

EFFECT OF HUMIDITY AND TEMPERATURE ON THE CURING AND AGING OF A ROOM TEMPERATURE EPOXY ADHESIVE

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1 Introduction

The business airplane industry has high esthetical standard concerning their interior design. A business airplane is distinguished by, among others, its luxurious components, and its breathtaking interior design. In luxurious aircraft, wood was formerly used to build the furniture. Nowadays, it is replaced by composites sandwich structures covered with wood veneer. These structures bring sophistication, lightness, and good mechanical properties to the interior furniture. Due to high costs and geometrical limitations it is difficult to manufacture composite sandwich structure in a single piece. In many engineering fields, it is therefore necessary to assemble small manufactured parts. The assembly can be made using bolted, riveted, or adhesive bonded joints. Adhesive bonded joints have the advantage of reducing the added mass and distributing uniformly the load transfer while improving the overall aesthetic of the part. Among all available adhesives, room temperature epoxy adhesives are increasingly used to bond joints. One of the main advantages using this type of epoxy is their rapid curing and high mechanical properties. Their low cost and good hygro-thermal properties make them a suitable choice for the aeronautic industry [1]. As example, the assembly and the fixation of the composites sandwich structures to the fuselage of business airplanes are made possible through fasteners composed of screws and metallic inserts. These are generally bonded inside the sandwich panels using a room temperature epoxy resin. Although this method reduces the added mass, it is actually a source of local surface defects. In fact,

defects often appear on the visible surface of furniture where inserts are located. Moreover, the defects tend to appear few months after the airplane delivery causing costly reparations. The sources of these defects can be mechanical (deformation due to an excessive tightening), chemical (shrinkage of the epoxy adhesive) or the result of hygro-thermal exposition of the adhesive.

In the literature, the impact of added water to epoxy resin has been widely investigated [2-4]. Thus, the influence of water on the polymerization kinetics and on the mechanical properties was analyzed [2, 4, 5]. Several researchers have also investigated the impact of water on cured epoxy and concluded that it increases the degree of polymerization [6]. It was also proven that its ultimate T_g decreases with increasing relative humidity [7]. It is well known that a low T_g can be harmful since the operating domain of the material is considerably reduced. If the influence of a direct water contact is known, only few scientific investigations have been done on the effect of humidity on neat or cured epoxy resin.

The goal of the present research was to investigate the influence of humidity on the polymerization of an epoxy adhesive and to evaluate the effect of hygro-thermal aging on a cured epoxy used for the assembly and fixation of airplane interior furniture.

In this paper, an experimental procedure was developed to study the influence of humidity on the polymerization of an epoxy adhesive. Gravimetric measurements were performed to assess the weight variation due to relative humidity. The cure kinetics was also evaluated using a differential scanning

calorimeter (DSC). Finally, tensile modulus was measured using a standard DMA under flexural configuration.

2 Materials and experimental procedures

The adhesive used in this study was a two-component room temperature epoxy.

2.1 Curing and aging methods

The first plan of experiments was intended to characterize the adhesive at ambient temperature.

The first part of this plan was devoted to the evaluation of the total enthalpy and the ultimate T_g of the adhesive. Thus, resin was hand mixed with the hardener. Few milligrams of liquid resin were then placed in DSC sealed pans and were totally cured with a heating ramp in order to obtain the total polymerization enthalpy. The application of a second heating ramp enabled the determination of the ultimate T_g .

The second part of the plan was elaborated in order to determine the evolution of the T_g and the degree of cure of the adhesive at ambient temperature for long period of time. Few milligrams of hand mixed resin were placed in ten (10) DSC sealed pans. One sample was tested each day at ambient temperature and humidity. The DSC parameters used are presented in section 2.2.2.

The second plan of experiments aimed at studying the influence of humidity during the cure of the epoxy. Resin was hand mixed with the hardener. The obtained blend was then put in silicone molds with 3 standard cavities (60x10x3mm) already coated with release agent. Four (4) molds were used to make twelve (12) samples. Each mold (with 3 samples) was placed in hygro-thermal aging chambers. The samples were cured at different humidity levels for 10 days. The different hygro-thermal conditions are summarized in Table 1.

The third plan of experiments was designed to the evaluation of hygro-thermal aging on cured epoxy. As in the first experiment, resin was mixed with the hardener and then put in silicone molds. Twelve (12) samples were subsequently cured at ambient temperature and humidity for 10 days. The samples were then aged for one (1) week in the hygro-

thermal aging chambers according to the parameters listed in **Table 2**.

2.2 Tests methods

2.2.1 Gravimetric measurements

Mass measurements of each sample were performed before and immediately after their exposition in hygro-thermal aging chambers. An analytical balance with an accuracy of 0.001 g was used in order to evaluate the absorbed humidity. The mass percentage of water absorbed by the resin $M(t)$ was calculated according to the equation:

$$M(t) = \frac{W_{final} - W_{initial}}{W_{initial}} * 100 \quad (1)$$

where, W_{final} was the resin weight after aging and $W_{initial}$ was the resin weight before aging.

2.2.2 Calorimetric analysis

A DSC Q2000 from TA Instruments was used to perform calorimetric measurements. Small pieces (few milligrams) were cut from each solid sample obtained from the second and the third plan of experiments and placed in DSC sealed pans. All tests were made with a heating ramp of 3 °C / min between 0 °C and 160 °C. T_g was determined by the inflexion point of the reversing heat flux curve. The residual enthalpy was obtained by the integration of the non-reversing heat flux curve. The degree of cure α was calculated with the following equation:

$$\alpha(\%) = 100 * \left(1 - \frac{\Delta H_{res}}{\Delta H_T}\right) \quad (2)$$

where, ΔH_{res} was the residual enthalpy and ΔH_T , the total enthalpy of the adhesive. All data were an average of 3 different samples.

2.2.3 Thermomechanical analysis

Mechanical properties were determined with a dynamical mechanical analyzer (DMA) Q800 from TA Instruments. Three point bending tests in static mode were performed to determine the Young's modulus E which corresponds to the slope of the stress-strain curve.

All data were an average of 3 different samples of each condition mentioned in **Table 1** and **Table 2**.

3 Results and discussion

3.1 Study of the epoxy adhesive at ambient temperature

The first DSC measurements of neat epoxy resin led to a total polymerization enthalpy of 350 J/g suggesting that the reaction is highly exothermic as seen in **Figure 1**. Moreover, the ultimate glass transition temperature (T_g) of 88 °C was determined by the inflexion point of the reversing heat flux curve as shown in **Figure 2**.

The second part of this study showed that this room-cured epoxy does not reach the full degree of cure after 10 days of curing at ambient temperature. **Figure 3** presents the degree of polymerization versus the exposition time at ambient temperature. It can be seen that the degree of polymerization varies between 60 % and 80% as the curing increases from one to 10 days. A plateau of polymerization is reached after just two days and the polymerization does not increase significantly thereafter. Moreover, **Figure 4** shows the glass transition temperature evolution with the exposure time at ambient temperature. As expected, the T_g follows the same trend as the degree of cure. It can be observed that the adhesive cured at room temperature has relatively low glass transition temperature ($T_g=50$ °C) after 10 days of polymerization. The value is significantly smaller than the ultimate T_g . This analysis suggests that this epoxy resin is still curing after very long period of time at ambient temperature. The kinetics and mechanical properties will be consequently more susceptible to change under certain hygro-thermal conditions.

3.2 Polymerization of epoxy samples under humid conditions at ambient temperature.

3.2.1 Weight variations

The gravimetric results did not show a significant increase of weight due to water absorption. However, for a relative humidity of 100 %RH, an increase of 1.7 wt% was obtained. **Figure 5** shows

the weight variation of epoxy as function of humidity. This corresponds to the percentage of water in the resin with respect to unaged resin. A negative absorption rate can be observed for the first three levels of relative humidity. Even at low humidity levels, it is uncommon to see such negative absorption. The adhesive seemed to lose weight when it polymerized in humid environment. However, at high humidity level, the water absorption became higher than the mass loss and the sample began to gain weight due to humidity. This kind of test requires a lot of time and many types of equipment thereby the amount of tests has been limited. However, a slightly increasing trend of the water absorption can be observed and the adhesive has absorbed 1.7% of mass due to humidity.

3.2.2 Kinetics properties

Figure 6 shows the residual enthalpy of the epoxy adhesive as function of the relative humidity exposure during the cure. The M-DSC results reported in this figure indicate that the residual enthalpy of reaction seems to slightly decrease with the increase of relative humidity. This conclusion can indicate that the presence of humidity leads to a different morphology of the resin and thus decreases the residual enthalpy. However, this conclusion cannot reinforce the results found in the literature stating that the presence of water tends to increase degree of cure [2, 4] and also accelerate the kinetic reaction rate [2-5] of other epoxy systems.

What distinguished this present study from literature is the way water was mixed with the neat resin. A direct interaction (water mixed into resin or immersed sample) would maximize the water effect leading to a higher degree of cure. It should also be noted that the reaction is made at ambient temperature. The mobility of water and resin molecules is therefore reduced. Thus, the conclusions exposed here can be different at elevated temperature.

3.2.3 Mechanical properties

This study showed that the Young's modulus decreases with increasing relative humidity. **Figure 7** represents the evolution of the Young's modulus as function of the relative humidity during the cure.

It can be seen that the modulus decreases by almost 25 % when the relative humidity reaches 100 %RH. These results were in accordance with previous researches [3] concluding that water absorption lead to a decrease of mechanical properties.

Since the moisture did not seem to influence the kinetic reaction, the decrease of the Young's modulus may be caused by either the presence of non-reacting water or voids. The water absorbed by the resin could be captured in between the polymer chains. But, as shown in the section 3.2.1 and 3.2.2, its reaction with resin molecules was not important enough to impact the polymerization. The decreasing mechanical properties can only be the result of entrapped gas inside polymerized resin. It is well known that the presence of only 1 % of voids can reduce the mechanical properties of composites material by almost 25 %. As mentioned before, due to the highly exothermic behavior of this epoxy, water molecules absorbed could have been transformed into vapor leading to voids and porosities formation.

3.3 Aging of polymerized epoxy

The aging procedure aimed at evaluating the behavior of polymerized epoxy exposed to different hygro-thermal conditions.

Previous studies showed that, the cross-linking process at ambient temperature did not reach the completion even after 10 days of polymerization for this resin (see section 3.1). For real application, the behavior of cured resin in some specific environment becomes very important. Thus, the measurements were performed with a polymerized epoxy at a degree of cure of $\alpha = 0.8$ (and $T_g = 50$ °C) which corresponds to a 10 days of cure at ambient conditions.

3.3.1 Weight variations

Figure 8 illustrates the polymerized resin weight gain (extent of water) as a function of relative humidity for two aging temperatures. The results showed an increase of weight with increasing relative humidity of around 2 wt%. The **Figure 9** shows the polymerised resin weight gain versus temperature for two values of relative humidity

during aging. It can be seen that an increase of aging temperature also increased the moisture absorption. At high temperature, the mobility of polymer chains as well as the activation energy of the water molecule is increased. It is therefore easier for water to penetrate the dense crosslinks network [8].

3.3.2 Kinetics properties

The weight variation and kinetics properties are gathered in **Table 3**. By analyzing these data, some conclusions can be made.

First, when the epoxy adhesive was aged at ambient temperature (25 °C), the presence of humidity (80 %RH versus 0 %RH) led to higher degree of cure (from 87.33 to 93.19 %) but the decrease of T_g was less significant (from 57.87 to 54.2 °C). The presence of water tends to increase the mobility of the polymer molecules and thus increases the plasticization effect. This latter effect is well known to decrease T_g [9]. However, the chains mobility simultaneously creates an additional polymerization which tends to increase the T_g . This has been demonstrated by Kajorncheappunngam and Al [6]. In fact, when an epoxy is partially polymerized, a water contact induces a repolymerization caused by chains mobility. Therefore, the result seems to reduce the T_g depression.

Secondly, at high temperature aging (60 °C) without humidity, the degree of cure was higher (98.79 %) because of cure temperature approaching the ultimate T_g value (see **Figure 2**). The corresponding T_g followed the trend up to 85.30 °C, since it is a function of degree of cure.

Thirdly, when samples were age at 60 °C and 80 %RH, degree of cure reached its highest value (99.34 %). This was a 1 % gain versus a 60 °C and 0 %RH aged sample. High temperature could thus slightly increase the degree of polymerization even when the cross-linking reaction of the polymer was controlled by diffusion. For the same aging conditions (60 °C and 80 %RH), T_g was 75.85 °C. Beside the fact that it was higher than the initial value (50 °C), it remained lower than the measured T_g at 60 °C and 0 %HR.

It seems that increasing the relative humidity increased the amount of water absorbed and lowered the T_g . This has been demonstrated by several authors [6, 7, 10]. In **Table 3**, it can be seen that high temperature aging caused a greater depression of T_g when we compare results from 0 %RH conditioning with 80 %RH. This observation was also done by Mijovic and Al.[8] and Xiao and Shanahan[11]. At high temperature, it was said previously that polymer chains and water molecules are in motion and the resin tended to absorb more water. The mechanism possibly increased the plasticization and thus, decreased T_g . Moreover, the high temperature aging initially causes a higher degree of cure. There is no additional polymerisation generated by adding water and thus the T_g depression is more important and is only caused by the plasticization effect.

To summarize, in the present study, not only a decrease of T_g was observed, but also an additional crosslinking at high relative humidity. Thus, the results obtained suggest that two phenomena occurred with water absorption. The results are in agreement with Zhou and Lucas [12, 13] studies in which it was demonstrated that the first mechanism consisted of water breaking hydrogen links and van der waals forces in resin and in fact, increased mobility. This created a T_g decrease [12]. The second mechanism depended on aging temperature and promoted secondary crosslinking [13].

3.3.3 Mechanical properties

A decrease of the Young's modulus by almost 20 % with increasing relative humidity (and thus the

absorbed water) was observed (see **Table 4**). The infiltration of water in the micro-voids [14-16] could be the cause of this decrease. The water absorption could also cause bubbles created by the epoxy additional polymerization. Voids contributed to facilitate the diffusion and elevated temperature increased molecular entropy. To summarize, even if the degree of cure increased with the relative humidity, the Young's modulus decreased due to the presence of voids.

4 Conclusions

In the present study, the effect of relative humidity at ambient temperature on the polymerization of an epoxy adhesive was analyzed. First, it was shown that residual enthalpy seems to be affected by the polymerization of the resin in humidified environment. Secondly, the effect of hygro-thermal aging on polymerized epoxy properties was examined. A slight decrease of T_g was observed, suggesting an additional polymerization of the adhesive caused by the combined temperature and humidity conditions. Furthermore, the Young's modulus decreased with the increase of relative humidity for the two cases studied, either by the presence of bubbles or by the presence of water entrapped in micro voids.

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Table 1. Hygro-thermal test conditions for uncured epoxy samples.

Polymerization 10 days		
Number of sample	Temperature (°C)	Humidity (%RH)
3	23	30
3	23	50
3	23	80
3	23	100

Table 2. Aging test conditions of cured epoxy samples.

Aging 1 week		
Number of sample	Temperature (°C)	Humidity (%RH)
3	25	0
3	60	0
3	25	80
3	60	80

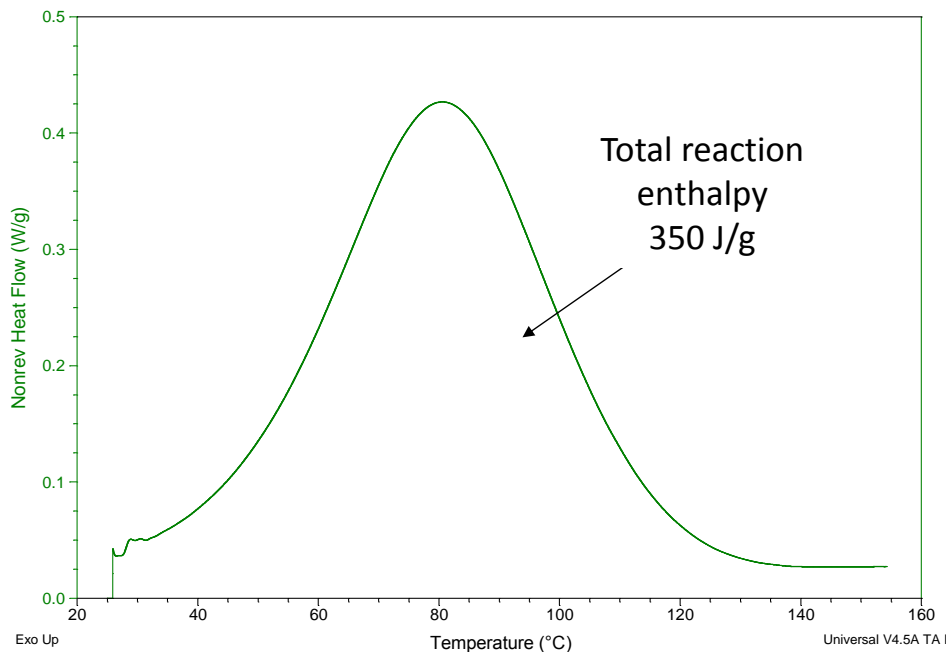


Fig. 1. DSC scan of epoxy adhesive at 3 °C/min.

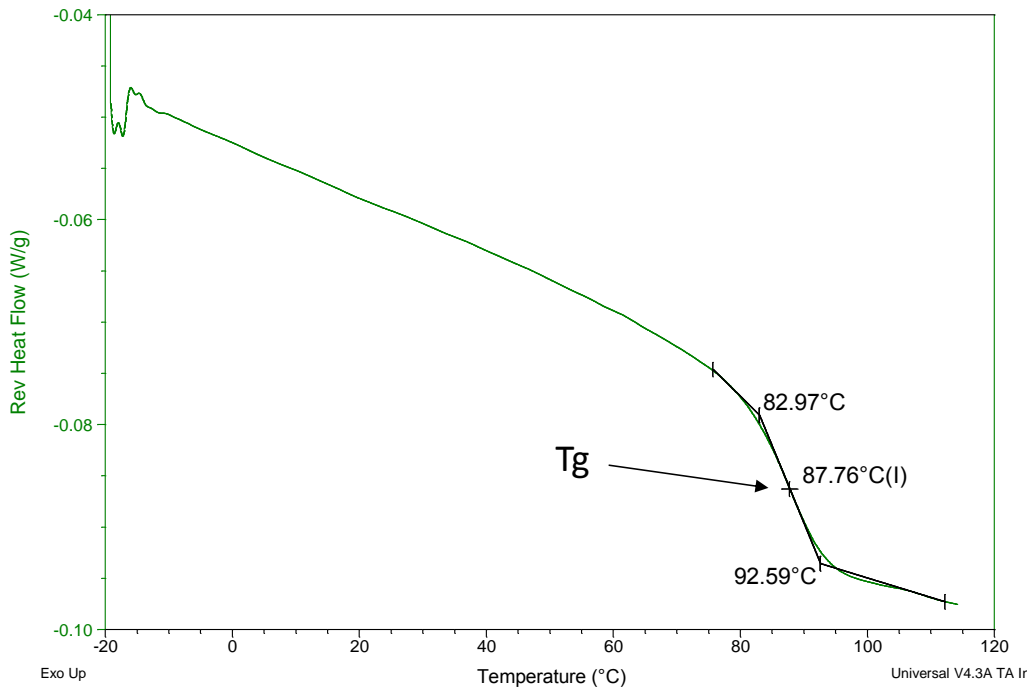


Fig. 2. Determination of Tg by MDSC.

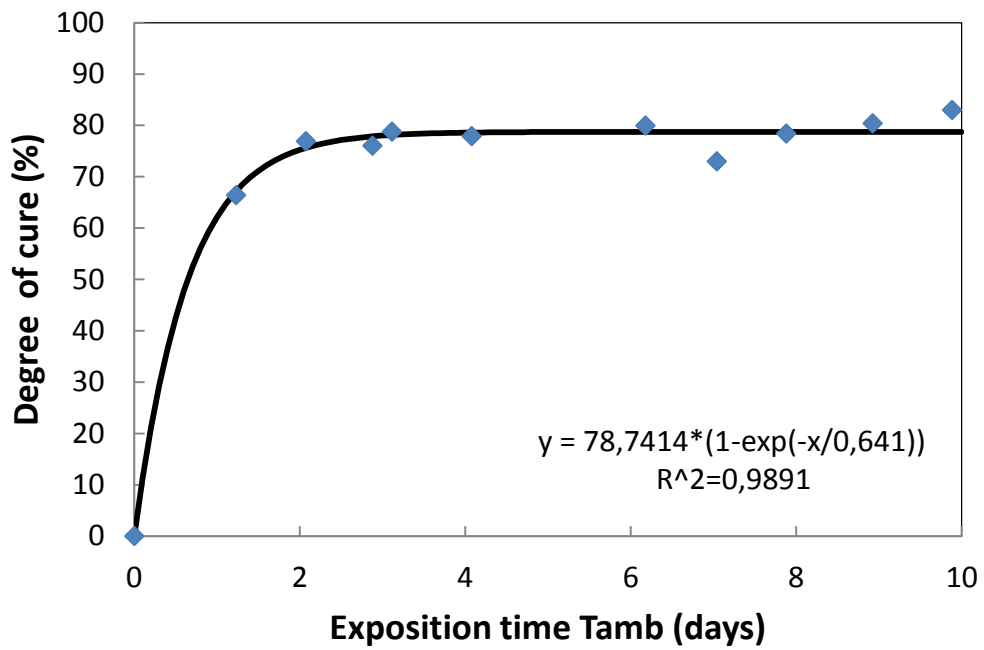


Fig. 3. Evolution of resin cure at ambient conditions (ie 23 °C).

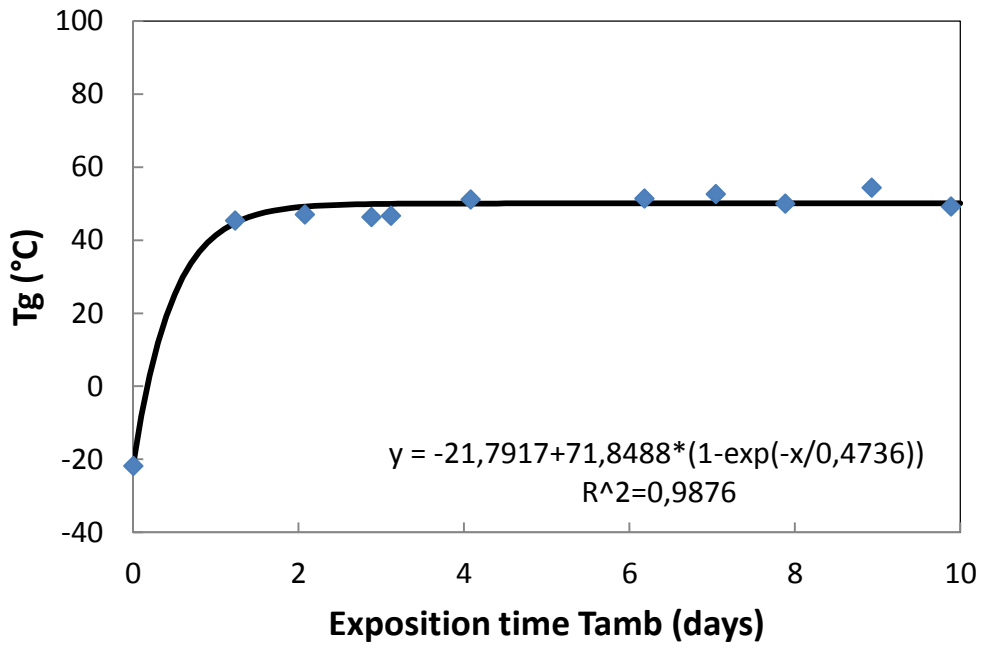


Fig. 4. Evolution of resin Tg at ambient conditions (ie 23 °C).

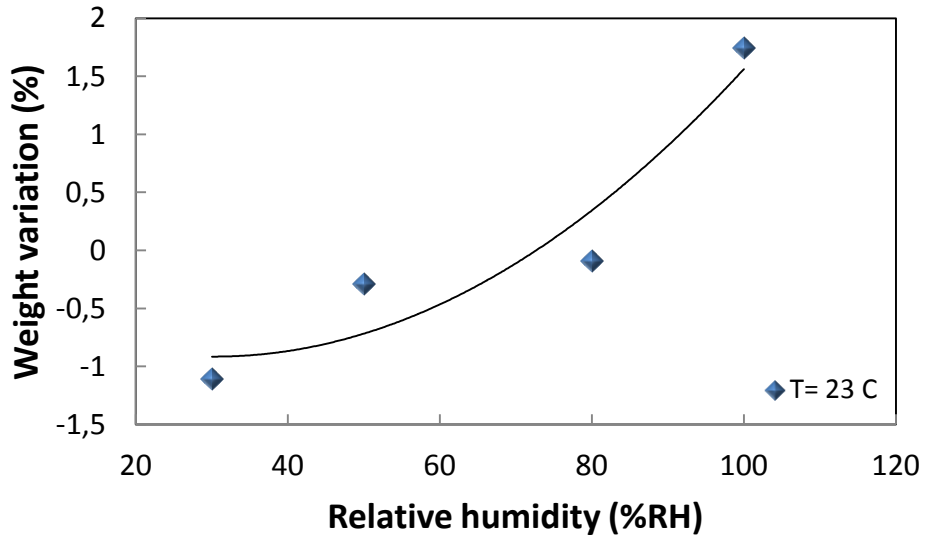


Fig. 5. Weight variation of epoxy adhesive cured under humid condition.

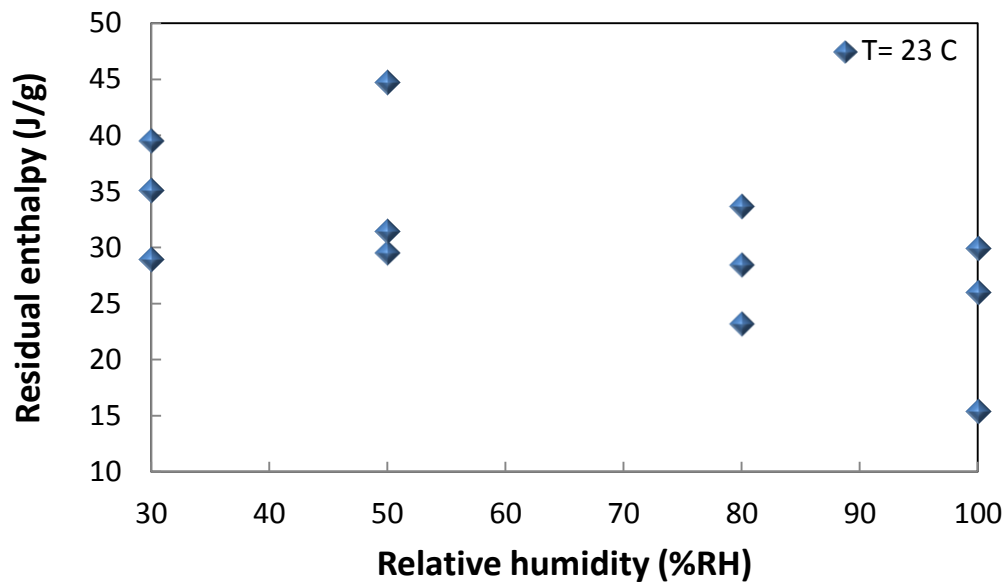


Fig. 6. Residual enthalpy of epoxy adhesive cured under humid condition.

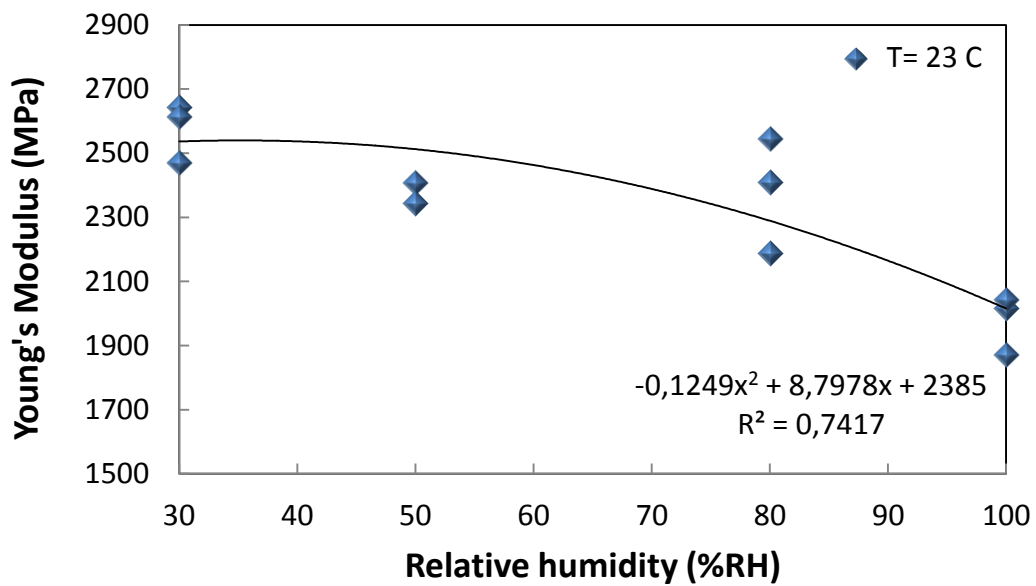


Fig. 7. Young's modulus of epoxy adhesive cured under humid condition.

Table 3. Degree of cure and T_g measured on polymerized samples after exposure to relative humidity and temperature conditions.

1week aging conditions		Results					
Temperature (°C)	Relative humidity (%)	Average weight variation (%)	Standard deviation	Average α (%)	Standard deviation	Average T_g (°C)	Standard deviation
25	0	-0.21	0.02	87,3	2,9	57,9	2,1
60	0	-0.52	0.03	98,8	0,3	85,3	2,1
25	80	0.44	0.03	93,2	0,9	54,2	0,8
60	80	1.41	0.04	99,3	0,2	75,9	1,7

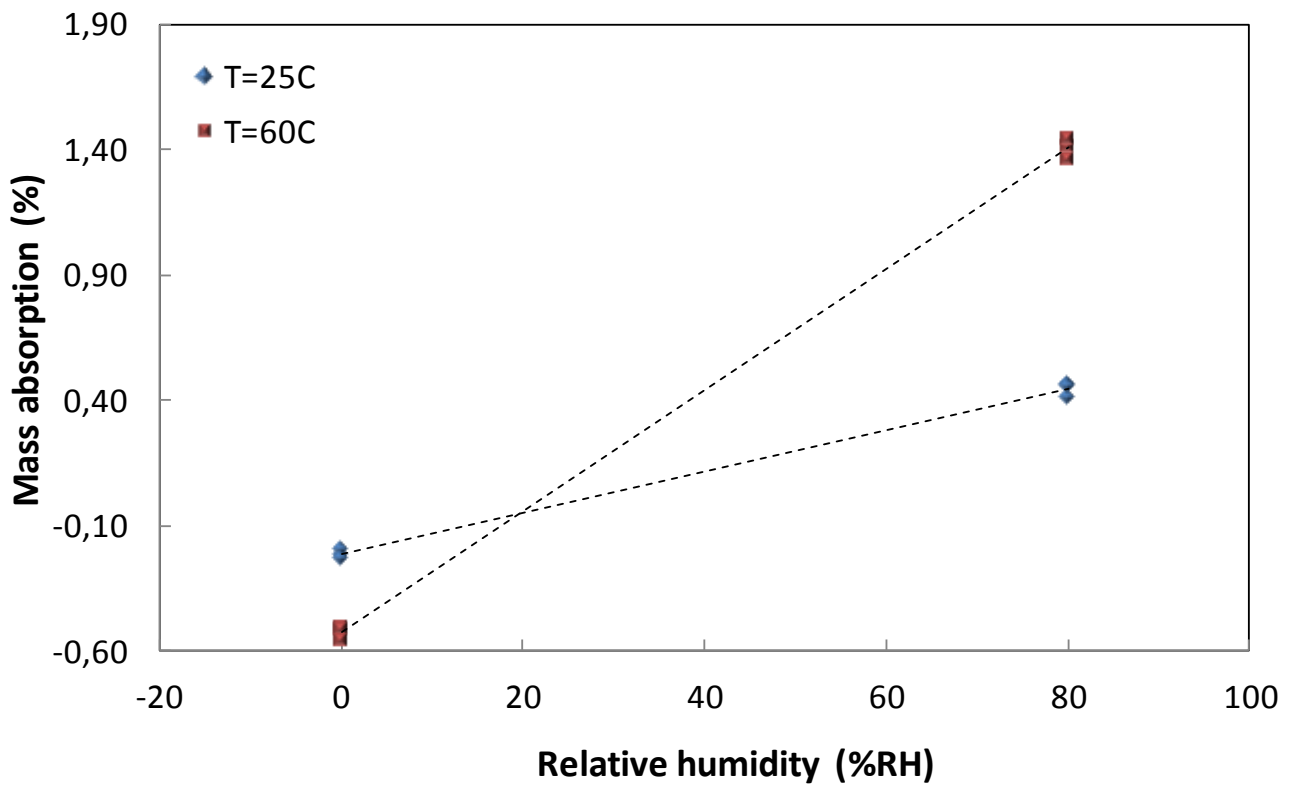


Fig. 8. Weight variation of polymerized sample aged under humid conditions for two aging temperatures.

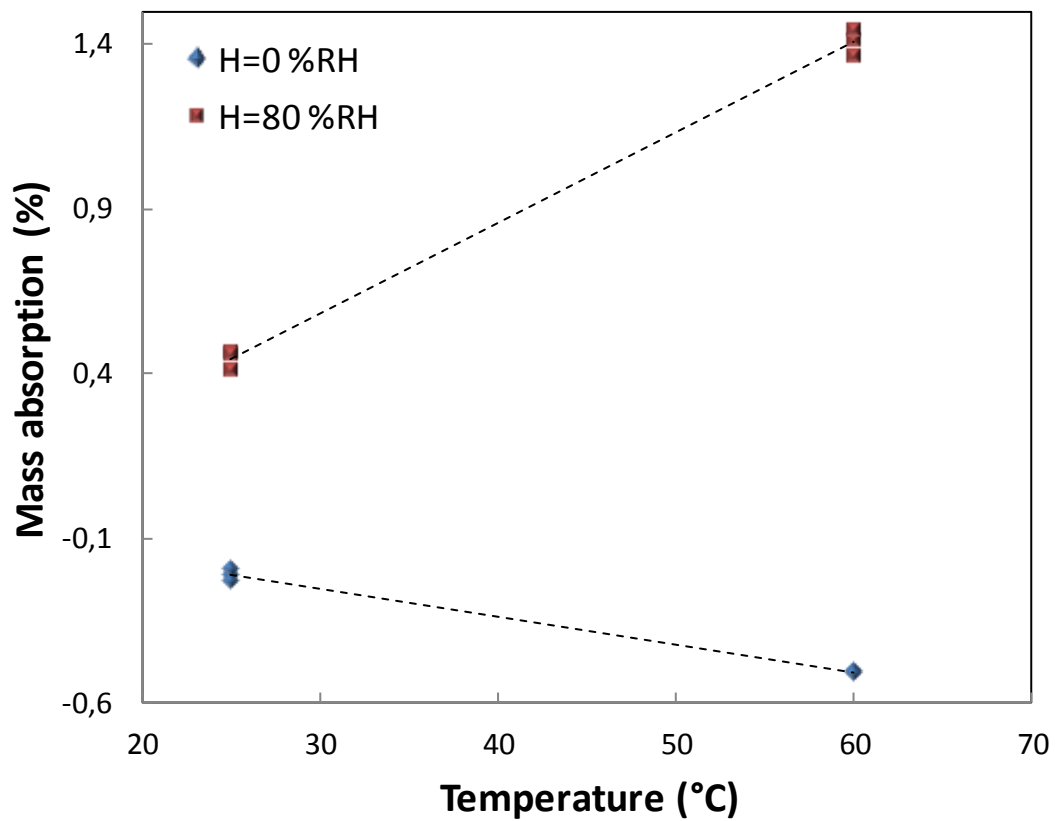


Fig. 9. Weight variation of polymerized sample aged under temperature conditions for two values of relative humidity.

Table 4 Flexural properties of polymerized epoxy adhesive after exposure to relative humidity and temperature conditions.

1week aging conditions		Results	
Temperature (°C)	Relative humidity (%)	Average Young modulus (MPa)	Standard deviation
25	0	2494	48
60	0	2190	86
25	80	2323	31
60	80	1997	234

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