Effect of Curing Agent Stoichiometry on Solvent Penetration in a Cured Epoxy

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The diglycidyl ether of bisphenol A was cured with triethylenetetramine at various resin to hardener ratios. The amount of curing agent ranged from 50% of the required amount to 120%. The sorption of a series of solvents which included water, methanol, acetone, isopropyl alcohol, ethyl acetate, 1,2-dichloroethane, and toluene was followed in a number of the cured epoxies. All experiments were performed at 40 °C for approximately 450 h. The epoxy cured with only 50% of the stoichiometric amount of hardener was most sensitive to all solvents except for isopropyl alcohol and water. Water sorption was insensitive to the amount of curing agent used. Isopropyl alcohol, was taken up by the cured epoxies, but at levels 1–2 orders of magnitude lower than other solvents. Kinetic data for solvent sorption was analyzed using Fick's diffusion equation.

Introduction

In the use of epoxy adhesives there is a wide variation in the manner in which each operator prepares the compound. Some of this is due to the way in which epoxies are packaged. For example, preweighed resin and hardener may be sealed in "blister" packs and emptied into a container and then mixed. Alternatively some of these "blister" packs are joined together with a separator between them. When the separator is removed the contents of the two sides are mixed in situ. Other epoxy materials come in tubes which call for squeezing out equal lengths of resin and harder before mixing. In fact, there are a myriad of ways in which manufacturers of epoxies suggest that two-component systems be put together.

Once the two components are together, the mixing process then adds another potential variation into the scheme. It is incumbent on each user to mix two relatively viscous materials thoroughly prior to application to surfaces. Nevertheless, some will spend half the time that others do in mixing; some will not scrupulously scrape down the sides of the container to ensure uniformity; some will use large blades for mixing; some will use thin sticks. What has become clear in our own use and in our observation of others is that the final product may end up being significantly different from person to person.

The main problem that can show up in such epoxy use is that some workers will end up with a resin to curing agent ratio that is considerably off-stoichiometry. That is, some mixes may contain insufficient hardener and others may contain excess hardener with possibly even local areas of each. Until there is some way to standardize component addition and mixing procedures these difficulties will continue to be experienced.

One of the primary concerns in the use of epoxy adhesives is their resistance to various chemicals they may be exposed to. The older literature (25 years or more) has some work on such exposure, particularly to various solvents.[1] The intrusion of solvent into polymers is a diffusion process and there are a number of excellent reviews on the phenomena of Fickian and non-Fickian sorption processes in polymers.[2,3] Alfrey[4] recognized the importance of the linear kinetics observed in some systems which he dubbed case II and thereby set off a flurry of research.[5] A compilation of diffusion constant data in many different polymers, not including epoxies, has recently appeared.[6]

Table I. Weights of Curing Agent (TETA) for 10.00 g of Epoxy Resin

TETA wt (g)	equiv of -NH	equiv of NH/ equiv of epoxy	T_g
0.62	0.0255	0.50	93.3
0.75	0.0308	0.60	109.2
0.87	0.0358	0.70	115.2
1.00	0.0411	0.80	118.6
1.12	0.0461	0.90	121.5
1.25	0.0514	1.00	123.3
1.49	0.0613	1.20	127.3

While there have been many studies on a variety of different polymers there has been relatively little work on solvent sorption in thermoset adhesives. To make some attempt to provide information in this neglected area, our work has centered on solvent penetration in cured epoxy networks.[7] A related area that to our knowledge has not been examined is how such solvent sensitivity varies as the resin to curing agent ratio is changed. The purpose of this work is to address that question.

Experimental Section

Samples of the diglycidyl ether of bisphenol A (DGEBPA, 10.00 g, 0.0513 equiv) were weighed into plastic dishes (2.5-in. diameter) together with appropriate amounts of triethylenetetramine (TETA). The DGEBPA had previously been titrated with HCl and shown to have an equivalent weight of 195. After mixing, 5.0 g of the resin/curing agent mixture was weighed into each of two aluminum dishes. See Table I for the composition of the samples. The following cure schedule was used. The mixtures were permitted to stand at room temperature for about 19 h and then placed in an oven at 120 °C for 24 h. A reasonable chemical structure for the repeat unit in the product polymer has been given in a previous publication.[7]

T_g's were determined for each cured specimen (see above) using a Perkin-Elmer DSC-4 differential scanning calorimeter. The T_g data are presented in Figure 1 and in the Table I. Fourier transform infrared spectra were taken of selected samples. There was no appreciable difference noted between the spectrum of the 50% sample and the 120% sample. In Figure 2 the absorption

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(1) See: Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1967. This contains a summary of solvent exposure data.

(2) See: Crank, J., Park, G. S., Eds. *Diffusion in Polymers*; Academic Press: New York, 1968 (discussion of various diffusion mechanisms and their kinetics).

(3) Fujita, H. *Fortschr. Hochpolym-Forsch.* **1961**, *Bd. 3*, 1.

(4) Alfrey, T. *Chem. Eng. News* **1965**, *43* (Oct 11) 64.

(5) Windle, A. H. In *Polymer Permeability*; Comyn, J., Ed.; Elsevier Applied Science Publishers, Ltd.: London, 1985; Chapter 3, p 75 (a good review of case II sorption).

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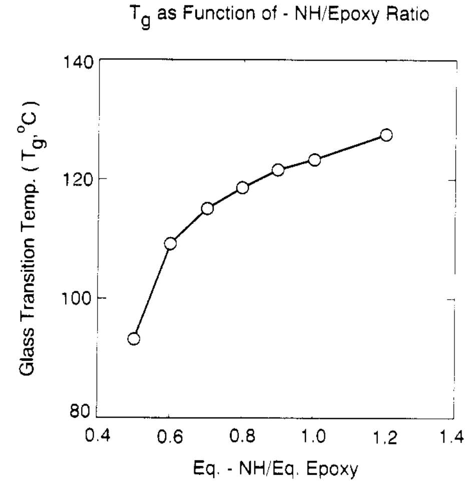

Figure 1. Glass transition temperatures vs amine/epoxy ratio.

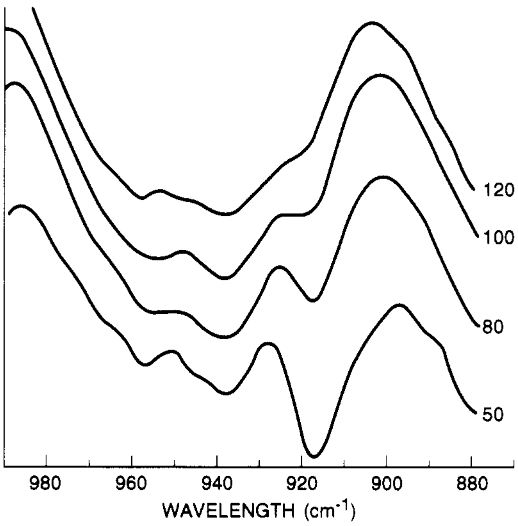

Figure 2. Infrared spectra of cured epoxies (the 916-cm^{-1} region) with various amine stoichiometries (50–120% equivalents).

line due to the epoxy group (916 cm^{-1}), one of the weakest lines in the spectrum, are shown for several different –NH/epoxy cure ratios.

The cured epoxy mixtures were broken up into irregularly shaped pieces. Samples of each, approximately 1–2 cm^2 and weighing between 0.3 and 0.7 g were placed in capped vials containing one of seven solvents. These included water, methanol, acetone, isopropyl alcohol, ethyl acetate, 1,2-dichloroethane, and toluene. Because sample thicknesses were all 1 mm, the front and back surface area was much greater than the surface area of the edges thus making direct comparison of the sorption curves from sample to sample reasonable. The vials were thermostatted at 40 ± 1 °C. Weight changes were obtained at various intervals by removing samples, blotting them dry, and weighing them to the nearest one hundredth of a milligram. Each sorption experiment was followed for over 450 h. These data are plotted as percent weight gain as a function of time$^{1/2}$ (see Figures 3–9). The curves shown are presented only to guide the eye and were not calculated from the data.

Results and Discussion

To analyze our sorption data use was made of the standard Fickian diffusion equation:

$$M_S = kt^n \qquad (1)$$

where M_S is the weight percent of penetrant absorbed at time t, k is a constant characteristic of the system, and the exponent n equals $^1/_2$. When other exponents are obtained different mechanisms are implied, thus, when n is 1 case II[8] (or transport dominated by relaxation processes) is in effect; for n between $^1/_2$ and 1 so called anomalous transport is observed; when n is greater than 1 super case II diffusion is seen.[9] The case II process is described by three characteristics: (a) a sharp advancing solvent front between the outer swollen rubbery shell and the internal glassy state; (b) the rubbery region is in a nearly equilibrium swelling state; (c) the boundary between the rubbery and glassy regions advances at a constant rate.[10] Therefore, the observed weight increase per unit cross section of the diffusion front varies linearly with time. Of course, in the case of glassy polymers combinations of several different mechanisms will result so that the simple plots of M_s vs $t^{1/2}$ or t can appear as complex functions rather than straight lines. Nevertheless, much useful information can be derived from such a treatment.

Table II. Specific Gravity at 22 °C of the Various Epoxies

% TETA	specific gravity	% TETA	specific gravity
50	1.188 ± 0.000	90	1.196 ± 0.015
60	1.180 ± 0.004	100	1.174 ± 0.002
70	1.178 ± 0.005	120	1.180 ± 0.003
80	1.194 ± 0.011		

In the sorption experiments contemplated here, it was necessary to make certain that the materials that were being examined were all in a similar physical state. Therefore, when the DGEBPA was cured with different stoichiometric amounts of TETA determinations of the T_g were undertaken. In Figure 1 the T_g data have been summarized. Thus, it is seen that for these amorphous, glassy polymers when the amount of curing agent is only 50% of the theoretical amount the T_g is 93.3 °C and when a 20% excess of TETA is used, the T_g increases to 127.3 °C. This indicates that substantial additional cross-linking takes place as the amount of TETA is increased and also that all of our sorption measurements were performed well below the glass transition temperature. The best-fit equation describing the curve in Figure 1 is

$$\frac{\text{NH}}{\text{EPOXY}} = 0.30214 + \frac{0.000638T_g}{1 - 0.00715T_g} \qquad (2)$$

Infrared spectra of several cured TETA/DGEBPA ratio mixtures are given in Figure 2. The region of interest, near 916 cm^{-1}, has been expanded so that the epoxy group absorption at that frequency can be seen easily. The amount of epoxy decreases progressively as the concentration of curing agent increases. However, even when there is a large excess of TETA available (e.g. 120%) there is still visible an absorption due to unreacted epoxy.

The specific gravity of each epoxy with different amounts of curing agent was measured by a water displacement method. These results are given in Table II. These data indicate that the network that forms in the cured DGEBPA is tightest near the 80–90% curing agent stoichiometry. This suggests that as the amine centers react with epoxy groups in the resin, the substituted (tertiary) amines themselves may then go on to react with additional oxirane and cause the network to be more highly cross-linked. Thus, even though 80–90% of the equivalent amine is added, more than 80–90% reaction may be taking place. We may also infer from these density data that there is a minimum amount of free volume present in the 80–90% amine equivalent samples. In passing we note

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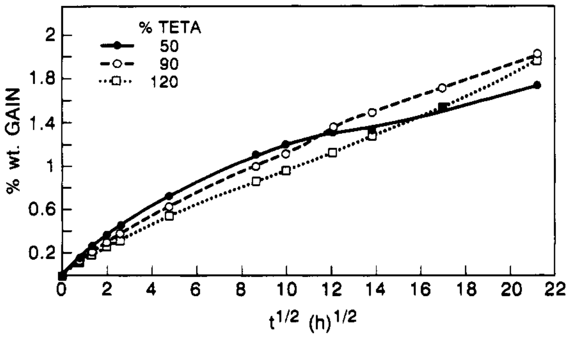

Figure 3. Water sorption (percent weight gain) vs hours$^{1/2}$ at 40 °C.

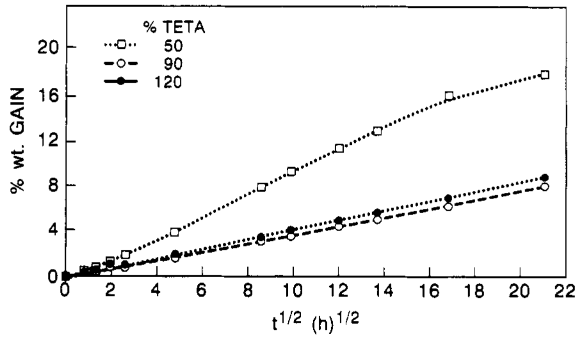

Figure 4. Methanol sorption (percent weight gain) vs hours$^{1/2}$ at 40 °C.

that the data of Figure 1, even up to an -NH/epoxy ratio of 1.2, show an increase in T_g. The usual explanation of a higher cross-link density as the T_g increases is inconsistent with the results of the density measurements. The explanation of this conflicting result may be that the samples used in the density determinations contain varying amounts of microvoids.

The polymer density at both the low end and high end of the curing agent concentration are about the same, suggesting that the network consisting of large amounts of ether bonds (low end) and the network made up of mostly amine bonds (high end) result in similar packing densities. At the low end there will be less -OH and -NH bonds than at the high end. Intuitively, then, hydrogen bonding or other interactions with polar solvents should be most important in the polymer where the amine curing agent concentration is greatest.

When the cured samples were exposed to the several solvents at 40 °C for various time periods weight gains were noted. Plots of the weight changes as functions of time permitted the investigation of the kinetics of the solvent sorption process. In previous work[7] the exponent of the diffusion equation was determined for TETA cured samples with stoichiometric amine. In this work, Fickian diffusion was assumed and plots for the various solvents are all shown with a time exponent of $^1/_2$. In general, the initial parts of the curves are linear although there are exceptions.

In the case of water, Figure 3, the surprising result was noted that the amount of curing agent present in the cured epoxy did not affect the amount of water taken up with time. Various authors have published research showing that epoxies do indeed interact with water and that the sorption process may be quite complicated.[11,12] While the evidence in these papers suggested both chemical reactivity with some epoxies and/or hydrogen bond formation with polar groups as viable mechanisms for water incorporation, our work seems to point to alternative possibilities. If hydrogen bond formation or reaction were operative, it seems likely that there would be a great difference in the amount of water picked up by the DGEBPA/TETA system when there was a deficiency of curing agent compared to when there was an excess. That is not the case. Therefore, we conclude that the water sorption process is more dependent on the physical state of the cured epoxy, in this case, than its chemical nature.

In the case of methanol sorption (Figure 4) the data for the 70, 90, 100, and 120% TETA mixtures are very similar. Only the 50, 90, and 120% lines are shown. For all TETA concentrations except the 50% mixture, very good fits to Fick's equation are found. In the 50% curing agent data a mixture of diffusion mechanisms can be found, based on the S-shape of the sorption curve. This is in contrast to the water data (Figure 3) which exhibit composite mechanisms throughout the entire range of TETA concentrations.

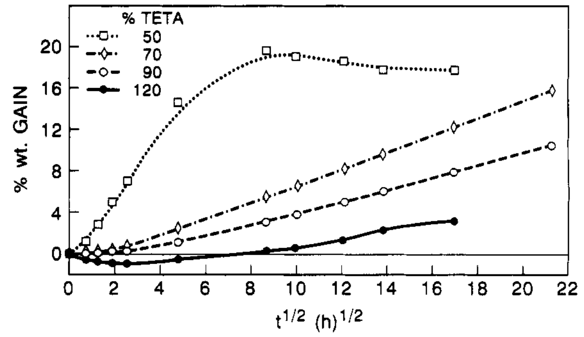

Figure 5. Acetone sorption (percent weight gain) vs hours$^{1/2}$ at 40 °C.

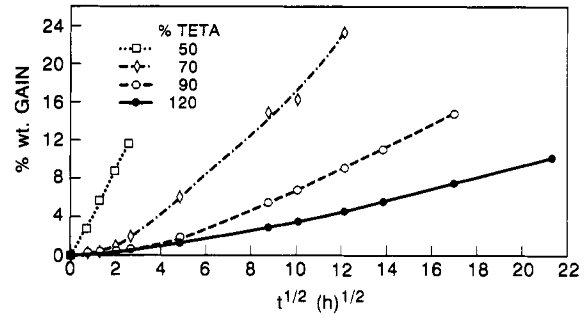

Figure 6. 1,2-Dichloroethane sorption (percent weight gain) vs hours$^{1/2}$ at 40 °C.

The picture of the uptake of acetone (Figure 5) and 1,2-dichloroethane (Figure 6) appears to follow a more predictable course. That is, that the more TETA that is used, the tighter the final network that is formed, and thus the the less solvent penetration observed. These results suggest that the chemical nature of the interaction of the epoxy with the solvent is not as important as the microstructural morphology. The latter apparently controls the entry of the solvents into the network. It should be noted at this point that the data presented are composites of solvent uptake effects together with extraction effects. This is more clearly shown in the 120% TETA curve showing acetone uptake. In the early stages the weight loss is greater than the weight gain and the curve goes below the 0% weight gain line. In our earlier work[7] hot toluene extraction of DGEBPA cured with a stoichiometric amount of TETA resulted in no weight loss. In this work extraction of the 50% and 90% TETA samples resulted

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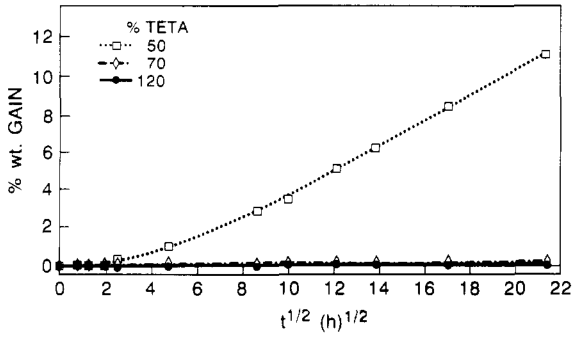

Figure 7. Toluene sorption (percent weight gain) vs hours$^{1/2}$ at 40 °C.

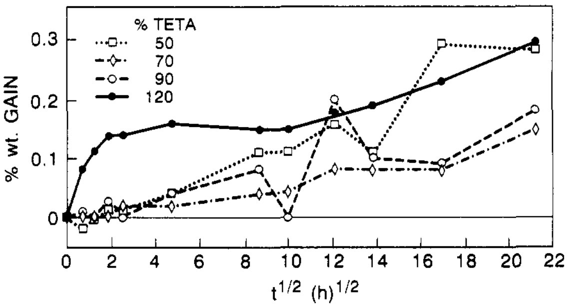

Figure 8. Isopropyl alcohol sorption (percent weight gain) vs hours$^{1/2}$ at 40 °C.

in no measurable weight loss.

As can be seen in the toluene data (Figure 7) it is only when the TETA is at 50% of the stoichiometric amount that sorption occurs. At the other concentrations of TETA 0% weight gain is observed over the course of the experiment. Isopropyl alcohol (Figure 8) is most unusual in that the amount of uptake is very small (<0.3%) at every TETA concentration. This effect was observed previously[7] for samples cured with a variety of curing agents with DGEBPA. Even here, when 50% TETA is used, resulting in a cured resin with the lowest T_g (about 93 °C) very little isopropyl alcohol is taken up. Under the same conditions nearly 18 wt % of methyl alcohol is absorbed (Figure 4). If solvent viscosity is the determining factor, then the least viscous solvent being the best penetrant might explain these alcohol results. Isopropyl alcohol is more than 3 times more viscous than methanol, implying that its diffusion will be proportionately slower. The final solvent, ethyl acetate (Figure 9), is absorbed fairly rapidly only when the curing agent is at 50% of the required amount for full reaction. At 70% TETA concentration, solvent uptake is very slow, approaching 6 wt % after nearly 450 h. All the ethyl acetate data appear to obey Fickian kinetics over a large portion of the sorption curve. In the 50% TETA sample more complicated processes are occurring at the very early stages and very late stages of data collection.

Some of the anomalies in the sorption processes seen at the 50% TETA concentrations might be due to the skewing of the amounts of tightly cross-linked microgel particles in the cured epoxy. This phenomenon of structural inhomogeneities in epoxies has been used to explain the shapes of moisture transport curves found in a DGEBPA epoxy cured with *m*-phenylenediamine.[13] The presence of these inhomogeneous regions have been measured by a variety of techniques, both direct and indirect. In particular, X-ray methods[14,15] and electron diffraction techniques[16] have provided compelling evidence that cured epoxy resins contain globular or nodular structures, on the order of 500 Å in diameter, with a higher density of cross-linking than the surrounding matrix in which they appear. On the basis of the thermal expansion and swelling behavior of an epoxy system exposed to water, it has been postulated[17] that three stages are involved in the sorption of moisture. First, water occupies the free volume in the polymer; second, a chemical interaction binds water to network sites; and last, water penetrates the dense nodules. While this work has not tested these hypotheses it is nevertheless reasonable to assume that many solvents, other than water, might behave in the same manner, especially those that are polar. In the composition containing the lowest amounts of curing agent there should be less of the densely cross-linked microgel particles and concomitantly greater amounts of the less dense matrix. These materials, with smaller amounts of TETA, do appear to be the most susceptible to solvent attack, consistent with the previous analysis.

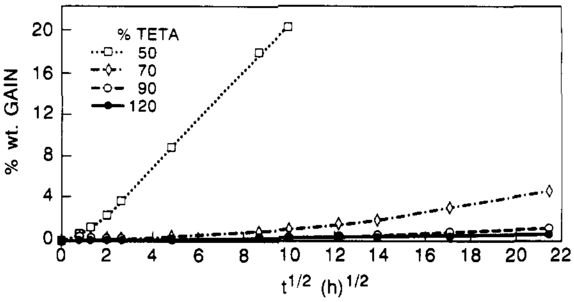

Figure 9. Ethyl acetate sorption (percent weight gain) vs hours$^{1/2}$ at 40 °C.

Although each epoxy resin–curing agent system will behave differently when exposed to various solvents and other chemicals some generalizations can be attempted. In the TETA–DGEBPA system it seems apparent that some solvents are particularly damaging to the cured epoxy. For the fully cured epoxy methanol, acetone, and 1,2-dichloroethane are the most intrusive, being absorbed after many hours, to greater than 10 wt %. This magnitude of sorption causes not only significant softening and weakening of the the adhesive bond but also general cracking and separation of epoxy pieces.

From the data presented here, it can be seen that there is a serious effect of insufficient curing agent on the epoxy network's susceptibility to solvent attack. It also appears that there is some leeway in preparing the TETA-cured epoxy as regards the adhesive's solvent sensitivity. In the cases of acetone, methanol, toluene, and ethyl acetate it is only when the curing agent goes below 70% of the required amount that the rate of solvent sorption increases rapidly. Excess curing agent, at least up to 120% of the stoichiometric amount, appears to enhance the ability of the cured epoxy to prevent solvent absorption. These results do not give us any insight into the other properties of epoxies, cured with different amine stoichiometries, that are of major concern, e.g., adhesive bond strength. Nevertheless, we have demonstrated that susceptibility of epoxies to solvent attack is dependent on the amount of curing agent that is used. This work strengthens the no-

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tion that extraordinary care must be taken when critical bonds are made that rely on epoxies. Accurate weighing of the resin and curing agent must be done. This should then be followed by a mixing process that has been tested to give uniform distribution of the epoxy components. Unless these precautions are taken, the joints that are formed will obviously be subject to attack and weakening by a variety of chemical agents.

Conclusions

The diglycidyl ether of bisphenol A was cured with triethylenetetramine at several concentrations of amine. The ratio of hardener -NH group to epoxy group spanned the range from a large deficiency (50%) to a large excess (120%). Infrared spectra indicate that even with a large excess of amine, a small amount of unreacted epoxy was present. Density measurements on the cured epoxy showed that the density went through a maximum when the amine concentration was near 90% of the theoretical amount.

Seven solvents, including water, methanol, acetone, isopropyl alcohol, ethyl acetate, 1,2-dichloroethane, and toluene, were used in sorption experiments with the various amine/epoxy ratio polymers. The most sensitive mixture of all solvents, except water and isopropyl alcohol, was the 50% amine material. This result was rationalized on the basis that the polymer containing a large deficiency of amine formed a less tightly cross-linked network (it had the lowest T_g), thereby providing more free volume and easier means of ingress. Water sorption was insensitive to the amount of curing agent used suggesting that association of the water to the cured epoxy, by hydrogen bonding, was not important.

Acknowledgment. The authors thanks Arturo Hale and Donald Dahringer for helpful discussions.

Registry No. (DGEBPA)(TETA) (copolymer), 73310-55-1; H_2O, 7732-18-5; MeOH, 67-56-1; H_3CCOCH_3, 67-64-1; $Cl(CH_2)_2Cl$, 107-06-2; PhMe, 108-88-3; $HOCH(CH_3)_2$, 67-63-0; H_3CCO_2Et, 141-78-6.

Photoisomerization of an Azobenzene in Sol–Gel Glass Films

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Sol–gel films of tetraethyl orthosilicate (TEOS) doped with 4-methoxy-4′-(2-hydroxyethoxy)azobenzene (MHAB) were prepared under various conditions. The trans–cis photoisomerization and the thermally induced cis–trans reversion of MHAB in the sol–gel films were studied and compared with that in poly(methyl methacrylate) (PMMA) film or in solution. An increased absorption between the π–π^* and the n–π^* absorption bands observed in sol–gel films doped with MHAB was attributed to hydrogen bond between the azo group and silanol groups. The cis fraction in the photostationary state in sol–gel films was much smaller than in PMMA. This suggests that the sol–gel matrix is more rigid than PMMA. The rigidity of the matrix in the sol–gel glass depends on the water concentration during its preparation.

Introduction

The sol–gel process is now a well-accepted technique for the preparation of various inorganic oxide glasses at low temperature without melting.[1-5] Such inorganic matrices are prepared by condensation–polymerization of a suitable metal alkoxide. For instance, the sol–gel process of TEOS can be described by

$$\text{hydrolysis} \quad Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$

$$\text{condensation} \quad Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$

Therefore, the overall reaction is

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$$

The sol–gel process consists of two main steps. In the first step, metal alkoxides hydrolyze at a low temperature to form a microporous glass with a large surface area. In the second step the porous glass is annealed at an elevated temperature in order to fill the pores. This results in a shrunken, nonporous glass. The porous glass obtained in the first stage is the precursor for the second stage and determines not only the properties of the final glass but also the annealing conditions. The porous glass is of particular interest because of its ability to trap organic photoactive molecules in the inorganic matrices.

Avnir et al. showed that organic molecules can be embedded in silica glasses by the sol–gel process[6-10] and the resulting materials may be used in such photochemical applications[11,12] as solid-state dye laser, nonlinear optical materials, and optical sensors. However, detailed information on the microscopic environment of organic molecules embedded in a matrix of silica gel glass by the sol–gel process has not been fully clarified since little is known about the mobility of organic molecules in the silica cage and about the interaction between the silica cage and the guest molecules.

Zink et al. have reported the preparation of silica and aluminosilicate gels doped with bipyridyltriscarbonylchlororhenium(I) and studied the changes in rigidity of sols

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