Water diffusion into epoxy resin: a 2D correlation ATR-FTIR investigation

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Abstract

The water diffusion process in a novolac epoxy resin (EP) was studied by 2D ATR-FTIR spectroscopy, the originally broad water OH bands in 1D-IR spectra can be effectively differentiated into three bands, located at 3610, 3460 and 3240 cm⁻¹, respectively. The bands at 3460 cm⁻¹ (antisymmetric) and 3240 cm⁻¹ (symmetric) are assigned to the OH stretching vibration of water fully hydrogen-bonded with other water molecules, while the 3610 cm⁻¹ band could be attributed to the stretching vibration of water partially hydrogen-bonded with epoxy resin. The mechanism of the water diffusion process in EP is also discussed.

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1. Introduction

Epoxy resins constitute a class of polymeric materials that are of significant technical relevance and are widely used in the microelectronics industry as the workhorse encapsulant and underfill agent in the mounting of chip assemblies to the printed circuit board. Furthermore, the printed circuit board itself is generally an epoxy/glass-fiber composite. However, in most application the epoxy-based component has the potential of being exposed to moist conditions or a humid environment. Absorbed moisture has deleterious effects on the physical properties of epoxy resins. The property of polymer surface bound water is different from that of bulk water due to its restricted motion [1] and is of great importance in many areas such as food packaging, protective clothing or separation membranes. The physical properties of polymers depend on a series of factors, one of the most important being their ability to absorb small molecules such as water. The absorbed water molecules change the melting and/or glass transition temperatures of the polymers and strongly influence their mechanical and electrical properties. Therefore, a good understanding of the transport mechanism of water in polymer is important for the selection of polymer materials and the tailoring of the properties of the films (both bulk and surface).
A number of experimental techniques have been used to study the diffusion process of small molecules in a polymer film by monitoring either the release from, uptake into, or permeation through the polymeric material. Besides the traditional gravimetric techniques, a great amount of work has been published using spectroscopic techniques to characterize the property of bound water, such as light scattering [2], neutron scattering [3], NMR [4], and FTIR and Raman spectroscopy [5,6]. Among the available spectroscopic methods, the usefulness of Fourier transform infrared spectroscopy has increasingly been demonstrated in recent years. Changes of frequency, intensity, and shape of the water-related bands have been interpreted in terms of bound and free water (up to four different water species in some systems), water clustering, water orientation, and water networking. However, the use of transmission mode in the infrared spectroscopy to measure the permeation of water through polymeric materials suffers from the problem of the unfavorably strong water absorptions in this spectral region. Therefore, the attenuated total reflection (ATR) method has been proposed for this purpose.

As a technique sensitive to the interaction between water and polymer, ATR-FTIR spectra have been quickly developed for studying the water diffusion behavior [7–11]. However, despite the apparent ease and rapidity of measuring FTIR spectra of water, the analysis of the spectra is not always straightforward and presents many problems. FTIR spectroscopy combined with some computational methods for resolution enhancement in OH bands has been pointed out as a powerful technique in water structure analysis. The earliest such methods proposed were second-derivative (SD) and Fourier self-deconvolution (FSD) [12,13]. The major improvement over previous methods has been achieved by introducing generalized 2D correlation spectroscopy to the studies [14].

The basic concept of constructing 2D IR spectra for perturbation-induced, time-dependent fluctuations of IR signals was first introduced by Noda [15]. A simple cross-correlation analysis was applied to sinusoidally varying dynamic IR signals to construct a set of 2D IR correlation spectra [16]. Later, Noda proposed a more generally applicable mathematical formalism, which allows to construct 2D correlation spectra from any transient or time-resolved variations of spectra having an arbitrary waveform [17]. This generalized 2D correlation spectroscopy was found to be applicable to intensity fluctuations not only in time but also of any other physical or chemical variable, such as temperature, pressure, electric field strength or concentration. Thus, it offers the possibility to study the dependence of vibrational spectra on any external perturbation in much greater detail than has previously been possible. Owing to the enhancement of the spectral resolution by spreading the peaks over the second dimension, it is possible to identify the spectral features not readily observable in the original data set [15–17]. Additionally, 2D correlation spectra include information about the relative rate of the spectral intensity changes taking place in the course of the perturbation [15] for different molecular functionalities.

2. Experimental

Time-resolved ATR-FTIR measurements of an epoxy resin (EP hereafter) film were performed at 24 °C using a Nicolet Nexus Smart ARK FTIR spectrometer equipped with a DTGS-KBr detector, solid cell accessories, and a ZnSe IRE crystal. The spectra were measured at 4 cm⁻¹ resolution and eight scans; the wavenumber range was 650–4000 cm⁻¹. The film-covered IRE crystal with a filter paper above the sample film was mounted in an ATR cell, and the spectra of the dry film was collected as background spectra; then without moving the sample, distilled water was injected into the filter paper while starting the data acquisition by a macro program. The 2D correlation analysis was performed using the software ‘2D Pocha’ composed by Daisuke Adachi.

3. Results and discussion

The O–H vibrational modes of liquid water lead to a very complicated vibrational spectrum,
complicated by both intermolecular and intramolecular hydrogen bonding. The fundamental stretching vibrations and the in-plane bending mode of water occur within the 3900–2800 cm\(^{-1}\) region and at around 1640 cm\(^{-1}\). Our discussion will focus on the 3900–2800 cm\(^{-1}\) spectral region, where the peaks are considerably more intense. In addition, more information about hydrogen bonding is expected from the analysis of the spectral region characteristic of the O–H stretching vibrations. A difficulty encountered in the analysis of these spectra arises from the fact that the spectrum of water in the 3900–2800 cm\(^{-1}\) region is superimposed onto a broad absorption band associated with the multiplicity of hydrogen bonding interactions of OH groups in the polymer network. The ATR-FTIR spectrum of pure water and time-evolved spectra for water diffusion into an EP resin in the spectral range 3900–2800 cm\(^{-1}\), are reported in Fig. 1. The major difference that is noted in the spectra as a result of the absorption of water is an increase in intensity of the broad \(\nu(\text{OH})\) band at about 3450 cm\(^{-1}\). For comparison, the FTIR-ATR spectrum of pure liquid water collected with the same IRE along with the spectrum of epoxy film exposed to water indicate that the broad OH stretching in pure liquid water centered at about 3400 cm\(^{-1}\).

The asynchronous correlation spectra of water in EP in the spectral range 2800–3700 cm\(^{-1}\) were shown in Fig. 2. The existence of three asynchronous crosspeaks (3610/3460, 3610/3240, 3460/3240 cm\(^{-1}\)) indicates that the wide water vibration band in the spectral region 3200–3800 cm\(^{-1}\) is split into 3 separate bands located at around 3610, 3460 and 3240 cm\(^{-1}\), which overlap in the 1D IR spectra. The two components at 3240 and 3460 cm\(^{-1}\) are believed to correspond to the absorbance from the strongly hydrogen-bonded and less strongly hydrogen-bonded hydroxyl groups that exist in liquid water, respectively [18]. The 3610 cm\(^{-1}\) band could due to a small population of water hydrogen bonded with epoxy resin (water–EP hydrogen bond). As the concentration of water in the polymer increases, this high wavenumber feature (3610 cm\(^{-1}\)) becomes less pronounced (the reason will be explained later). If we compare the peak locations of the hydrogen bonded component OH bands of the water in epoxy film and the pure water, the peak positions for the water in epoxy film are approximately 50 cm\(^{-1}\) higher than that for pure liquid water, respectively. Both the increase of the high wavenumber feature (3610 cm\(^{-1}\)) and the positive shift of the water–water hydrogen bonded OH stretching bands are indicative of the weakening water–water hydrogen bonding of the

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Fig. 1. Time-dependent ATR-FTIR spectra of pure water and sorbed water in EP.

Fig. 2. Asynchronous 2D correlation IR spectra of EP in the spectral range 2800–3700 cm\(^{-1}\).
water molecules in the epoxy film versus that of pure liquid water. The sign of asynchronous correlation peak \( v_1/v_2 \) gives information about the sequential order of intensity changes between band \( v_1 \) and band \( v_2 \). According to Noda [17], if \( v_1 > v_2 \), and the sign of the asynchronous band \( v_1/v_2 \) is positive (unshaded area), band \( v_1 \) will vary prior to band \( v_2 \), while the negative asynchronous band (shaded area) implies the opposite phenomena. According to this rule, the positive asynchronous bands at 3610/3240 and 3460/3240 cm\(^{-1}\) in the left upper triangle reveal that the change of the population of the high wavenumber feature (3610 cm\(^{-1}\)) and the weak hydrogen bonded OH species (3460 cm\(^{-1}\)) occur earlier than the change of the population of the strong hydrogen bonded OH-species (3240 cm\(^{-1}\)); while the negative 3610/3460 cm\(^{-1}\) band suggests that the 3460 cm\(^{-1}\) band varies prior to the 3610 cm\(^{-1}\) band.

During the diffusion process, water molecules may form hydrogen bond with epoxy resin, consequently, some of the water–water hydrogen bonds have to be compromised. The positive shift in the OH stretching band is an indication of the interactions between water molecules and the carbonyl oxygen in the epoxy matrix and thus a weakening of the water–water hydrogen bonding. In the early stage of the water diffusion, water molecules are surrounded by the epoxy resin and have more possibility to form water–EP hydrogen bond, therefore, the population of the 3610 cm\(^{-1}\) band is relatively high. However, different aggregates of water are assumed in a dynamic equilibrium, the increase of the 3610 cm\(^{-1}\) population (water hydrogen bonded with EP) occurs only after the weak hydrogen bonded water permeated into the EP bulk and partly dissolved, that is the reason why the 3460 cm\(^{-1}\) band varies prior to the 3610 cm\(^{-1}\) band.

As the water concentration increases, the equilibrium gradually shifts back in favor of more water–water hydrogen bond versus the water–EP hydrogen bond and the high wavenumber feature (3610 cm\(^{-1}\)) becomes relatively less pronounced. At the later stage of diffusion, the confined structure of the EP resin presumably limits the movement of water molecules and forces the water molecules to form cluster (stronger hydrogen bonded) with other water molecules, the relative population of the 3240 cm\(^{-1}\) band begins to increase.

### 4. Conclusion

A 2D ATR-FTIR spectroscopic study on the water diffusion process in an epoxy resin has been carried out to study the complex mechanism of water diffusion process in an epoxy resin. The originally broad water OH bands in 1D-IR spectra can be effectively differentiated into three bands, 3610, 3460 and 3240 cm\(^{-1}\). From the asynchronicity between these bands, following sequences of spectral changes can be derived: 3460 cm\(^{-1}\) (weak water–water hydrogen bonded) > (earlier than) 3610 cm\(^{-1}\) (water–EP hydrogen bonded) > (earlier than) 3240 cm\(^{-1}\) (strong water–water hydrogen bonded).

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