# Interfacial Interaction in Polyimide/Silica Hybrid Composites by Fluorescence Spectroscopy

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In this paper, we report that the interfacial interaction in polyimide (PI)/silica hybrid composites can be characterized by a fluorescence spectroscopy. We found that silica shows different effects on the fluorescence behavior of polyimide based on biphenyltetracarboximide (BPDA) depending on the type of diamine, that is, whether it is oxydiphenyldiamine (ODA) or phenylenediamine (PDA). The polyimide/silica hybrid composite films were prepared by thermal imidization and sol−gel method from tetraethoxy silane (TEOS). For the polyamic acid (PAA)/TEOS solutions, the interfacial interaction was discussed in terms of the intermolecular hydrogen bonding between PAA and $Si(OH)_4$ or complexation between a solvent, *N*-methylpyrrolidinone (NMP), and PAA. Significant changes in the fluorescence wavelength as well as intensity were observed by the presence of silica particles in the case of BPDA−PDA/silica composite films as compared to the case of BPDA−ODA/silica composite films. We found that silica has some interaction with BPDA−PDA but no interaction with BPDA−ODA in PI films. The interfacial interaction between silica and BPDA−PDA or BPDA−ODA was explained by different electron-donating strength of the diamines, here, PDA and ODA.

## Introduction

Organic/inorganic hybrid composites constitute emerging advanced materials since they combine unique properties from the inorganic and organic components. Among the polymers that have been used as matrix materials for the hybrid composites are epoxy resins,[1] poly(dimethylsiloxane) (PDMS),[2,3] and poly(methyl methacrylate).[4]

Since the first report of Nandi et al.,[5] aromatic polyimides have been considered to be suitable matrix polymers for hybrid composites for advanced technological applications in the microelectronics and aircraft industries, because they possess excellent chemical, physical, thermal, and mechanical properties due to the phenyl and imide moieties of the backbone.[6−9] In addition, silica has been most extensively investigated as an inorganic component in hybrid composites because of the expected interesting catalytic and electronic applications.[5] An important advantage of the sol−gel synthesis route for polyimide/silica composites is that the poly(amic acid) organic matrix acts to prevent agglomeration of the silica, which can lead to nanometer scale silica clusters in the composites or, as often stated, “nanocomposites”. During the sol−gel reaction of metal alkoxides such as tetraalkoxy silane, polyimide films are formed by spin-casting solutions containing the soluble poly(amic acid) precursor, followed by thermal imidization. This is a complex process involving chain orientation, solvent evaporation, chemical reaction, and structural relaxation, as well as the interaction between the metal alkoxide and the polyamic acid or polyimide. Consequently, the relationship between final film structure and processing conditions is of considerable practical significance.

Several authors have reported on the structure and properties of the polyimide/silica composites.[10−14] Previous works on polyimide/silica hybrid films have demonstrated that the properties of the polyimide matrix can be influenced by the presence of the silica.[10−14] In particular, both the glass-transition and thermal-

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decomposition temperature increase with increasing silica content. In addition, an increase of the silica content causes an increase of the density, storage modulus, and linear thermal expansion coefficient.[13,14]

Fluorescence spectroscopy is known to be very useful in the investigation of the dynamics and structure of solid polymers and is complementary to the X-ray methods.[3,15−19] Although fluorescence spectroscopy has also been used to investigate the interfacial interaction or miscibility in polymer blends,[20] very little has been published on the fluorescence spectroscopic studies of organic/inorganic hybrid composites. Leezenberg and Frank[3] were the first to utilize fluorescence spectroscopy in organic/inorganic hybrid composites. They reported on the fluorescence spectroscopy of dansyl-labeled cross-link junctions in PDMS networks as a function of the sol−gel formation of silica.

To the best of our knowledge, however, no paper has dealt with the investigation of interfacial structure of polyimide/silica hybrid composites using fluorescence spectroscopy, even though several papers, mainly by Hasegawa et al.[15] and Frank et al.,[16] have been published on the use of fluorescence spectroscopy to investigate the state of organization of polyimide. In this work, we report that silica has different effects on the fluorescence behavior of polyimide based on biphenyltetracarboximide (BPDA), depending on the type of diamine: oxydianiline (ODA) or phenylenediamine (PDA). We propose that the difference is due to different interfacial interaction of ODA or PDA with silica. We found that fluorescence spectroscopy is a useful tool for determining the interfacial interaction between inorganic particles and polymer matrix for hybrid composites.

## Experimental Section

**Materials.** 3,3′,4,4′-Biphenyl tetracarboxylic dianhydride (BPDA, TCI Chemicals) was recrystallized and vacuum-dried at 200 °C for 24 h before use. Sublimed *p*-PDA, 4,4′-ODA, anhydrous *N*-methyl pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), hydrochloric acid (HCl), and tetraethyl orthosilicate (TEOS) were purchased from Aldrich and were used as received.

**Table 1. Preparation of Polyimide/Silica Hybrid Films**

| | PAA[a] (g) | TEOS (g) | silica[b] (wt %) |
|---|---|---|---|
| PI | 6.667 | 0 | 0 |
| PI/Si5 | 6.667 | 0.05 | 1.42 |
| PI/Si10 | 6.667 | 0.10 | 2.80 |
| PI/Si20 | 6.667 | 0.20 | 5.45 |
| PI/Si30 | 6.667 | 0.30 | 7.96 |
| PI/Si50 | 6.667 | 0.50 | 12.60 |
| PI/Si75 | 6.667 | 0.75 | 12.78 |
| PI/Si100 | 6.667 | 1.00 | 22.38 |

[a] 15 wt % solution in NMP. [b] Calculated silica content (wt %) in the hybrid films assuming that the gel reaction was completed.

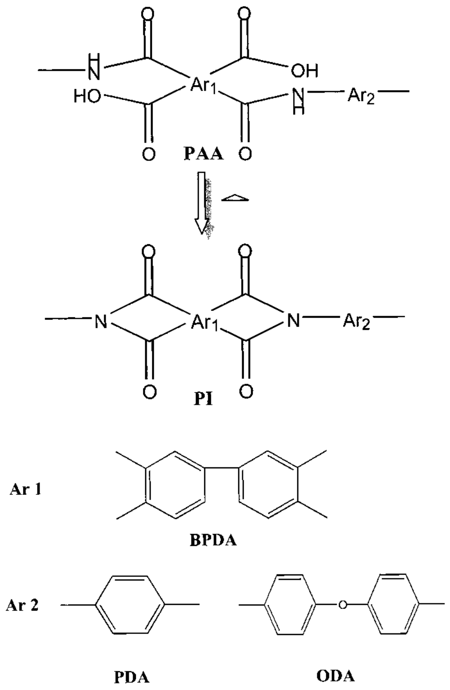

**Figure 1.** Chemistry of thermal imidization of BPDA−PDA and BPDA−ODA polyimides from their PAA precursors.

**Preparation of PAA Solutions and PI/Si Hybrid Films.** Poly(amic acid) (PAA) was polymerized by adding an equimolar amount of BPDA powder into the NMP solution of PDA or ODA with continuous stirring at room temperature for a few hours. Various quantities of TEOS with water and HCl as catalyst were then added into the PAA solution (15 wt %). The weight ratio of TEOS to PAA varied from 0.05 to 1.(see Table 1 for notation.) The heterogeneous solution was stirred for 1 day until the solution became homogeneous. The resulting homogeneous mixtures were spun on glass plates or quartz wafers to prepare the PAA−TEOS as-spun films. The PI/Si hybrid films were obtained by successive heating of the corresponding precursor PAA−TEOS as-spun films. The PAA−TEOS as-spun films after drying at 80 °C for 30 min were heated to 200 °C for 30 min followed by 350 °C for 1 h in a laminar flow convection oven (Blue M) under nitrogen purge. Then, the films were cooled to room temperature at a rate of 10 °C/min. The chemistry of thermal imidization in this work is illustrated in Figure 1. The PI/Si hybrid films were denoted as PI and PI/Si5, 10, 20, 30, 50, 75, and 100, where the number means the weight percent of silica based on PI (Table 1). For example, PI/Si5 means that the weight ratio of silica to PI is 0.05.

**Characterization.** *1. Fluorescence Spectroscopy.* The emission and excitation spectra of the films as well as solutions were measured using a fluorescence spectrometer (FS 900CDT spectrometer, Edinburgh Instruments). All measurements were made at room temperature using 1 mm slit widths. Films were excited in a front-face arrangement to minimize self-absorption. Fluorescence intensity was corrected to account for variations in PMT sensitivity and absorption using a rhodamine B standard solution. Seven measurements were performed and signal-averaged.

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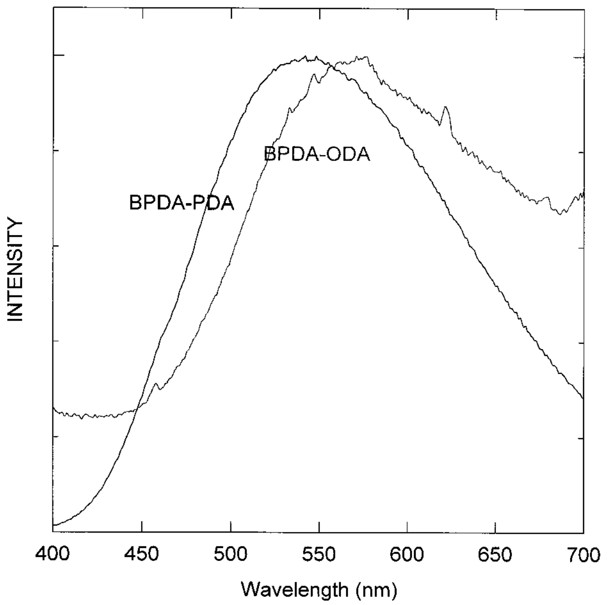

**Figure 2.** Emission spectra of the BPDA–PDA and ODA PI films, which were excited at 350 nm.

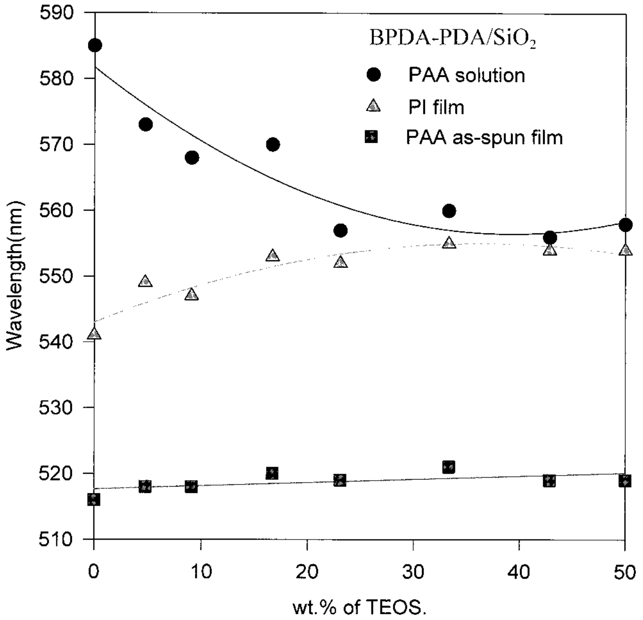

**Figure 3.** Wavelength of emission peak of BPDA–PDA PAA/TEOS solution, PAA/TEOS as-spun film, or in PI/Si film states as a function of TEOS content. The emission peaks of BPDA–PDA PAA/TEOS solutions were obtained with the excitation wavelength of 480 nm.

*2. Fourier Transform Infrared Spectroscopy (FTIR).* Infrared analyses of solutions were performed with an Analect FX-6160 FTIR spectrophotometer. Thirty-two scans at a resolution of 2 cm$^{-1}$ were signal-averaged.

## Results and Discussion

Figure 2 presents the emission spectra of the BPDA–PDA and BPDA–ODA PI films, which were excited at 350 nm, one of the stronger excitation peaks in the excitation band. Broad structureless peaks occur at approximately 542 and 571 nm, respectively.

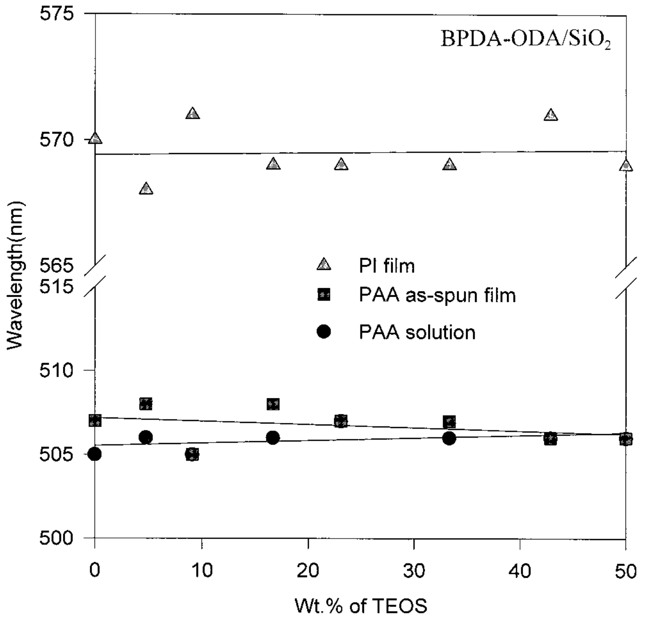

**Figure 4.** Wavelength of emission peak of BPDA–ODA PAA/TEOS solution, PAA/TEOS as-spun film, or in PI/Si film states as a function of TEOS content. The emission peaks of BPDA–PDA PAA/TEOS solutions were obtained with the excitation wavelength of 400 nm.

Figures 3 and 4 show the wavelength of the emission peak of BPDA–PDA PAA/TEOS solution or BPDA–ODA PAA/TEOS solution, PAA/TEOS as-spun film, or PI/Si composite film as a function of TEOS content, respectively. In this figure, the emission peaks of BPDA–PDA PAA/TEOS and BPDA–ODA PAA/TEOS solutions were obtained with excitation wavelengths of 480 and 400 nm, respectively. The redshift of the emission peak of PI/Si composite films in comparison to PAA/TEOS as-spun films for both BPDA–PDA and BPDA–ODA systems is not unusual; this arises due to changes in the molecular packing and in-plane orientation of the systems as the processing converts the PAA/TEOS as-spun films to PI/Si composite films during thermal imidization. The redshift is reported to be due to the intra- or intermolecular charge-transfer complex formation between the phenyl (electron donor) and imide moieties (electron acceptor).[15–17,19] One can see, however, that clear differences exist between the two figures. The main differences are summarized as follows: (1) For the BPDA–PDA and BPDA–PDA/TEOS solutions, there is a large redshift (up to 50–70 nm) in emission wavelength compared to those of PAA or PAA/TEOS as-spun films over the entire TEOS content range investigated, whereas for the BPDA–ODA PAA and BPDA–ODA PAA/TEOS solutions and PAA/TEOS as-spun films before thermal imidization, emission peaks remain at almost the same wavelength. (2) On increasing the silica content, the wavelength of the emission peak of the BPDA–PDA PAA solution decreases, but that of the BPDA–PDA PAA/TEOS as-spun films and PI/Si composite films increases, whereas the wavelength of the emission peak of the BPDA–ODA PAA solutions is not changed significantly with increasing TEOS or silica content, regardless of their sample states, whether it is in solution, in PAA as-spun film, or in PI film.

The results in Figures 3 and 4 strongly suggest that the interaction between silica and BPDA–PDA or BPDA–ODA is different in the polyimide/silica hybrid composite systems; moreover, the interaction is different depending on the sample states.

The preparation of the PI/Si hybrid composites includes the sol−gel reaction of TEOS, drying of the PAA as-spun film, and thermal imidization. Thus, the photophysical behavior of polyimide/silica hybrid composites as well as their final morphology and physical properties can be influenced in many ways by the chemistry before and after the sol−gel reaction and thermal imidization. In the solution state, the hybrid system contains PAA, NMP, and $Si(OH)_4$, which comes from TEOS by sol−gel reaction. After thermal imidization, there is no NMP in the system and most of the $Si(OH)_4$ is transformed to a silica network. Thus, we may expect that the interfacial interaction between silica and polyimide is governed by the competition between the NMP−PAA interaction and the $Si(OH)_4$−PAA interaction for the PAA/TEOS solution, whereas it is determined only by the interaction between silica and PI for the PI/Si hybrid composite films.

The large redshift in the emission wavelength for the BPDA−PDA PAA solution in comparison to PAA/TEOS as-spun films and PI/Si films provides evidence for the complexation between NMP and BPDA−PDA PAA. Rojstaczer et al.[21] found that the solidification of the PAA precursor mixtures, due to complex formation between NMP and carboxylic acid moieties or amine moieties of PAA, plays a major role in determining the morphology of the fully imidized mixtures. Complexation between PAA and NMP is very important also in the kinetics study of polyimide curing.[22] The decomplexation of PAA from NMP proceeds when the PAA film is exposed at higher temperature, because of decreasing solvent diffusion with imidization.[23] It may be assumed that when the PAA as-spun film is imidized at higher temperature, several structural changes occur simultaneously and competitively, including complexation or decomplexation between NMP and PAA, and molecular ordering of PAA to imide depending on the degree of imidization as well as the solvent removal rate. On increasing TEOS contents, large blueshift is observed up to 30 wt %, Blueshift is usually observed in the emission spectra of a polymer solution in comparison to that of its corresponding solid polymer film, due to so-called “the dilution effect,” when there are electronic interactions between fluorophores in the systems.[24,25] The result of Figure 3 suggests that the blueshift with increasing TEOS contents comes from the dilution of electronic interaction between NMP and BPDA−PDA PAA by TEOS in the excited state as well as the decreasing complexation in the ground state. On the other hand, in Figure 4, the complexation seems not to be strong (defined here as “loose”) in the case of BPDA−ODA PAA, and thus, the loose complexation is not much affected by the presence of silica, regardless of TEOS content.

TEOS is readily hydrolyzed to $Si(OH)_4$ by water in the presence of an acid catalyst such as HCl. The hydrolysis reaction is very fast even in the NMP solution of TEOS and BPDA−PDA or BPDA−ODA PAA. The hydrolysis reaction proceeds rapidly even in other acid or base catalyst systems. Then, the intermolecular hydrogen bonding exists between the hydroxy group in the hydrolyzed TEOS and carboxylic acid in BPDA in both BPDA−PDA and BPDA−ODA systems.

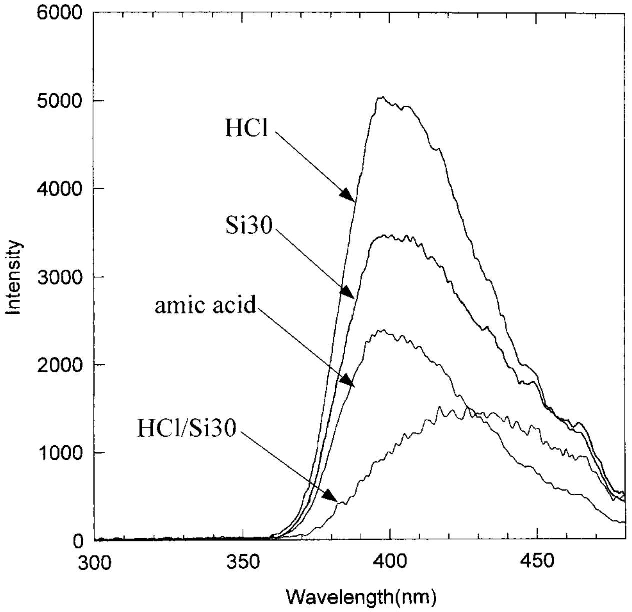

**Figure 5.** The excitation spectra of BPDA−ODA PAA/HCl solution without TEOS, BPDA−ODA PAA/TEOS solution without HCl, and BPDA−ODA PAA/HCl/TEOS solution, as well as BPDA−ODA PAA solution without HCl and TEOS.

The existence of intermolecular hydrogen bonding can be proven if we examine the excitation spectra of BPDA−ODA PAA solution with or without HCl or TEOS. Figure 5 shows the excitation spectra of BPDA−ODA PAA/HCl solution without TEOS, BPDA−ODA PAA/TEOS solution without HCl, and BPDA−ODA PAA/HCl/TEOS solution, as well as the BPDA−ODA PAA solution without HCl and TEOS. In this figure, the concentration of TEOS is 30 wt %. The BPDA−ODA PAA solution only with HCl and TEOS (denoted as Si30) together shows a redshift in the excitation spectrum, whereas no peak shift was observed for PAA/TEOS solution without HCl or PAA/HCl solution without TEOS. Since TEOS is readily changed to $Si(OH)_4$ in the presence of HCl catalyst, the redshift in the excitation peak is caused only by the intermolecular hydrogen bonding between the hydrolyzed TEOS, i.e., $Si(OH)_4$ and PAA, regardless of whether the hydrolysis is complete or partially done. This may be true although TEOS is not completely hydrolyzed, since the same experimental results are obtained for different pH solutions by using other acid or base catalysts such as formic acid and *t*-ethylamine or for different concentrations of TEOS.

Figure 6 shows the excitation spectra of BPDA−ODA PAA solutions with or without TEOS when DMSO was used as a solvent, which were emitted at 550 nm. In this figure, the content of TEOS is 30 wt %. It is noteworthy that even when aprotic DMSO was used as a solvent instead of NMP, such a redshift was also observed when TEOS was added to the PAA solution in the presence of HCl. This is further evidence that the redshift is due to the interaction between PAA and

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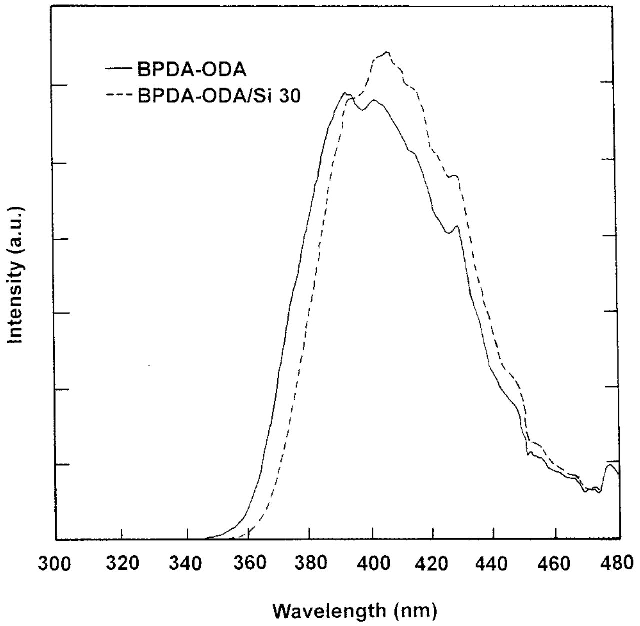

**Figure 6.** Excitation spectra of BPDA−ODA PAA solutions with or without TEOS when DMSO was used as a solvent, which were emitted at 550 nm. The content of TEOS is 30 wt %.

TEOS, i.e., the hydrogen bonding. The redshift in the excitation spectra with a constant emission spectra has been also reported for intramolecularly hydrogen-bonded molecules such as 2-(2′-hydroxyphenyl) benzothiazole, upon photoexcitation to the first singlet excited state, with excited-state intramolecular proton transfer.[26] The result of Figure 6 implies that the complexation between NMP and PAA did not play a role for the redshift in Figure 5. Such redshift in the excitation peak was not clearly observed in the case of BPDA−PDA PAA/silica composite solutions.

Let us consider why BPDA−PDA/silica and BPDA−ODA/silica composite systems exhibit such different photophysical behavior, as shown in Figures 3 and 4, under the same experimental conditions. We note that the only difference between the two composite systems is the use of different diamines, PDA and ODA. The difference in physical properties such as glass-transition temperature and tensile modulus between BPDA−PDA and BPDA−ODA is not small, since the ODA moiety is much more flexible than the PDA moiety because of the presence of the ether linkage.[27] In this work, we found that the difference between PDA and ODA also gives rise a profound effect on the photophysical properties of the polyimide systems consisting of either of the diamines.

The results of Figures 3−6 imply that in BPDA−PDA /silica systems the complexation between NMP and PAA is very tight, but the intermolecular hydrogen bonding between hydrolyzed TEOS (i.e., $Si(OH)_4$) and carboxylic acid in PAA is weak. On the contrary, in BPDA−ODA/TEOS systems, the complexation is loose but the hydrogen bonding is strong; When PAA solution is imidized to PI films, however, the interaction between silica and polyimide is important and the interfacial interaction between BPDA−PDA and silica is stronger than that between BPDA−ODA and silica, since decomplexation takes place during the imidization process and the system has no complexation effect. This can be proven by the fact that on increasing the silica content, the BPDA−PDA exhibits an increasing redshift in the emission peak but the BPDA−ODA PI/Si composite films do not.

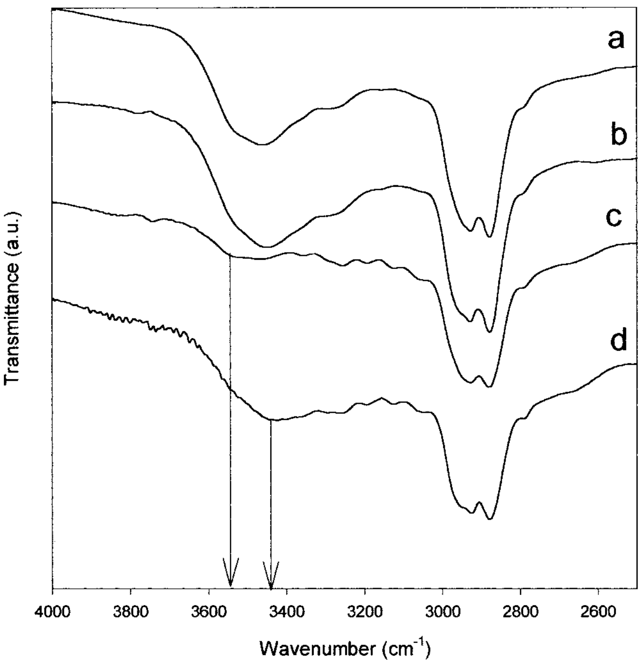

**Figure 7.** IR spectra of BPDA−PDA PAA and BPDA−ODA PAA solutions with or without TEOS in the wavelength ranges over 2500−4000 cm$^{-1}$: (a) BPDA−PDA PAA, (b) BPDA−PDA PAA/TEOS, (c) BPDA−ODA PAA, and (d) BPDA−ODA PAA/TEOS solutions. The content of TEOS is 30 wt %.

Figure 7 shows the IR spectra of BPDA−PDA PAA and BPDA−ODA PAA solutions with or without 30 wt % of TEOS in the wavelength range of 2500−4000 cm$^{-1}$. Intense peaks were observed around 3450 cm$^{-1}$, in the case of BPDA−PDA PAA solutions (spectra a and b, Figure 7), regardless of the presence of TEOS, whereas weak broad peaks were observed around 3540 and 3450 cm$^{-1}$ for BPDA−ODA PAA solutions with (spectrum d, Figure 7) or without (spectrum c, Figure 7) TEOS, respectively. The intensity and the wavelength of the peak were almost identical for both BPDA−PDA solutions with (spectrum b, Figure 7) and without (spectrum a, Figure 7) TEOS. On the other hand, it is noteworthy that in the case of BPDA−ODA PAA solutions the peak around 3540 cm$^{-1}$ was shifted to slightly lower wavelength, i.e., 3450 cm$^{-1}$, and the peak intensity around 3450 cm$^{-1}$ was remarkably increased when TEOS was added in the solution. (The maxima of the peaks were indicated as arrows.) If we consider the chemical environment in both BPDA−PDA and BPDA−ODA solutions with or without TEOS, the peak around 3450 cm$^{-1}$ corresponds to the presence of hydrogen bonding, whereas the peak around 3540 cm$^{-1}$ corresponds to free hydroxyl group in the system. The strong peak around 3450 cm$^{-1}$ in the case of BPDA−PDA PAA solution (spectrum a, Figure 7) may be attributed to the hydrogen bonding by the tight complexation between PAA and

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NMP. The population of free hydroxyl groups is small, and instead the complexation is dominant in the solution system. In this case, the hydrogen bonding between PAA and TEOS, if any, may be overlapped with the complexation in the BPDA−PDA PAA/TEOS solution. In the case of BPDA−ODA PAA solution, however, the weak intensity of the peak around 3540 $cm^{-1}$ with no trace of peaks around 3450 $cm^{-1}$ means that there may exist free hydroxyl groups and the hydrogen bonding is rarely formed in the solution; i.e., the complexation between PAA and NMP is very loose. Instead, the shift of the peak around 3540−3450 $cm^{-1}$, when TEOS is present in the BPDA−ODA PAA solution, is ascribed mainly to the hydrogen bonding between PAA and TEOS, more exactly, between hydrolyzed TEOS (i.e., $Si(OH)_4$) and carboxylic acid in PAA. It may be expected that the loose complexation between PAA and NMP becomes much weaker in the presence of TEOS. The IR results are in good agreement with the fluorescence spectral results.

We argue that the difference comes from the different electron-donor strengths of PDA and ODA. Although both PDA and ODA act as electron donors, the electron-donor ability of ODA is weaker than that of PDA because of the ether linkage of the former, and thus, PDA possesses a higher amine basicity ($pK_b = 7.92$) than ODA ($pK_b = 8.80$).[28] The positive charge character of hydrogen in the amine moiety of ODA is assumed to be weaker than that of PDA because of the lone-pair electrons of oxygen in the ether linkage. Then, the hydrogen of NH as well as the carboxylic acid moieties in the electron-richer PDA can produce a tight complex with the carbonyl group in NMP, and the intermolecular hydrogen bonding between $Si(OH)_4$ and carboxylic acid in PAA is screened by the strong complexation. On the contrary, in the BPDA−ODA/TEOS composite solution, the intermolecular hydrogen bonding predominates, because the complexation is loose due to the relatively weak positive charge character of hydrogen in the NH moiety by the electron-poorer donor property of ODA. In the PI films, however, the solvent complexation effect is vanished. Instead, there exists only the interaction between silica with BPDA−PDA PI or BPDA−ODA PI. The different interactions of BPDA−PDA or BPDA−ODA PI with silica, which have been changed from silica sol during sol−gel reaction and thermal imidization, are not unusual if we consider that the electron-richer PDA has stronger interaction with electron-accepting silica than ODA does because of the stronger electron-donor ability of PDA than ODA.

## Conclusion

In this work, we have observed different fluorescence behavior in the effect of silica on the interfacial interaction of polyimide/silica hybrid films as well as polyamic acid solutions, depending on the kinds of diamine, whether it is PDA or ODA for the same BPDA dianhydride system. We found that silica has some interaction with BPDA−PDA but no interaction with BPDA−ODA in PI films. The interfacial interaction between silica and BPDA−PDA or BPDA−ODA is due to different electron-donating strength of diamines, PDA and ODA, in terms of the competitive intermolecular hydrogen bonding between PAA and $Si(OH)_4$ and complexation between NMP and polyamic acid. Further fluorescence studies are now underway to provide more details on the interfacial interaction between polyamic acid or polyimide and silica, as well as the morphology of the systems, and the effect of silica on the state of organization of the polyimide matrix.

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