Transparent Anti-Stain Coatings with Good Thermal and Mechanical Properties Based on Polyimide-Silica Nanohybrids

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In this work, we synthesized polyimide/silica hybrid materials via sol–gel method using a fluorinated poly(amic acid) silane precursor and a variety of perfluorosilane contents. We studied the influence of a hybrid coating film with the following characteristics; hydrophobicity, oleophobicity, optical transparency, and surface hardness of the coating films. The hybrid coatings with the fluorosilane contents up to 10 wt% are optically transparent and present good thermal stability with a degradation temperature of > 500 °C as well as a glass transition of > 300 °C. Both water contact angle and oil contact angle increase rapidly with introducing small amount of the fluorosilane in the hybrids and reaches the maximum of 115° and 61°, respectively. The hardness of the hybrid coatings increases up to 5H with an increase of the FTES content in the hybrids. These colorless, transparent, and thermally stable hybrid materials could be suitable for applications as anti-stain coatings.

Keywords: Anti-Stain Coating, Polyimide, Silica, Fluorosilane, Hybrid.

1. INTRODUCTION

Anti-stain coatings with hydrophobic, oil-repellent, and stain-resistant surface have attracted significant attention because of recent recognition of their potential applications in various industries such as textiles, construction, automobiles, electronics, and so on.¹⁻⁴ Many strong detergents and ecologically less friendly solvents used to clean the stains we want removed do harm to the environment. The anti-stain nature can be controlled by two important elements; surface energy and surface property.⁵,⁶ Fluorine is well-known as the most effective element for low surface energy substances because it has small atomic radius and strongest electronegativity among all atoms and forms a covalent bond with carbon to generate low surface energy on the surface.⁷ Therefore fluorine-containing polymers have made important contributions as coating materials owing to their low surface energy and their outstanding properties, such as chemical inertness and thermal stability, in a variety of environments.⁸,⁹ Polyimide (PI) is well-known as a super-engineering plastic with excellent resistance to environmental circumstance. They have good thermal stability, such as high Tg of > 300 °C and high decomposition temperature of > 500 °C, mechanical toughness, and outstanding electrical properties.¹⁰⁻¹² Therefore PI has been used in many applications such as films, adhesives, fibers, wire-coating enamels, and resin matrices for composites.¹³,¹⁴ Despite with its advantageous properties, it generally demonstrates strong coloration from yellowish brown to blackish brown due to the characteristic absorption tailings in the visible region.¹⁵ To overcome this coloration problem, fluorinated PIs such as 6FDA/TFDB PI prepared from 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2-bis(trifluoro-methyl)-4,4’-diaminobiphenyl (TFDB) have been extensively studied to apply to colorless optical materials.¹⁶⁻¹⁸ They exhibit high transparency in the visible region and colorlessness as well as high thermal stability. Fluorine moieties of the PIs located on the surface can decrease surface energy and impart water and oil repellence at the same time. In addition to the low surface energy, the required surface properties of a coating include good adhesion with a substrate, improved surface hardness, and...
good optical transparency for the practical application. Organic–inorganic hybrid systems have been recognized as a new class of high performance materials because these systems provide to combine the advantageous properties of inorganic materials such as high modulus, thermal stability, and surface hardness with the ductility and low temperature processing characteristics of the organic polymers. In this work, we synthesize polyimide/silica hybrid anti-stain coatings via sol–gel method using a fluorinated poly(amic acid) silane precursor and a variety of perfluorosilane contents. The aim of this work was to study the influence of a hybrid coating film with the following characteristics: hydrophobicity, oleophobicity, optical transparency, and surface hardness of the coating films.

2. EXPERIMENTAL DETAILS

2.1. Materials

Fluorinated dianhydride and diamine monomers were used to synthesize poly(amic acid) (PAA). A fluorinated dianhydride, 2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA, Aldrich) and a fluorinated diamine, 2,2-Bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (HFDA, Tokyo Chemical Industry) were purified by sublimation under reduced pressure. Two silane precursors such as p-aminophenyl triethoxysilane (APTES, Aldrich) and perfluoroalkylethyltriethoxysilane (FTES, Gelest) were added into the PAA silane precursor solutions. Figure 2 shows the ATR-FTIR spectra of the PI/silica hybrid anti-stain films. The absence of absorption bands at around 1780 and 1720 cm\(^{-1}\) indicates that the imide ring of PI moieties of the hybrid films are completely imidized.

2.2. Synthesis of Poly(Amic Acid) (PAA)

Silane Precursor

Typically, PAA silane precursor was synthesized by addition polymerization between dianhydrides and diamine in DMAc as described in scheme 1. HFDA (5.18 g, 10 mmol) was dissolved in DMAc (28 mL). 6FDA (8.89 g, 20 mmol) was added to the HFDA solution and the mixture was stirred for 24 hours. All the handlings were conducted at a room temperature in a glove box purged by nitrogen. Finally, the resulted PAA silane precursor solution was stored in a glove box prior to the following use because the precursor solution is sensitive to moisture.

2.3. Fabrication of Polyimide/Silica Hybrid Anti-Stain Coatings

To prepare PI/silica hybrid coatings, various amounts of the perfluorosilane (FTES) were added into the PAA silane precursor. After the mixture was stirred for 3 hours, these precursor solutions were spin-coated onto clean and dried glass substrates at 2000 rpm. The as-cast films were soft-baked at 80 °C for 1 hour and thermally cured at 250 °C for 1 hour. The average thicknesses of the obtained composite films were around 10 μm. All of the films were stored in desiccators prior to the analysis.

2.4. Measurements

Attenuated total reflection (ATR)-FTIR spectra were recorded with a Nicolet Avatar-320 FTIR spectrometer with 32 scans per spectrum with 2 cm\(^{-1}\) resolution. A robust single-reflection accessory (Thunderdome, Spectra-Tech Co., Ltd.) with a germanium IRE (\(n = 4.0\), incidence angle = 45°) was used for the ATR measurements. Thermogravimetric analysis (TGA) was performed on Shimadzu DTG-60 thermal analyzer. The samples were heated at a heating rate of 10 °C min\(^{-1}\) from 50 to 900 °C. Differential scanning calorimetry (DSC) was conducted with Shimadzu DSC-60 differential scanning calorimeter. The samples were heated at 10 °C min\(^{-1}\) from 50 to 400 °C. The TGA and DSC measurements were conducted under a nitrogen flow. Ultraviolet-visible (UV-Vis) absorption spectra were measured for the synthesized PI films with thickness of 15 μm on a HITACHI U-3500 spectrophotometer optimized with a spectral width of 200–800 nm, a resolution of 0.5 nm, and a scanning rate of 120 nm min\(^{-1}\). Water contact angles of prepared films were measured using a manual contact angle goniometer. Water droplet was gently placed onto the films and the average value measured over five different locations for each sample was taken. Surface hardness was characterized by pencil test according to ASTM methods. Anti-stain property was evaluated by visual inspection of the scum on the anti-stain coatings after erasing the letters written by water-based pen and oil-based pen, respectively. It was done by rubbing the written letter by three times on three different locations for each sample using a paper tissue.

3. RESULTS AND DISCUSSION

As shown in Figure 1, PI/silica hybrid coating films were prepared by thermal treatment of their precursor solutions which contain the PAA silane precursors and FTES in DMAc. Figure 2 shows the ATR-FTIR spectra of the PI/silica hybrid anti-stain films. The absorption bands at around 1700 cm\(^{-1}\), which are assignable to the carbonyl stretching of PAAs, clearly indicates the PI moieties of the hybrid films are completely imidized. The absorption bands at around 1780 and 1720 cm\(^{-1}\) are assigned to the carbonyl symmetric and asymmetric stretching of imide groups, respectively. The bands at around 1485 cm\(^{-1}\) can be assigned to the benzene ring vibrations of aromatic amine moiety. The absorbance peaks of C–N–C component in imide rings, observed at about 1372 cm\(^{-1}\), indicates that the imide ring of the PI moieties was successfully generated after thermal
Fig. 1. Preparation of the PI/Silica hybrids (PISx) where x describes amount of FTES (wt%) in the hybrid materials.

treatment at 250 °C. The stretching peak appeared at around 1090 cm\(^{-1}\) which is assigned to the Si–O–Si or Si–O–C indicates that silica phase exists in the polyimide matrix. However the absorbance intensity is not clearly distinguishable according to the contents of the fluoro-
lane precursor.

As displayed in the inset of Figure 3, the PI/silica hybrid anti-stain coating with the FTES content of 10 wt% was highly transparent. Colorlessness and transparency are absolutely important to apply for anti-stain coating because the anti-stain film is generally fabricated onto other colored coating layers or transparent substrates such as glasses or transparent plastic films. As is well known, polyimide demonstrates strong coloration from yellowish brown to blackish brown due to the strong intra-and inter-
molecular charge transfer complex (CTC) interaction of polyimide backbones which have electron donor moieties and electron acceptor moieties alternatively in the same chain. However, some fluorinated polyimide was reported to exhibit colorlessness and transparency because the flu-
orine in the PI chain can reduce electron density of the PI backbone.\(^{16,17}\) Note that fluorine has small atomic radius and strongest electronegativity among all atoms and can form a strong covalent bond with carbon. The strong electronegativity can withdraw electron from the con-
jugated aromatic backbone to increase its optical band gap. In addition, the good thermal stability of fluorocar-
bon introduced in PI backbone just slightly decreased thermal stability compared to fully aromatic PI. The optical transmittance spectra of the hybrid films with the thicknesses of approximately 5 \(\mu m\) are shown in Figure 3. These spectra are useful to understand the difference in the transparency at the visible wavelength range. Note that the absorption edges of the hybrid films produced from only PAA silane precursor is observed at around 413 nm, which are marginally shifted to the shorter wavelengths with the increase of the loaded FTES contents in the hybrid films. The transmittances at 500 nm of the hybrid films with the FTES contents of 0, 4, and 10 wt% were 97, 95, and 94 nm, respectively. They were slightly decreased with the increase of the FTES contents in the hybrid films. However, in case of the hybrid films with higher loading over 15 wt%, the transmittance of the films were significantly decreased. This might be due to the light scattering by the large silica particles generated in the hybrid films. From the point of view of optical transparency, 10 wt% in FTES content was a maximum for practical use in this study.

The thermal properties of the hybrid films were evaluated with the glass transition temperatures (\(T_g\)) observed by DSC and the decomposition temperatures with 5% weight loss (\(T_d^{5\%}\)) observed by TGA. No apparent glass transitions were detected up to around 280 °C (Fig. 4(a)).

Fig. 2. FT-IR spectra of (a) PIS, (b) PISO2, (c) PISO4, (d) PISO10, and PISO30 after imidization at 250 °C for an hour.

Fig. 3. Optical transmittance spectra of the PI/silica hybrids. The inset displays the transparent PISO10 which contains 10 wt% of FTES in the PI/Silica hybrids.
Compared with the PIS, the hybrids with high content of FTES exhibit significantly weak change in heat flow above \(\sim 300\, ^\circ\text{C}\), indicating enhancement in the thermal stability of the hybrids. It might be due to the inorganic silica moieties which are homogeneously dispersed in the hybrid matrix. Figure 4(b) displays the thermal stability of the hybrid materials. All the PI/silica hybrid coating materials demonstrate good thermal stability with the degradation temperature \((T_d)\) of around 528 \(^\circ\text{C}\). The small weight loss observed at around 285 \(^\circ\text{C}\) might be caused by the additional reaction of the remaining silanol groups of the hybrids.

Anti-stain properties are usually attributed to the ability of surface to repel water and oils. Figures 5(a) and (b) show the effect of FTES content in the hybrid coating films on the hydrophobicity and oleophobicity, respectively. The PIS is weakly hydrophobic. Therefore \(n\)-hexadecane readily spread on the coating’s surface. The water contact angle increases abruptly with an increase in the FTES in the hybrids and increases slowly to the maximum of around 115\(^\circ\). The contact angle using \(n\)-hexadecane droplet also increases significantly with introducing small amount of the FTES in the hybrids and reaches a maximum of 61\(^\circ\) at 10 wt% of the FTES. The drastic changes in surface properties of the hybrid coatings might be due to the low surface energy of the fluorocarbone originated from the FTES. From these surface properties, the optimized content of the FTES can be estimated to be around 10 wt%.

Surface hardness covering several properties such as resistance to deformation, friction and abrasion is one of the most important properties in the practical applications of the anti-stain coating materials. The hardness determined using the pencil test, a rapid and inexpensive method to determine the film hardness of a coating on a substrate, has been used in the coating industry for many years. The measurement of pencil hardness begins with the hardest pencil and continues down the scale to determine the minimum hardness able to scratch the surface of the hybrid films (ASTM D 3363-74). The scratch hardness of the typical PI such as Kapton exhibits 1 H as described in Figure 6(a). The hardness of the hybrid coatings increases up to 5 H with the increase of the FTES content in the hybrid coating. Generally, inorganic moieties in organic–inorganic hybrid systems have been recognized to improve mechanical properties such as modulus and...
surface hardness. Considering the requirement of $>4$ H in surface hardness for a practical use, the hybrid films with $>4$ wt% content of the FTES are desirable.

To characterize anti-stain properties on the hybrid coating film, a simple writing–erasing test using water- and oil-based pens were performed. This test was conducted repeatedly up to 6 times as shown in Figure 6(b). Compared to a glass substrate, the hybrid coatings were hard to write using water-based pen and all letters written on the hybrid coatings were erased easily by a common toilet paper. When oil-based pen was used instead of water-based pen, the letters written on the hybrid films were clear, indicating that the hybrid coatings are hydrophobic rather than hydrophilic. All letters written by oil-based pen on the hybrid coatings were also removed without any surface scratches, whereas the hybrid coatings with higher content of the FTES are easier to erase the stained letters. These good anti-stain properties on the hybrid coatings might be attributed to low surface energy by the fluorine originated from fluorinated PI and fluorosilane in addition to the enhanced surface hardness.

4. CONCLUSIONS

We synthesize polyimide/silica hybrid anti-stain coatings via sol–gel method using a fluorinated poly(amic acid) silane precursor and a variety of perfluorosilane (FTES) contents. The hybrid coatings with a FTES content of $<10$ wt% were highly transparent and colorless. Good thermal stability was exhibited with a glass transition of $>300$ °C and a degradation temperature of $>500$ °C. Both water and oil contact angle increase rapidly with introducing small amount of the FTES in the hybrids and reaches a maximum of 115° and 61°, respectively. The hardness of the hybrid coatings increases up to 5H with an increase of the FTES content in the hybrid coating. The stains written by water and oil-based pen on the hybrid coatings were erased easily by a common tissue paper. These good anti-stain properties on the hybrid coatings can be attributed to low surface energy by the fluorine originated from fluorinated PI and fluorosilane in addition to the enhanced surface hardness. Finally, these colorless, transparent, and thermally stable hybrid materials could be suitable for applications as anti-stain coatings.

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References and Notes

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