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Two-dimensional ATR-FTIR Spectroscopic Study on the Water Diffusion Behavior in Polyimide/Silica Nanocomposite

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To consider the reliability and performance of electronic devices based on polyimide derivatives, dynamic water sorption and diffusion behavior in a polyimide derivative: poly(4'4'-oxydiphenylene pyromellitimide) (PMDA-ODA)/silica nanocomposite was investigated by two-dimensional ATR-FTIR spectroscopy, by which three states of water molecules owning different H-bonding strength were distinguished. The amounts and strength of H-bonding also played a significant role in determining the diffusion rate of the different states of water molecules. The type of aggregated water molecules which also formed H-bonding with silicic acid (residues) or polyimide system was the last one diffusing to the polymer side in contact with the ATR crystal element because the polymeric matrix blocked their diffusion to a great extent. The diffusion coefficient was also estimated to gain the information of the dynamic diffusion behavior.

Key words: Two-dimensional ATR-FTIR spectroscopy, Polyimide/silica nanocomposite, H-bonding

I. INTRODUCTION

Polyimide (PI) derivatives have attracted many research efforts for their potential applications in microelectronics, photonics, optics and aerospace industries, owing to their high thermal stability, excellent mechanical properties, good dielectric properties and high chemical resistance [1]. Among the varied properties of PI derivatives investigated, its water sorption characteristic is one of the most important subjects with regard to the reliability and performance of electronic devices based on PIs, because water causes metal corrosion, failure of the adhesion to metals and degradation of dielectric properties [2]. That is, the detailed investigation of the behavior of the water molecules adsorbed and transported in PI derivatives is very important from the point of view of fundamental study as well as industrial applications. Over the past decades, there have been many studies reporting the water sorption behaviors in PI film, and varied techniques have been applied in the corresponding research work such as gas permeation analysis [3], electro-microbalance [4] and residual stress analysis [5].

A novel technique, two-dimensional (2D) correlation spectroscopy proposed by Noda [6-8], was used in monitoring the dynamic diffusion behavior of water in a PI film. Compared with one-dimensional (1D) spectroscopy, 2D correlation spectroscopy has two obvious advantages in analyzing the spectra intensities shown in the relevant spectra. On one hand, 2D spectrum can distinguish the weak and overlapped bands from

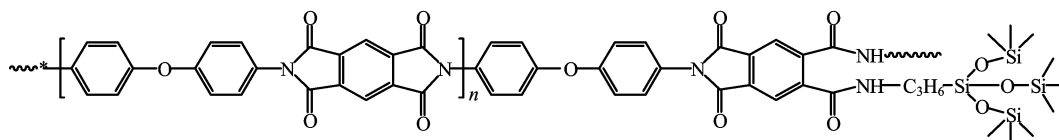
the broad bands in an original 1D spectrum [6]. On the other hand, it can provide information about the sequential order of the intensity change occurred in 1D spectra, which is very important in the explanation of the interactions between varied groups or molecules. Thus, 2D correlation spectroscopy is usually viewed as a useful tool to aid in the interpretation of complex 1D spectra [8].

The stretching vibration mode of O-H as the characteristic band of water was studied by ATR-FTIR spectroscopy in this work. ATR-FTIR is a very common method to study the penetrant diffusion in polymers [9]. The motion sequential order of the varied intensities (O-H stretching) was obtained using 2D ATR-FTIR spectra, which provided some hints of the dynamic behavior of water sorption and diffusion in one PI film.

A PI derivative selected in this work was poly(4'4'-oxydiphenylene pyromellitimide) (PMDA-ODA)/silica nanocomposite (the chemical structure is depicted in Scheme 1). Nanoparticles are usually used as additives for their low melting point, special optical properties, and unusual mechanical properties [10-13]. Silica has been widely used as a kind of inorganic nanoparticle in hybrid composites to reinforce various properties of the matrix polymer, here, the matrix referred to PMDA-ODA [14-16].

For the sake of convenience, the PMDA-ODA/silica nanocomposite studied in this work was simply called PISA. "PI" refers to PMDA-ODA, "S" refers to silica, and "A" refers to γ -aminopropyl-triethoxysilane (APTES), a coupling agent connecting PMDA-ODA and the silica particles. The amounts of silica and APTES in PISA were 20% and 4%, respectively. It is important to note that the role of the coupling agent used here is to improve the compatibility between

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Scheme 1 The chemical structure of PISA.

PI and inorganic phase, control the size of the silica nanocomposite and achieve a much better dispersion of it in the PI network [17].

To summarize, the purpose of this work is to probe the dynamic diffusion behavior of water adsorbed in PISA film by 2D ATR-FTIR spectroscopy.

II. EXPERIMENTS

A. Diffusion measurements by time-resolved ATR-FTIR

All time-resolved ATR-FTIR measurements were carried out at 26 °C using a Nicolet Nexus Smart ARK FTIR spectrometer equipped with a DTGS detector, solid cell accessories, and a ZnSe IRE crystal. The IRE crystal covered by the sample film with a filter paper on it was mounted in an ATR cell, and distilled water was then injected into the filter paper while starting the data acquisition using a macro program. The spectra were collected at a resolution of 4 cm^{-1} with 16 scans. The time interval between two successive spectra was about 40 s. The original measured wavenumber range was 650–4000 cm^{-1} , however, the water diffusion behavior is the key information wanted, only the spectral range 3750–2650 cm^{-1} (O–H stretching mode) of PISA is shown in Fig.1. All the original spectra were baseline corrected using Omnic 5.1 software.

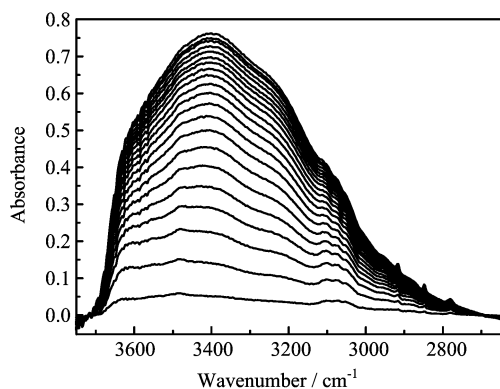


FIG. 1 The infrared spectra of PISA film (the time interval between two successive spectra was about 160 s).

B. Two-dimensional correlation analysis

The infrared spectra chosen for 2D correlation analysis were the subtraction spectra of the wet sample films and the dry film at equal time intervals. The software

for two-dimensional correlation analysis in this is 2D Pocha, composed by Daisuke Adachi (Kwansei Gakuin University). The time averaged 1D reference spectra are at the side and top of the map. In the 2D correlation maps, unshaded regions are defined as the positive correlation intensities, whereas shaded regions are defined as negative ones.

III. RESULTS AND DISCUSSION

A. The states of water molecules

Figure 1 shows the O–H stretching vibration mode of the water molecules pervading the PISA film. For the sake of overloading the figure, the time interval between two successive spectra plotted was about 160 s. It is important to note that we did not stop monitoring the diffusion process until equilibrium was reached. With the increase of the water molecules transported in PISA film, the intensity of the O–H stretching vibration mode increased continuously. Unfortunately, except for a large broad band centered around 3400 cm^{-1} , any detailed information about the dynamic diffusion behavior of water molecules could not be gained.

Therefore, 2D ATR-FTIR correlation spectra first were plotted to distinguish various O–H stretching vibration modes overlapped in the broad O–H band centered around 3400 cm^{-1} in Fig.1. As mentioned above, the subtraction spectra of wet PISA film and dry film at equal intervals were used to perform the 2D IR correlation analysis. Figure 2 (a) and (b) plot the 2D synchronous and asynchronous contour map, respectively. According to the rules of Noda [8], the broad auto-peak centering around 3400 cm^{-1} that appears on the diagonal line in Fig.2(a) suggests that O–H stretching mode of the water molecules had a strong response to the perturbation in the process of the water diffusion, indicating the number of water molecules transported in PISA film increased nonlinearly with elapsed time.

In the 2D asynchronous spectrum, a shoulder band centering around 3236 cm^{-1} shares strong positive asynchronous cross-peaks with bands 3610, 3506 and 3433 cm^{-1} , respectively. And a weak negative cross-peak Ψ (3506/3433 cm^{-1}) is also seen in Fig.2(b). These asynchronous spectral signals mean that at least four O–H stretching modes, three relatively sharp bands at 3610, 3506, 3433 cm^{-1} and a shoulder band centering around 3236 cm^{-1} , were separated precisely from the original 1D overlapped O–H stretching band. Also, some weak asynchronous signals appeared at 2990

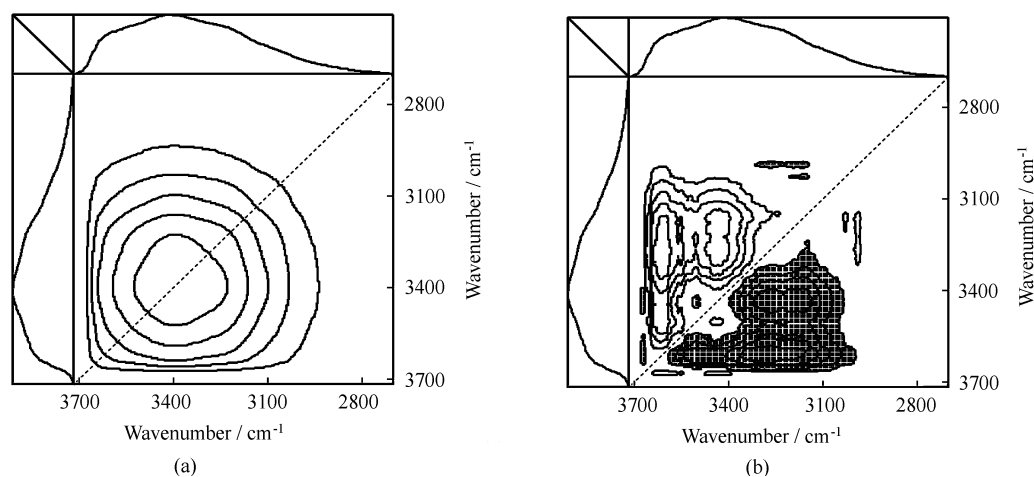


FIG. 2 The 2D (a) synchronous (b) asynchronous infrared spectrum of PISA.

and 3024 cm^{-1} . However, the bands at 2990 and 3024 cm^{-1} are attributed to the C–H stretching mode, and accordingly are beyond our discussion in this work. A more detailed information about them will be given in our next work.

The motion sequential order of these four O–H bands was further investigated by the 2D correlation analysis. The appearance of an asynchronous cross-peak $\Psi(\nu_1/\nu_2)$ illustrates the bands ν_1 and ν_2 vary out of phase with each other according to the rules of 2D correlation spectroscopy [8]. If a synchronous cross-peak $\Phi(\nu_1/\nu_2) > 0$ and $\nu_1 > \nu_2$, a positive asynchronous cross-peak $\Psi(\nu_1/\nu_2)$ indicates that the intensity change at ν_1 occurs predominantly before ν_2 , and a negative one means an opposite behavior. However, if $\nu_1 < \nu_2$, this rule is reversed [6]. For example, in the left triangle of Fig.2(b), $\nu_1 > \nu_2$, the strong positive cross-peak $\Psi(3610/3236\text{ cm}^{-1})$ shows that during the water diffusion process, the intensity of the band at 3610 cm^{-1} changed prior to that of the band at 3236 cm^{-1} , whereas the weak negative cross-peak $\Psi(3506/3433\text{ cm}^{-1})$ suggests that the intensity change of the band at 3506 cm^{-1} occurred slightly later than that of the band at 3433 cm^{-1} . Other cross-peaks also obey this rule. Consequently, by sorting out the temporal relations indicated in the cross-peaks, the motion sequential order of the intensity change of these four O–H stretching bands was: $3610\text{ cm}^{-1} \rightarrow 3433\text{ cm}^{-1} \approx 3506\text{ cm}^{-1} \rightarrow 3236\text{ cm}^{-1}$. It is of particular note that the negative asynchronous cross-peak $\Psi(3506/3433\text{ cm}^{-1})$ was so weak that in this sequential order, the occurrence of the intensity change of the bands at 3433 and 3506 cm^{-1} under the external perturbation was observed at almost the same time.

According to the literature [18–21], the O–H stretching vibrations in water are predicted to exhibit sequential red shift with the increasing strength of the hydrogen bond. Thus, the band at 3610 cm^{-1} could be attributed to the water molecules without H-bonding, and

in this work, it was simply called “free water”. (In fact, this kind of water interacts with each other with very weak hydrogen bonding; the hydrogen bond is so weak that this kind of water behaves just like free water.) The band at 3236 cm^{-1} indicates the water molecules aggregated with strong H-bonding, and the other bands indicate the water molecules clustered with moderately strong H-bonding. In the ATR-FTIR experiment, the ZnSe IRE crystal (ATR element) only monitored the water molecules diffusing to the polymer side in contact with the crystal, thus the above-mentioned sequential order means that in the water diffusion process in PISA membrane, the diffusion rate of “free water” was faster than that of the aggregated water, and water molecules aggregated with the strongest H-bonding was the last one monitored by the ATR crystal element. It should be noted that in this work, the H-bonding referred to several formations: H-bonding formed between the water molecules; H-bonding formed between water molecules and silicic acid (residues); and H-bonding formed between water molecules and PI system.

Due to the large volume of the aggregated water molecules, it is reasonable to think that in the polymeric matrix, the aggregated water had significantly lower diffusivity than the “free water”. As for the aggregated water molecules which also formed H-bonding with silicic acid (residues) or PI system, the polymeric matrix blocked the diffusion of them to a great extent, leading to this state of water being the last one diffusing to the polymer side in contact with the ATR crystal element. In a word, the polymeric system (PISA) induced the adsorption of water molecules, but blocked the further diffusion of them.

B. Estimation of diffusion coefficient

The amounts of water molecules in PISA and the corresponding diffusion coefficient was further estimated.

The Fickian equation was used to calculate the diffusion coefficient of water from ATR-FTIR spectra [9].

$$\frac{A_t}{A_\infty} = 1 - \frac{8\gamma}{\pi[1 - \exp(2L\gamma)]} \cdot \sum_{n=0}^{\infty} \left\{ \frac{\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right]}{(2n+1) \left[4\gamma^2 + \left(\frac{(2n+1)\pi^2}{2L}\right)^2\right]} \cdot \left[\frac{(2n+1)\pi}{2L} \exp(-\gamma 2L) + (-1)^n 2\gamma\right] \right\} \quad (1)$$

In the equation, A_t is the absorbance of O–H stretching band at time t , A_∞ is the absorbance at equilibrium, γ is the penetration depth of the evanescent wave, L is the thickness of the PISA film (15 μm , invariable), and D is the diffusion coefficient. D was calculated by a nonlinear curve fitting to the equation. Two new parameters: a and m are defined as follows: a is the zero correction parameter, m is the equilibrium water uptake (it corresponds to A_∞). The fitting curve and results are shown in Fig.3. The fitting results was $a = -1.96831$, $D = 2.7604 \times 10^{-9} \text{cm}^2/\text{s}$, $m = 1159.5205$, $L = 15 \mu\text{m}$. This method was very convenient to estimate the diffusion coefficient.

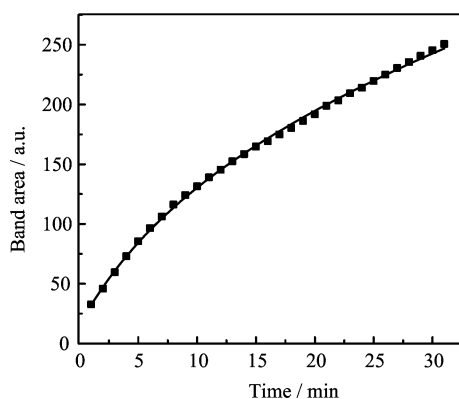


FIG. 3 The fitting curve of sorbed water in PISA.

IV. CONCLUSION

Two-dimensional ATR-FTIR correlation spectroscopy was applied to investigate the dynamic diffusion behavior of water molecules transported in the PMDA-ODA/silica nanocomposite. 2D correlation analysis illustrated that at least three states of water molecules with different strengths of hydrogen-bonding pervading the polymeric matrix. The amounts and strength of H-bonding played a significant role in determining the diffusion rate of the different states of water molecules. The diffusion coefficient of water molecules

was also calculated by a nonlinear curve fitting to the Fickian equation to gain some dynamic diffusion information. This work provided some suggestions in designing and optimizing the PI derivatives used in the microelectronics industry.

V. ACKNOWLEDGMENTS

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