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Preparation and Photophysics of Polyimide/Silica Organic/Inorganic Hybrid Composites

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SUMMARY: In this work, polyimide/silica hybrid composites were prepared by the sol-gel reaction of tetraethoxysilane(TEOS) and the thermal imidization of poly(amic acid) from 3,3',4,4'-biphenyltetracarboxylic dianhydride(BPDA) and 4,4'-oxydianiline(ODA), and their photophysical properties were investigated using a fluorescence spectroscopy. It was found that the intrinsic fluorescence of poly(4,4'-oxydiphenylene-3,3'4,4'-biphenyltetracarboximide) (BPDA-ODA) such as emission intensity and emission wavelength depends strongly on the changes in the molecular conformations during the sol-gel reaction and the thermal imidization. In conclusion, we found that the fluorescence spectroscopy can provide an insight into how the intermolecular or intramolecular interaction of polyimide in the hybrid composite system is affected by the silica contents, depending on the sample states.

Introduction

The organic/inorganic hybrid composites constitute emerging advanced materials since they combine unique properties from the inorganic and organic components[1-4]. Recently, Nandi, et al[2] reported that aromatic polyimides can be a suitable matrix polymer for hybrid composites in advanced technological applications in the microelectronics and aircraft industries, since they possess high thermal stability, and excellent chemical, physical, and mechanical properties. In addition, silica has been most extensively investigated as an inorganic component for the hybrid composites because of the expected interesting catalytic and electronic applications[2].

Two methods of achieving the polyimide/silica hybrid composites are the direct addition of the oxide particles and the use of a precursor such as tetraalkoxysilane that produces the oxide particles during the second stage of thermal curing. The second approach, which may be accomplished with the sol-gel process, results very small particles with a more homogeneous distribution[3].

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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$^{5)}$. Fluorescence spectroscopy has been widely used in the studies to reveal the molecular orientation of polyimide *per se* and to see the effects of curing conditions on the thermal imidization of poly(amic acid)s$^{5\text{-}11)}$. In the present study, therefore, we wish to learn how fluorescence spectroscopy can provide insight into whether the state of organization of the polyimide matrix is altered by the presence of silica or how the intermolecular or intramolecular interaction in the hybrid composite systems depends on the sample states.

Previous works on polyimide/silica hybrid composites have demonstrated that the properties of the polyimide matrix such as dielectric and tensile properties can be influenced by the presence of the silica$^{2),4)}$. Recently, we found that the polyimide morphology which had been investigated by atomic force microscopy and small angle X-ray scattering(SAXS) techniques is also significantly affected by the presence of silica and the types of the polyimide precursors$^{12)}$.

Since the preparation of the polyimide/silica hybrid composites for this work includes the sol-gel reaction of tetraalkoxysilane, drying of the poly(amic acid) as-spun film, and thermal imidization, the molecular conformation of polyimide and the aggregate state of the inorganic silica particles as well as the dimension of silica networks are affected by several factors such as complexation between a solvent and poly(amic acid), chain orientation, chemical reaction, structural relaxation, and the interaction between silica and poly(amic acid) in solution or polyimide.

The photophysical behavior of the polyimide/silica hybrid composites will be therefore influenced by the presence of tetraalkoxysilane or silica gel in many ways depending on their interaction with poly(amic acid) in solution or poly(amic acid) as-spun film as well as polyimide.

We report here the effect of silica contents on the fluorescence behavior of the hybrid composite systems before and after sol-gel reaction of tetraethoxysilane(TEOS) to silica and/or thermal imidization to poly(4,4'-oxydiphenylene-3,3'4,4'-biphenyltetracarboximide) (BPDA-ODA) for which the emission intensity and emission wavelength depend strongly on the changes in the molecular conformations during sample preparation.

Experimental

Materials and Sample Preparation. 3,3',4,4'-biphenyltetracarboxylic dianhydirde (BPDA, TCI Chemicals) was recrystallized and vacuum-dried at 200°C for 24h before use. 4,4'-oxydianiline (ODA, Aldrich), and anhydrous N-methyl pyrrolidinone(NMP, Aldrich) were used as received. Tetraethylorthosilicate(TEOS) obtained from Aldrich and was used as received.

The BPDA-ODA poly(amic acid) (hereafter PAA, unless otherwise noted.) was prepared by adding an equimolar amount of BPDA powder into the NMP solution of ODA with continuous stirring at room temperature for several hours. The preparation of the BPDA-ODA polyimide-silica (hereafter PI-Silica, unless otherwise specified.) hybrid films is shown in scheme I. Various quantities of TEOS, water and HCl catalyst were then added into the poly(amic acid) solution (15wt.%). The weight ratio of TEOS to PAA varied from 0.05 to 1. 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-Silica "as-spun" hybrid films. The PI-Silica hybrid films were obtained by successive heating the corresponding precursor PAA-Silica "as-spun" hybrid films. The PAA-Silica as-spun films after drying at 80°C for 30min were heated to 200°C for 30min followed by 350°C for 1h in a laminar flow forced air convection oven (Blue M) under nitrogen purge. Then the films were cooled to room temperature at a rate of 10°C/min. Fig. 1 shows the chemical structure of BPDA-ODA polyimide.

Measurement. The emission and excitation spectra of the films and solutions were measured at room temperature using a fluorescence spectrometer (FS 900CDT spectrometer, Edinburgh Instruments). The UV-Vis spectrometer (8452A diode array spectrometer, Hewlett Packard) was used for recording the absorption of films and solutions.

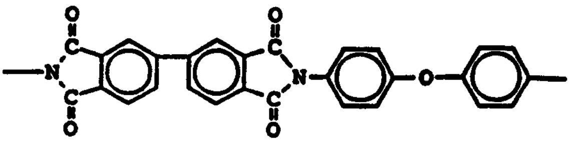
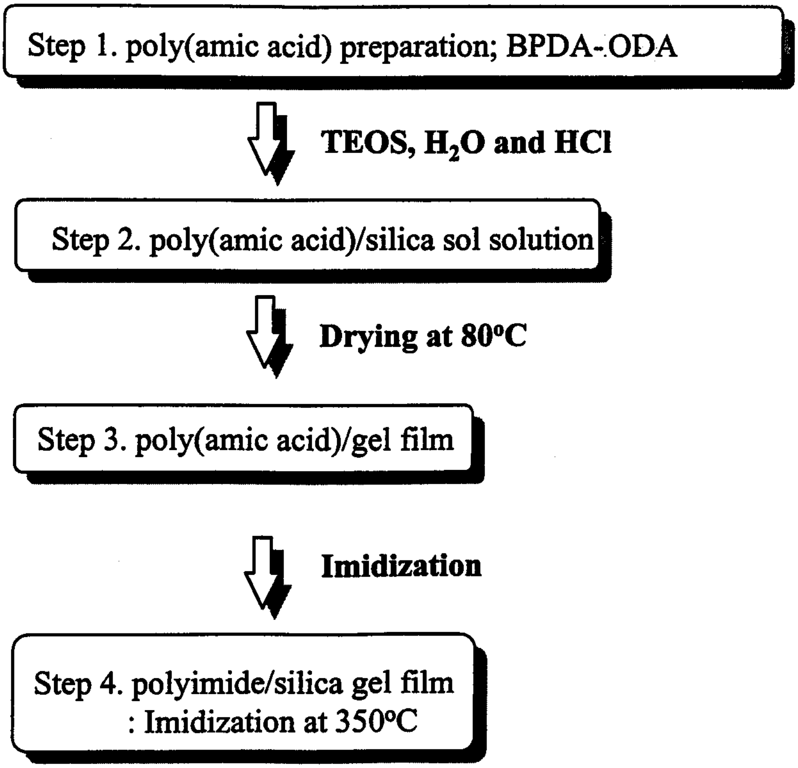


Fig. 1. Chemical structure of BPDA-ODA PI



Scheme I: The preparation of polyimide-silica hybrid films

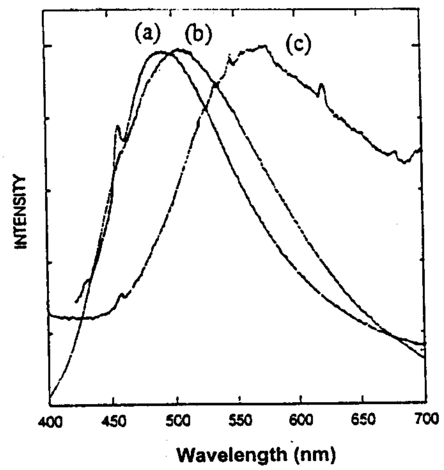


Fig.2. The emission spectra of the PAA solution in NMP (a), PAA as-spun film(b), and PI film(c), which were excited at 350 nm, one of the stronger excitation peaks in the excitation band, for PAA and PI films, and at 400 nm for PAA solution, respectively.

Results and Discussion

Fig. 2 illustrates the emission spectra of the PAA solution in NMP (a), PAA as-spun film(b), and PI film(c), which were excited at 350 nm, one of the stronger excitation peaks in the excitation band, for PAA and PI films, and at 400 nm for PAA solution, respectively. Broad structureless peaks were observed at approximately 505 nm, 509 nm and 570 nm for PAA solution, PAA as-spun film and PI films, respectively.

Even though no literature reports on the exact peak assignment of the chromophores in BPDA-ODA, we can deduce the nature of the chromophores in BPDA-ODA by reviewing literatures which deal with fluorescence of the polyimides or their model compounds either precursor of which is the same as BPDA-ODA such as poly(4,4'-

oxydiphenylenepyromellitimide) (PMDA-ODA), poly(4,4'-oxydiphenylene-3,3'4,4'-benzophenonetetracarboximide) (BTDA-ODA), and poly(1,4-phenylene-3,3'4,4'-biphenyltetracarboximide) (BPDA-PDA). Previous workers have proposed that intermolecular and/or intramolecular charge transfer complexes (CTC) exist and give rise to the fluorescence in those polyimides5-11). The intensity of the CTC depends not only on the nature of chromophores but also on the thermal imidization conditions.

For the PI film, broad and structureless excitation peaks, measured with 550 nm emission, were observed around 350 and 480 nm, while broad emission peak of the PI film was observed around 570 nm for both short-wavelength (350 nm) and long-wavelength(480 nm) excitation. Similar excitation and emission spectra were also reported by Hasegawa, et al6). It is generally accepted that polyimide fluorescence usually arises from CTC's that form between electron donor (diamine) and electron acceptor (diimide) segment pairs7), 11). It is believed for the BPDA-ODA PI the emission peak is due to the intermolecular CTC11). We note that the emission peaks of PI films were observed at much longer wavelength than those of PAA as-spun films as well as PAA solution. The change of fluorescence of the PAA as-spun film to PI film is of course due to the structural development such as in-plane orientation and molecular packing6-11). Hasegawa et al.8) reported that the changes in the fluorescence intensity are due to the energy transfer from PAA units to PI units as imidization proceeds. Wachman and Frank11) reported that the fluorescence is a measure of some aspect of the molecular rearrangement between the polyimide chains depending on the curing temperature. Bessonov, et al.13) reported that the interaction between the highest occupied molecular orbital(HOMO) of the amine, bearing a lone electron pair, with the lowest unoccupied molecular orbital(LUMO) of the dianhydride is very important for the imidization reaction since they are closest in energies.

It was reported by the authors14) that in case of BPDA-PDA(p-phenylenediamine) the emission peak is observed at much longer wavelength for BPDA-PDA PAA solution than is for BPDA-PDA as-spun film as well as BPDA-PDA PI film, meaning the formation of tight complexation between solvent, NMP, and PAA. However, such difference in the emission peak wavelength was not clearly observed for BPDA-ODA. The result indicates that the complex between BPDA-ODA PAA and NMP is not tight.

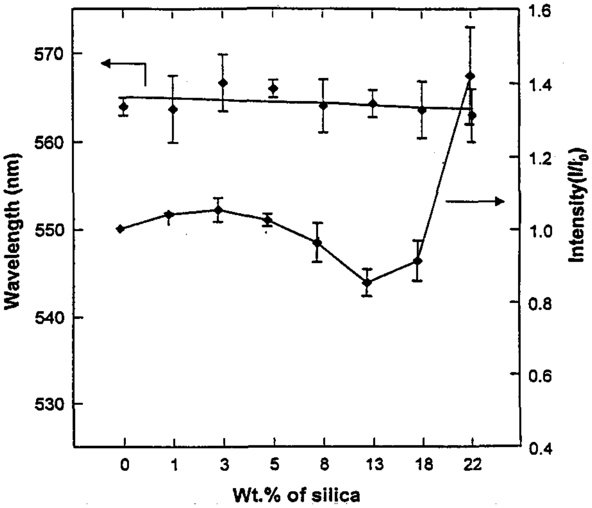


Fig. 3. The effect of silica contents on the emission wavelength and intensity of PI/Silica composite films. The content of silica was calculated assuming that the gel reaction from TEOS to silica was completed.

Brekner and Feger15) reported that imidization is hindered by the complexation, if any. They reported that the hydrogen-bonded complex formed between the solvent NMP and PAA can prevent the reactive groups of the PAA from getting into the conformation required for imidization to occur.

The decomplexation of amic acid from NMP proceeds when the PAA film is exposed at higher temperature, because of decreasing solvent diffusion with degree of imidization. It may be assumed that when the PAA film was soft-baked at 80 °C, several structural changes occur simultaneously and competitively including complexation and/or decomplexation between NMP and amic acid, and molecular ordering of amic acid to imide depending on the degree of imidization as well as solvent removal rate.

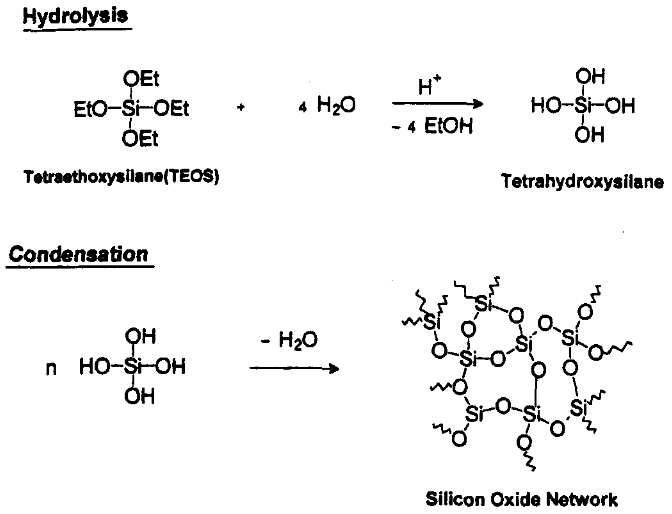


Fig.4. Sol-gel process of TEOS. Hydrolysis and condensation occur simultaneously[12).

Fig. 3 shows the effect of silica contents on the emission wavelength and intensity of PI/Silica composite films. In this figure, the wt. % of silica was calculated assuming that the gel reaction from TEOS to silica was completed. The error bar is the range of intensities for seven measurements. On increasing silica content, the wavelength was not much changed but the intensity slightly decreased except at high silica content.

The results of Fig. 3 suggests that the interaction between PI and silica particles is not strong. The result implies that the intermolecular and/or intramolecular charge transfer from HOMO energy level of ODA to the LUMO of imide (BPDA) is strong enough to hinder the interfacial interaction between the PI and the electron accepting silica. It was reported by the authors[14), however, that the emission maximum of the BPDA-PDA polyimide film was red-shifted with increasing silica contents, meaning that interfacial interaction exists between the PI and silica. The decreasing behavior of the emission intensity with increasing silica contents is due to the reduced population of charge transfer complex in the PI because of the nonfluorescent silica particles.

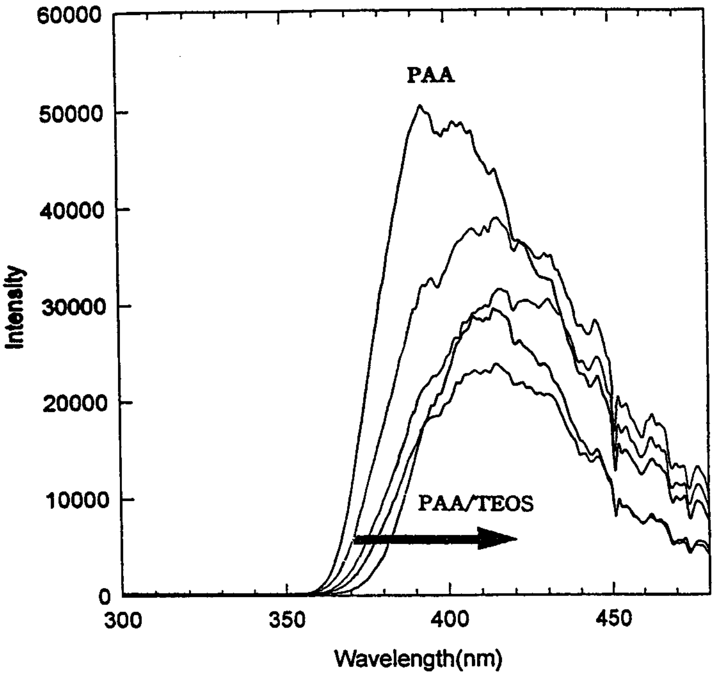


Fig. 5. The excitation spectra of the PAA/TEOS solutions with different TEOS contents. The arrow indicates the increasing TEOS contents. The emission was monitored at 500 nm.

Too many silica particles exhibit some scattering effect because of poor interaction between the PI and silica particles. In Fig.3, the very high emission intensity of the PI/Silica composite film, when the silica content is highest (about 22% of silica), is due to scattering from silica particles.

TEOS is readily hydrolyzed to $Si(OH)_4$ by water in the presence of an acid catalyst such as HCl, as shown in Fig. 4. The hydrolysis reaction is very fast even in the NMP solution of TEOS and PAA. Then the intermolecular hydrogen bonding exists between the hydroxy group in the hydrolyzed TEOS and carboxylic acid in BPDA in PAA systems.

Fig. 5 shows the excitation spectra of the PAA/TEOS solutions with different TEOS contents. In this figure, the emission was monitored at 500 nm. One can see that regardless of the TEOS contents, the wavelength of the excitation peak of the PAA/TEOS solution is red-shifted to the almost same wavelength, when compared to the PAA solution without a catalyst, HCl as well as TEOS.

Since TEOS is readily changed to $Si(OH)_4$ in the presence of a catalyst, the red-shift in the excitation peak is caused by the intermolecular hydrogen bonding between the hydrolyzed TEOS, *i.e.* $Si(OH)_4$ and PAA, regardless of whether the hydrolysis is completely 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. Details on this point are described elsewhere14).

Conclusion

The fluorescence spectroscopic analysis in this work showed that in BPDA-ODA PAA/TEOS solutions, the complexation between NMP and PAA is not tight but the hydrogen bonding between $Si(OH)_4$ and PAA is strong. When PAA solution is imidized to PI films, however, the interfacial interaction between PAA and silica is not strong, though decomplexation takes place during the imidization process and the system has no complexation effect.

In summary, we have observed some interesting fluorescence behavior to give an insight on the interfacial interaction in the polyimide/silica hybrid film, depending on the sample state, whether it is PAA solution, PAA as-spun film or PI film. Further fluorescence studies are now under way to provide more details on the interfacial interaction between poly(amic 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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