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Transient color changes in oxidative-stable fluorinated polyimide film for flexible display substrates

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Abstract

The stable optical properties of high transmittance and low yellow index are required of polyimide film as a flexible display substrate, but thermal process could result in its color change by thermal imidization. To prevent the color change, anti-oxidants have been used, but as yet though, the effect of oxidation in polyimide has remained unexplored. We explore the yellow index and absorbance changes of fluorinated polyimide after thermal imidization to determine the color change kinetics. Furthermore, we investigated the effect of anti-oxidants on film color change, representing that anti-oxidants even accelerate the color change due to their decomposition. Both experimental findings and density functional theory calculations suggest that the oxidative stability for the thermal imidization could have a modest impact, and in turn yellow index is less dependent on the oxidation of fluorinated polyimide, attributed to mild interaction between fluorinated polyimide and oxygen insufficient to form strong oxidation of diamine groups.

Keywords: fluorinated polyimide; charge transfer complex; anti-oxidant; density functional theory

1. Introduction

Glass is the most commonly used substrates for electronic devices, but is not suitable for the flexible display due to their weightiness, rigidity, and fragile nature with high thickness^{1,2}. Highly transparent polymer films having high thermal and mechanical stability have been widely researched for applications in prospective flexible substrates of electronic devices and micro-

optical devices in the field of displays, memory, lighting, solar cells, sensors, waveguides, etc., where glass is utilized^{3, 4}. To replace glass substrates, flexible film substrates have been intensively studied to keep the merits of glass, i.e., clarity, dimensional stability, thermal stability, solvent resistance, low coefficient of thermal expansion (CTE), and a smooth surface^{2, 5}. In addition, plastic substrates require of optically transparent and thermally stable polymer film after high temperature fabrication because fabrication process at high temperature can cause the color change and decomposition of polymeric materials, losing their optical properties³. Thus, extensively well-known transparent films (e.g., poly(ethylene naphthalates), poly(ethylene terephthalate), poly(ether sulfones), and polycarbonates) are rarely suitable for the flexible display in despite of their outstanding optical properties^{4, 6}. Among the available candidates, polyimide (PI) films are one of the most promising, attributed to their high thermal stability, flexibility, chemical inertness^{7, 8}. The color of PI films, however, generally becomes pale yellow to brown due to their absorption characteristics tailings in the visible region, caused by the intra and intermolecular charge transfer (CT) interactions of the PI backbones, as shown in Fig. 1³.

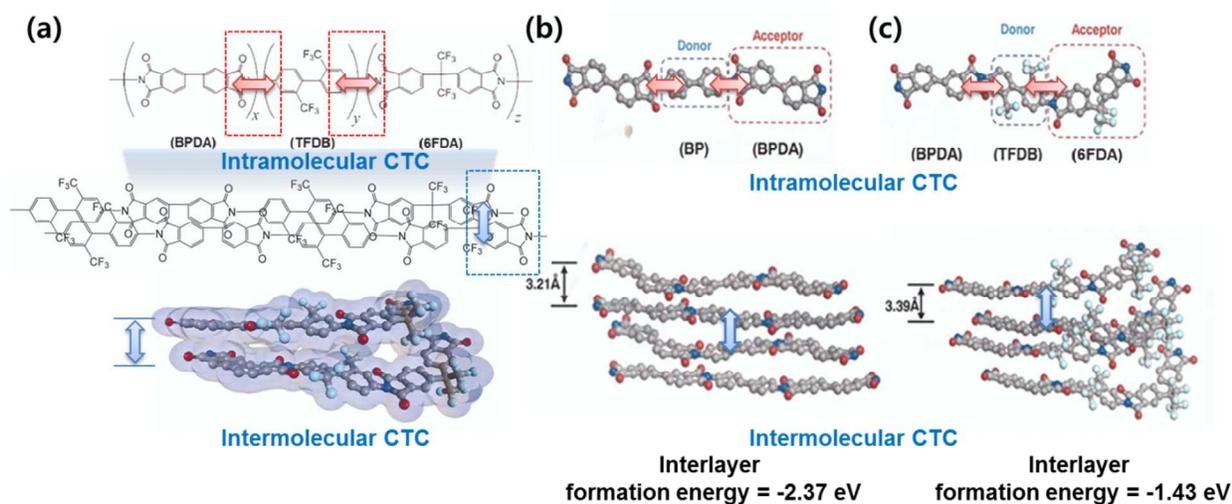


Figure 1. (a) Schematic diagram of intra/inter-molecular charge transfer complex (CTC);

optimized molecular geometry of (b) polyimide intra/inter-molecular CTC and (c) fluorinated polyimide using density functional theory (DFT) calculation. Note that red and blue describe intramolecular and intermolecular CTC, respectively. Interlayer binding energy denotes the binding energy between polymer chains. Distance is the average distance between polymer chains.

To resolve the issue of yellowish color change, extensive studies of many alicyclic or fluorinated PI (FPI) have been given close attention to diminish charge transfer complex (CTC) formation and imidization. Among many types of modified PIs, this study selected such a fluorinated polyimide (FPI), composed of 2,2'-Bis-(3,4-Dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)-3,3',4,4'-Biphenyl tetracarboxylic dianhydride-(BPDA)-2,2'-Bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) since fluorinated side groups in 6FDA and TFDB weaken their intra- or inter-molecular interaction, leading to the high thermo-mechanical property (Fig. 1b)^{9, 10}. Aside from the usual improvement process of film properties (e.g., chemical modification of film, thermal treatment), the use of anti-oxidants in keeping the clear color (yellow index < 5 at 50 um thickness) has been applied to the poly(amic acid) (PAA) solution during thermal imidization^{7, 11}. After thermal treatment process, however, the thermal instability of anti-oxidants at temperature over 330 °C may lead to the initiation of the film color change deteriorating the optical property of the film. Therefore, it is important to determine the effect of anti-oxidants on the resistance of PI oxidation at high temperature.

Herein, the aim of this study is to gain a better understanding of the PI oxidation chemistry and use this information to develop feasibly flexible display substrates. Hence, we figured out which factors influence the film colors between an oxidation of remaining amine in the film and the formation of charge transfer complex, attributed to the conjugation between PI

chains. Initially, we investigated the color change kinetics of fluorinated PI (FPI), composed of 6FDA-BPDA-TFDB, in the temperature range of 300 – 390 °C because the film color tends to change yellow at temperature over 300 °C. We discussed the optical characteristics of yellow index and absorption intensity depending on various temperature and exposure time. Furthermore, we focused on the effect of anti-oxidant on film color change in the environmentally-controlled condition such as temperature and atmosphere during thermal imidization (air or N₂ only). In particular, in order to achieve fundamental understanding of oxidation activity at PI and FPI at atomistic level, density functional theory (DFT) calculations were utilized to provide a comprehensive analysis of such O₂/ N₂ binding properties to PI and FPI through investigating the molecular geometry and electronic properties of O₂/ N₂ binding to those PI films. These results in turn support how gas adsorption would influence the inter-molecular attractive interaction between those PIs' chains associated with imidization.

2. Experimental

2.1. Materials

Polyamic acid (PAA) solution was prepared from the molar ratio of 6FDA:BPDA:TFDB = 1:3:4, as shown in Fig. 1(b). To improve the processibility on solvent casting machine for this solution, we applied the chemical imidization (CI) to PAA solution. 1.4 equivalents of Pyridine to PAA solution was added to PAA solution, which leads to 70 % chemical imidization. To fabricate the transparent film, we introduced such an additive, anti-oxidant, to the PAA solution to minimize the color change. We utilized the anti-oxidant of Irganox® 3114, 1010 and 565, supplied by Ciba®. Irganox® 3114 is composed of 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione with a molecular weight of 784 g/mol at the melting point

of 218 – 223 °C. Irganox® 1010 is Pentaerythritol Tetrakis [3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate] with 1178 g/mol, at the melting point of 110 – 125 °C. Irganox® 565 is 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol with a molecular weight of 589 mol/g at the melting point of 91 – 96 °C. 3 wt % of the antioxidants were added to PAA solution.

2.2. Film fabrication

PAA and PAA with anti-oxidants (PPA with Irganox® 3114, 1010 and 565) solutions were cast on the glass substrate of which size is 10 x 10 cm with an automatic film applicator. The rate of applying the solution on the glass substrate is 3~ 4 mm/sec due to its high viscosity (~100,000 cPS) to make the solution surface as flat as possible. The films were dried on the hot plate at about 60 °C for 30 min to keep the surface smooth without bubbles. After the drying process, PAA films were easy to be detached from the glass substrates. The Film thickness is fixed ~50 µm and the amount of polyimide (related to degree of imidization) would be higher than 95%. For thermal imidization process, these films were heated up to 300 °C under N₂ environment. It is clearly note that these thermally treated films provide highly optical transparency in the visible region and high solvent resistance against organic solvents with a high thermal stability.

2.3 Characterization

Optical properties of yellow Index (YI) and absorption intensity (AI) were analyzed with a CM-3600D spectrophotometer (KONICA MINOLTA Inc.) to figure out the film color

alteration with heat treatment time and temperature. To investigate temperature effect on the color change of PI films, the annealing temperature has been changed from 300 °C to 390 °C at the intervals of 30 °C for 30, 60, 90 and 120 min under N₂ and air atmosphere to control the heating condition accurately in TGA equipment (TA Q800®). TA instrument DMA Q800 was utilized to evaluate the transition characteristic of PI films (5mm x 20 mm of film size). In DMA measurement, a strain of 0.1 % and 1 Hz oscillation were applied for the measurement of storage and loss modulus change as a function of temperature. Sample was scanned up to 390°C at a heating rate of 5 °C/min under N₂ purge.

2.4 Computational details

In this study, DFT calculations were performed to evaluate the O₂ / N₂ binding properties on fluorinated PI and non-functionalized PI without periodic slab models. DFT has been widely used to describe the interactions between gas molecules and organic materials.¹²⁻¹⁴ Geometry optimizations were performed using the DMol³ module of Materials Studio from Accelrys¹⁵ with the General Gradient Approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional¹⁶. We used all-electron Kohn-Sham wave functions and the DNP numerical basis set for this study. The optimized unit structures of non-functionalized PI and fluorinated PI are shown in Fig. 1b and (c), respectively. Once the optimized unit structures were obtained, O₂ or N₂ gas molecules are introduced to be bound. Self-consistent field (SCF) convergence, 1×10^{-5} Ha is obtained.

The O₂ / N₂ binding energy (ΔE_b) on the mineral surface was calculated by the following definition:

$$\Delta E_b = E_{\text{film}+\text{O}_2/\text{N}_2} - (E_{\text{film}} + E_{\text{O}_2/\text{N}_2}) \quad (1)$$

where ΔE_b denotes the binding energy of O_2/N_2 on fluorinated PI or non-functionalized PI, $E_{\text{film}+\text{O}_2/\text{N}_2}$, E_{film} , and $E_{\text{O}_2/\text{N}_2}$ are the energy of the O_2/N_2 bound on fluorinated PI or non-functionalized PI, the energy of fluorinated PI or non-functionalized PI without O_2/N_2 and the energy of a single molecule of O_2/N_2 , respectively.

3. Results and discussions

3.1 Color change kinetics on the basis of yellow index

After fluorinated polyimide (FPI) was synthesized, we initially evaluate its yellow index (YI) change at thermal exposure time and various temperatures, as shown in Fig. 2a. At 300 °C, the thermal imidization has already undergone, but in turn modest level of YI change after 30 min inferred that the FPI is able to withstand at the temperature below 300 °C without degrading. Dynamic mechanical analysis (DMA) profile shows that with an increase of temperature, further thermal imidization unambiguously initiates and prevails, which derives to accelerate the formation of charge transfer complex (CTC) affecting YI changes, associated with glass transition temperature of the film (Fig. 2b). Storage modulus continuously decreases whereas loss modulus shows bell-shape profile. In particular, broadly increased β -transition at 240 °C provides active chain rotations around benzidine bonds in TFDB units¹⁷⁻¹⁹. It is clearly found that thermal imidization promotes the conjugation between PI chains, and in turn CTC is enhanced with the reduction of free volume enough to show glass transition at 330 °C, which are good agreement with the YI changes at around 330 °C. Thus, it is worthy to note that thermal

treatment increases the rate of imidization, which leads to the availability of suitable conformations for the formation of a charge transfer complex (CTC) between dianhydride and diamine groups.

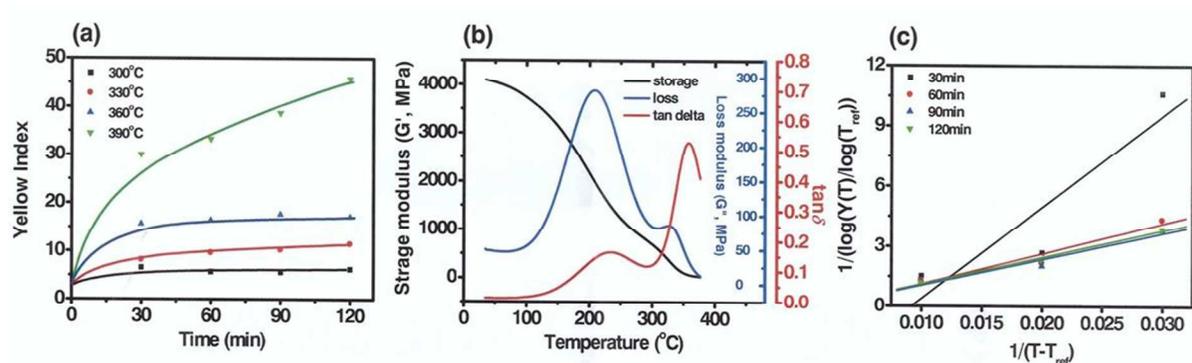


Figure 2. (a) Yellow index change of the fluorinated polyimide film at various temperature and thermal exposure time, (b) Dynamic mechanical analysis (DMA) profile of fluorinate polyimide, (c) An empirical modeling associated with yellow index–temperature using Williams–Landel–Ferry (WLF) equation. Green and blue curve at DMA profile denote storage modulus and loss modulus, respectively. Note that experimental results were obtained under N₂ atmosphere.

On the basis of YI change for 30 min, we can estimate and predict the YI change at each 30, 60, 90, 120 min using Williams–Landel–Ferry (WLF) model at various temperature ranges. WLF formalism for fitting YI is described as follows:²⁰

$$\log \frac{YI(T)}{YI(T_{ref})} = \frac{-C_1(T-T_{ref})}{C_2+(T-T_{ref})} \quad (2)$$

where $YI(T)$ denotes yellow index at the desired temperature (T), T_{ref} is the reference temperature of 300 °C, $YI(T_{ref})$ is yellow index at 300 °C, C_1 and C_2 are empirical constants adjusted to fit the values of $YI(T)$. Then, we rearranged the equation into $1/(T-T_{ref})$ vs $1/\log(YI(T)/YI(T_{ref}))$, as shown

in Fig. 2c. According to the fitted plots, It should be noted that the rate of thermal imidization reduced as the duration of thermal treatment undergoes further, which supports that thermal imidization has already taken place within 30 min at temperature over 330 °C. Those thermal imidization at high temperature accelerates more YI change, eventually diminishing the transmittance. As transmittance decreases, the wavelength of the transmitted light is longer than that of blue light, which suggests that CIE tristimulus value of red and green color is higher than that of blue one postulating YI change behavior associated with transmittance.

3.2 Anti-oxidant effects on film color change

During thermal treatment process, the film color change accelerates, leading to the change of optical properties. Hence, we carried out the introduction of various anti-oxidants or atmosphere control using air/N₂ to elucidate the insight into their effects for keeping clear color even after thermal imidization. First, we investigated the effect of anti-oxidants (e.g., Irganox[®] 3114, 1010, and 565) on FPI film color change associated with YI change, as shown in Fig. 3. Anti-oxidant could be useful for preventing the yellowish color change on general polymeric films, but on PI film, the temperature of thermal treatment for imidization would be higher than that of melting temperature for anti-oxidants (i.e. Irganox[®] 3114, 1010, and 565= 220, 12, and 94°C, respectively). Thus, it is inferred that Irganox[®] 1010 provides small weight loss, but all anti-oxidants are thermally unstable at temperature over 330 °C during thermal imidization, resulting from the weight loss (2-8 wt.%) as temperature elevates (Fig. 3a). Herein, on the basis of YI change, we investigated the role of anti-oxidants on FPI film color change. For the film

with Irganox[®] 3114 and 1010, YI dramatically goes as far as to increase up to 75 within 30 min, and in turn YI approaches the plateau state (Fig. 3b, 3c). It is found that anti-oxidant barely plays a critical role on the prevention of film color change, as we anticipated. Only FPI film with Irganox[®] 565 shows relatively low YI (45.2) at 390 °C for 120 min, which is close to YI (45.8) for that without anti-oxidant (Fig. 3d). It may be attributed to lower rate of weight loss, leading to the relatively high thermal stability. The thermal instability of anti-oxidants in FPI film can ironically cause their decomposition and evaporation, even accelerating film color change compared to FPI film without anti-oxidants instead. All those results announced that the use of the anti-oxidant for thermal imidization does not clearly diminish the color change of the film, but even facilitates the color change to more yellowish, forming charge transfer complex.

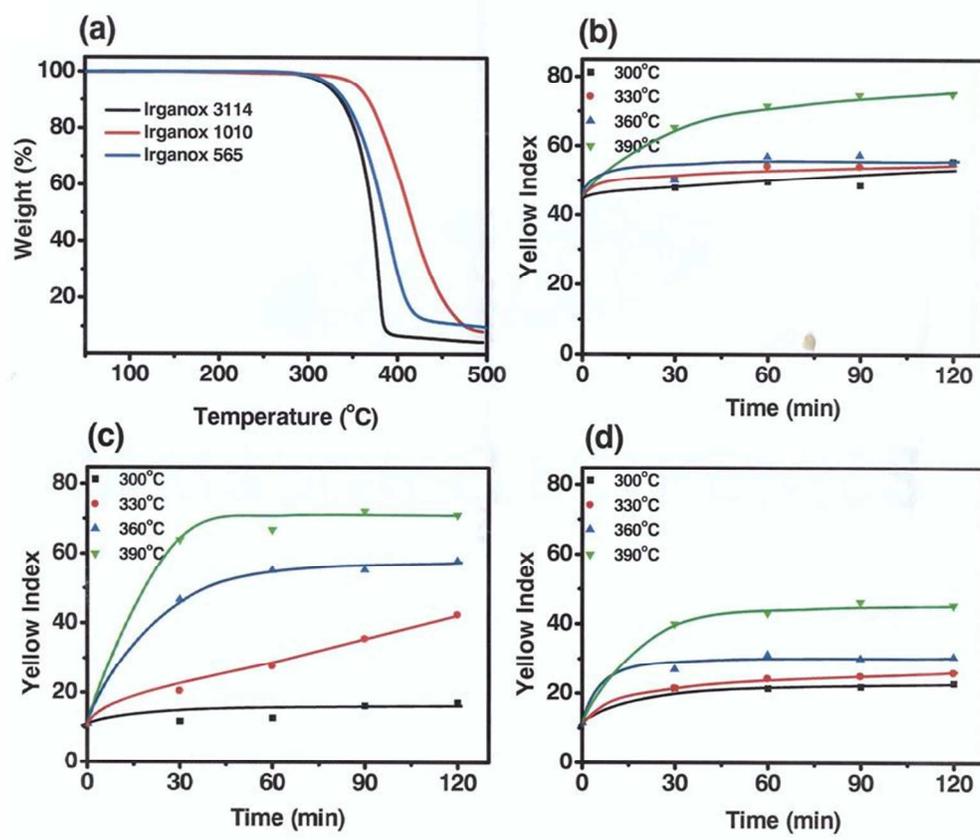


Figure 3. (a) Thermogravimetric analysis (TGA) profiles for various anti-oxidant, and Yellow index change of the fluorinated polyimide film with anti-oxidants such as (b) Irganox[®] 3114, (c) Irganox[®] 1010, (d) Irganox[®] 565 at various temperature and thermal exposure time.

3.3 Atmospheric process effects on film color change

Film color change could be more dependent on air environment than on N₂ environment since the amine oxidation in use of oxygen is known as critical factor to accelerate the film color change. If amine oxidation plays an important role in film color change, YI change at the condition of air environment would be expected to higher than that at the condition of N₂ environment. In order to determine the oxidation effect on the film color change, we performed the environmentally-controlled effect changing the atmosphere of N₂ to air during thermal treatment process in terms of YI change of FPI film (a) without anti-oxidant and (b) with Irganox[®] 3114, as shown in Fig. 4. Overall, it is found YI change with Irganox[®] 3114 shows much higher change than that without anti-oxidant because anti-oxidant became thermally more unstable at temperature over 330 °C and oxidized to exhibit yellowish color even under air environment markedly. In addition, the similar results for other anti-oxidants were observed, which was not shown in the manuscript.

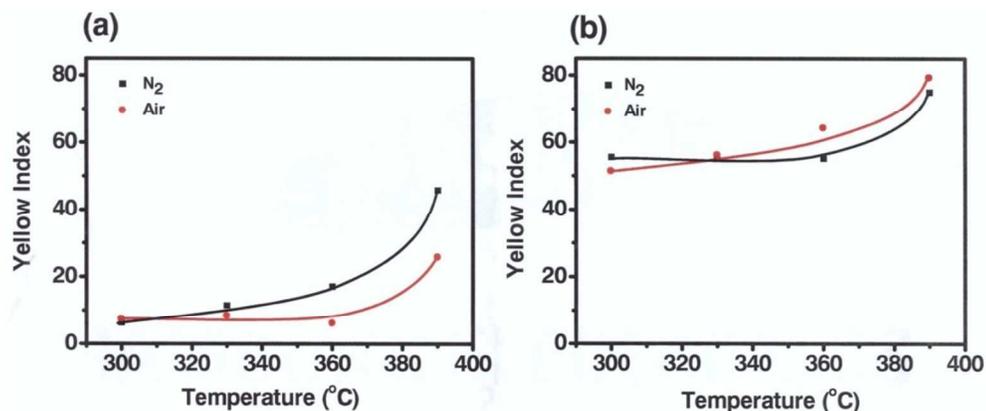


Figure 4. Yellow index change of the fluorinated polyimide film (a) without anti-oxidant and (b) with anti-oxidant (Irganox[®] 3114) under N₂ and air environment during thermal treatment at different temperatures. Note that experimental results were obtained after the exposure of 1h.

Surprisingly, YI change of FPI film without anti-oxidant accelerates strongly at the condition of N₂ environment compared to air environment as temperature increases over 330 °C even if an effect of both gas conditions at 300 °C is immaterial. This result is consistent with the thermal degradation of another type of FPI (PETI-5 and AFR700B), which suggests that PI resin and composite undergo modest oxidation even when using air environment⁹. It could be inferred that at temperature over 330 °C where glass transition temperature of FPI used in this study, N₂ environment even tends to provide more favorable condition for conjugation between PI chains, leading to the CTC formations. This N₂ environment might stabilize the thermal imidization more effectively compared to air environment, suggesting that the oxidation does not significantly influence the film color change, and even provide the beneficial role on FPI film without anti-oxidant. Contrary to this conjecture, the FPI film with anti-oxidant (Irganox[®] 3114) provides the modest degree of YI difference between N₂ and air environment, but YI at the condition of air environment is higher than that at the condition of N₂ environment. All these

aspects, namely, increased intermolecular interaction, increased yellow index changing the color from transparent to yellow during thermal treatment lose the use of anti-oxidants highly attractive.

3.4 Density functional theory (DFT) calculation of O₂/N₂ adsorption on PIs

It has been noted that the yellowish color change is attributed to intra/intermolecular CTC formation where imidization takes place. Hence, in order to investigate a better understanding of CTC formation and oxidation activity at PI and FPI at atomistic level, density functional theory (DFT) calculations were carried out to provide a comprehensive analysis of interaction characteristics of PIs and such O₂/ N₂ binding properties to PI and FPI including electronic properties, as shown in Fig. 1 and Fig. 5, respectively. The optimized geometry of both PI (a) and FPI (b) represents the chain-chain interaction for the layer arrangement of PIs where the dianhydride and the diamine groups of the one chain are correspondingly interacted with alongside those groups of another chain. It is found that the binding energy between such chains of PI (-2.37 eV) is quite higher than that of FPI (-1.43 eV) since fluorinated groups (CF₃) in TFDB and 6FDA sections release the distance to place them in the void space between chains and keep the interactive orientation with weaker interlayer formation energy. The distance between chains of FPI (3.39 Å) is longer than that of PI (3.21 Å), which strongly supports that fluorinated side groups in 6FDA and TFDB spaces intra/intermolecular polymer structure^{21,22}.

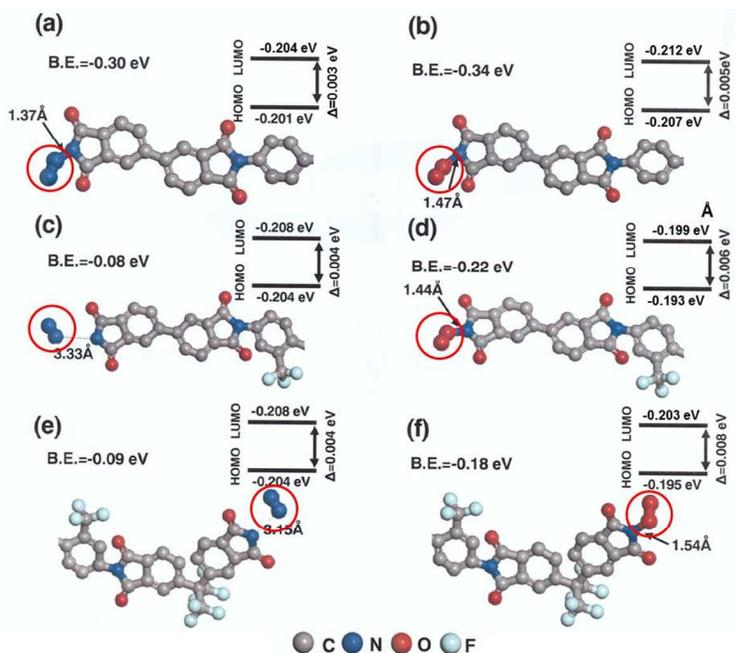


Figure 5. Optimized Geometry of polyimide with (a) N_2 adsorption, (b) O_2 adsorption, and fluorinated polyimide with (c) N_2 adsorption at BPDA side, (d) O_2 adsorption at BPDA side, (e) N_2 adsorption at 6FPA side, (f) O_2 adsorption at 6FPA side using DFT calculation.

The presented fluorinated groups in the dianhydride may disrupt the packing arrangement by inhibiting the polar attraction between CF_3 of one chain and dianhydride/diamine of another chain. Such groups in turn lead to only reduce the packing density diminishing their intra or intermolecular interaction. In addition, such gas (O_2/N_2) adsorption on PIs are utilized to explain the predominating effect of oxidation on PIs since the presence of such strong electronic interactions between O_2 and PI is responsible for its enhanced color change. O_2/N_2 environments interact with FPI through relatively weak interactions as compared to PI, which is good agreement with the experiment. It is clear that fluorinate groups make O_2/N_2 interaction unattractive. The results are consistent with the interpretation of the energy trends in terms of molecular orbitals. Relatively, a broad HOMO-LUMO band gap and small adsorption energy of

O₂/N₂ on FPI support that the oxidation of diamine groups is less preferable as compared to PI.

4. Conclusion

This investigation evaluates the yellow index characteristics of fluorinated polyimide film, composed of 6FDA-BPDA-TFDB to clarify the effect of temperature and thermal exposure time. It is induced that the thermal treatment time should be within 30 min under around 350 °C to keep colorless properties of the film. Indeed, anti-oxidants could not prevent the color change on account of their decomposition at the temperature for thermal treatment, which may lead to erroneous reliability estimation in such their role. In addition, both experimental and DFT calculated findings suggest that the oxidation of film is a relatively minor factor to form diamine oxidation in fluorinated monomers of the fluorinated polyimide due to mild interaction between polyimide and oxygen. In particular, DFT calculation illustrates a basic understanding of charge transfer complex formation in polyimide, which supports that fluorinated groups in FPI inserted into intra/intermolecular spacing in polymer structure diminish both intra-and intermolecular CTCs. It is clearly announced that the color change from transparent to yellow is the intra- and intermolecular charge transfer complex during thermal imidization, attributed to the conjugation between polymer chains. These studies highlight the need of an additional treatment for yellow index change to be further exploited in polyimide fabrication on a broader scale.

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Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of manuscript.

Notes

The authors declare no competing financial interest.

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