Analysis of the Correlation between Optical Transmission Loss and Weight Loss of Thermally Deteriorated Epoxy Resins Using Near Infrared Spectroscopy

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ABSTRACT: The correlation between the optical transmission loss and the weight loss of thermally deteriorated epoxy resins was analyzed using near infrared (NIR) spectroscopy. Using three types of acid anhydride cured epoxy resins, the optical transmission losses at 850 nm of each resin and their weight losses were measured during the accelerated heating tests. At longer heating times the color of each resin darkens and its weight decreases, i.e., the values of the optical transmission loss and the weight loss are both increasing gradually. Both of tendencies are similar in magnitude, and the optical transmission loss of each resin has a good correlation with its weight loss. It is postulated that the cross-linking was increased in the resin by the thermal oxidation reaction, and that the simultaneous elimination reaction occurs from the surface. As the thermally oxidized structure is more conjugated, the optical transmission loss is increased in the shorter wavelength region, and thus theoretically, one can predict the weight loss of the thermally deteriorated epoxy resins non-destructively by measuring the optical transmission loss using NIR. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 14–19, 2000

Key words: optical transmission loss; thermal deterioration; weight loss; epoxy resin; near infrared

INTRODUCTION

In electric equipment, many types of epoxy resins with superior thermal stability are used as insulating materials and adhesives.[1] These resins are exposed to a variety of stresses that can deteriorate their physical properties during long-term use. Such stresses include temperature, voltage, mechanical, and/or environmental force. In particular, thermal stress affects both the weight and the mechanical strength of a resin significantly, and generally thermally deteriorated resins darken in color. The main cause of darkening is the increase of the electronic transition absorption α_e due to thermal oxidation of the resin.[2] The α_e spectrum has a peak in the ultraviolet (UV) range, and decreases exponentially with increasing in wavelength.[3] We have been investigating the spectroscopic properties of thermally deteriorated resins, and have devised a method to evaluate the extent of deterioration of a resin by measuring the tail absorption of the α_e spectrum in the visible (VIS) to the near infrared (NIR) range quantitatively.[4,5] For transparent materials, the deterioration can be evaluated via the transmission method using the optical transmission loss per unit optical path length,[4] and for opaque ones, it can be evaluated via the reflecting method.[5] Furthermore, the residual life of a resin can be predicted theoretically for each technique based on chemical kinetics.
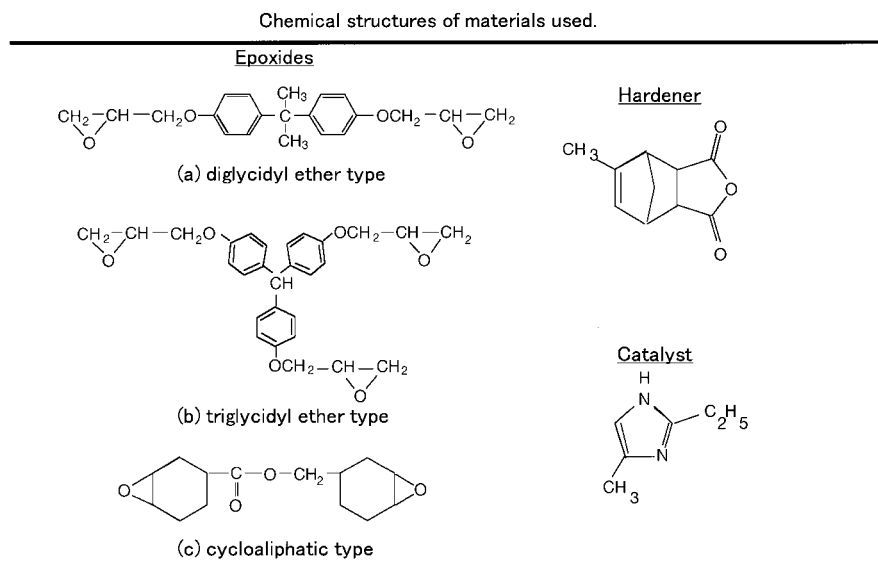
Scheme 1

In this paper, the correlation between the optical transmission losses per unit optical path length at 850 nm and the weight losses of three types of thermally deteriorated epoxy resins were analyzed using NIR spectroscopy.

EXPERIMENTAL

Materials and Preparation

Scheme 1 shows the chemical structures of the materials used. Methyl nadic acid anhydride is used as a hardener, and (a) the diglycidyl ether of diphenyl propane (i.e., bisphenol A type epoxide), (b) the triglycidyl ether of tris(hydroxyphenyl) methane, and (c) a cycloaliphatic epoxide are used as epoxides. Cured resins were obtained by mixing and heating a mixture of the epoxide, hardener, and 0.5 wt % of 2-ethyl-4-methylimidazole as a catalyst. The equivalent ratio of (acid anhydride)/(epoxide) is 0.95. Cure conditions of the resins was 175°C for 4 h, and the average thickness of the obtained resin plates was about 2 mm.

Measurement of Weight Loss

Weight losses of the resin plates were measured using sample pieces of approximately 25 mm × 15 mm × 2 mm in size. After vacuum drying at 110°C for 8 h, the control weight w_0 (g) was measured. The sample was then heated in the oven, and at an arbitrary time the sample weight w (g) was measured. The percentage weight loss of the thermally deteriorated sample is calculated by eq. (1):

$$\text{Weight loss} = 100 \cdot (w - w_0)/w_0 \qquad (1)$$

Measurement of Optical Transmission Loss

Optical transmission losses of the epoxy resins were calculated from the absorbance of the sample plates using a spectrophotometer (Hitachi, Ltd.; 330 type) in the 600–2000 nm wavelength range. The optical transmission loss α_λ (dB/mm) at the wavelength λ (nm) by a unit optical path length (1.0 mm) was calculated from eq. (2)[4]:

$$\alpha_\lambda = 10 \cdot A'_\lambda = 10 \cdot A_\lambda/t \qquad (2)$$

where A_λ is the absorbance at λ (nm), t (mm) is the thickness of the resin plate, and $A'_\lambda = A_\lambda/t$. Using α_λ per unit optical path length ensures that the same values can be obtained when the extent of deterioration of samples are equal, even if their thickness is different.

Measurement of Dynamic Viscoelasticity

Using a dynamic mechanical analyzer (DMA) (Rheology Engineering, Co.; DVE Rheospectror DVE-V4 type), the temperature dependence of the storage modulus (E′), loss modulus (E″), and mechanical loss tangent (tan δ) were measured by a
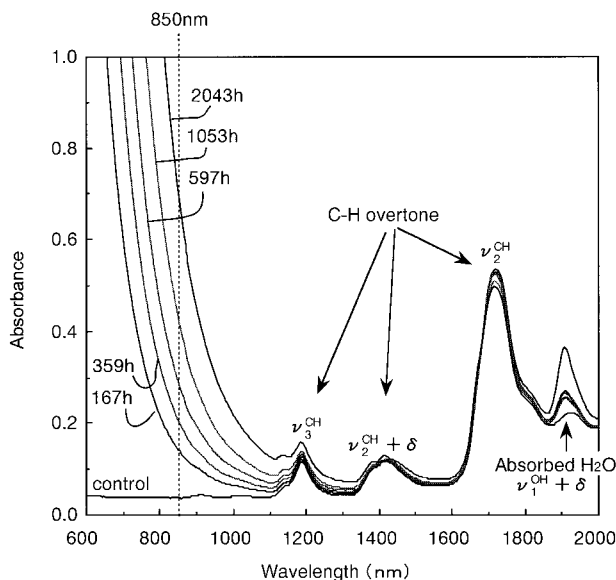
Figure 1 Absorbance spectra of thermally deteriorated epoxy resin (diglycidyl ether type (a)) heated at 180°C in air.

tensile vibration test. Samples were rectangular strips of approximately 25 mm × 5 mm × 2 mm in size, and the employed vibrational frequency was 10 Hz on a longitudinal direction. The heating rate was 2°C/min in an atmosphere.

RESULTS AND DISCUSSION

Spectra Change of Thermally Deteriorated Epoxy Resins

Figure 1 shows the absorbance spectra of a thermally deteriorated epoxy resin (diglycidyl ether type, (a)), using a heating temperature of 180°C. As the heating time is increased, absorbance increases exponentially at the shorter wavelength, but little change was observed over 1300 nm. The spectral changes for the other epoxy resins are similar to that of Figure 1. The wavelength dependence in the shorter wavelength range of the absorbance spectra is called the Urbach rule[6] and is given by eq. (3):

$$\alpha_e = Ao \cdot \exp(Bo/\lambda) \tag{3}$$

where α_e is an electronic transition absorption loss, Ao and Bo are material constants, and λ (nm) is the wavelength.[3] The main contributor to the absorbance spectra of resins is the α_e in the VIS wavelength range, which is caused by the

presence of the specific chemical double bonds. Typically there are two kinds of electronic transition absorptions, those due to the $\pi \rightarrow \pi^*$ transition of the carbon-carbon double bond (C=C), and those due to the n$\rightarrow \pi^*$ transition of the carbonyl group (C=O). It is theorized that for the thermally deteriorated resins, as the cross-linking densities increase due to thermal oxidation reactions, the extent of conjugation in the compounds is also increased, and that α_e thus increases exponentially according to eq. (3). The increasing absorption peaks around 1900 nm are due to absorbed water, which is independent of thermal deterioration, that is the combination tone ($\nu_1^{OH} + \delta^{OH}$) of the fundamental stretching vibration (ν_1^{OH}) and the bending vibration (δ^{OH}) of O-H bond. The stable absorption peaks at 1200, 1400, and 1700 nm are due to higher harmonics of C-H molecular vibration. To be exact, the absorption at 1700 nm is the second overtone of stretching vibration (ν_2^{CH}) of C-H bond, the absorption at 1400 nm is the combination tone ($\nu_2^{CH} + \delta^{CH}$) of the second overtone of stretching vibration (ν_2^{CH}) and the bending vibration (δ^{CH}) of C-H bond, and the absorption at 1200 nm is the third overtone of stretching vibration (ν_3^{CH}) of C-H bond.[7,8] It is significant, however, that the color change of the resins cannot be observed by eye, because most of the visible light is absorbed by the deteriorated resin and the spectra change is detected only in the NIR range. Therefore, the correlation between the optical transmission loss and the weight loss can only be discussed using NIR spectroscopy.

Correlation Between Optical Transmission Loss and Weight Loss

Next, the optical transmission losses α_λ (dB/mm) at 850 (nm) of the thermally deteriorated epoxy resins were calculated. Figures 2 to 4 show the heating time dependence of the weight loss and the optical transmission losses at 850 nm of the three types of thermally deteriorated epoxy resins. Both the values of the weight loss and the α_λ increased gradually during the heating of each epoxy resin and the two tendencies are similar, the optical transmission loss of each resin having a good correlation with the weight loss. Figure 5 shows the correlation between the weight loss (wt %) and the optical transmission loss at 850 nm (dB/mm) of the three types of thermally deteriorated epoxy resins. The optical transmission loss of each resin has a good correlation with the
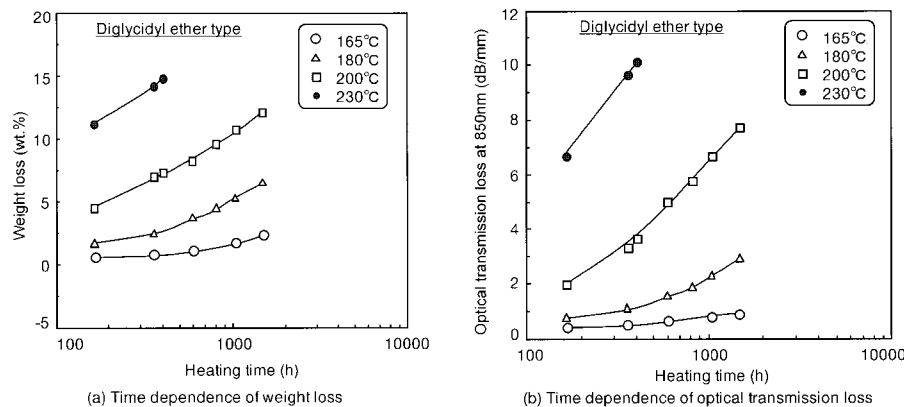
(a) Time dependence of weight loss

(b) Time dependence of optical transmission loss

Figure 2   Time dependence of the weight loss (wt %) and the optical transmission loss at 850 nm (dB/mm) of the thermally deteriorated diglycidyl ether type epoxy resin. (a) Time dependence of weight loss; (b) time dependence of optical transmission loss. Heating temperature: 165, 180, 200, and 230°C in air.

weight loss, respectively. This suggests that the optical transmission loss can be used as a nondestructive diagnostic parameter to evaluate thermal deterioration.

Figure 6 shows the temperature dependence of the storage modulus E′ (Pa) and loss tangent (tan δ) of the thermally deteriorated diglycidyl ether type epoxy resin heated at 180°C in air. The glass transition of E′-curve shifted to higher temperatures and the rubber modulus increased with increased heating time. This indicates that the cross-linking densities in the resins are increased by the thermal oxidation reaction, the rigidity of the resins becoming higher. Similarly, the temperature dependence of the tan δ-curve peaks shifted to higher temperatures until the heating

time is 1053 h, but the peak height decreased gradually and the peak width increased. This again indicates that the thermally deteriorated resins became more rigid, because of their increased cross-linking densities. The reason why peak temperature decreased at a heating time of 2043 h is that although the cross-linking structure was produced in the resin by the thermal oxidation reaction, the simultaneous elimination reaction occurred from the surface. To confirm this theory, the weight loss dependence of the peak temperature of tan δ of the thermally deteriorated diglycidyl ether type epoxy resin is shown in Figure 7. Up to a weight loss of 5 wt %, the peak temperatures of tan δ increase, but the peak temperatures of tan δ decrease over 6 wt %.

(a) Time dependence of weight loss
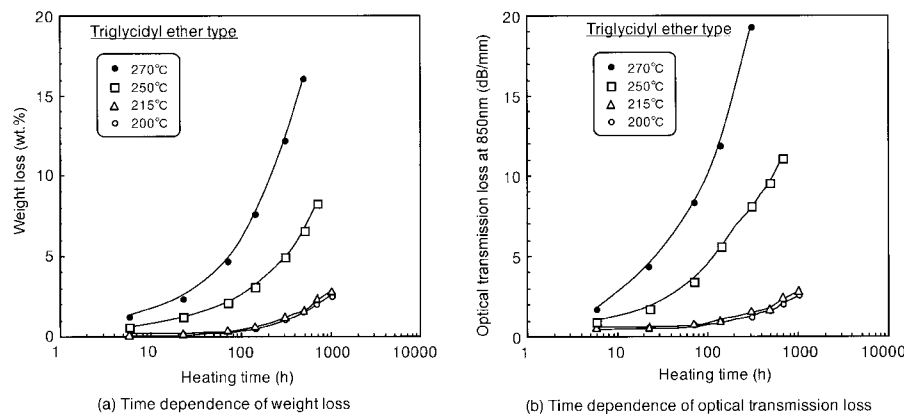
(b) Time dependence of optical transmission loss

Figure 3   Time dependence of the weight loss (wt %) and the optical transmission loss at 850 nm (dB/mm) of the thermally deteriorated triglycidyl ether type epoxy resin. (a) Time dependence of weight loss; (b) time dependence of optical transmission loss. Heating temperature: 200, 215, 250, and 270°C in air.
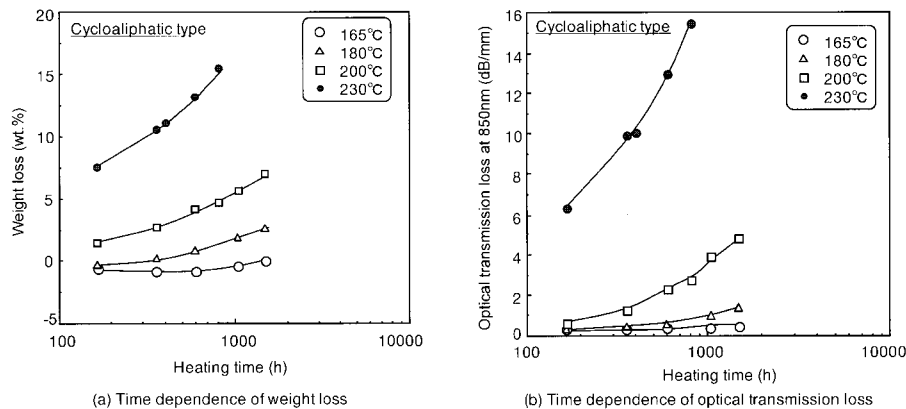
(a) Time dependence of weight loss

(b) Time dependence of optical transmission loss

Figure 4 Time dependence of the weight loss (wt %) and the optical transmission loss at 850 nm (dB/mm) of the thermally deteriorated cycloaliphatic type epoxy resin. (a) Time dependence of weight loss; (b) time dependence of optical transmission loss. Heating temperature: 165, 180, 200, and 230°C in air.

It is postulated that the cross-linking reaction occurs more quickly than the elimination reaction in former region, and the opposite phenomenon occurs in the latter region.

CONCLUSIONS

The correlation between the optical transmission loss in the NIR range and the weight loss of thermally deteriorated epoxy resins was analyzed us-ing NIR spectroscopy. Using three types of acid anhydride cured epoxy resins, the optical transmission losses at 850 nm per unit optical path length of each resin and their weight losses were measured during accelerated heating tests. As heating time is increased, the color of each resin darkens and its weight decreases, so that the values of the optical transmission loss and the weight loss are increasing gradually. Both of the tendencies are similar in magnitude and the optical transmission loss of each resin has a good correlation with the respective weight loss. It is theorized that the cross-linking structure was increased in the resin by the thermal oxidation re-
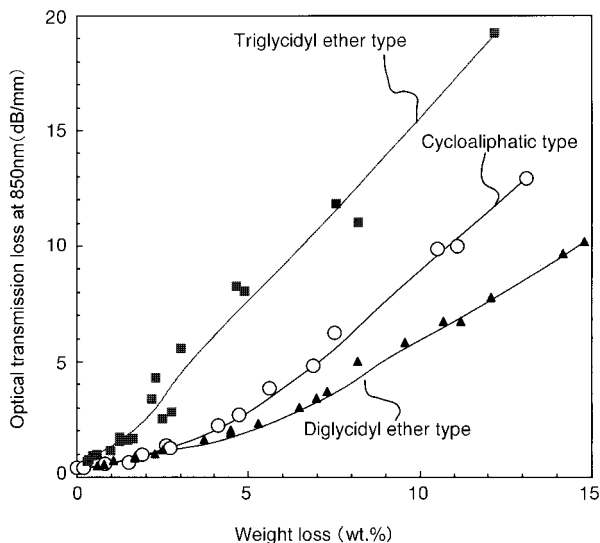

Figure 5 Correlation between the weight loss (wt %) and the optical transmission loss at 850 nm (dB/mm) of thermally deteriorated three types of epoxy resins. (▲) Diglycidyl ether type; (■) Triglycidyl ether type; (○) Cycloaliphatic type.
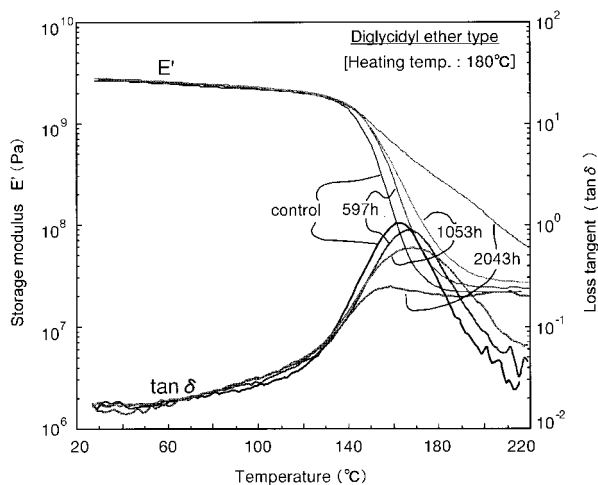

Figure 6 Temperature dependence of the storage modulus E′ (Pa) and loss tangent (tan δ) of the thermally deteriorated diglycidyl ether type epoxy resin heating at 180°C in air.
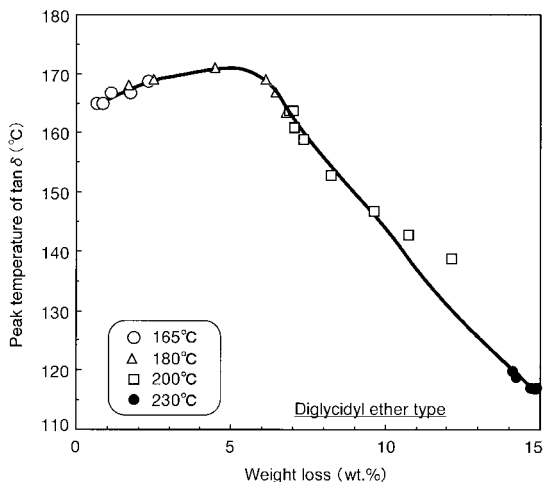
Figure 7 Weight loss dependence of peak temperature of tan δ of the thermally deteriorated diglycidyl ether type epoxy resin.

action and that a simultaneous elimination reaction occurs from the surface. As the thermally oxidized structure is more highly conjugated, the optical transmission loss is increased in the UV–visible region. Theoretically, one can predict the weight loss of the thermally deteriorated epoxy resins nondestructively by measuring the optical transmission loss at NIR.

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