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The effects of hydroxyl groups on the thermal and optical properties of poly(amide-imide)s with high adhesion for transparent films

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ABSTRACT

In this study, transparent thin films for coating material are synthesized by adding bulky CF_3 and hydroxyl groups intro into poly(amide-imide)s. As expected, these poly(amide-imide)s show higher shear adhesion and higher glass transition temperatures than the neat poly(amide-imide) due to hydrogen bonding of the hydroxyl groups. In addition, the modification to the poly(amide-imide) structure leads to only slight decreases in transmittance and yellow index.

Consequently, the successful synthesis of poly(amide-imide)s with wide applications as transparent coating materials due to their optical properties and high adhesion is demonstrated. Transparent flexible display and coating products can be manufactured with poly(amide-imide)s having high reliability and a low chance of cracking due to their favorable thermal properties.

1. Introduction

Polyimide(PI), initially developed as an aerospace material by NASA in the 1970s, has been extensively studied and applied to number of different industries [1,2]. PI is actively used in electronic devices, such as semiconductors and integrated circuits, for continued development of technology-focused industries. Furthermore, based on its high performances and flexibility, PI can be applied to display and coating materials.

Flexible PI films are used as a replacing material to glass/metal substrate with better workability and safety from crack problems. Also, PI has many structure combinations depending on the monomers. Therefore, thin film with high adhesion and flexibility can be synthesized easily by introducing hydrogen bond agent into PI structure.

However, PI has a highly conjugated aromatic structure, giving it low transmittance and a strong brown color due to high amounts of charge transfer complexes(CTC) [3]. PIs can be used in the display and coating industries, but only when using transparent and colorless films.

To reduce CTC content and remove the associated color, most previous studies have added fluorine group to the main chain [4,5]. The modification of polymer with *cis*- and trans- or ortho-, meta-, and para- structures can also change the polymer matrix and its thermal and optical properties [6]. These modifications can yield transparent polymer films, but their mechanical properties and adhesion must also be considered to fully realize the application of such film. To improve the mechanical and adhesion properties of polymer, hydroxyl groups can be introduced into the main chain. Hydrogen bonding and other intermolecular forces between amide and imide groups enhance the mechanical properties and adhesion of these polymers [7].

In this study, poly(amide-imide) (PAI) was synthesized with different molar ratios of amide and hydroxyl groups, in order to remove color and improve the mechanical properties and adhesion of this polymer. The resultant transparent PAIs having good hardness can be used in various applications such as in displays, coating materials, transparent films and integrated circuits.

2. Experimental

2.1. Materials

For the synthesis of precursor solutions, 4,4′-(hexafluoroisopropylidene) diphthalic anhydride(6FDA), dodecanedioic dihydrazide, and 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (AHHFP) were purchased from Tokyo Chemical Industry Co. N,N-dimethyl acetamide (DMAc) was purchased from Duksan Chemical Co., Korea. All reagents were used without further purification.

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Table 1
Molar ratios of polyimide and PAI random copolymer.

Monomer	6FDA	Dodecanedioic dihydrazide	AHHFP	Note
Mole ratio	10	10	0	6 D:A 10:0
	10	9	1	6 D:A 9:1
	10	7.5	2.5	6 D:A 7.5:2.5
	10	5	5	6 D:A 5:5

2.2. Preparation of precursor solutions for PAIs

Synthesizing the precursor solutions of PAI involves three steps. First, n mole of dodecanedioic dihydrazide and m mole of AHHFP were dissolved in DMAc in various ratios (Table 1). Second, (n + m) mole of 6FDA were added to the solution at 20 °C. Third, the mixture was stirred at 0 °C for 4.5 h in an ice bath and then at 20 °C for 12 h. The resulting solution contained 20 wt% solute in DMAc. The molecular weight of synthesized precursor were measured with gel permeation chromatography. 6 D:A 10:0 showed M_n: 3114 Da, M_w: 9170 Da, PDI: 2.95. 6 D:A 9:1 showed M_n: 3194 Da, M_w: 9593 Da, PDI: 3.035. 6 D:A 7.5:2.5 showed M_n: 1889 Da, M_w: 5533 Da, PDI: 2.93. 6 D:A 5:5 showed M_n: 1032 Da, M_w: 2397 Da, PDI: 2.32.

The solution was spin-coated on a glass plate at a thickness of 10–15 μm. PAI films were cured for temperature/time combinations of 100 °C/1 h, 150 °C/0.5 h, 200 °C/0.5 h, and 250 °C/2.5 h (in air). Temperature was increased at a rate 2 °C/min. The synthetic pathway of PAI is described in Scheme 1.

2.3. Characterization

^{1}H- and ^{13}C-nuclear magnet resonance spectrometer (NMR) spectra of the PAIs were measured with an Jeol JNM-LA400 with LFG(JEOL) instrument.

The molecular weight of the PAIs was measured with an EcoSEC HLC-8320 GPC (Tosoh) instrument.

Fourier transforms infrared (FT-IR) spectra of the PAIs were measured with an Excalibur Series FT-IR (DIGILAB Co., USA) instrument.

The thermal stabilities of the PAIs were obtained using a Q50 thermogravimetric analyzer (TGA) (TA Instrument Co., USA) in the temperature range from 35 to 800 °C at a heating rate of 20 °C/min in a nitrogen atmosphere. The temperature at 5% weight loss ($T_{5\%}$) of the PAIs were measured with TGA.

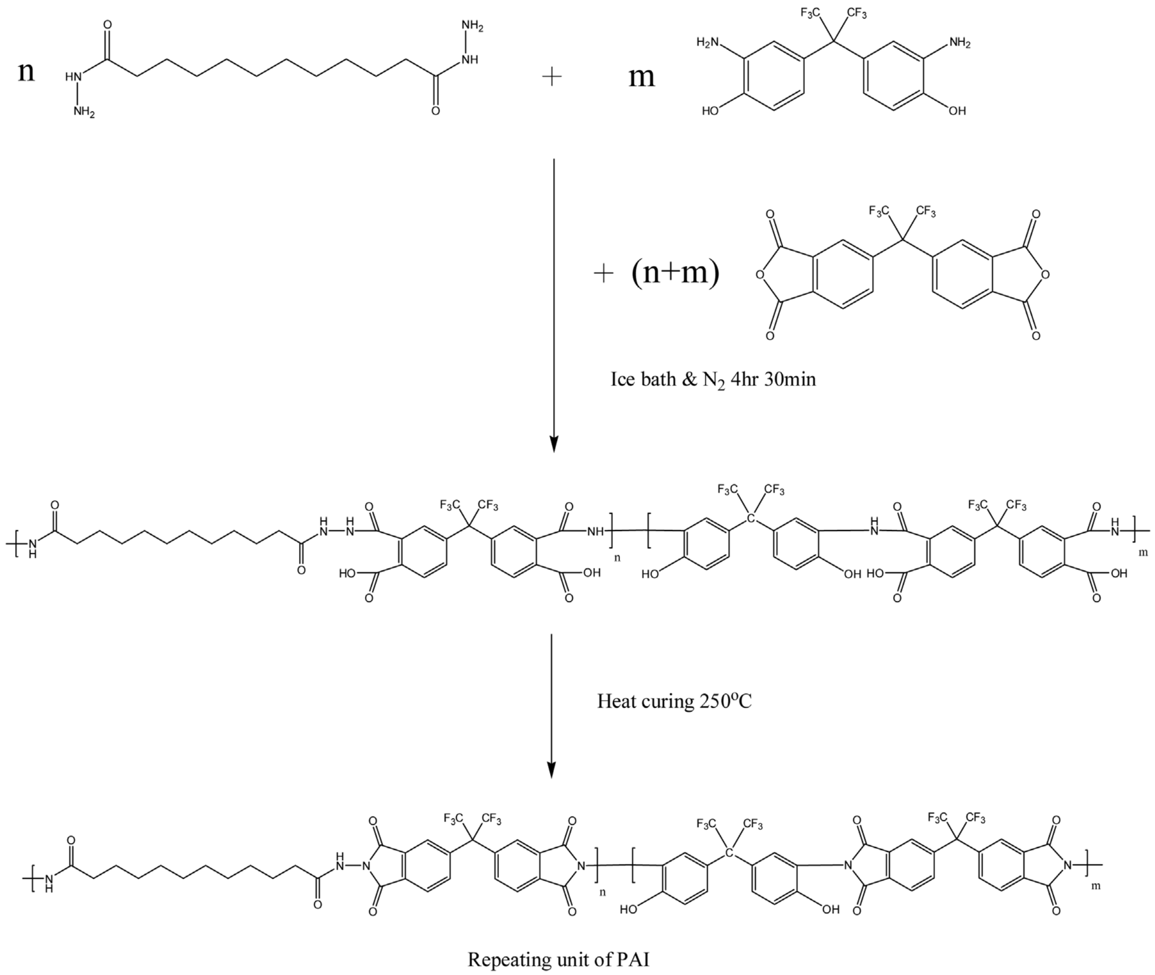
The glass transition temperatures (T_g) of the PAIs were investigated with a Q10 differential scanning calorimeter (DSC) (TA Instrument Co., USA) in a nitrogen atmosphere. The samples were heated at a rate of 10 °C/min from 25 to 300 °C.

Ultraviolet-visible (UV-vis) spectra of the PAIs in the range of 200 ~ 800 nm were measured with a UV–vis spectrophotometer (V530, JASCO Co., Japan).

The yellow indices of PAIs were measured with a Minolta spectrophotometer (CM-3500D, KONICA MINOLTA). The ASTM D1925 method was used for calculation of yellow index. X, Y and Z are the tristimulus values.

$$\text{YellowIndex} = 100\frac{1.274641506X - 1.057434092Z}{Y} \quad (1)$$

The mechanical properties and adhesion of PAIs were measured with a universal testing machine(UTM)(Mecmesin, multitest 5-i).



Scheme 1. Synthetic pathway of PAIs.