows the refractive index for polyimide blends, copolyimides, and homopolyimides against the composition. The refractive index decreases smoothly with increasing 6FDA content. Therefore, we can prepare any copolyimide whose refractive index is between 1.556 and 1.647. It is difficult to measure the refractive index of the polyimide blends at a light wavelength of 589.3. This may be due to fluctuations in the refractive index.

4. Conclusion

We prepared (6FDA/TFDB)/(PMDA/TFDB) polyimide blends and 6FDA/PMDA/TFDB copolyimides. The 6FDA/TFDB polyimide is well mixed with PMDA/TFDB polyimide in the blend film. For microelectronics, a polyimide blend can be made to match the CTE of a substrate. The 6FDA/PMDA/TFDB copolyimides can also be used for optical components, as it is easy to control their refractive index.

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