

Crosslinking Studies in Plasticized Epoxies by Means of Dynamic Measurements

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Synopsis

A class of amine-cured epoxy resins containing various amounts of polysulfide plasticizer were subjected to dynamic testing during curing at high temperature. Both E modulus and loss factor were determined simultaneously. It was proved that the method allowed for rapid determination of the general pattern of the crosslinking procedure and the necessary curing time and, in general, that dynamic methods are most suitable for the mechanical characterization of polymers under curing at each stage of the curing cycle.

INTRODUCTION

Epoxy resins, apart from their applicability as structural materials, are most suitable for manufacturing models of structural components or composite systems, in particular, for photomechanical applications. This is due not only to their general properties such as linear mechanical behavior, transparency, etc., but also to the possibility of modification of their mechanical and optical properties in a very wide range by using suitable modifiers. In order to achieve this, as well as to control the polymerization process, accelerators, reactive or nonreactive diluents, and plasticizers can be applied. Rheo-optical properties of plasticized epoxy resins have been investigated by Theocaris and his co-workers.¹⁻³

During the polymerization process, "conversion" occurs (disappearance of reactive groups) as well as crosslinking, i.e., coupling of the molecules into three-dimensional networks through reactive side chains to form the desired thermoset system. As polymerization proceeds, there is a continuous change of the mechanical, optical, etc., properties of the material. For example, stiffness is increasing, energy dissipation per unit volume under sinusoidal loading is decreasing, while transition temperature is increasing.^{4,5} For a plasticized cured polymer, plastification has the reverse effect on its properties: with increasing plasticizer percentage, mechanical moduli decrease, energy dissipation increases, and transition shifts to lower temperatures.

The variation of properties during curing is greatly affected by the curing procedure. For example, curing can be effected by means of ultraviolet radiation or processing at high temperature in an inert atmosphere. In this latter case, curing temperature is a very important factor for the variation in

properties. Curing can also be effected at ambient temperature, at a much slower rate. Consequently, uncured or incompletely cured polymers have their properties changing continuously with time at a rate depending on the actual storage conditions. Stable situation can only be reached after the completion of the curing process.

In the literature are mentioned attempts to use the variation of properties of polymeric materials under cure for experimental applications, as, for example, in three-dimensional photoelasticity⁶ or in manufacturing photoelastic specimens in plate form with continuously varying properties along a linear dimension.⁷ This is obtained by having the plate specimen slowly sliding out of the oven so that various parts of the specimens have been subjected to high temperature for different time intervals, which results in different properties. However, for the reasons already mentioned, experimental work with incompletely cured polymers is of very limited reliability.

On the contrary, reliable results can only be obtained with completely cured polymers, and complete curing is obviously a necessary condition. Therefore, for a given curing method, it is important to know when the curing cycle for the material considered has been completed. Several authors have worked on the investigation of curing procedures by various methods.^{8,9}

Chemical methods of analysis, although they provide an insight of the molecular structure, become inoperative toward the end of the curing cycle because their sensitivity decreases. Measurements of physical parameters, such as mechanical or optical ones, are in this case more advantageous, as applied in conjunction with existing theories correlating molecular structure with the respective properties.¹⁰

Dynamic measurements leading to the determination of a complex modulus of the material provide, in fact, two parameters: a dynamic modulus and a loss factor ($\tan \delta$), both of which are frequency-dependent and respond with different sensitivity toward crosslinking changes. Thus, a powerful device for detection and evaluation of the latter is provided. Dynamic mechanical properties of cured epoxy resins have been studied, even at nonstoichiometric compositions, with curing agent^{11,12} and for different network structures.¹²

In this work, the curing process of a class of amine-cured epoxy resins is investigated, in particular, for various amounts of a polysulfide employed as plasticizing agent.

EXPERIMENTAL

As prepolymer for the thermoset system, a diglycidyl ether of bisphenol A resin was used, Epikote 828 (Shell Co.), with an epoxy equivalent 185–192, a molecular weight between 370 and 384, and a viscosity of 15,000 cP at 25°C.¹¹

As curing agent, 8 phr by weight triethylene tetramine was employed, i.e., a highly reactive primary aliphatic amine capable of curing diglycidyl ethers at room temperature. The amount of curing agent critically affects the physical properties of the cured resin.

As plasticizer, a polysulfide of the type Thiokol LP-3 was applied, i.e., a primary plasticizer completely compatible with the resin considered. This plasticizer has a molecular weight of 1000, 2% crosslinking, a specific gravity of 1.27, and a viscosity of 700–1.200 cP at room temperature.

Polysulfides of low molecular weight and of the general structure HS—R—SH react with the epoxy groups to cause chain extensions but not cross-linking, and hardeners must, therefore, be added in the amounts required. However, in the presence of a primary aliphatic amine, the reactivity is increased, so that low amounts of plasticizer (up to 40 phr) reduce the pot life, which, for higher amounts, increases rapidly.⁴

The materials investigated in this work are denoted in the following as 100-P-8, meaning amount of prepolymer, plasticizer, and curing agent, respectively, where P, in phr, has been given the values of 0, 5, 10, 15, and 20.

The materials were produced as follows: The prepolymer was heated up to about 30°C to decrease viscosity. Proper amounts of curing agent and plasticizer were then added, and the mixture, after being stirred thoroughly, was put in a vacuum chamber for degassing. Subsequently, it was put into a rectangular Plexiglas mold 250 × 250 × 5 mm. The pot life, i.e., the gelation time, was of the order of at least 15 min at 25°C.

The molding was removed 24 hr later, and beam specimens 248 × 17 × 7 mm were machined from each specimen. Tests were carried out on a standard Brüel and Kjaer Complex Modulus Apparatus, Type 3090, at ambient temperature as follows:

Each specimen was first tested immediately after its manufacturing. It was then put in an oven at 90°C for 10 min and subsequently removed from the oven, left for about 2 hr to cool to ambient temperature, and then tested again. Then, it was put again into the oven for another 10-min curing period at 90°C, and so on, until the complex modulus of the material was not affected by the repeated curing periods any more.

The notation employed in the following corresponds to the expression

$$E^*(\omega) = E'(\omega) [1 + i \tan \delta(\omega)]$$

where $E^*(\omega)$ is the complex Young's modulus of the material, $E'(\omega)$ is the storage modulus, $\delta(\omega)$ is phase lag between stress and strain, and ω is frequency. All tests were performed at frequencies varying between 50 and 70 c/s. Over this range, the above parameters were practically independent of frequency.

RESULTS

In Figure 1, the densities and the polymerization shrinkage of plasticized specimens are shown. In particular, curve a shows the change in density of the solid material 24 hr after casting and just before starting the curing-and-testing procedure. Curve b gives the density of liquid phase as evaluated according to the rule of mixtures. From curves a and b, i.e., from the change in density, the variation of polymerization shrinkage for the uncured, i.e., the solidified material can be calculated, and this is shown with the curve c. It is worth noticing that addition of plasticizer up to an amount of 14% results in decreased shrinkage as compared with the unplasticized material. For higher percentage of plasticizer, shrinkage increases rapidly.

Curve d shows the density change as determined at the end of each curing cycle, and curve e shows the respective variation of shrinkage. Again, one

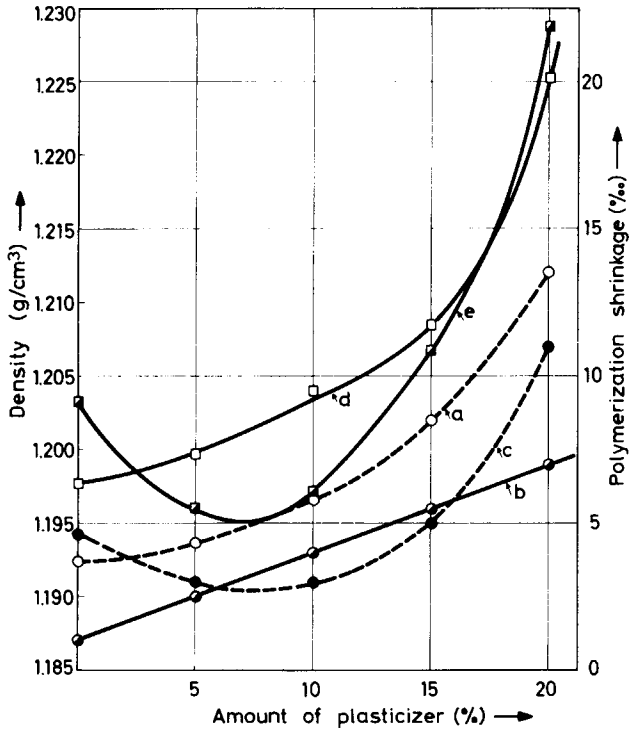


Fig. 1. Densities and polymerization shrinkage for plasticized specimens: (a) density of uncured material; (b) density of the liquid phase according to the law of mixtures; (c) polymerization shrinkage for uncured material; (d) density of cured material; (e) polymerization shrinkage of cured material. Densities of constituents, in g/cm^3 : prepolymer, 1.20; curing agent, 1.00; plasticizing agent, 1.27.

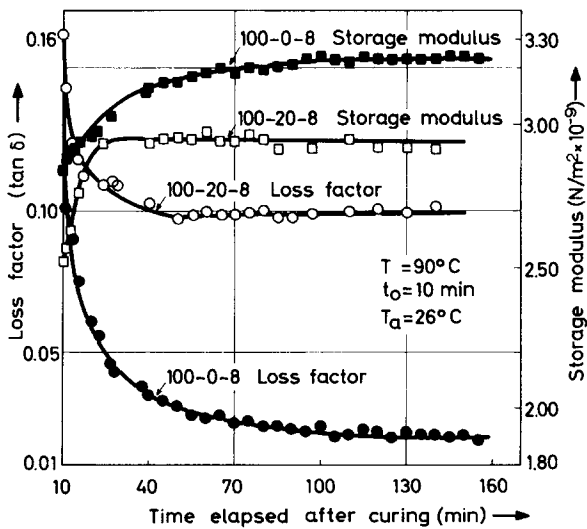


Fig. 2. Effect of the first curing cycle on complex modulus.

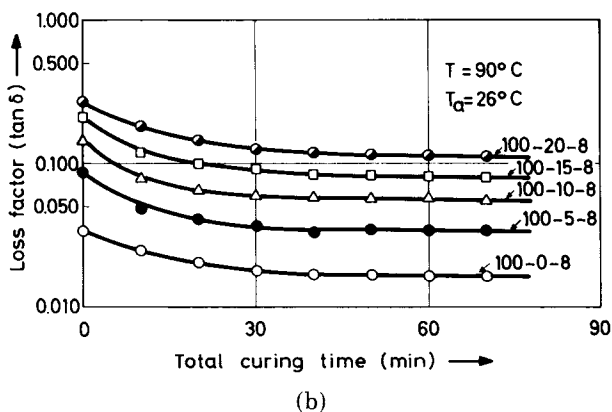
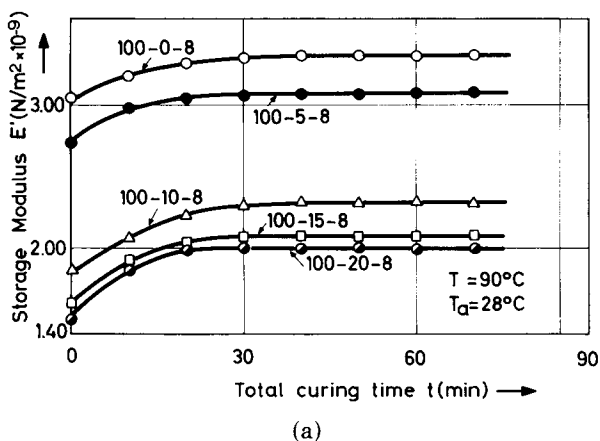


Fig. 3. Storage modulus (a) and loss factor (b) plotted vs. total curing time for various amounts of plasticizer.

notices that ultimate shrinkage decreases considerably for less than 14% amount of plasticizer, while it increases rapidly above that amount.

In Figure 2, the effect of the first curing cycle on the complex modulus for a 100-0-8 and 100-20-8 specimen is shown. Namely, the specimen was taken out of the oven, left for 10 min to cool down, and then subjected to testing every 2 to 5 min. Values of storage moduli and loss factors have been plotted against time elapsed from the end of the 10-min curing. All parameters appear to vary rapidly, especially within the first half hour. This variation is due both to further cooling down of the specimen (although the specimen must have lost the major part of its heat content within its first 10 min at ambient temperature) and also to the fact that crosslinking procedure continues after the imposed heat input (10 min at 90°C). In general, the storage modulus reaches an equilibrium faster than the loss factor. In particular, both parameters of the plasticized specimen reach equilibrium much faster than the unplasticized one. Assuming that no considerable difference in thermal conductivity exists between the two materials, one can conclude that the presence of plasticizer leads to a rapid attenuation of the reaction.

In Figure 3, the storage modulus (a) and loss factor (b) are plotted versus curing time (i.e., the sum of 10-min intervals of curing) for specimens with different degrees of plastification. Given that, after every curing cycle, each specimen remained for about 2 hr at ambient temperature while polymerization process was advancing according to Figure 2, the total curing time, as defined here, corresponds to slightly longer time of uninterrupted curing at 90°C. The latter can be estimated from the activation energy of the reaction, which in the present case is of the order of 13.0 kcal/mole.

Curves corresponding to different amounts of plasticizer appear to run parallel both for the storage modulus and the loss factor; and for all compositions, the curing is completed within 30 min. (For photomechanical purposes, in addition to complete curing, stress-free specimens are required. Curing process and stress removal (annealing) are usually obtained simultaneously by means of programmed thermal processing of several days duration.) Addition of plasticizer between 5% and 10% appears to produce a dramatic change in storage modulus. As mentioned, this is the range in which curing shrinkage decreases with increasing plasticizer percentage. Loss factor follows, almost proportionally, plasticizer percentage.

In Figure 4, the storage modulus (4a) and the loss factor (4b) have been plotted versus per cent plasticizer for different curing times. Again, in the range between 5% and 10% plasticizer, very high slopes of the respective curves appear.

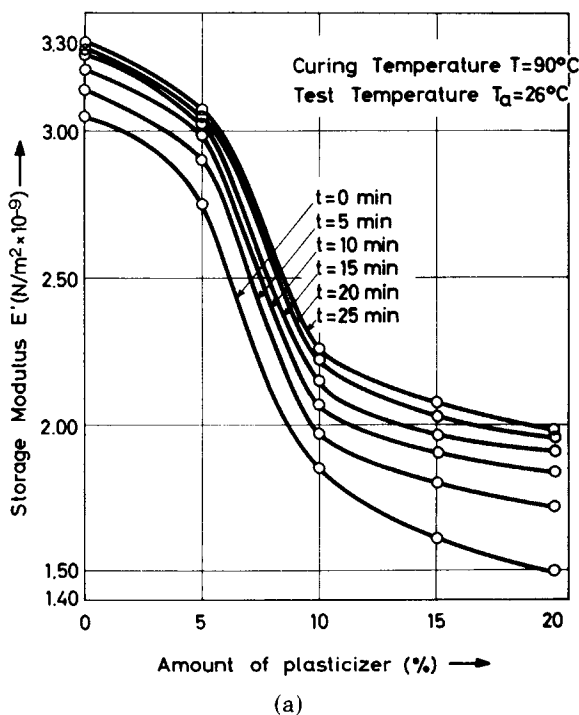


Fig. 4 (continued)

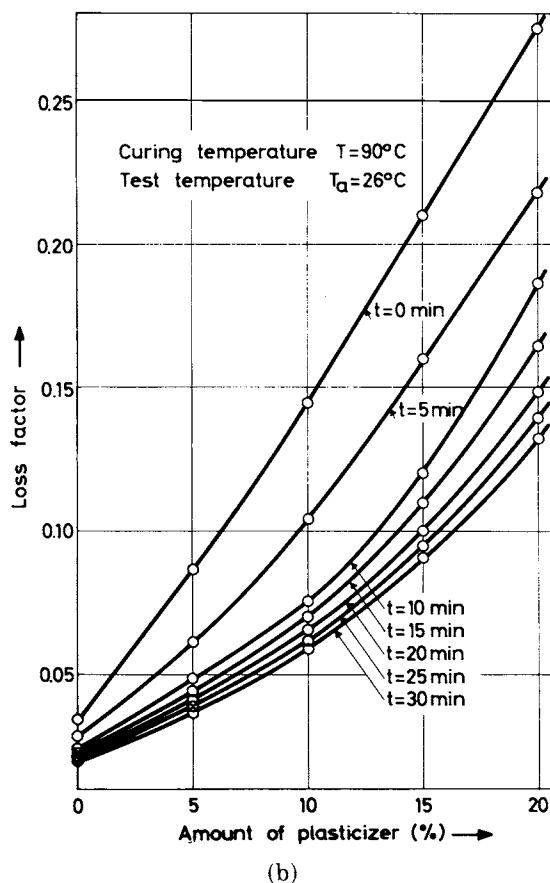


Fig. 4. Storage modulus (a) and loss factor (b) plotted vs. plasticizer percentage for different total curing times.

DISCUSSION AND CONCLUSIONS

From the above results it follows that by the method employed in this work, an accurate determination of the general pattern of the crosslinking process is possible for the materials considered, as well as determination of the curing time required under given conditions. However, for the complete mechanical characterization of the partly cured resins, additional data are required, such as response over a wide frequency range for various strain levels.

The present method, being a resonance method, can only vary the testing frequency by changing the free length of the beam specimen, i.e., a very limited possibility, and also it is working for loss factors less than 0.20. Linearity can always be assumed, because very low strain levels are involved.

A forced vibration method, working under the actual curing conditions, e.g., at high temperature, not limited by the geometry or the mechanical properties of the specimen, would provide the necessary data concerning the viscoelastic behavior of the materials considered. Such a method should be able to sweep the predetermined frequency range sufficiently fast, so that no appreciable change of the properties of the material would occur during the

test because of the advancing crosslinking. Such a condition cannot be fulfilled by long-time experiments, such as creep or relaxation tests of partly cured polymers. In the last cases, the properties of the materials tested would change, not only owing to the time-dependent viscoelastic behavior of the material, but also to varying crosslinking. Obviously, no reliable results can be obtained by such methods.

Cured epoxies with high degree of crosslinking are linear viscoelastic materials with their glass transition temperature well above ambient temperature. With partly cured or highly plasticized polymers, the latter is shifted toward ambient. The mechanical behavior of the materials is then characterized by entropy elasticity, as is the case with cured polymers at their rubbery state. On the contrary, uncrosslinked or highly plasticized polymers exhibit elastic behavior at low temperatures (well below ambient) or high strain rates, e.g., high frequencies.

In conclusion, the change in the mechanical properties of polymers under curing can be satisfactorily determined by means of dynamic measurements, which can provide a powerful tool for the investigation of the crosslinking process.

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