EFFECTS OF AGING ON EPOXY-BASED RAPID TOOLING MATERIALS

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Abstract

This study shows the effects of aging on epoxy-based rapid tooling materials. Two epoxy-acrylate resins used for stereolithography and one aluminum powder-filled epoxy used for the high speed machining of plastic injection molds were selected to investigate their aging behavior in different environments. Four different conditions, each characterized by a specific relative humidity, were used to perform a seven week long aging study. Temperature was kept constant at 30°C. Both stereolithographic resins showed a drop in mechanical properties and in their glass transition temperatures in wet environments, whereas aging time showed little influence on these properties. Moisture uptake is mainly responsible for that drop and coefficients of water diffusion were determined. On the other hand, the aluminum powder-filled epoxy showed little humidity-dependent drop in mechanical properties and in its glass transition temperature during aging. This result correlates well with the very low moisture absorption of this material.

Introduction

Prototype tooling for injection molding applications needs to have a long lifetime regardless of storage conditions. Many RP's materials are polymer-based. It is imperative therefore that test methods be developed in order to predict the long-term durability of these materials in different environments. This study (Ottemer, 2001) focuses on three materials that can be used for soft tooling for injection molding applications: Somos SL7110, Ciba SL7510, and Vantico Renboard Ren Shape-Express 2000. Both SL7110 and SL7510 are epoxy-acrylate photopolymers for stereolithographic systems manufactured by 3D-Systems. Ren Shape-Express 2000 is an extremely fast milling aluminum powder-filled epoxy for prototype and short run tooling. These three materials are representative of the current trend in polymer-based rapid tooling materials.

Aging of polymers

Aging is the term given to various processes that degrade polymers over time. During aging, one or more environmental stress factors act on the bulk polymer. The effects of these stress factors are translated to the microscopic/molecular level where changes occur in the polymer network or chain. Allred (1981) used the glass transition temperature as an indicator of any physical changes in the resin due to aging.

Hydrolytic aging is the greatest concern as contact with water is almost unavoidable. Moisture has the most significant effect on the reduction in the properties of these materials. Moisture exposure has two important components:

- Diffusion of water into the sample: the moisture absorption of a resin can be attributed to the water's affinity for the highly polar functional groups in the cured resin.
- Plasticization of the resin: on a molecular level the effect of water associating with polar groups is to decrease the hydrogen bonding between polymer chains which causes plasticization of the resin (Roe, 1991).

Time-humidity superposition principle

Moisture accelerates the aging process in the same way as temperature. A time-moisture principle has been proposed by Knauss and Kenner (1980) where the effect of moisture could be explained by the time-humidity superposition principle using a shift factor as shown in Equation 1.

$$\log(a(c)) = -\frac{B_1(c - c_0)}{B_2 + c - c_0} \tag{1}$$

Where a(c) is the shift factor; B_1, B_2 are constants determined by regression; c, c_0 are the moisture concentrations at time t, and at an arbitrary reference time, respectively.

Sample Preparation

Samples made of SL7110 for tensile, diffusion, and DMA tests were built with 3D-Systems's stereolithography machine SLA250. Samples made of SL7510 were built with a SLA3500. Parts were all built vertically on the platform. After part formation, the excess resin was removed by rinsing with tripropylene glycol monomethylether, followed by a rinse in isopropyl alcohol. Then the parts were post-cured for 60 minutes with UV light and for 120 minutes in a thermal oven at 80ºC. RenBoard was shaped into samples using a conventional milling machine.

Study of Moisture Diffusion

Time dependence of coefficient of diffusion

The diffusion behavior of glassy polymers cannot be described adequately by a concentration-dependent form of Fick's law with constant boundary conditions. Deviations from Fickian behavior are considered to be associated with the finite rates at which the polymer structure changes in response to the sorption or desorption of penetrant molecules. This viscous behavior of the polymer makes the diffusion time-dependent. Three different equations were used to fit the data because the diffusion behavior of the resin systems did not strictly follow any well-known model. Coefficients of diffusion were determined by plotting the short-time, average, and long-time diffusion data using equations from Crank (1975). For short times, Equation 2 was used.

$$\frac{M_t}{M_\infty} = \left(\frac{16 D_s t}{\pi L^2}\right)^{\frac{1}{2}} \quad (2)$$

Where M_t is the mass uptake at time t, M_∞ is the mass uptake at infinite time, D_s is the coefficient of short-term diffusion, t is the time, and L is the thickness of sample. Coefficients of long-time diffusion were computed using Equation 3, where D_l is the long term diffusion coefficient.

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\exp\left(\frac{-D_l \pi^2 t}{4L^2}\right) \quad (3)$$

Then, assuming that the coefficient of diffusion is independent of solvent concentration, an estimated average of this coefficient can be derived with an error being about 0.001 percent using Equation 4 where the value of (t/L^2) for which $M_t/M_\infty = 1/2$ is defined as the half-time, $(t/L^2)_{1/2}$.

$$D_{av} = \frac{0.049}{\left(t/L^2\right)_{1/2}} \quad (4)$$

Moisture uptake measurements:

ASTM D-570 is a standard test practice for water absorption. Eight standard specimens of each material were made. The dry weights of the samples were recorded with an accuracy of 0.1 mg. Then half of each kind of sample were put in pure water (humidity=100% and T=30ºC) and the remaining half in saturated salt-water. This aqueous solution has an equivalent relative humidity of 75.1±0.1% at 30°C, according to the ASTM E104. However, this solution is not totally equivalent to a 75.1% RH environment because the osmotic pressure created by Na^+ and Cl^- ions will affect the leaching out of the polymer.

The samples were weighed at 2 hrs, 4 hrs, 6 hrs (RenBoard), 8 hrs (RenBoard), 24 hrs, one week, and every two weeks until they absorbed less than 1% of the total weight gain or 5 mg per two weeks, whichever was greater. After all the test samples reached the termination criteria, they were placed in a dessicator overnight, and then reweighed in order to observe any leaching out of the materials. Figure 1 shows the weight gain versus time of the three materials. By comparing the main trends of the mass uptakes for the three materials, it appears that SL7510 absorbs the most water and RenBoard the least. Also, the infinite moisture absorption for both SL7110 and SL7510 is lower when immersed into salt-water, equivalent to a 75.1% RH environment, than in distilled water. That was not observed with RenBoard.

The coefficients of diffusion are shown in Table I. These values are consistent with values of coefficients of diffusion of water in other commercial resins (Becker and Colton, 2000). RenBoard shows an odd behavior - the coefficients of diffusion for salt-water immersion are higher than those for water-immersion. This may be due to a chemical interaction between ions (Na^+,Cl^-) and the aluminum filler. Moreover a change of color from gray to brown has also been observed after 1 week of salt-water immersion and after 3 weeks of water-immersion. Only SL7510 immersed into water has shown some significant leaching out (3% of material loss).

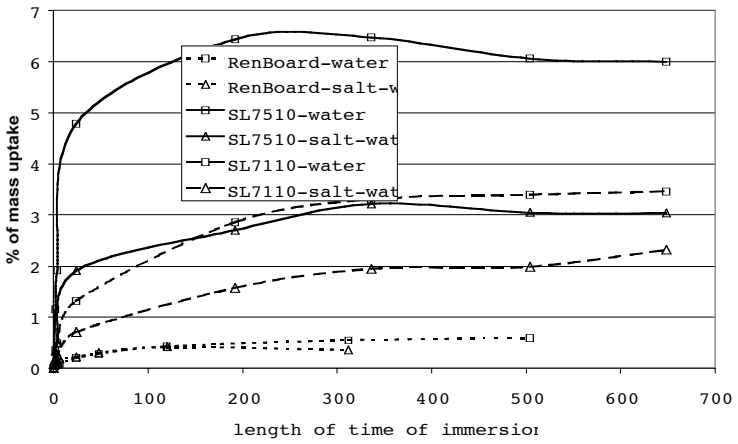

Figure 1: Water uptake

Table I: Coefficients of diffusion

mm^2/s	D short	D average	D long
SL7510 - 100%RH	10.0E-7	21.8E-7	13.8E-7
SL7510 - 75%RH	3.1E-7	9.2E-7	8.6E-7
SL7110 - 100%RH	3.3E-7	9.4E-7	2.3E-7
SL7110 - 75%RH	2.1E-7	5.4E-7	1.4E-7
RenBoard - 100%RH	2.1E-7	8.5E-7	2.5E-7
RenBoard - 75%RH	10.7E-7	20.7E-7	7.4E-7

Aging study

Eighty-four samples of each material were immersed in distilled water at 30°C. The same number of samples were put in a bath of saturated aqueous salt solution, equivalent to a 75.1% RH environment at 30°C. Another set of samples were exposed to ambient atmosphere kept at 30°C (dry-bulb temperature) by the use of a ventilated thermal oven. The RH of the environment varied other time due to weather conditions. It was 30±5% at 30ºC during the aging study on SL7510, 23±5% at 30ºC during the study of SL7110, and 20±6% at 30ºC during the study of RenBoard. Finally, a dessicator placed in the oven provided dry conditions for the last set of samples.

Mechanical properties:

At specified aging times, two sets of three samples of each material were removed and dynamical mechanical analysis (DMA) and tensile test were performed.

Storage modulus E' and Glass Transition Temperature T_g.

These characterizations were made with DMA testing (DMA 2980, TA Instruments, New Castle, DE) in the single cantilever flexural mode at a frequency of 1Hz and an amplitude of deformation of 20 _m. E' and T_g were recorded during a temperature ramp of 3°C/min from 30°C to 130°C for both SL7110 and SL7510 and from 30°C to 270°C for RenBoard. T_g was measured at the peak of tan_=E"/E'.

Young's modulus and ultimate tensile properties

Standard ASTM D638 was used as a guideline for the mechanical testing procedure. A tensile testing machine (Instron 4466, Canton MA) with a 10 kN load cell was used, and an extensometer was mounted on the sample. The cross head speed was 0.25 cm/min. Both strain and load were recorded.

Aging behavior of SL7510 and SL7110:

The evolution of the glass transition temperature is a good indicator of the aging behavior of a material. Figure 2 shows the evolution of the T_g of SL7510. After an induction period of around 400 hr due to diffusion of water inside the materials (area I on Figure 2), the T_g becomes time-independent and shows a marked decrease with RH due to the effect of moisture uptake on the material (area II on Figure 2). From 96ºC for the dry environment, the T_g of SL7510 drops down to 55ºC for the wet environment. This drop is an indication that the resin is being plasticized by moisture uptake.

The results of the mechanical tests are similar for both SL resins, showing a drop in properties in wet environments, except for the yield strain which remains mostly unaffected and constant, whatever the aging time or the RH of the environment.

After a 400 hr induction period, aged SL7510 samples show a 66% decrease in ultimate tensile strength from dry to wet environments. Initial properties were UTS = 54.5 MPa, E = 2407 MPa, E' = 2200 MPa, and ultimate strain = 5.75%. On the other hand, the tensile strength remains constant for the dry environment, with a slight increase observed. The storage modulus, E', and the Young's modulus, E, of SL7510 also reveal the same behavior (Figure 3): first an induction period followed by a time-independent, RH-dependent stage. It also is observed that the ultimate and yield strengths of SL7510 decrease with RH in the same way as T_g, E', and E.

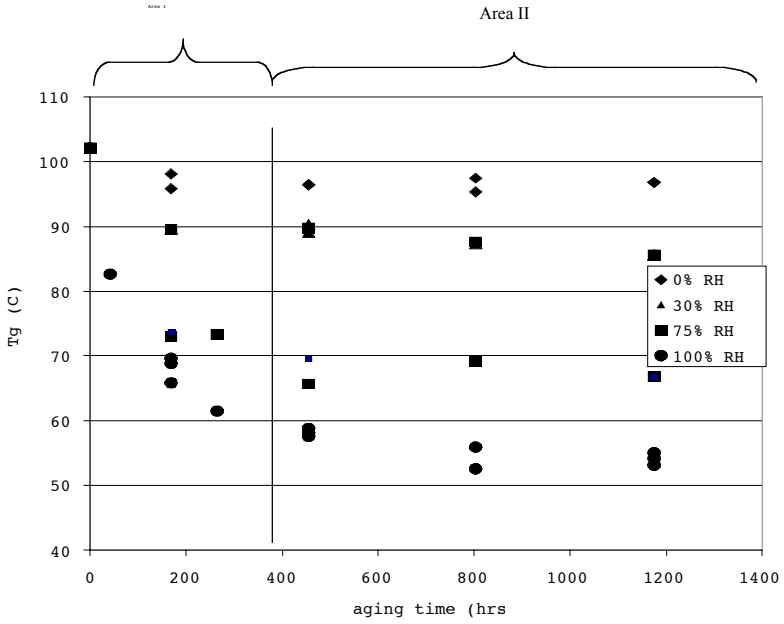

Figure 2: Tg of SL7510

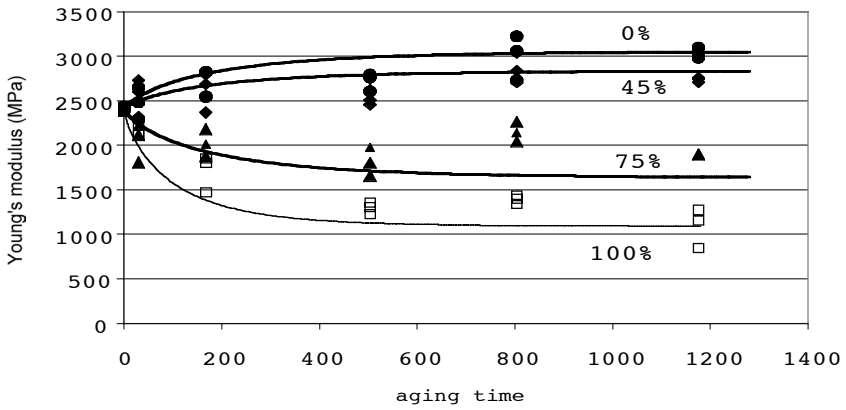

Figure 3: Young's modulus of SL7510

The same overall behavior is observed for SL7110, but to a lesser extent. Its initial values were UTS = 52 MPa, E = 2450 MPa, E' = 2000 MPa, and ultimate tensile strain = 4.6%. After an induction period of around 400 hr, the T_g becomes more time-independent and shows a marked decrease with RH (Figure 4). From 108ºC for the dry environment, the T_g drops down to 75ºC for the wet environment. The mechanical test results indicate the same, showing a drop in properties in wet environments, but here the properties are ruled by a 200 hr induction stage. The ultimate tensile strength is 25.3% higher than initially in dry and ambient environments, remains constant when immersed into the 75.1% RH environment, and drops 12% from its unaged value when submitted to the wet environment.

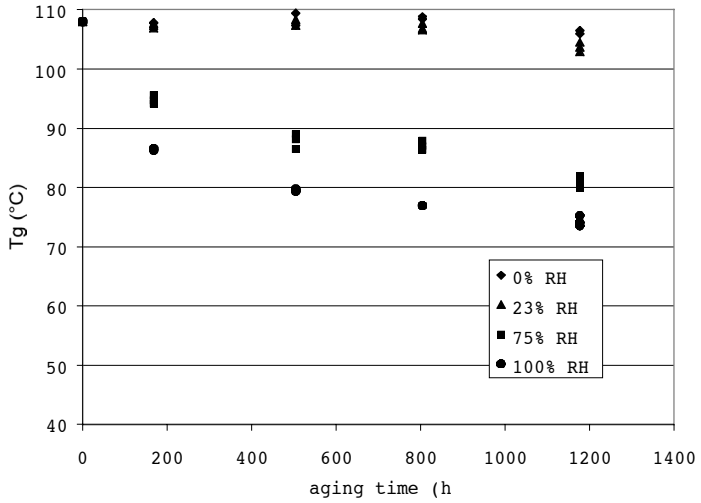

Figure 4: Tg of SL7110

Aging behavior of RenBoard:

RenBoard does not behave like the two other materials. The initial values were UTS = 52 MPa, E = 15000 MPa, E' = 6026 MPa, and the ultimate tensile strain = 0.83%. Figure 5 shows the evolution of the T_g of RenBoard with aging time. The variations observed are not significant. The T_g remains quite constant at 248ºC whatever the aging time or the RH of the environment. The mechanical results indicate the same, showing almost no significant variations. Whatever the aging time or the RH, the material failed in a brittle manner. This is different from the behavior of SL7510 and SL7110.

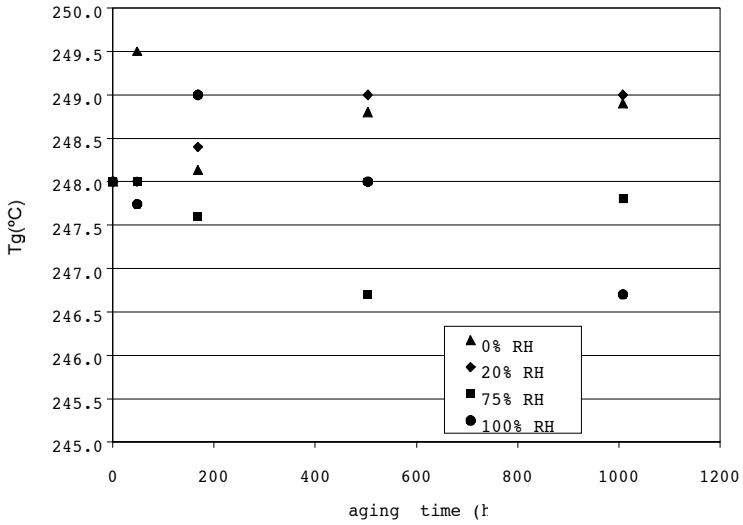

Figure 5: Tg of Renboard

Conclusions

The aging behaviors of three epoxy-based rapid tooling materials were investigated under four different moisture environments at 30ºC over seven weeks. Two were stereolithographic resins and showed a drop in mechanical properties and in their glass transition temperatures in wet environments, whereas aging time had no significant influence on these properties. The magnitude of the drop of mechanical properties was found to be related directly to the magnitude of the moisture uptake by the material. The properties (T_g and mechanical properties) first undergo an induction period led by moisture absorption and then reach asymptotic values, which are functions of the infinite mass-uptakes. The higher the moisture absorption, the more affected are the properties. The third material, an aluminum-filled epoxy, did not show significant humidity-dependent drops in mechanical properties and in its glass transition temperature. This result correlates well with the very low moisture absorption ability found for this material.

Acknowledgments

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