Preparation of Polyimide with Pendant Glycidyl Groups for Cationic Electrodeposition Coatings and Evaluation of Their Properties

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Owing to the paradigm shift in energy systems from petroleum to electricity to realize sustainable society, the development of high-performance electrical devices has become increasingly important. The development of insulating materials with thermal stability and facile electrodeposition is essential for the production of high-performance next-generation electric devices because such electric devices cannot be coated with a conventional dip coating method. There are few reports on the development of polyimides with electrodeposition ability. Thus, we have reported that anionic electrodeposition coating was successfully performed using poly(amide acid) (PAA) nanoparticles that can be converted to polyimides (PI) upon thermal annealing. A hybrid coating using polyimide/bentonite with an inorganic filler was also produced, and the resulting electrodeposition films were thermostable at temperatures higher than 450 °C. However, PAAs are usually subjected to hydrolysis, and so their pot life is not long. In this study, we developed cationic electrodeposition materials with solvent-soluble PIs with pendant epoxy groups. The developed materials served as good insulation coatings on substrates and exhibited excellent thermostability.

Keywords: Electrodeposition, Polyimide, Glycidyl group

1. Introduction

With the paradigm shift in energy systems from petroleum to electricity owing to sustainability considerations, the development of high-performance electrical devices has become increasingly important. The motors of electric vehicles are currently driven at voltages of 700 V. However, the next-generation standard is expected to become much higher because electric power is defined as the product of electric current and electric voltage, and because the electric current cannot be increased due to the problems caused by Joule heating. Thus, next-generation insulating materials must have strong resistance against electric surges induced by inverter circuits to prevent their degradation and breakdown and excellent thermostability [1].

Conventional electric motor coils are fabricated by winding enamel wires around iron cores, where the enamel wires consist of copper wire insulated by poly(amide-imide)s or polyimides by the dip coating method. Recently, novel electric motors have been invented that consist of rectangle-shaped coils instead of conventional motor coils. The line product ratio of the novel coil is much higher, and the total electric flux lines are more homogeneous than those of conventional motor coils; thus, their motor performance and stability are drastically increased [2]. However, such rectangular-shaped substrates cannot be covered using conventional insulating coating techniques, such as the dipping method, because surface tension causes defects in the
coatings at the edges. This problem hinders their practical application.

Electrodeposition coating is a coating technique in which an electric voltage is applied to the substrates when electrodes are immersed in a suspension of charged particles, and charged particles are electrophorated onto the substrate, which allows the substrate to be coated without defects [3]. Therefore, the development of polyimides with an electrodeposition ability is crucial for the production of high-performance next-generation electric devices to realize sustainable society.

There are some commercially available polyimide materials with the electrodeposition ability, but their performance is limited [4,5]. To our knowledge, there are few articles that reported the development of polyimides with the electrodeposition ability [6].

We have reported that an anionic electrodeposition coating was successfully performed using several types of ammonium salts of PAA nanoparticles [7,8] that can be converted to polyimide coatings by thermal annealing after electrodeposition (Fig. 1) [9]. Hybrid electrodeposition coating using inorganic fillers, such as bentonites, was also performed, and the inorganic content of the electrodeposited film was as high as 40%. The resulting electrodeposited coating layer was sufficiently thermostable up to 450 °C.

A disadvantage of the anionic electrodeposition material is that PAAs are subjected to hydrolysis in aqueous media, which shortens the pot life of the material. Another disadvantage of PAAs is that they induce corrosion of the electrode during the electrodeposition when using a copper as the substrate. Therefore, the development of polyimide with a cationic electrodeposition ability is desirable. Thus, we designed novel solvent-soluble polyimide with pendant dimethylaminobenzoic groups for cationic electrodeposition with excellent thermostability, insulating properties, and strong resistance against hydrolysis [10]. In this study, we developed novel polyimide with pendant glycidyl groups, which can be modified with amines to obtain cationic polyimide particles for electrophoration. In addition, the properties of the obtained electrodeposited coatings are described.

2. Experimental

2.1. Apparatus

Thermal analysis was performed using a thermal gravimetric-differential thermal analyzer (TG-DTA, SHIMADZU DTG-60) at a heating rate of 10 °C/min under nitrogen flow (50 mL/min). The particle size and zeta potential of polyimides were measured with a HORIBA nano Partica SZ-100. Electrodeposition was performed using a TESIO PA250-0.42B as an electric source, and copper plates were used as electrodes. Electrodeposition particles were prepared using a syringe pump YSP-101. 1H-NMR was recorded on a Bruker Ascend™ 400 MHz Spectrometer using tetramethylsilane as an internal standard and DMSO-d6 as the solvent. IR spectra was measured on a SHIMADZU IRAffinity-1S spectrometer.

2.2. Reagents

4,4’-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (AHHFP), 3,3’,4,4’-benzophenonetetracarboxylic acid dianhydride (BTDA), 2,2-bis(3-amino-4-hydroxyphenyl) propane (AHPP), and diethanolamine were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and used without further purification. 1-Methyl-2-pyrrolidone (NMP) was purchased from FUJIFILM Wako Pure Chemical Co. and dried over molecular sieves 4A before use. Epichlorohydrin, toluene, calcium chloride, and lactic acid were purchased from FUJIFILM Wako Pure Chemical Co. and used without further purification.

2.3. Preparation of PI(6FDA/AHHFP)

AHFFP (7.3252 g, 20 mmol) was dissolved in 70 mL of NMP in a three-necked flask, where 6FDA (8.8847 g, 20 mmol) was slowly added with stirring at 0 °C for 2 h to give poly(amide acid), PAA(6FDA/AHHFP). Toluene (35 mL) was added to the PAA solution, and azeotropic dehydration was performed for 2 h by reflux. The product was purified twice by reprecipitation into water and dried in vacuum.

\[ \text{PAA(6FDA/AHHFP)} \]

1H-NMR [400 MHz, DMSO-d6, 25 °C]: δ 7.06–7.27 (m, 4H, –ArH), 7.49 (s, 2H, –ArH),
7.73 (s, 2H, –ArH), 7.94 (d, J = 6.8 Hz, 2H, –ArH), 8.13 (d, J = 8.0 Hz, 2H, –ArH).

2.4. Preparation of PI(6FDA/ep-AHHFP)

PI(6FDA/AHHFP) (2.87 g, 3.7 mmol) was dissolved in epichlorohydrin (30 mL) in the presence of benzyltrimethylammonium chloride (BTMA) (0.10 g) in a three-necked flask, which was stirred at 100 °C for 1 h. Then, the excess of epichlorohydrin was removed under vacuum, and the product was obtained by reprecipitation into water to give PI(6FDA/ep-AHHFP).

$^1$H-NMR [400 MHz, DMSO- $d_6$, 25 °C]: $\delta$ 2.59 (m, 2H, –CH$_2$–in epoxy ring), 2.72 (m, 2H, –CH$_2$–in epoxy ring), 3.19 (m, 2H, –O–CH$_2$), 3.98 (m, 2H, –O–CH$_2$), 4.44 (m, 2H, –O–CH$_2$), 7.36–8.15 (m, 12H, –ArH).

2.5. Preparation of PI(BTDA/AHPP)

AHPP (10.3254 g, 40 mmol) was dissolved in NMP (130 mL), and then BTDA (12.8891 g, 40 mmol) was slowly added to the solution at 0 °C, followed by stirring at room temperature overnight to yield PAA(BTDA/AHPP). Toluene (75 mL) was added to the PAA solution, and azeotropic dehydration was performed for 3 h. NMP (130 mL) was added to the obtained PI(BTDA/AHPP) solution, and the product was purified twice by reprecipitation in water.

$^1$H-NMR [400 MHz, DMSO- $d_6$, 25 °C]: $\delta$ 1.60 (s, 6H, –C–CH$_3$), 9.72 (s, 2H, –Ar–OH), 6.90–8.26 (m, 12H, –ArH).

2.6. Preparation of PI(BTDA/ep-AHPP)

Epichlorohydrin (100 mL) and BTMA (1.0 g) were added to the residual solution of PI(BTDA/AHPP) (186 g), and the mixture was stirred at 100 °C for 1.5 h. Then, the excess of epichlorohydrin was removed under vacuum, and the product was obtained by reprecipitation into methanol.

2.7. Preparation of PI(6FDA/ep-AHHFP) particles

Amine modification of polyimide with pendant glycidyl groups was performed by heating the mixture of diethanolamine (4.63 g, 44 mmol) and PI(6FDA/ep-AHHFP) (15.39 g, 17 mmol) in NMP (80 mL) at 120 °C for 60 min. Then 0.305 g of amine-modified PI was diluted with NMP (1.58 g), and lactic acid (0.522 g, 5.8 mmol) was added to yield the corresponding ammonium cation. A total of 20 mL of water was slowly added to yield a suspension of PI particles.

2.8. Preparation of PI(BTDA/ep-AHPP) particles

Amine modification of PI(BTDA/ep-AHPP) was performed by heating the mixture of diethanolamine (0.440 g, 4.2 mmol), and PI(BTDA/ep-AHPP) (1.314 g, 2.0 mmol) in NMP (12 mL) at 100 °C for 60 min. Lactic acid (0.512 g, 5.7 mmol) was added to 0.300 g of amine-modified PI, and methanol (20 mL) was slowly added to yield a suspension of PI particles.

2.9. Electrodeposition procedure

The PI nanoparticle suspension was poured into a stainless steel cup (which served as the anode), and a copper plate (1 cm × 1 cm) (which served as the cathode) was immersed in the solution. The distance between the plate and the edge of the cup was 1.5 cm. Electric voltage was implied to the electrodes using a stationary voltage electric source.

3. Results and discussion

3.1. Preparation and electrodeposition of PI(6FDA/AHHFP) with pendant epoxy groups

PI(6FDA/AHHFP) was prepared by the polycondensation of 6FDA and AHHFP in NMP at 0 °C, followed by azeotropic dehydration with toluene (Fig. 2). The structure of the polymer was identified by IR and $^1$H NMR spectra, the details

![Fig. 2. Preparation scheme and structure of solvent-soluble polyimides with pendant glycidyl groups.](image-url)
of which were described in the experimental section. Next, glycidyl groups were introduced on the side of PI(6FDA/AHHFP) by the reaction with epichlorohydrin at 100 °C for 1 h in the presence of benzyltrimethylammonium chloride (BTMA) as a phase transfer catalyst [11–13]. The $^1$H-NMR spectrum shows aromatic protons at 7.36–8.15 ppm, and methylene protons with adjacent oxygen atoms at 3.98 ppm, 4.44 ppm, 2.59 ppm, 2.72 ppm, and 3.19 ppm. Epoxy groups are known to perform ring opening reactions in the presence of carboxylic acids at elevated temperatures, where the methylene protons, which are adjacent to oxygen atom, should be observed near 4 ppm in the NMR spectrum. The methylene protons at 2–3 ppm in the present experiment can be assigned to strained methylenes, which shows that glycidyl groups were introduced without ring opening under present conditions.

The obtained epoxy-modified PI, PI(6FDA/ep-AHHFP) was treated with diethanolamine at 120 °C for 1 h and yielded amine-modified PI, PI(6FDA/N-AHHFP). The pH of the solution was adjusted to be 4 with lactic acid and then water was slowly added to the solution. The solution became turbid during water addition, which demonstrated the formation of PI nanoparticles. Figure 3 shows the appearance of the PI(6FDA/N-AHHFP) suspension. The mode radius of the PI(6FDA/N-AHHFP) particles was 620 nm, and the zeta potential was +40 mV, which shows that the suspension was very stable and the particles did not precipitate (Fig. 4).

Electrodeposition was performed at 5 V for 15 min using the electrodeposition solution of PI(6FDA/N-AHHFP), and the initial electric current was 20 mA. Figure 5 shows the photos of the electrodeposited electrodes without and with the thermal treatment at 200 °C for 30 min. A mat white coating layer due to light scattering by the PI particles was observed on the surface of the electrode after electrodeposition without the thermal treatment. After the thermal treatment, the coating layer became a homogeneous PI-colored coating with a smooth and densely packed surface owing to re-solvation into residual NMP, and molecular relaxation. The electrodeposition coating showed good insulating ability, as confirmed by the pinhole test [9].

Figure 6 shows the thermogravimetric analysis of the electrodeposited PI(6FDA/AHHFP) coating on the substrate. The polymer weight gradually decreased, and the 10% weight loss temperature was determined to be 322 °C. We prepared another polyimide with the electrodeposition ability, PI(BTDA/AHPP)-DAA, bearing pendant dimethylaminobenzoic acid groups; the 10% weight loss temperature was 308 °C [14]. The difference in the detected temperature is the effect of the pendant dimethylaminobenzoic groups.

3.2. Preparation and electrodeposition of PI(BTDA/AHPP) with pendant epoxy groups

In the previous section, we showed that
electrodeposition can be performed with amine-modified polyimide with pendant epoxy groups, PI(6FDA/N-AHHFP). Thus, another polyimide without fluorine groups was prepared, and investigated from the viewpoint of cost.

The preparation of PI(BTDA/AHPP) was similar to that of PI(6FDA/AHHFP) (Fig. 2), and epoxy modification was performed. Amine modification was performed by reacting diethanolamine at 100 °C for 1.5 h and yielded amine-modified PI, PI(BTDA/N-AHPP). Then, lactic acid was added to protonate the amine groups.

The preparation of PI nanoparticles was performed by adding water, which is similar to the approach used for PI(6FDA/AHHFP), however, polymer aggregation was obtained even if the water was added very slowly. Therefore, several poor solvents that are suitable for the preparation of PI(BTDA/AHPP) particle were investigated (e.g., ethanol and THF) to find that the nanoparticle suspension was successfully obtained using methanol as the poor solvent.

The mode radius of the particles was 130 nm, and the zeta potential was +50 mV, which is explained by the lack of electron negative fluorne groups. The electrodeposition suspension was sufficiently stable.

Electrodeposition was performed by the stationary voltage of 5 V for 15 min to produce an electrodeposited coating on the electrode. Figure 7 shows the relationship between precipitation weight and the accumulated amount of implied electric charge density, which shows that the amount of deposition linearly depends on the amount of charge. The coulomb effect of the electrodeposition of this sample was calculated to be 2.3 mg coulomb⁻¹.

Figure 8 shows the thermogravimetric analysis of the deposited coating on the substrate. The organic materials were burned out at 600 °C after the measurement to confirm the initial sample amount. No change in weight loss was observed until 250 °C, while a gradual decrease was observed at higher temperature. The 10% weight loss temperature was determined to be 312 °C, which is slightly lower than that of PI(6FDA/N-AHHFP). The thermostability of PI(6FDA/N-AHHFP) is explained by the strong C-F bond that does not degrade via hydrogen abstraction at higher temperature.

4. Conclusion

Solvent-soluble PIs with pendant glycidyl groups were synthesized, and their nanoparticles with diameters of 130–620 nm were prepared by poor-solvent addition. Electrodeposition was performed under stationary voltage conditions to produce electrodeposited coatings on copper substrates (which served as the cathode) without
corrosion. Their 10% weight loss temperatures were 312–322 °C, which indicates good thermostability and excellent insulation ability. The cationic electrodeposition materials are advantageous because they have long pot life and prevent electrode corrosion compared to that of PAAs. These materials are expected to help realize next-generation high-performance electric devices for sustainable society.

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