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A study of water absorption characteristics of DGEBA/DDS resin system using near infra-red spectroscopy

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Summary

Water absorption and desorption of the diglycidyl ether of bisphenol A (DGEBA)/4,4'-diaminodiphenyl sulfone (DDS) resin systems, cured isothermally at three different temperatures (160, 180 and 220°C), were monitored at 80°C, as a function of soaking and drying times. New near infra-red spectroscopic (NIR) technique as well as the conventional gravimetric method were used.

The data from two different techniques were reasonably identical showing that the new NIR technique is valid. The resin systems cured at higher temperature absorbed more water. The degree of structural packing of the network systems has been estimated from the observations in water absorption characteristics.

Introduction

Water resistance has been considered an extremely important property for those epoxy resins that are used in structural applications, and has attracted many studies (1-3). The water absorption characteristics of epoxy resins have also been used as an indicator of the degree of structural packing of the epoxy network on the basis of the reported water absorption mechanism (3-6).

The most widely used method in water absorption studies is the gravimetric method in which the changes in sample weight resulted from water absorption are simply measured on a normal laboratory balance. In this study water absorption and desorption characteristics of the standard DGEBA/DDS resin systems are studied by new NIR technique as well as the conventional gravimetric method. The data from two different techniques are compared each other to prove the validity of the new NIR technique.

Experimental

An intimate mixture of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Epikote 8283, Shell Chemicals, Mn=380) and an amine curing agent, 4.4'-diaminodiphenyl sulfone (DDS, Anchor Chemicals, Mn=248) (stoichiometric formulation based on the functionality of two reactant monomers) was prepared under vacuum. In this procedure the calculated amounts of the resin and the DDS monomers were placed in a 500ml round bottomed flask and then connected to a rotating evaporator with an adjustable vacuum box. In order to minimize curing during the mixing process, the heating time was reduced to 30 minutes, starting from a temperature of 80°C and finishing at 120°C, using a silicone oil bath. The flask was rotated at a constant speed during the process. When the temperature reached 120°C, the mixture became a clear transparent solution. It was allowed to remain at that

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temperature until free from bubbles and then poured into preheated Teflon moulds before being placed in an air oven for curing. This mixing procedure has two advantages over the conventional procedure in which the mixing is carried out in air. One is that moisture from the environment can not be absorbed into the mixture, and any moisture initially present in the reactants is removed by the vacuum conditions. The other advantage is that a separate degassing process is not needed.

The cure conditions employed in this study were isothermal, single-step cures ranging in set temperatures from 160°C to 220°C; the cure time was standardized at 6 hrs in order to isolate the influence of cure temperature, and hence to obtain the variation in structural packing (cross-linking density) of the cured resin systems.

Five rectangular samples of 50 x 10 x 2.4 mm were machined from each cured resin plaques, and used consistently for the tests by gravimetric method and NIR technique. The infra-red apparatus employed in this study was an Alpha Centauri FTIR Spectrophotometer (Mattson Instruments Inc,.USA) for recording near infra-red absorption spectra in the region from 11000 to 4000 cm^{-1}. The operating conditions for obtaining the spectra involved 32 scans at a resolution of 8 cm^{-1}.

Water absorption and desorption were monitored at 80°C. For absorption the samples were immersed in a water bath filled with distiled water. After a certain period the samples were removed from the water, dried the surfaces by the aid of tissue, and then the weight gains were measured on a balance. The same samples were used immediately for near infra-red spectroscopic scanning, and then placed back to the bath for the second time period and so on. For monitoring the desorption the saturated samples were dried in a vacuum oven at 80°C which is the temperature used in absorption study. The weight loss was measured at every intervals, and the samples were also used for near infra-red spectroscopic scanning. In gravimetric analysis the measured densities of resin samples and the known density of water (taken as 1 g/cm^3 at room temperature) were used in the

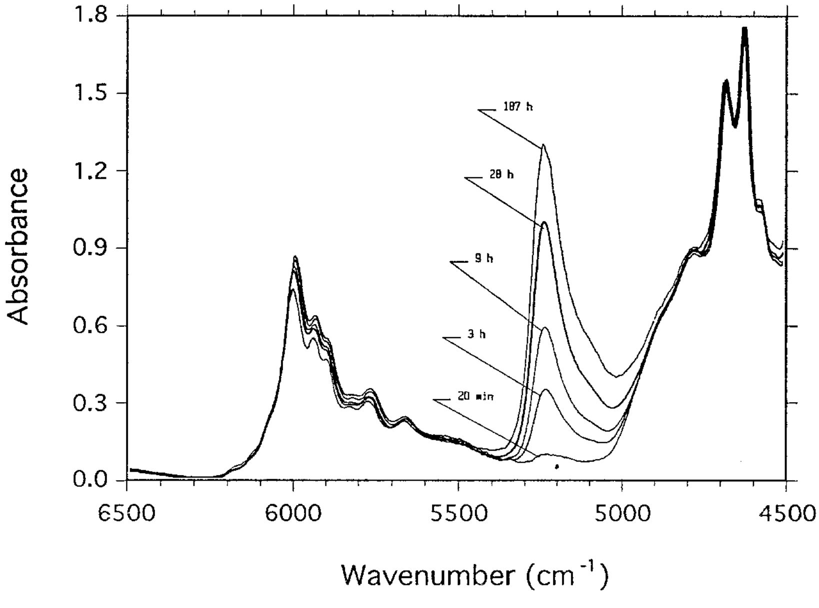

Fig. 1: Overlaid near infra-red absorption spectra for DGEBA/DDS resin system cured at 220°C during water absorption. Note that the band at 5230 cm^{-1} corresponding to the contribution of water molecules increases as the soaking time (marked on the curves) increases.

calculation of volume percents from weight changes. In NIR analysis the changes in the area of the band for water molecules, which appears at 5230 cm^{-1}, as shown in Fig.1, were monitored and converted to volume percents. The details of the quantitative analysis method of near infra-red spectroscopic data are described in our recent publication (7).

Results and discussion

The data of water absorption and desorption, obtained gravimetrically, are shown in Fig. 2 as a function of soaking and drying times. The time scale for desorption curve is not shown, but begins in the opposite direction from the end point of the absorption curve. It can be seen from both of the absorption and desorption curves that the slope is much greater in the early stage and becomes smaller and then finally levels off in the later stage. The contours of the curves for absorption and desorption are quite similar, but in detailed comparison the absorption was slightly more rapid than desorption in the same temperature cured sample. 0.1-0.2 vol % of water, depending on the cure temperature, remains when the samples are dried to the starting point of the absorption. In addition, as the cure temperature increases the water absorption and desorption become more rapid, and the equilibrium water content increases.

As mentioned earlier, water absorption characteristics can be related to the degree of structural packing of the network. This approach is based on the following well known water absorption mechanism: At the early stage of absorption process, the water molecules occupy free volume entrapped in the cross-linked network. At a later stage, some of the water molecules remaining in the free volume disrupt the polar groups such as hydroxyls, attached to the network, and become hydrogen bonded water. The former water is called bulk, unbound water and the latter is termed bound water. Therefore, the epoxy network which has larger free volume and/or more polar groups can absorb more water. Our experimental result, shown in Fig. 2, implies that the highly cross-linked systems, cured at higher temperatures, contain greater free volume and/or more polar groups. This can be explained as follows: In addition to the -OH groups attached to the backbone of the oligomeric epoxy monomer more -OH groups are produced by ring opening during the cure. As a result, the number of -OH groups in the cross-linked network increases in proportion to its cross-linking density. But the implication in our work that the highly cross-linked system would have greater free volume in the glassy state can be considered an anomalous result. This has been reported elsewhere where the cross-linking density of the network was controlled by varying reactant ratio or cure time (2, 5, 8).

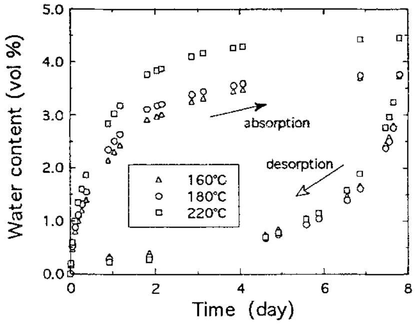

Fig. 2: The changes in water content versus time (during the absorption and desorption at 80°C) obtained by gravimetric method for DGEBA/DDS resin systems. The time for desorption begins in the opposite direction from the end point of absorption.

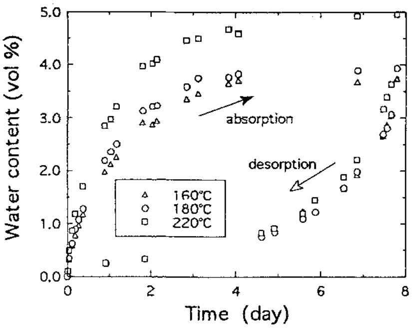

Fig. 3: The changes in water content versus time (during the absorption and desorption at 80°C) obtained by NIR technique for DGEBA/DDS resin systems. The time for desorption begins in the opposite direction from the end point of absorption.

The anomalous cross-linking density and free volume relations have been explained by Gillham (1) by monitoring the changes in specific volume as a function of the temperature for a partially and fully cured resin systems, which were prepared by curing at the different temperatures, T_1 and T_2. In the rubbery state above $T_{g\infty}$, the specific volume for the more highly cross-linked system is lower. As the systems are cooled through $T_{g\infty}$, the specific volume versus temperature curves cross, resulting in a higher specific volume for the more highly cross-linked system. On the other hand, it is known that the specific volume is proportional to the free volume because of: (i) the specific volume equals the sum of the free volume and the occupied volume and (ii) the occupied volume does not change noticeably in a chemically arrested cross-linked network. Consequently, the more highly cross-linked system contains greater free volume in the glassy state, where the experimental works of present study were carried out (80°C). In addition, the greater free volume for more highly cross-linked system is believed to be attributed to the higher steric hindrance associated with the higher number of cross-linkages (shrinking of the network is more restricted during the cooling process).

In parallel with the observations in water absorption and desorption characteristics, a decreasing room temperature bulk density with increasing cross-linking density, observed in our separate study (9) and others (2, 5, 8), implies again that the more highly cross-linked system has greater free volume.

The data of water absorption and desorption from NIR technique are shown in Fig. 3. In NIR data analysis band area/vol % was calculated by deviding the band area for water molecule at 5230 cm^{-1} by vol % of the respective system from gravimetric method.

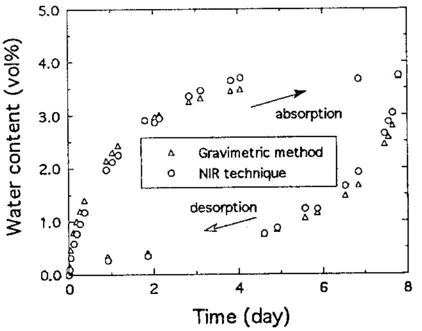

Fig. 4: The comparison of the data from two different techniques (gravimetric method and NIR technique) for DGEBA/DDS resin system cured at 160°C.

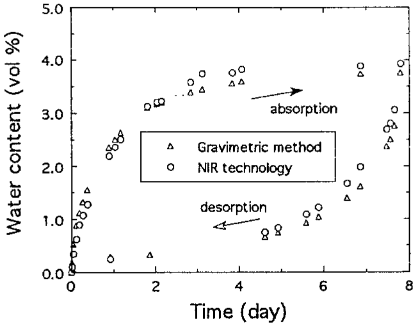

Fig. 5: The comparison of the data from two different techniques (gravimetric method and NIR technique) for DGEBA/DDS resin system cured at 180°C.

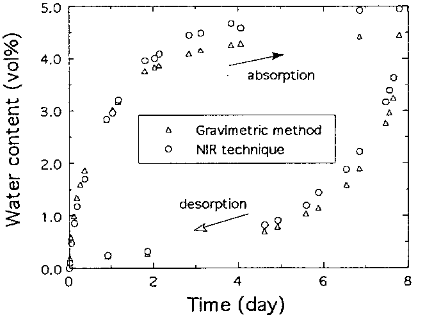

Fig. 6: The comparison of the data from two different techniques (gravimetric method and NIR technique) for DGEBA/DDS resin system cured at 220°C.

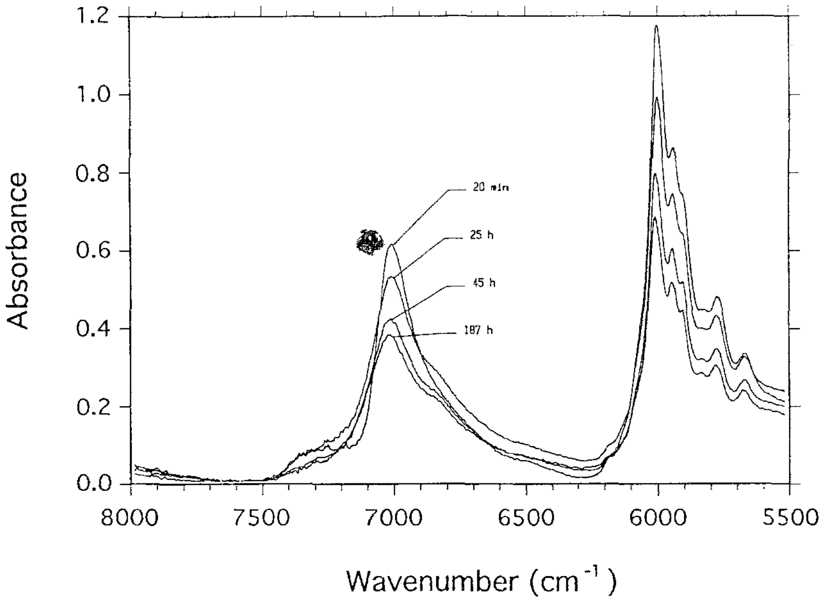

Fig. 7: Overlaid near infra-red absorption spectra of OH group band at 6990 cm^{-1} for DGEBA/DDS resin system cured at 220°C during water absorption. The soaking time is marked on the curves.

The average value was 15.959/vol %. Finally, NIR water vol % could be obtained by deviding the band area by 15.959. Although the equilibrium water contents from NIR technique, as can be seen from Fig. 4-6, are slightly higher than those from gravimetric method, the contours of the overall data curves from two different techniques are quite similar. This consistent tendency shows the validity of our new NIR technique for water absorption characteristic study. Other noteworthy thing, observed from NIR absorption spectra, is the broadening of the OH group band at 6990 cm^{-1} with increasing soaking time, as shown in Fig. 7. It is more significant in the later stage of water absorption. This phenomenon is considered to be due to the production of the hydrogen-bonded OH groups. However, any noticeable change in the area of OH group band was not observed.

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