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Hygrothermal Aging of Amine Epoxy: Reversible Static and Fatigue Properties

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Abstract: Fiber-reinforced polymers (FRP) are widely used in structural applications. Long-term properties of such materials exposed to water are of high concern and interest, especially for subsea and offshore applications. The objective of this study is to identify the mechanisms and to identify whether drop in properties of diamine-cured mixed DGEBA-HDDGE is reversible upon drying the material to its initial water content. The properties of interest are mechanical strength, elastic properties and fatigue performance, as well as changes in chemical structure. The effect of absorbed water on the properties of the resin is evaluated, and hygrothermal effects and aging mechanisms are discussed. Furthermore, it is shown experimentally that the tension fatigue S-N curve of a wet epoxy resin can be estimated by shifting the S-N curve of a dry material proportionally to a reduction in static tensile strength due to hygrothermal effects.

Keywords: epoxy; hygrothermal aging; plasticization; strength; fatigue

1 Introduction

Epoxy resins are well known for their relatively high strength, stiffness, low volatility, chemical resistance, and low shrinkage on curing [1, 2]. Glycidyl ether derivatives of bisphenol A, i.e. DGEBA, are the most widely used epoxy resins in structural applications and constitute more than 75% of epoxy resins sold worldwide [3]. These epoxy resins are widely used as matrices for composite materials, i.e. fiber-reinforced polymers (FRP), as well as adhesives, organic surface coatings and encapsulating agents [1, 4]. FRPs are often exposed to water or humid air environments, where water molecules can migrate in the polymeric matrix and modify their physical and mechanical properties [1]. Highly crosslinked amine-cured epoxy resins are hydrophilic and their properties can significantly deteriorate upon water uptake [2, 5–13]. A degradation of the matrix-dominated properties of epoxy-based glass fiber composites is also expected when they are exposed to and saturated with water [14, 15]. Such effects are of special interest for offshore and marine industries, but also for many other industries, such as the renewable energy sector, i.e. wind turbines, where FRPs are widely used [16, 17]. The number of articles concerning aging of this particular mixed resin (DGEBA/HDDGE/IPDA/POPA) is very limited [17].

Water has a double effect on the polymer networks depending on its concentration [12]. At the beginning of the hygrothermal process, absorbed water causes the relaxation of residual stress and the acceleration of additional crosslinking, both of which may be responsible for the increase of the mechanical properties [12, 14, 18]. T_g can be regarded as the most useful parameter revealing material degradation [19]. The more flexible the polymer chains, the lower the T_g [12]. A decrease in T_g is generally attributed to plasticization and deterioration (i.e. chain scission), while an increase in T_g is derived from additional crosslinking [14]. The degradation of the tensile strength can be attributed to the plasticization and deterioration of the resin [14, 20]. The percentage reduction in the tensile strength of epoxies is related to the hydrophilicity of the resin blend, which may be measured by Hoy's solubility parameter for hydrogen bonding [21]. Fatigue life reduction is still not completely understood, and while some authors report significant degradation, others do not observe noticeable changes after water absorption [17].

Hygrothermal process may induce both reversible and irreversible changes in the epoxy [14, 22]. Irreversible changes persist after re-drying the material [17]. It seems that chemical processes involved in hygrothermal aging of

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epoxies are generally irreversible and persist even after the material is dried [17]. Irreversible damage in epoxies may occur due to susceptibility of the polymer to hydrolysis, oxidation, and change of the effective average crosslinked molecular weight. For some epoxy systems, water at elevated temperatures can attack the crosslinked network, causing chain scission and the leaching of segments [23]. Crosslinking reactions can also continue in an epoxy over time resulting in increased stiffness, since water causes an acceleration of the resin-hardener reaction [22, 24].

V.O. Startsev et al studied the effect of outdoor exposure on epoxies and assessed reversible effects of moisture. They have found that strength of the studied epoxies decreased by 20-40% due to plasticization [25].

Plasticization, due to water uptake, is commonly placed in the physical aging category. Authors believe that this is not fully correct, and, instead, offer a distinction between hygrothermal aging and hygrothermal effects. Aging can be defined as processes which cause changes in material properties and that are directly time-dependent. Processes which are also dependent on other terms, such as concentration (e.g. related to mass transport phenomena), are termed as hygrothermal effects, where other terms might or might not be time-dependent themselves.

The aim of this paper is to investigate whether static and fatigue properties of a commonly used DGEBA/HDDGE/IPDA/POPA amine epoxy resin are reversible or not after re-drying the material.

2 Materials

Amine-cured epoxy resin was prepared using reagents Epikote Resin RIMR 135 (Hexion) and Epikure Curing Agent MGS RIMH 137 (Hexion) in a ratio of 100:30 by weight (stoichiometrically). The epoxy value of the resin is 0.54-0.60 equivalent/100 g. The amine value of the hardener is 400-600 mg KOH/g [24]. The mixture was degassed in a vacuum chamber for 0.5 h in order to remove bubbles. The epoxy system consists of the following compounds: bisphenol A diglycidyl ether (DGEBA), 1,6-hexanediol diglycidyl ether (HDDGE), poly(oxypropylene)diamine (POPA) and isophorondiamine (IPDA).

The resin was casted into moulds to make rectangular DMTA ($40 \times 7 \times 2$ mm^3) and dogbone-shaped ($200 \times 30 \times 2$ mm^3 with 20 mm width in the most narrow part) specimens according to ISO 6721 and ISO 527 [26, 27]. The geometry of dogbone specimens equipped with strain gauges (gauge length 6 mm; Tokyo Sokki Kenkyujo Co., Ltd., Japan) is shown in Figure 1. The resin was degassed before pouring. The specimens were cured at room temperature for 24 h and post-cured in an air oven (Lehmkuhls Verksteder, Norway) at 80 °C for 16 h. The specimens were removed from the moulds' grooves and cut into the desired length with a vertical bandsaw. After cutting the epoxy specimens were ground using sandpaper (FEPA P60, grain size 269 μm). The specified dimensions from ISO 6721 and ISO 527 [26, 27] were achieved within 5% tolerance.

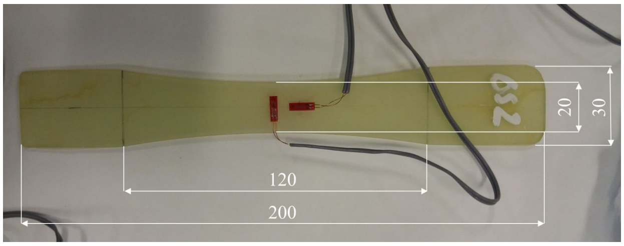

Figure 1: Geometry of dogbone specimens used for static tensile and fatigue tests. The placement of strain gauges is indicated.

The placement of strain gauges as shown in Figure 1 allowed to measure strains in both the direction of the applied load and the direction normal to it, thus enabling the calculation of Poisson's ratio.

3 Experimental

3.1 Conditioning of resin specimens in distilled water and drying

The epoxy specimens were tested dry, saturated in water and re-dried. Specimens were conditioned in a heated distilled water (60 ± 1 °C) bath for a period of two months (equilibrium was achieved after a few weeks; see Figure 2). The water content was measured by FT-NIR spectroscopy [28] and by the more widely used weight gain method [29]. Specimens were weighed using analytical scales AG204 (± 0.1 mg; Mettler Toledo, USA). Both methods gave about the same results, but the FT-NIR method has the advantage of providing a true water content using the method described in another paper [28]. The true water content shows the amount of water in respect to the absolutely dry material and is defined in Equation 1.

$$\begin{aligned} W^{\star}(t) &\equiv \frac{m_{water}(t)}{m_{absolutely\ dry}} \cdot 100\% \\ &= \left(\frac{m(t) - m_{absolutely\ dry}}{m_{absolutely\ dry}}\right) \cdot 100\% \end{aligned} \tag{1}$$

where m_{water} is a moisture mass, $m_{absolutely\ dry}$ is a mass of resin with 0% moisture content, m is a total mass of resin with moisture.

Already at the initial stage, the ‘dry’ material has a true water content of about 0.63% [28], meaning that it has some initial water present being in equilibrium with water vapour in the air. The evolution of true water content in time during hygrothermal conditioning, drying and reconditioning in air atmosphere to initial water content is presented in Figure 2.

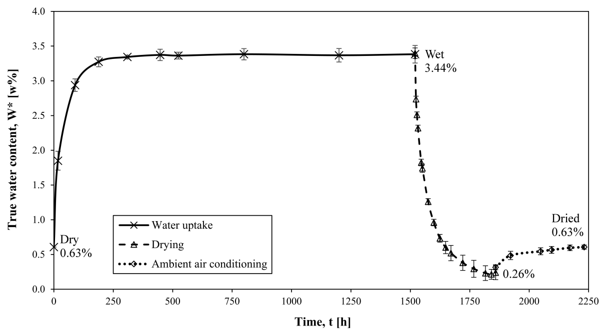

Figure 2: Evolution of true water content of amine-cured epoxy resin during water uptake, drying and conditioning in air.

The drying of saturated specimens was performed in a drying cabinet PK-410 (ESAB, UK) at 60 ± 1 °C in air atmosphere with natural convection and relative humidity of 13 RH%.

3.2 Glass transition temperature determination

Dynamic Mechanical Thermal Analysis (DMTA) tests for determination of glass transition temperature (T_g) were conducted using Netzsch GABO qualimeter Eplexor equipped with a 1.5 kN load cell (Netzsch GABO Instruments, Germany) operated in tension in displacement control with a constant static strain of 0.4% and a cyclic strain of 0.1% applied with a frequency of 1 Hz. The temperature sweep range was from 20 up to 120 °C with a heating rate of 1 °C/min. T_g is determined as the point of inflection in the temperature sweep of the storage modulus plot [26]. Evaporation of water for the wet specimens was avoided by conducting measurements in the water environment, ensuring that the specimens have been saturated during the whole process.

3.3 Mechanical testing

Tensile tests were conducted using a servo hydraulic test machine Instron model 1342 (Instron, International: USA/UK). the displacement rate was set to 1 mm/min. Fatigue tests were done using the same equipment. The testing frequency was chosen in order to keep a constant strain rate of 0.05%/min. Tests were performed at R ratio of 0.1. The temperature during the tests was about 23 °C (room temperature). Tensile tests were performed with 4 specimens for each configuration (dry, wet and dried). Average values and experimental scatter were reported for ultimate tensile strength, Young’s modulus and Poisson’s ratio for each group. In fatigue, between 11 and 13 dogbone specimens were used for obtaining S-N curves for each case (dry, wet and dried).

4 Results and discussion

4.1 Change of mechanical properties due to water uptake

In order to investigate the influence of the hygrothermal process and water content on the mechanical properties, static tensile and tension fatigue tests were performed.

4.1.1 Reversibility of mechanical properties in static tension

Static tensile test results are illustrated in stress-strain curves shown in Figure 3. The dry material has an ultimate tensile strength (UTS) of 60.5 ± 2.7 MPa. All scatter is given as one standard deviation. After the hygrothermal aging process, the UTS decreased to 48.5 ± 3.3 MPa, resulting in a relative decrease of about 20% on average. Results indicate that the material regained its initial strength and Young’s modulus after redrying (and conditioning in air to its initial water content). It should be noted, that dried material has a slightly higher strength (66.4 ± 3.0 MPa) than the initial (60.5 ± 2.7 MPa), although the effect is within the standard deviations. A possible explanation to this phenomenon could be residual crosslinking or polymer relaxation [17]. It should be noted that not only the UTS of the dry and re-dried specimens were the same, but also the entire shape of the stress strain curve was very similar.

Poisson’s ratios are reported in Figure 5. The Poisson’s ratio was calculated as the ratio of strains measured via strain gauges in directions normal to applied load and in

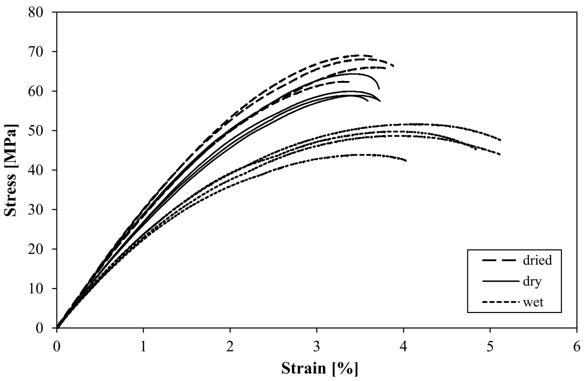

Figure 3: Stress-strain curves of dry, conditioned and dried epoxy specimens.

the direction of tension. Results show that Poisson's ratio increases for saturated epoxy but returns to the initial values after drying to the initial water content, indicating that this effect is reversible. An increase in Poisson's ratio of epoxy due to absorbed water is consistent with literature [30]. The authors believe that such increase in Poisson's ratio might be due to the absorbed almost incompressible water or the reduction of glass transition temperature (T_g) due to the plasticizing action [30,31]. Theocaris has shown that the Poisson's ratio of epoxy increases with higher plasticizer content even at room temperature below T_g [30]. The T_g of dry, saturated and re-dried epoxy was 81.7, 59.1 and 84.7 °C, respectively.

The strain to failure (ϵ_{max}) is identical for dry and dried epoxy, being 3.71 ± 0.10% and 3.69 ± 0.22% respectively, while being much higher for saturated epoxy (4.78 ± 0.51%). Dogbone specimens failed in the middle as shown in Figure 4. It was a brittle fracture and shattering often occurred for dry and re-dried specimens, while failure was less brittle for saturated epoxy. On the micro level failure is believed to occur due to a combination of crosslink bond breakage and disentanglement of macromolecular chains. The specimen placement in the machine along with the failure are shown in Figure 4.

Mechanical and elastic properties of dry, wet and dried epoxy are shown in Table 1. The average values of ultimate tensile strength (UTS), Young's modulus (E), strain to failure (ϵ_{max}) and Poisson's ratios are reported along with the statistics indicating experimental scatter (Table 1).

Figure 4: Placement and failure of the specimen in the test machine.

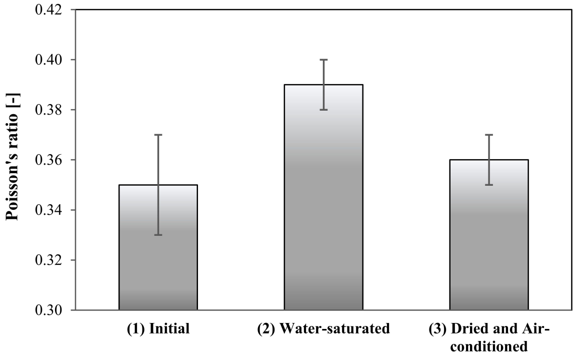

Figure 5: Poisson's ratio of initial (dry), wet and dried epoxy specimens.

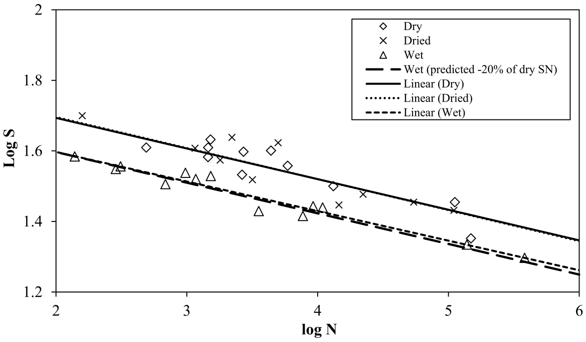

Figure 6: S-N curves of initial (dry), saturated and dried epoxy specimens in log-log scales.

4.1.2 Reversibility of mechanical properties in tension fatigue

Tension fatigue results are shown in Figure 6 and Figure 7 in log S-log N and linear S-N scales, respectively, where maximum stress S is in MPa and number of cycles to failure N is unitless. The R ratio was 0.1. The results of the fatigue

Table 1: Mechanical and elastic properties of dry, wet and dried epoxy.

Material	UTS [MPa]	E [MPa]	ϵ_{max} [%]	Poisson's ratio [-]
Dry	60.5 ± 2.7	2908.8 ± 126.6	3.71 ± 0.10	0.35 ± 0.02
Dried	66.4 ± 3.0	3237.5 ± 126.3	3.69 ± 0.22	0.36 ± 0.01
Wet	48.5 ± 3.3	2588.9 ± 252.3	4.78 ± 0.51	0.39 ± 0.01

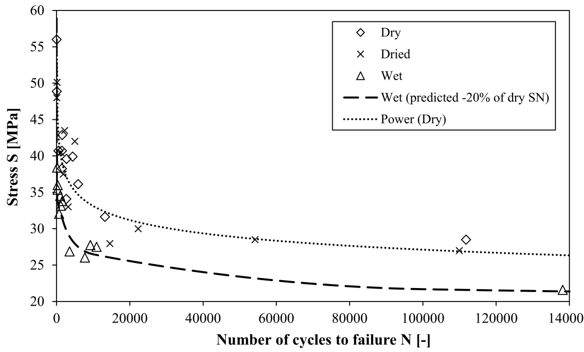

Figure 7: S-N curves of initial (dry), saturated and dried epoxy specimens in linear scales.

tests show that the S-N curve of the wet epoxy shifted down by 20% without a change in slope. The slope was obtained by linear regression of the log-log curve with the number of cycles being the dependent variable. Regression equations are shown in Table 2.

The fact that the slope of the S-N curve did not change, and the drop is the same as for the static data indicates that fatigue of wet epoxy can be simply predicted by measuring static strength changes of wet specimens.

The S-N curve of the re-dried epoxy was the same (within experimental scatter) as the original S-N curve of the dry material. This effect indicates reversibility, as was already observed for the static data.

5 Aging mechanisms and hygrothermal effects

For epoxy-amine networks [17], two possible major hygrothermal degradation mechanisms might occur: plasticization (hygrothermal effect) and chain scission (hygrothermal aging). Other failure mechanisms may also happen [14, 15, 17, 22, 32–34], but are considered of minor importance to this study, such as thermo-oxidation, photo-oxidation, additional crosslinking (residual curing), secondary crosslinking between the epoxy and water molecules, leaching of additives, polymer relaxation, swelling-induced microcracking and formation of microcracks through absorption/desorption cycles. Multiple aging mechanisms and hygrothermal effects may also combine.

Results of this study indicate that plasticization (hygrothermal effect) is fully reversible for the studied epoxy.

No chain scission was observed. The T_g of dry, saturated and re-dried epoxy was 81.7, 59.1 and 84.7 °C, respectively. The T_g of saturated specimen decreased due to plasticization. There was only a slight increase in T_g after re-drying compared to the dry epoxy, indicating that no major changes in chemical structure have occurred during hygrothermal aging. In case of chemical degradation (chain scission) a T_g value would have decreased, which is opposite to what was observed. A slight increase in T_g of the dried material can be explained due to additional crosslinking taking place or polymer relaxation [14, 17].

6 Conclusions

Exposure of the amine-cured epoxy to water caused the material to swell. The absorption of water had detrimental, but reversible effects on static strength and cyclic fatigue properties. Similar values of dry and re-dried specimen T_g serve as an indicator that no chemical degradation (chain scission) has occurred.

The ultimate tensile strength of the resin decreased by 20% relative to the initial dry value due to plasticization by water. The strength of dried epoxy is comparable to that of the initial dry epoxy, indicating the reversibility in mechanical properties.

Poisson's ratio increased for conditioned epoxy, but returned to the initial values after drying, also indicating that the effect of water conditioning is reversible. The increase of Poisson's ratio is believed to be due to the absorbed almost incompressible water or due to the reduction of glass transition temperature (T_g) due to the plasticizing action. The results of fatigue tests indicated that the S-N curve of a wet epoxy also shifted by 20% without a change in slope. The S-N curves of dry and dried material

Table 2: Linear regression of fatigue data.

Linear models	Regression equation	Determination coefficient R^2
Dry (linear)	log N = -11.5207 log S + 21.5115	0.89
Dried (linear)	log N = -11.3895 log S + 21.3121	0.82
Wet (linear)	log N = -11.9332 log S + 21.0585	0.95
Wet (linear predicted from static data)	log N = -11.5207 log S + 20.3952	0.90

were identical, further proving the reversibility in mechanical properties.

It is shown experimentally that the tension fatigue S-N curve of a wet epoxy resin can be estimated by shifting the S-N curve of a dry material proportionally to a reduction in static tensile strength due to hygrothermal effects.

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List of symbols

W*	Moisture content in the resin (w%)
m_{water}	Moisture mass in the resin (g)
$m_{absolutelydry}$	Mass of an absolutely dry resin specimen (g)
m	Measured mass of a resin specimen (g)
T_g	Glass transition temperature (°C)
t	Time (s)
ϵ_{max}	Linear strain to failure (%)
E	Young’s modulus (MPa)
S	Stress (MPa)
N	Number of cycles before specimen fails in fatigue (-)
UTS	Ultimate tensile strength (MPa)
DMTA	Dynamic mechanical testing analysis
FT-NIR	Fourier transform near infrared spectroscopy

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A Appendix Fatigue raw data

Table 3: Fatigue raw data. S represents maximum stress in MPa. The R ratio was 0.1.

DRY			DRIED			WET		
Specimen	N [-]	S [MPa]	Specimen	N [-]	S [MPa]	Specimen	N [-]	S [MPa]
1	21	56.0	1	158	50.1	1	139	38.4
2	53	48.9	2	53	48.0	2	311	36.0
3	1515	42.9	3	2210	43.5	3	286	35.4
4	489	40.7	4	4986	42.0	4	974	34.5
5	1455	40.7	5	1155	40.5	5	1524	33.8
6	4392	39.9	6	1798	37.5	6	1169	33.2
7	2711	39.6	7	3171	33.0	7	686	32.1
8	1451	38.3	8	22265	30.0	8	9219	27.8
9	5896	36.1	9	54185	28.5	9	10911	27.5
10	2643	34.1	10	14538	28.0	10	3543	26.9
11	13183	31.6	11	109947	27.0	11	7710	26.0
12	111785	28.5				12	138162	21.6
13	148408	22.5				13	381758	19.8