Blush Resistance of Polyimide Coating Fluids

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A series of 6,6-PIs are soluble highly heat resistant aromatic polyimides, but they have a problem that cast solution (coating fluids) are blushed because 6,6-PI uses NMP as the solvent. In this study, we investigated to solve the problem of blushing without changing NMP and without lowering the heat resistance of the soluble PI. We examined structure control method and additive method, and succeeded to make blush resistant coating fluids maintaining high glass transition temperature using NMP as the solvent.

**Keywords:** Blushing, soluble polyimide, coating fluid, heat resistant, aromatic polyimide

1. Introduction

Aromatic polyimides (PIs) are well accepted as the most important thermally stable polymer [1] because of their superior properties, such as excellent thermal and mechanical properties, low dielectric constant and chemical resistance. PI also has excellent molecular design flexibility because of the wide variation of monomers available. One of the representative PI is Kapton-H, which is made from pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (DADE) [2]. Itatani synthesized biphenyltetracarboxylic dianhydride (BPDA), and used BPDA for the synthesis of Upilex [3]. These typical aromatic PIs have excellent properties, but encounter processing difficulty due to the poor solubility in organic solvents. As the common method for the preparation of PI films, soluble precursor poly(amide acid) (PAA) is used for casting, followed by imidization. However, this process has some problems such as void formation, especially for the thick films, and instability of PAA due to the hydrolysis by moisture.

These problems can be solved by using soluble PI. Generally, soluble PIs can be synthesized by using special monomers, which are very often expensive. Furthermore, thermal properties of these soluble PIs are often low. Aiming to prepare highly heat resistant and soluble aromatic polyimides using PMDA and BPDA, which are usually difficult to prepare soluble PI, we developed a novel three-step method to control the sequence as shown in Scheme 1 [4]. The composition of typical 6,6-PI is \{[(PMDA), (DADE), (BPDA), (DAT), ]\} and was named 6,6-PI. Various 6,6-PIs can be obtained by changing the structure and sequence of the monomers. 6,6-PI is a series of high performance soluble PI. But soluble PI, in general, has a problem that the coating fluid causes blushing. This is because highly hydrophilic amide solvents such as NMP absorb water and PI aggregates on the surface. When the coating fluid causes blushing, physical properties of the PI films are lowered. The previous studies of the conventional soluble PIs cleared this problem by changing the solvent from NMP to the mixture of anisole and NMP [5], to the less hydrophilic solvents such as γ-butyrolactone [6]. However, the new solvent system lowers solubility of PI than NMP. Therefore, highly soluble PI has to be used. For that purpose, flexible linkages such as aliphatic group [5], urethane group [6], and silicone [7] were introduced and gave highly soluble but low heat resistant PIs.

In this paper, we tried to solve the problem of blushing without changing the solvent and without lowering the heat resistance of the soluble PI, 6,6-PI. Our aim is to synthesize the coating fluids that resist blushing for more than 10 minutes maintaining high glass transition temperature ($T_g$ >350 °C). We examined two different methods. One

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Scheme 1. Synthesis of typical 6,6-PI, Solpit-S
is to control the structure of the soluble PI (structure control method) and the other is to add various additives (additive method).

2. Experimental
2.1. Reagents
PMDA, bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetra-carboxylic dianhydride (BCD), 2,4-diaminotoluene (DAT), p-cresol, 4-hydroxybenzoic acid, N,N-dibutyl-m-aminophenol, hydroquinone, bisphenol-A, 3,5-dihydroxybenzoic acid, phloroglucinol, N,N-di oxyethyl-m-toluidine, N-ethyl-N-2-hydroxyethyl-m-toluidine, N,N-bis(2-hydroxyethyl)-m-toluidine, p-toluenesulfonic acid, 1,4-diazobicyclo[2.2.2]octane, and 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) were obtained from Tokyo Kasei Kogyo (Tokyo, Japan) and were used as received. DADE, bis(4-aminophenyl)sulfone (ASN), bis(3-aminophenyl)sulfone (m-ASN), 3,3'-dihydroxybenzidine (HOAB), 9,9-bis(4-aminophenyl)fluorene (FDA), 1,3-bis(4-aminophenoxo)benzene (m-TPE), and bis(3-aminooxyethyl)sulfone (HOSO₂AB) were obtained from Wakayama Seika Kogyo (Wakayama, Japan) and were used as received. 3,3',4,4'-Biphenyldiacarbonyl dianhydride (BPDA) was purchased from UBE Industries (Tokyo, Japan) and was used as received. γ-Valerolactone, pyridine, 1-methyl-2-pyrrolidinoline (NMP), and toluene were obtained from Wako Pure Chemical Industries (Osaka, Tokyo) and were used as received.

2.2. Preparation of 6,6-PI
Preparation procedure of the typical 6,6-PI, Solpit-S, is shown below as an example. Into a 500 ml separable flask equipped with nitrogen inlet and mechanical stirrer, DADE (4.00 g, 20 mmol) and 60.0 g of NMP were added. The mixture was kept stirring until clear solution was obtained. BPDA (2.94 g, 10 mmol) was added to the solution and the wall of the flask was washed with a mixture of toluene (20.0 g) and NMP (20.0 g) containing pyridine (2.0 mmol) and γ-valerolactone (2.0 mmol). The reaction mixture was stirred for 1h at 180 °C to give a transparent dark-red imide oligomer solution. After cooling down to room temperature, PMDA (40 mmol), DAT (20 mmol) and 80.0 g of NMP were added, and stirred for 30 minutes at room temperature. Finally, BPDA (10 mmol), DAT (20 mmol), and 74.8 g of NMP were added, and stirred for 3h at 180 °C for imidization. Water was removed as an azeotropic solvent. A transparent dark-brown Solpit-S solution containing 10 wt% solid content was obtained.

Other 6,6-PIs were prepared in the same way using different monomers.

2.3. Measurements
IR spectra were obtained using a Jasco Fourier Transform IR-420 spectrophotometer. Molecular weights were measured by a gel permeation chromatography (GPC) in NMP using a Tosoh HLC-8320 GPC system and polystyrene standards for calibration. Thermogravimetric analysis (TGA) was performed with a Rigaku Thermo Plus TG8120 at a heating rate of 5 °C/min under nitrogen. Tensile properties were recorded with Imada Seisaku-sho Model SV-3 at a crosshead speed of 1 mm/min using films of 2 cm long. The tensile properties of each sample were determined from an average of at least 10 tests. Dynamic mechanical analysis (DMA) was conducted on a Seiko Instruments model EXSTAR DMS6100 at 1 Hz from room temperature to 450 °C at a heating rate of 5 °C/min.

3. Results and Discussion
3.1. Structure control method
3.1.1. Synthesis of blush resistant 6,6-PIs
Table 1 shows the composition of the 6,6-PIs examined in this study. In the case of typical 6,6-PI, Solpit-S, when the 10 wt% NMP solution was cast on a glass plate, the coating fluid was unstable and blushed within 1 minute. In the case of adhesion grade 6,6-PI (Solpit-A), the coating fluid was very stable and blushed after more than 1 hour.

First of all, we investigated which functional group is effective for the prevention of blushing. Distinctive components of Solpit-A are HOSO₂AB that contains hydroxyl and sulfonic groups, and m-TPE that contains ether group (Fig. 1). Therefore, novel 6,6-PIs (PI-1 and PI-2) that contain HOSO₂AB and m-TPE were prepared, and blush resistance was examined. As a result, PI-1 that contains HOSO₂AB was much more blush resistant than PI-2 that contains m-TPE. HOSO₂AB contains hydroxyl and sulfonic group as hydrophilic functional groups. To identify the effective functional group for preventing blushing, novel 6,6-PIs (PI-3, 4, 5) were prepared using diamine that contains hydroxyl group (HOAB), and diamines that contain sulfonic group (ASN and m-ASN), respectively. The comparison of the effect of prevention of blushing (Table 1) showed that HOAB was much more effective than ASN or m-ASN. Therefore, it was made clear that hydroxyl group is the key functional group to prevent
Fig. 1. Chemical structures of some diamines.

Table 1. Blushing test of 6,6-PIs.

<table>
<thead>
<tr>
<th>Code</th>
<th>Structure</th>
<th>Blushing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solpit-S</td>
<td>(BPDA+2DADE)(4PMDA+2DAT)(BPDA+2DAT)</td>
<td>1</td>
</tr>
<tr>
<td>Solpit-A</td>
<td>(2PMDA+HOSO₂AB)(2BCD+4DADE)(2BPDA+m-TPE)</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>PI-1</td>
<td>(BPDA+2DADE)(4PMDA+2DAT)(BPDA+2HOSO₂AB)</td>
<td>30</td>
</tr>
<tr>
<td>PI-2</td>
<td>(BPDA+2DADE)(4PMDA+2DAT)(BPDA+2m-TPE)</td>
<td>1</td>
</tr>
<tr>
<td>PI-3</td>
<td>(BPDA+2DADE)(4PMDA+2FDA)(BPDA+2HOAB)</td>
<td>30</td>
</tr>
<tr>
<td>PI-4</td>
<td>(BPDA+2DADE)(4PMDA+2FDA)(BPDA+2ASN)</td>
<td>3</td>
</tr>
<tr>
<td>PI-5</td>
<td>(BPDA+2DADE)(4PMDA+2FDA)(BPDA+2m-ASN)</td>
<td>5</td>
</tr>
<tr>
<td>PI-6</td>
<td>(BPDA+2DADE)(4PMDA+2HOSO₂AB)(BPDA+2DAT)</td>
<td>20</td>
</tr>
<tr>
<td>PI-7</td>
<td>(BPDA+2DADE)(4PMDA+2HOSO₂AB)(BPDA+2HOSO₂AB)</td>
<td>&gt; 60</td>
</tr>
</tbody>
</table>

blushing. However, the solubility of PI-3 was not high enough, and HOAB was easily oxidized. Therefore, we concluded that HOSO₂AB is the monomer for preventing blushing.

Based on the above examination, we prepared several 6,6-PIs using HOSO₂AB (PI-1, 6, 7) as shown in Table 1. The NMP solutions of the 6,6-PIs were cast on glass plates and blushing time was measured. As a result, all the coating fluids of the new 6,6-PIs containing HOSO₂AB were stable, and blushing times were extended to over 20 minutes.

3.1.2. Thermal properties of 6,6-PI films

To examine the thermal properties of the 6,6-PIs, the viscoelastic measurements were performed. The glass transition temperatures ($T_g$) of the blush resistant 6,6-PIs (PI-1, 6, 7) were very high, and in the range of 390 - 391 °C (Fig. 2). The storage

Fig. 2. Viscoelastic analyses of 6,6-PIs.
Table 2. Thermal properties of 6,6-PIs.

<table>
<thead>
<tr>
<th>Code</th>
<th>Structure</th>
<th>$T_g$ a) °C</th>
<th>$T_5$ b) °C</th>
<th>$T_{10}$ °C</th>
<th>Char Yield b) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solpit-S</td>
<td>(BPDA+2DADE)(4PMDA+2DAT)(BPDA+2DAT)</td>
<td>427</td>
<td>532</td>
<td>556</td>
<td>65</td>
</tr>
<tr>
<td>Solpit-A</td>
<td>(2PMDA+HOSO$_2$AB)(2BCD+4DADE)(2BPDA+m-TPE)</td>
<td>360</td>
<td>420</td>
<td>455</td>
<td>54</td>
</tr>
<tr>
<td>PI-1</td>
<td>(BPDA+2DADE)(4PMDA+2DAT)(BPDA+2HOSO$_2$AB)</td>
<td>391</td>
<td>425</td>
<td>470</td>
<td>58</td>
</tr>
<tr>
<td>PI-6</td>
<td>(BPDA+2DADE)(4PMDA+2HOSO$_2$AB)(BPDA+2DAT)</td>
<td>391</td>
<td>426</td>
<td>472</td>
<td>59</td>
</tr>
<tr>
<td>PI-7</td>
<td>(BPDA+2DADE)(4PMDA+2HOSO$_2$AB)(BPDA+2HOSO$_2$AB)</td>
<td>390</td>
<td>420</td>
<td>445</td>
<td>56</td>
</tr>
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</table>

a) estimated from tan δ. b) at 650 °C under nitrogen.

The modulus ($E'$) value of the 6,6-PIs was also higher than that of Solpit-S.

Thermal stability of the 6,6-PIs was examined by TGA (Fig. 3 and Table 2). The 5 and 10% weight loss temperatures ($T_5$ and $T_{10}$) of the 6,6-PIs containing HOSO$_2$AB were, though lower than those of Solpit-S, higher than 420 and 445 °C, respectively.

3.2. Additive method

3.2.1. Effect of additives on blush resistance

As an alternative method, we examined “additive method”, in which additives are expected to work for preventing blushing without changing the chemical structure of the standard 6,6-PI, Solpit-S. We examined several additives as shown in Fig. 4.
Since phenolic functionality was shown to be effective as described before in the 6,6-PIs using HOSO₂AB and HOAB, various phenols were examined. 10 wt% NMP solutions of the additives were added to the 10 wt% NMP solution of Solpit-S, so that the weight ratio of additive and Solpit-S is 1:9. The clear solution was cast on glass plate and blushing time was measured. As a result, phenols were only slightly effective, and blushing time was less than 3 minutes.

Toluidines that are effective for accelerating curing and for preventing blushing of adhesives [8] were examined. Toluidines showed slightly better blush resistance, but blushing time was still 4 minutes for all the toluidines.

Catalysts used for the synthesis of urethane [9] and epoxy [10] (Fig. 4) were also examined. Blushing times were 2 minutes for p-toluenesulfonic acid (pKₐ = -2.8), and 4 minutes for 1,4-diazobicyclo[2.2.2]octane (pKₐ = 5.18), and not so effective. The most effective additive was DBU (pKₐ = ca. 2), and blushing time of Solpit-S in the presence of DBU was increased to more than 30 minutes.

3.2.2. Thermal properties of Solpit-S films with additives

10 wt% NMP solution of Solpit-S that contains 10 wt% DBU was cast on a glass plate, cured in an air oven at 150 °C and then at 300 °C for 1h each. The film was black opaque. Thermal stability of Solpit-S that contains DBU was examined by TGA (Fig. 5). It was found that T₅降低了 to 420 °C. DBU is strongly basic catalyst, and DBU may cleave the molecular chain of PI [11]. In fact, molecular weight of the coating fluid of Solpit-S that contain DBU, after leaving at room temperature for 30 minutes, dropped from 35,000 to only 9,000.

4. Conclusions

We examined 2 methods for the preparation of blush resistant 6,6-PI using NMP solvent. In the structure control method, hydroxyl groups were found to be effective, and we succeeded to prepare blush resistant 6,6-PIs by introducing HOSO₂AB. Blushing time was extended to more than 20 minutes and T₅ lowered to 350 °C. In the additive method, DBU was most effective, and the Solpit-S solution containing 10 wt% DBU showed blushing time more than 30 minutes. However, DBU cleaved molecular chain of PI because of the strongly basic DBU.

References