

Low CTE and Improved Toughness of PMDA/PDA-based Polyimide Composites

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ABSTRACT

Asymmetric biphenyl type polyimide (PI) derived from 2,3,3',4'-biphenyl tetracarboxylic dianhydride (a-BPDA) and 4,4'-oxydianiline (ODA), a-BPDA/ODA, was used a matrix polymer for rod-like polyimide, PMDA/PDA (PMDA: pyromellitic dianhydride, PDA: p-phenylenediamine). The film toughness of PMDA/PDA was significantly improved by blending a small amount of a-BPDA/ODA (10 wt%). Additionally, this blend film showed a considerably low CTE (2.0 ppm) and no glass transition. On the other hand, when the symmetric biphenyl type PI counterpart, s-BPDA/ODA was used as a flexible component, the blend film was still very brittle and exhibited a CTE (7.2 ppm) higher than that of the blend containing a-BPDA/ODA. These results are probably attributed to the difference of the miscibility for two blend systems. By applying a unique fluorescence character of perylenetetracarboxydiimide (PEDI) bound to the flexible PI main chain, we revealed that the blend containing a-BPDA/ODA is miscible but the blend containing s-BPDA/ODA is not, indicating that a-BPDA/ODA is matrix polymer much better than s-BPDA/ODA.

INTRODUCTION

We have so far studied the dynamic mechanical properties of a-BPDA-based homo PIs.[1,2] These PIs have some interesting characters: (1) T_g higher than the corresponding s-BPDA PI counterparts, (2) sudden E' decrease at the T_g (softening), and (3) no crystallization

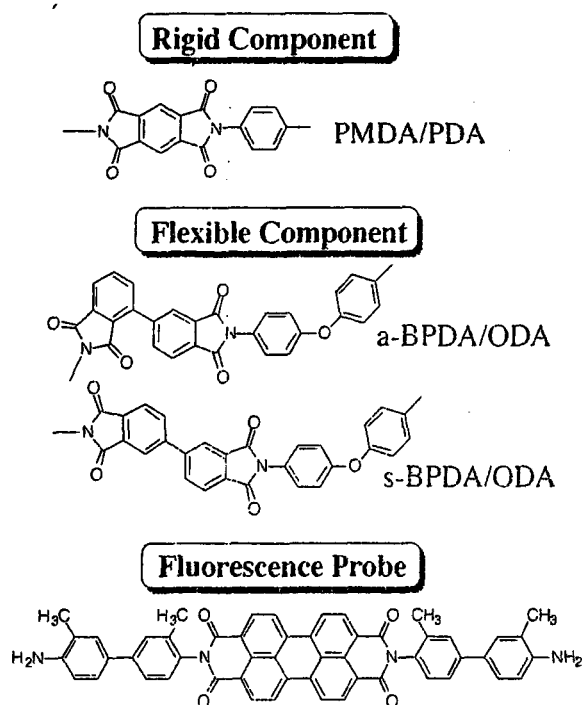


Fig. 1 Chemical structures of polyimides and fluorescence probe used.

behavior. Applying these asymmetric PIs to a matrix polymer for semi-rigid s-BPDA/PDA made possible to improve the insufficient thermal processability intrinsic to s-BPDA/PDA without a decrease in the T_g : The blend of s-BPDA/PDA with a-BPDA/ODA (80/20) exhibited thermal plasticity, whereas the blend of s-BPDA/PDA with s-BPDA/ODA (80/20) did not. The result is attributed to crystallization of the s-BPDA/ODA component in the latter blend by annealing at 400 °C.

In this paper, a-BPDA/ODA was used as a matrix polymer for PMDA/PDA with a rod-like chain structure. PMDA/PDA is expected from its structure to show very low coefficient of thermal expansion (CTE) and very high modulus. But, unfortunately, this PI film prepared through thermal imidization of the precursor, polyamic acid (PAA), is known to be too brittle for practical use, despite that the PAA film is highly tough. Comparison with the blend containing s-BPDA/ODA manifests how a-BPDA/ODA is a good matrix polymer for PMDA/PDA.

EXPERIMENTAL SECTION

a-BPDA[3] monomer was supplied by Dr. H. Yamaguchi of Ube Industries, Co. **Figure 1** shows the reduced viscosities of PAAs (0.5 wt% in DMAc at 25 °C) and the chemical structures of PIs used. The DMAc solutions of PAA (10 wt%) were bar-coated on a substrate and then dried at 60 °C for 2 h in an air convection oven. The PAA films obtained were thermally imidized at 400 °C for 1 h on a substrate. PAA binary blend films were prepared by casting at 60 °C immediately after prompt mixing of two kinds of the PAA solutions for 10 min at room temperature to suppress transamidation.

CTE of PI specimens (10 mm long, 5 mm wide, 10–15 μm thick) were measured as the average within 100–250 °C for the in-plane direction on a thermomechanical analyzer (Mac Science TMA-4010) with a load (0.5 g per thickness of 1 μm) in a nitrogen flow. Storage modulus E' and loss energy E'' were measured as a function of temperature using the same apparatus with a heating rate of 5 °C min^{-1} and a load frequency (sinusoidal) of 0.1 Hz in N_2 . For the CTE and the dynamic mechanical measurements, the PI films cured on a substrate were annealed additionally at the T_g-5 °C for 1 h in a free-standing state to remove the residual stress.

The degree of in-plane orientation (IPO) of PAA and PI chains of the rigid component was determined by means of the tilt angle dichroic measurements[4] for PEDI-bound PMDA/PDA. Miscibility was judged from the blend composition dependence of the fluorescence yield (Φ_f) for the blend films composed of PEDI-labeled BPDA/ODA and dye-free PMDA/PDA.

Reflection more WAXD measurements for PI films were conducted at room

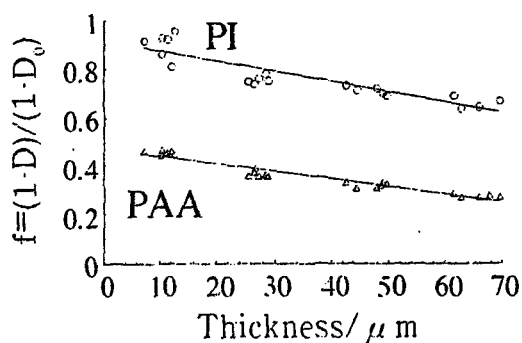


Fig. 2 The degree of in-plane orientation of PAA and PI chains as a function of film thickness for homo PMDA/PDA.

temperature on Rigaku XRD-RAD2C (CuK α , 20 mA, 40 kV) with a sampling step of 0.1° and a scan rate of 5° min⁻¹.

RESULTS AND DISCUSSION

Improved Toughness of PMDA/PDA Film by Blending a-BPDA/ODA.

As mentioned previously, the brittle PMDA/PDA film can not be utilized for practical use. However, this PI film is expected to have considerably low CTE, although actually one can not measure the CTE of the very brittle film cured on a substrate. Fortunately, we have a technique for conveniently estimating the IPO value, which is directly related to the CTE, for the PMDA/PDA films cured on a substrate. Figure 2 shows IPO of PAA and PI as a function of film thickness for the homo PMDA/PDA system. This indicates obviously that the PI chains highly align parallel to the film plane, thus suggesting very low CTE. When the PMDA/PDA film was cured in a free-standing state, the dynamic mechanical measurement could be barely conducted. As illustrated in Figure 3a, no glass transition was observed within our experimental range up to 450 °C.

We tried to improve the brittleness of the PMDA/PDA film by blending a small amount of a flexible PI without preventing the low CTE character intrinsic to PMDA/PDA. The blend of PMDA/PDA (90 wt%) and a-BPDA/ODA (10 wt%) significantly improved the film toughness and showed no glass transition as well as PMDA/PDA homopolymer. Table 1 lists the elongation at the break point for the blend film. On the other hand, the blend film containing the same composition of s-BPDA/ODA was still very brittle. Then we considered that the significant difference of the film toughness for these blend systems may result from the difference of miscibility.

Miscibility of the blends of PMDA/PDA with a- or s-BPDA/ODA.

One can readily suppose that rod-like PMDA/PDA has little entanglement, which is related to the viscosity character of polymeric solids. Enough entanglement between rigid and flexible components would relaxes the internal stress, consequently improves the film toughness. In other words, the miscibility between rigid/flexible components would be related to the film toughness.

Miscibility of polymer blends is often judged on the basis of so-called T_g -criteria by

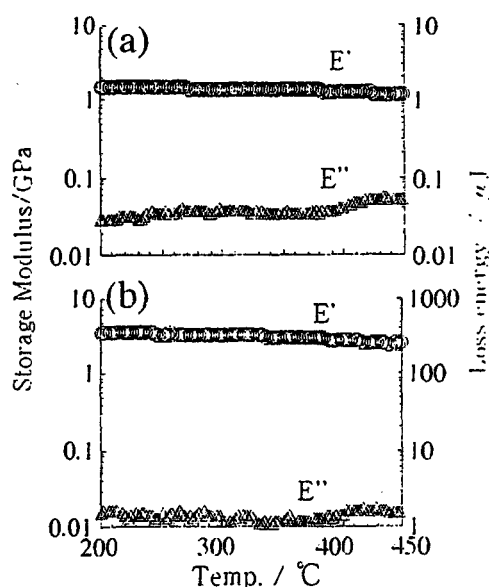


Fig. 3 Dynamic storage modulus (E') and loss energy (E'') as a function of temperature for PI films cured at 400 °C for 1 h in a free-standing state: (a) homo PMDA/PDA and (b) blend composed of PMDA/PDA (90 %) and a-BPDA/ODA (10 %).

thermal analyses such as DSC and DMA. However, these ways are not suitable for the present systems in which the blends show no appreciable glass transition as demonstrated in **Figure 3b**. Our approach for miscibility judgment is to apply a unique fluorescence behavior of PEDI probe. We demonstrated that the fluorescence yield of PEDI bound to the aromatic PI main chains depends strongly on the charge transfer character of the host PIs: PEDI in the BPDA/ODA chains is highly fluorescent but practically non-fluorescent in PMDA/PDA.[5] When the phase separation occurred in the blend PEDI-labeled a-BPDA/ODA

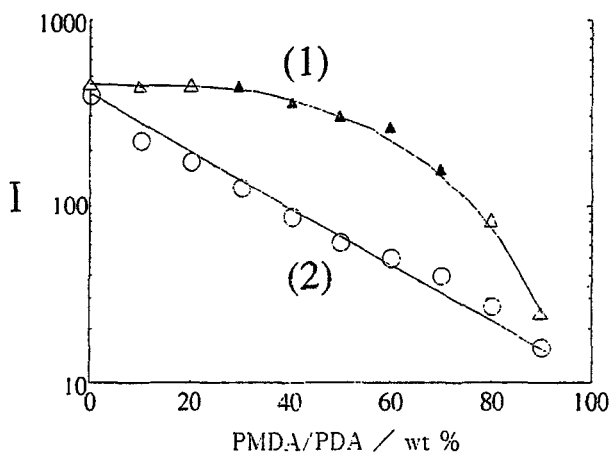


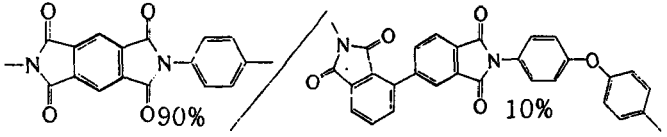
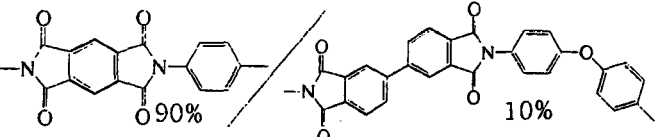
Fig. 4 Dependence of the normalized PEDI fluorescence intensity on the PMDA/PDA blend composition: (1) blend of PMDA/PDA with s-BPDA/ODA, (2) blend of PMDA/PDA with a-BPDA/ODA.

with dye-free PMDA/PDA, the blend should show the strong PEDI fluorescence as well as in a-BPDA/ODA homopolymer. On the other hand, good miscibility should lead to the fluorescence quenching due to molecular contact between PEDI bound to a-BPDA/ODA and the PMDA/PDA chains as a quencher. This means that the PEDI fluorescence intensity is a miscibility-indicator. **Figure 4** displays the PEDI fluorescence intensity normalized for the absorbance, $I (\propto \Phi_f)$, of two blend systems as a function of the PMDA/PDA content. The blends containing a-BPDA/ODA provided optically transparent films over the whole composition range, and the fluorescence intensity decreased markedly with increasing PMDA content. On the other hand, the blend films containing s-BPDA/ODA became opaque within PMDA/PDA = 30–70 wt%, and the fluorescence intensity decreased gradually. The intensity-composition curve of the former system was always lower than that of the latter. These results obviously indicate that the blend system containing a-BPDA/ODA has much better miscibility than that containing s-BPDA/ODA. The difference of miscibility for these blend systems is most likely attributed to the difference of crystallization ability for the flexible components. s-BPDA/ODA is crystallizable upon annealing at $T > 300$ °C, but a-BPDA/ODA is amorphous regardless of the annealing temperature.[2,6] For the former blend, in other words, crystallization of s-BPDA/ODA also causes demixing (phase separation).

The WAXD measurements demonstrated that the crystallinity of PMDA/PDA was affected by the miscibility of the blends: In the reflection geometry mode, the homo PMDA/PDA film shows a peak around 21°. The peak broadened slightly by blending s-BPDA/ODA (10 wt%). The miscible blend containing a-BPDA/ODA provided the broader peak, indicating that crystallization of PMDA/PDA is partially prevented in the

miscible blend. The result corresponds to the relation between film toughness and miscibility for two blend systems.

Table 1 CTE and the elongation at break of the blend films (90/10).

| | | CTE/ppm | $\Delta L / \%$ |
|---|--|------------------|-----------------|
|  | | 2.0 | 6.0 |
| | | 13 μ m thick | |
|  | | 7.2 | 0 |
| | | 14 μ m thick | |

CTE of the blends of PMDA/PDA with *a*- or *s*-BPDA/ODA.

Table 1 also lists the values of CTE for two blend systems. It should be noted that the miscible blend film (90/10) containing *a*-BPDA/ODA gave a considerably low CTE (= 2.0 ppm) and the value was much lower than that of the blend with *s*-BPDA/ODA. We expected first that the lower CTE for the miscible system is probably due to the higher IPO of the rod-like component, since there is no difference of the CTE values for two flexible components (ca. 60 ppm). However, in fact, no appreciable difference of the IPO in the PMDA/PDA chains was observed for two blend systems (90/10). Another possible explanation for the difference of CTE is that the *s*-BPDA/ODA phase in the immiscible blend contributes more strongly to the total thermal expansion than the molecularly dispersed *a*-BPDA/ODA chains in the miscible blend. In other words, the miscibility between rod-like/flexible components also influences significantly the CTE of the blend films.

Thus, *a*-BPDA/ODA was successfully applied as a matrix polymer for rod-like PMDA/PDA and made possible to form a PI film possessing both the considerably low CTE and enough toughness.

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