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Characterization of Interaction of Water in Epoxy by UV Reflection Spectroscopy

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ABSTRACT: Water uptake in diglycidyl ether of butanediol (DGEB) epoxy cured with 4,4′-diaminodiphenyl sulfone (DDS) was studied using UV reflection spectroscopy. There is a progressive shift to longer wavelength of approximately 13 nm for the DDS reflection peak at 338 nm upon exposure to water, apparently due to hydrogen bonding of water to DDS through the SO_2 group. The fraction of hydrogen-bonded DDS through SO_2 with water was estimated by spectral deconvolution, and subsequently the fraction of hydrogen-bonded water to DDS through SO_2 was obtained. When the epoxy is saturated with water containing 9 wt % of epoxy, the SO_2 group in DDS is fully hydrogen bonded, while 32% of absorbed water is hydrogen bonded to the SO_2 group of DDS. Since hydrogen bonding of water to the tertiary amino group of DDS does not show up in UV reflection spectra, the fractions of hydrogen-bonded water are smaller than the values published recently by NIR studies, which account for both types of hydrogen-bonded water.

Introduction

Epoxy resins are the main matrix resins used for high-performance composites and adhesives and coatings for high-temperature performance. A major problem with epoxy resins is the water absorption from a humid environment, which has detrimental effects on its physical properties such as mechanical[1] and dielectric properties.[2]

Water sorption has been studied by various characterization techniques such as IR,[3] NIR,[3] NMR,[4] dielectric,[2] and dynamic mechanical techniques.[2] These studies suggest that sorbed water is made up of two species: (1) water bound to epoxy by hydrogen bonds and (2) small clusters of water presumably going into microvoids.

In a recently published paper based on NIR studies, approximately 30% of water is found to be hydrogen bonded to a diamine curing agent even during early stages of water uptake. It reaches up to 40% at equilibrium uptake,[3] apparently without disturbing the hydrogen-bonded epoxy network. On the basis of careful NIR studies, Musto et al. proposed that water can form hydrogen bonds with either the tertiary amino group or the SO_2 group of the curing agent, 4,4′-diaminodiphenyl sulfone (DDS). Characterization of water in polymers in terms of bound water vs unbound clusters is important since bound water in the polymer matrix rather than the total amount of water uptake is expected to lower the T_g of the polymer.[5]

It is important to develop other analytical methods to compare with the results of the NIR spectroscopic technique and to offer other advantages that are difficult to achieve by NIR, such as in-situ characterization capability. In this study, a UV reflection spectroscopic technique is demonstrated as such a method. While NIR looks at the water molecules in epoxy, UV spectra show changes in epoxy structure due to its interaction with water.

It is well-known that UV spectra are very sensitive to solvent polarity.[6] Absorption due to the $\pi \rightarrow \pi^*$ transition usually exhibits a red shift to longer wavelength while the weak absorption due to the $\pi \rightarrow \pi^*$ transition shows a blue shift to shorter wavelength, with increasing polarity of the solvent. When hydrogen bonding is formed between solute and solvents such as water or alcohol, even greater spectral shifts have been observed in the UV spectral region for the $\pi \rightarrow \pi^*$ transition with water producing the largest red shift.[7a] We will take advantage of such a shift in this study when epoxy absorbs water.

Epoxy resins contain high concentrations of intrinsic UV chromophores, making UV transmission spectra difficult to obtain except for very thin (<1000 Å) samples. For thick films, coatings, or composites, the UV external reflection technique is useful, since it probes in the range of a few hundred angstroms[8] and thus is not affected by the coating substrate or reinforcing fiber in composites. We have demonstrated the use of UV reflection spectroscopy for cure monitoring in epoxy networks as well as imidization monitoring in polyimides based on the spectral shifts of curing agents and imide/amic acid deconvolution, respectively.[9a] In-situ cure monitoring in epoxy composites was also reported by using bifurcated fiber-optic attachment for UV reflection.[9b]

In this paper, we will report on the water sensitivity of UV reflection spectroscopy to characterize the interaction of water in epoxy films. On the basis of spectral deconvolution, we estimate the fraction of hydrogen-bonded DDS through the SO_2 group and, subsequently, the fraction of hydrogen-bonded water to the SO_2 group of DDS.

Experimental Section

Moisture Absorption Measurements. A stoichiometric mixture of diglycidyl ether of butanediol, DGEB, and DDS was cured at 160 °C for 3 h and showed complete cure by the IR and UV reflection technique.[9] DGEB−DDS epoxy film with about 1 mm thickness was cut into 1.5 in. square pieces and immersed in a sealed deionized water flask. At specific time intervals, the films were removed from the water and quickly dried with a cloth, and the weight was measured with a Mettler AE 200 balance.

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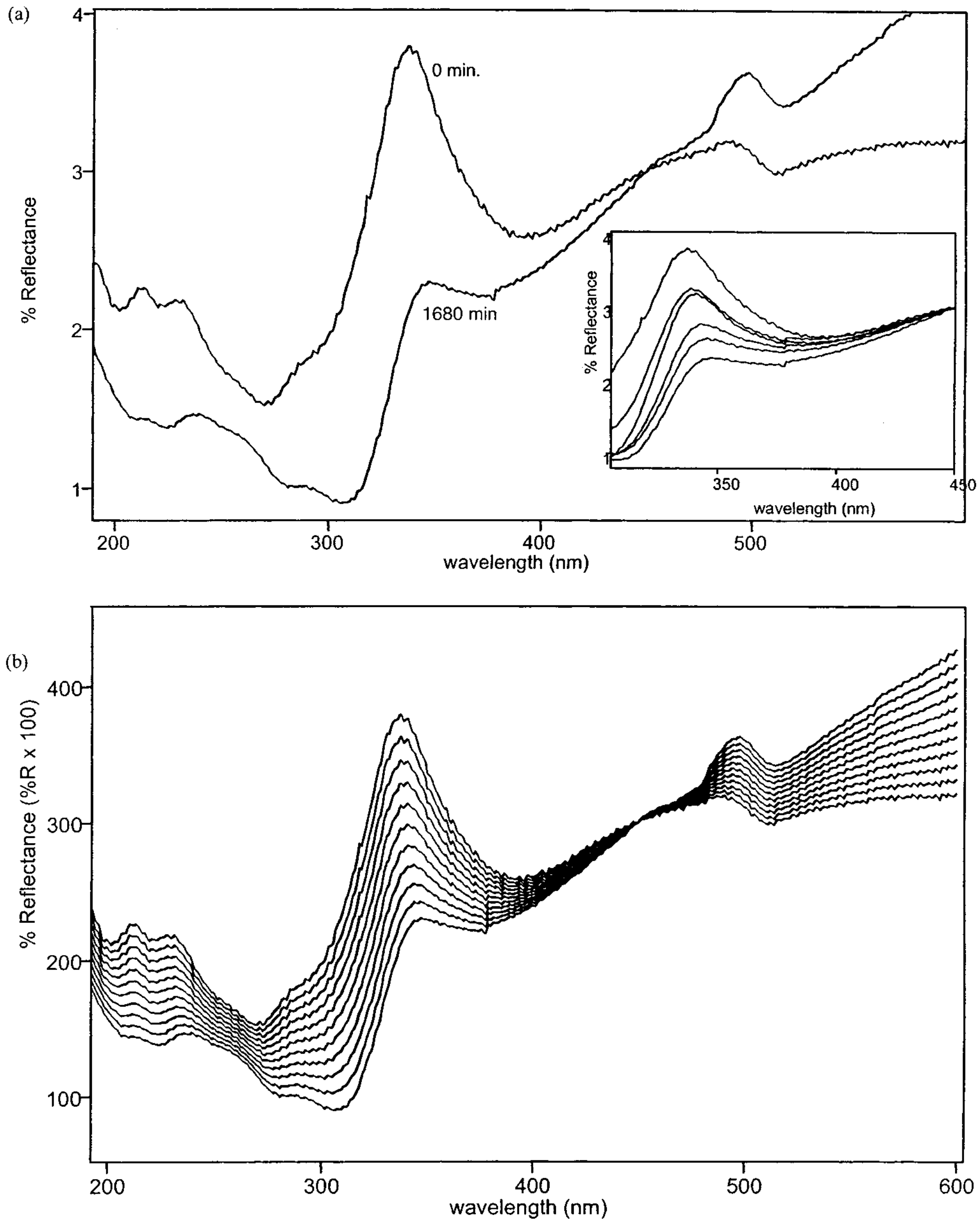

Figure 1. (a) UV reflection spectra of DGEB/DDS epoxy as a function of immersion time in water at room temperature (inset: $t = 0$, 30, 90, 360, 540, and 1680 min from top to bottom). **(b)** Simulated mixture spectra of 0% and 100% H-bonded DDS (0% H-bond/100% H-bond: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100 from top to bottom).

UV Reflection Measurements. After measuring the weight, UV reflection spectra were taken on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer with a specular reflection accessory which has a 6° angle of incidence. Simulated spectra and spectral deconvolution were performed using PLSPlus/IQ software from Galactic, Inc.

Results and Discussion

Figure 1a shows the changes in the entire UV reflection spectra of DDS cured diepoxide, diglycidyl ether of butanediol (DGEB) at $t = 0$ and $t = 1680$ min of water immersion. There are three main peaks visible, the predominant one located at 338 nm. The peak at 338 nm is due to the tertiary amine form of DDS,[9] which is obtained after reaction with DGEB. DGEB does not contribute in this spectral region. As seen in the inset to Figure 1a, with increasing water immersion time, the peak at 338 nm is progressively red-shifted to longer wavelengths up to 13 nm after 1680 min of immersion in water, with reduced reflectance that is expected due to the decreased extinction coefficient observed in $\pi \rightarrow \pi^*$ transitions in polar enviroment.[10] Since this peak shows the greatest sensitivity to water sorption, we will use it to analyze the water uptake in epoxy. The spectra as well as weight gain (9 wt %) changes little beyond this immersion time. Furthermore, room temperature drying which results in 40% loss of water does not change the spectra. Since H-bonded water is expected to be more difficult to remove than unbound water,[3] we will assume the spectra after 1680 min of water immersion to be that of H-bonded DDS.

We have attempted to approximately determine the fraction of DDS H-bonded with water. In a stoichiometric mixture of epoxy, 2 mol of DGEB (404 g) reacts with 1 mol of DDS (248 g). At 9 wt % of water uptake (59 g), as observed after 1680 min, there is approximately 3.2 mol of water for 1 mol of DDS in the cured epoxy. Musto et al. have found by NIR that ~40% of water is H-bonded to DDS at equilibrium, meaning that 1.3 mol

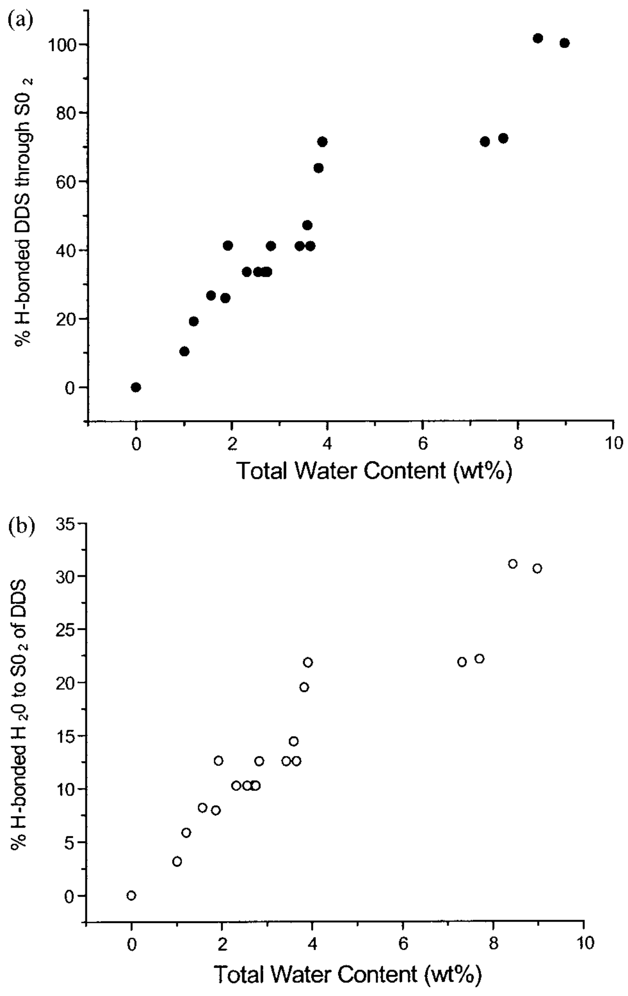

Figure 2. (a) Plot of % H-bonded DDS through SO_2 group as a function of total water content obtained after spectral deconvolution of Figure 1. **(b)** Plot of H-bonded water to SO_2 group of DDS calculated from data in (a). (The error in these values is about 5%.)

of water is H-bonded to 1 mol of DDS at equilibrium water uptake. Since water can form H-bonds with either the tertiary amino group or the SO_2 group of DDS, it is reasonable that there is an excess molar amount of H-bonded water in comparison to the amount of H-bonded DDS. It was shown by Ungnade that electron-withdrawing substituents such as SO_2 would produce a large red shift in water, while electron-donating substituents on benzene such as tertiary amino group would not.[7b] Thus, the lower spectrum in Figure 1a is likely to represent that of H-bonded DDS through SO_2. For nonbonded DDS, we can use the spectrum of epoxy prior to immersion in water (the top spectrum in Figure 1a). Using these two spectra, we generated the mixture spectra for different ratios of free vs H-bonded DDS through SO_2 as shown in Figure 1b. These simulated spectra exhibit similar spectral shifts as observed in Figure 1a. Therefore, we may deconvolute the spectra assuming a mixture of two species. The experimental spectra in Figure 1a were deconvoluted in order to estimate the fraction of H-bonded DDS through SO_2 as a function of immersion time, as illustrated in Figure 2a. We note that there is a sharp increase in the fraction of H-bonded DDS through SO_2 during the initial exposure to water, followed by a more gradual increase until the 100% H-bonded fraction is reached.

From these results, we can attempt to calculate the fraction of water which is H-bonded to the DDS through the SO_2 group. According to Musto et al.,[3] one water molecule forms double hydrogen bonds with one SO_2 group. Therefore, the mole fraction of H-bonded DDS through SO_2 group, x_{DDS}, obtained from Figure 2a will be the same as the number of moles of H-bonded water to the SO_2 group of DDS, x_{H_2O}, in a stoichiometric epoxy containing 1 mol of DDS.

$$x_{H_2O} = x_{DDS} \tag{1}$$

The fraction of H-bonded water to SO_2 group of DDS, X_{H-bond,H_2O}, can then be easily calculated as follows:

$$X_{H-bond,H_2O} = \frac{(x_{H_2O})(m_{H_2O})}{w_{H_2O}} \tag{2}$$

where m_{H_2O} is the molecular weight of water and w_{H_2O} is the total weight of water absorbed (59 g) for a stoichiometric epoxy with 1 mol of DDS. Figure 2b shows a plot of the weight fraction of H-bonded water to the SO_2 group of DDS according to eq 2. We can compare these values of H-bonded water in epoxy to those recently published by Musto et al. by NIR studies.[3] The first thing noticed is that the total water content in our epoxy films is greater (by ~2%) than that found by Musto et al.,[3] due to the aliphatic epoxy used in our study compared to their tetrafunctional aromatic epoxy (TGDDM). They also observed a quick rise in percent hydrogen-bonded water (32%) at an early stage of water uptake (>1%), while we observe more gradual increase. Additionally, we find that the fraction of H-bonded water at saturation is about 32%, which is less than seen by Musto et al.[3] Since NIR measurement includes water H-bonded to the amino group as well as to the SO_2 group of DDS, it is reasonable that our value which results mainly from H-bonded water to the SO_2 group of DDS is lower.

Conclusion

Through this study, we have demonstrated the effectiveness and sensitivity of UV reflection spectroscopy in water sorption studies. By taking advantage of the spectral changes that occur during water sorption, we can estimate the fraction of H-bonded DDS through SO_2 as well as H-bonded water to SO_2 group of DDS in the epoxy system. From here, we can apply this technique to other polymers, such as polyimides, as well as composites based on these systems. Additionally, and most importantly, we can then use a bifurcated fiber-optic attachment for UV reflection[9b] to monitor water sorption in situ.

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