Cohesive Properties of Environmentally Degraded Epoxy Adhesives

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Abstract

Adhesives are increasingly being used in the aerospace and automotive industries. They allow for light weight vehicles, fuel savings and reduced emissions. However, the environmental degradation of adhesive joints is a major setback in its wider implementation. Moisture degradation of adhesive joints includes plasticization, attacking of the interface, swelling of the adhesive and consequent creation of residual stresses. The main factors affecting the strength of adhesive joints under high and low temperatures are the degradation of the adhesive mechanical properties and the creation of residual stresses.

To model the long term mechanical behaviour of adhesive joints, the temperature and moisture dependent properties of the adhesives must be known. However, few studies focus on the combined moisture and temperature degradation, which difficults the prediction of the long term mechanical behaviour of these joints. In this study the prediction of moisture and temperature dependent cohesive properties of a structural adhesive is analysed.

Author Keywords. Temperature Degradation, Moisture Degradation, Cohesive Zone Modelling

Type: Research Article

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1. Introduction

Structural adhesives are increasingly being used in several industries. Adhesive joints allow for uniform stress distributions, higher fatigue resistance and for joining dissimilar materials (Banea et al. 2014). The only viable way of joining fiber reinforced plastics is with a structural adhesive. This translates into stronger and lighter and fatigue resistant structures. Adhesive joints are increasingly being used in civil engineering, particularly in timber structures (Carbas et al. 2015). Transport industries in particular are very interested in this kind of technology as it allows higher energy efficiencies and reduced emissions.

The automotive industry in particular has been investing in the development of adhesive bonding in recent years. Automotive manufacturers are interested in reducing the weight of their vehicles in order to improve their efficiency and reduce emissions. However, vehicles must be able to withstand important loads during their lifetime, probably the most demanding for the adhesive joint being impact loads, that are caused when the vehicle crashes. These stresses must be withstood under a great variety of temperatures (usually between -40ºC and

80ºC) and relative humidity, so that the safety of the passengers can be assured. Moisture is absorbed by the adhesive in two different ways: as free water or as bound water. Free water occupies the free spaces of the adhesive and is responsible for plasticization while bound water forms single or multiple hydrogen bonds with the adhesive's polymer chain, resulting in swelling of the adhesive, plasticization and consequent decrease of strength and glass transition temperature (Tg) (Viana et al. 2016). Usually, if the water uptake is done at low temperatures, as soon as the adhesive is dried, its mechanical properties are usually recovered. It is frequently, therefore, a reversible process.

High temperatures are also responsible for degrading the adhesive properties. Sometimes for short exposure times, the adhesive joint's properties are improved due to post cure effects. However, after a certain amount of time, its properties start to decrease (Li et al. 2015).

The environmental degradation of adhesive joints is still a major setback in their wide implementation. Studies have been made regarding the moisture and temperature degradation of adhesives, which include reduction of their mechanical properties, induced plasticization and decrease of Tg. The deleterious effects are usually greater in adhesive joints due to the creation of residual stresses between the adhesive and the adherends and due to the degradation of the interface between the adhesive and the adherends, which may cause interfacial failure. In order to improve the strength of the adhesive-adherend interface, a suitable surface treatment should be used.

Cohesive zone models (CZM) have been used together with standard finite element analyses to predict the mechanical behaviour of adhesive joints (Avendaño et al. 2016; Fernandes et al. 2017; Sugiman, Crocombe, and Aschroft 2013). These models have the advantage of combining stress/strain based criteria with fracture mechanics, accurately predicting the behaviour of the material. CZM can predict the formation and propagation of cracks. As soon as the strength of the material is reached, softening initiates. Depending on the properties of the material, several cohesive laws can be used to simulate the softening of the material. These include triangular, linear-parabolic, polynomial, exponential and trapezoidal laws. Although the cohesive laws can be adjusted to better fir the behaviour of the material, the triangular CZM, shown in Figure 1, due to its simplicity, is very widely used and provides good results for most of the real situations (Liljedahl et al. 2006).
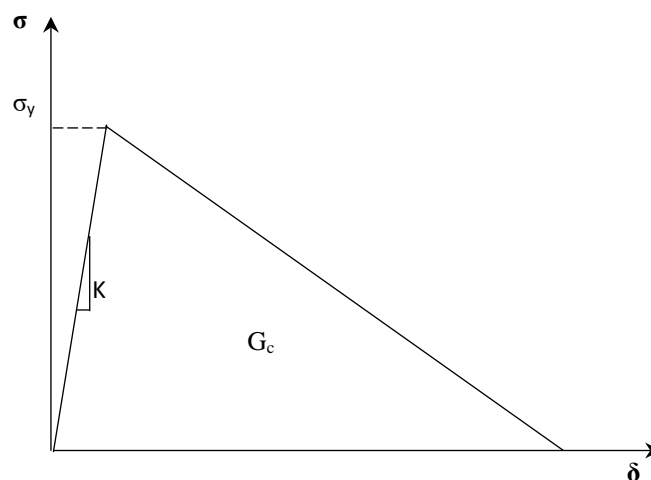

Figure 1: Triangular cohesive zone law

In order to model the adhesive using cohesive zone models, at least three properties, which are necessary for the definition of the CZM triangle must be known:

1. The yield stress (σ_y) of the adhesive;
2. The toughness (G_c), which is the area of the triangle;
3. The rigidity (K), which is normally set to a very high value (Turon et al. 2007).

This paper focuses on the prediction the material properties as a function of temperature and moisture, taking into account experimental results obtained in previous studies (Viana et al. 2017a; Viana et al. 2017b).

2. Materials and Methods

The epoxy adhesive XNR 6852-1, supplied by NAGASE CHEMTEX® (Osaka, Japan) was analysed. This adhesive is a one-part system that cures at 150oC for 3 h. Previous studies regarding this adhesive have addressed the determination of the cohesive properties of this material as a function of its water uptake and test temperature (Viana et al. 2017a; Viana et al. 2017b).

The tensile yield strength and Young's modulus of this adhesive were determined in previous studies (Viana et al. 2017a; Viana et al. 2017b) using dogbone bulk tensile specimens and its toughness was determined using small double cantilever beam (DCB) specimens. The results that were obtained are shown in Table 1. Additional parameters, such as its glass transition temperature (T_g) were also determined and are useful in the present study.

		Temperature (oC)		
		-40	23	80
Moisture uptake (%)	0	102.42	54.351	10.86
	0.86	95.1788	47.1098	3.6188
	1.18	92.4844	44.4154	0.9244

Table 1: Yield stress of the studied adhesive as a function of moisture and temperature

The mode I toughness of the adhesive was measured using DCB specimens. However, due to degradation of the interface, some joints suffered adhesive failure, which means that one is not measuring the toughness of the adhesive, but the toughness of the interface instead. The value of the interfacial fracture toughness will not be discussed in this study. The results that were obtained are shown in Table 2.

		Temperature (oC)		
		-40	23	80
Moisture uptake (%)	0	3.93	6.7	7.82
	0.86	2.18	4.57	2.29
	1.18	3.78	2.75	1.52

Table 2: Fracture toughness of the studied adhesive as a function of moisture and temperature.
The values in bold were obtained from specimens that suffered adhesive failure

Also the T_g of the adhesive was measured as a function of moisture uptake (Table 3 shows the results that were obtain). This is an important parameter, as above T_g there is a molecular rearrangement that causes the adhesive to have a completely distinct behaviour.

Tg (oC)	117.4	112.9	102.4
Moisture uptake (%)	0	0.86	1.18

Table 3: Tg as a function of moisture uptake

3. Results

3.1. Evolution of T_g as a function of moisture uptake

In this study, the Tg of the adhesive showed a linear behaviour as a function of the fourth power of moisture uptake, as shown in Equation 1 and in Figure 2.

$$T_g = 117.4 - 8.23H^4 \qquad (1)$$

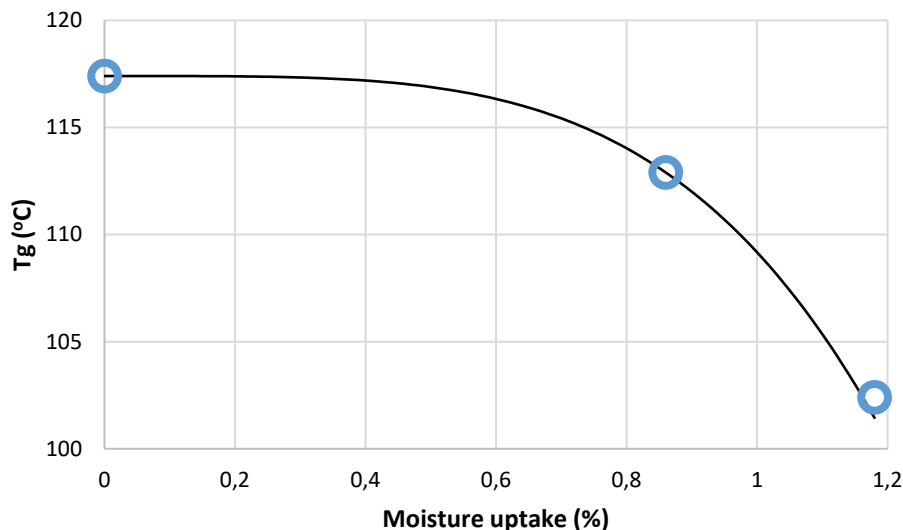Where H is the percentage of moisture uptake of the adhesive.

Figure 2: Evolution of Tg as a function of moisture uptake

This simple relationship will be used in the following sections to estimate the T_g of the adhesive.

3.2. Evolution of the cohesive properties as a function of T and T_g

As water is absorbed by adhesives, its T_g decreases. Some authors claim that the decrease of mechanical properties of moisture degraded structural adhesives is directly due to this decrease in T_g and that the decrease in T_g by a specific amount is equivalent to increasing the environmental temperature by the same amount (Jurf and Vinson 1985). The mechanical properties of the adhesives would therefore only depend on $(T_g - T)$.

Three simple equations able to describe the dependency of the yield stress and the fracture toughness of the studied adhesive were analysed:

$$P = C_0 - C_1(T_g - T) \qquad (2)$$

$$P = C_0 - C_1(T_g - T) - C_2(T_g - T)^2 \qquad (3)$$

$$P = C_0 - C_1 \times T - C_2 \times H \qquad (4)$$

Where P is the property to be determined (either yield strength or fracture toughness). C_0, C_1 and C_2 are constants that must be determined. These constants were determined using the software Eureqa®.

The equation should be as simple as possible, so that the least amount of constants that must be determined is as little as possible. The proposed equations have varying degrees of complexity. Equation 4 and 3 require three constants to be determined, while Equation 2 only requires two. However, with increased complexity, the equation is expected to give more accurate results. The results given by each equation, as well as the relative error are presented below.

Equation 2

Equation 2 is the most simple. It takes into account only the temperature and the T_g of the adhesive (which indirectly relates to its moisture uptake). Constants C_0 and C_1 computed using the software Eureqa® for the prediction of the yield stress and fracture toughness are shown in Table 4.

Yield stress		Fracture toughness	
C_0	C_1	C_0	C_1
15.4	0.75	9.83	0.0418

Table 4: Constants determined to describe the behavior of the adhesive according to Equation 2

The predicted values for the yield stress and fracture toughness according to Equation 2 are shown in Table 5. The values in bold represent values that were not correctly predicted.

		Yield Stress Prediction				Fracture Toughness Prediction		
		Temperature (oC)				Temperature (oC)		
		-40	23	80		-40	23	80
Moisture (%)	0	102.7	55.4	12.7	0	3.3	5.9	8.3
	0.86	99.3	52.1	9.3	0.86	3.4		
	1.18	90.7	43.4	0.68	1.18	3.9		

Table 5: Yield stress and fracture toughness prediction according to Equation 2

Table 6 shows the relative error associated to the prediction according to Equation 1. The values in bold represent values with high relative error, which were not correctly predicted.

		Relative Error (%)				Relative Error (%)		
		Temperature (oC)				Temperature (oC)		
		-40	23	80		-40	23	80
	0	5.1	2.3	16.3	0	17.3	12.2	5.7
Moisture (%)	0.86	4.2	7.5	423.9	0.86	57.7		
	1.18	1.8	5.0	27.6	1.18	3.6		

Table 6: Relative error associated with the yield stress and fracture toughness calculation using Equation 2

Equation 3

Equation 3 is an attempt to improve the results obtained with Equation 2. It introduces a third constant and is slightly more complex. The constants that were computed with the software Eureqa® are shown in Table 7.

Yield Stress			Fracture Toughness		
C_0	C_1	C_2	C_0	C_1	C_2
-24.8	-1	0.0014	8.58	0	0.000233

Table 7: Constants determined to describe the behaviour of the adhesive according to Equation 3

Table 8 shows the yield stress and fracture toughness computed using Equation 3. The values presented in bold correspond to conditions in which a good correlation was not possible to obtain.

		Yield Stress Prediction				Fracture Toughness Prediction		
		Temperature (oC)				Temperature (oC)		
		-40	23	80		-40	23	80
Moisture (%)	0	97.9	57.1	10.6	0	2.8	6.5	8.3
	0.86	95.4	53.8	6.6	0.86	3.1		
	1.18	89.2	45.8	-3.1	1.18	3.9		

Table 8: Yield stress and fracture toughness prediction
according to Equation 3

Table 9 shows the relative error associated with the yield stress and fracture toughness prediction using Equation 3. The values in bold represent situations in which there is high error and in which a good correlation was not obtained.

		Relative Error (%)				Relative Error (%)		
		Temperature (oC)				Temperature (oC)		
		-40	23	80		-40	23	80
Moisture (%)	0	0.3	0.77	2.2	0	28.6	2.9	5.6
	0.86	0.15	11.1	272.0	0.86	43.7		
	1.18	3.3	0.096	429.0	1.18	2.0		

Table 9: Relative error associated with the yield stress and fracture toughness
calculation using Equation 3

Equation 4

Equation 4 depends on the temperature and moisture uptake of the adhesive and, unlike the previous equations, it does not directly depend on the T_g of the adhesive. It has three coefficients, which are shown in Table 10 and were computed using the software Eureqa®.

Yield Stress			Fracture Toughness		
C_0	C_1	C_2	C_0	C_1	C_2
71.9	0.763	8.42	5.46	0.044	0.485

Table 10: Constants determined to describe the behaviour of the adhesive
according to Equation 4

The yield strength and fracture toughness values are shown in Table 11. The relative error associated with each of these results is shown in Table 12.

		Yield Stress Prediction				Fracture Toughness Prediction		
		Temperature (oC)				Temperature (oC)		
		-40	23	80		-40	23	80
Moisture (%)	0	102.4	54.4	10.9	0	3.7	6.5	8.98
	0.86	95.2	47.1	3.6	0.86	4.1		
	1.18	92.5	44.4	0.92	1.18	4.3		

Table 11: Yield stress and fracture toughness prediction
according to Equation 4

Moisture (%)	Relative Error (%)				Relative Error (%)		
	Temperature (oC)				Temperature (oC)		
	-40	23	80		-40	23	80
	0	4.9	4.1	0.18	0	5.9	3.4	14.9
	0.86	0.054	2.7	104.5	0.86	88.9		
	1.18	0.20	2.9	2.0	1.18	13.0		

Table 12: Relative error associated with the yield stress and fracture toughness calculation using Equation 4

4. Discussion

Generally, every equation that was analyzed was able to predict the yield stress of the adhesive under every environmental condition. The exception is when the adhesive was being tested at 80ºC after having been aged. This is probably due to the increased influence of creep in the adhesive behaviour, which was not taken into account in this study. As the adhesive is tested at higher temperatures, it gets more susceptible to time-dependent deformation. This phenomenon is increasingly important if the adhesive has a lower T_g, as in the case of aged adhesive specimens. In order to improve the accuracy of these predictions, a time-dependent parameter would have to be considered in the study.

The adhesive's fracture toughness was also generally accurately predicted by the proposed equations. Strangely, the fracture toughness of 0.86% moisture uptake specimens tested at -40ºC was not possible to predict using any of the proposed equations. The best result was given by Equation 3, with a relative error of 43.7%. Unfortunately, due to restrictions of the experimental study, it was not possible to compare the result of the proposed equations in every considered environmental condition.

Although each equation had different degrees of complexity, the accuracy of the predictions did not differ significantly, which indicates that even with the simplest proposed equation, good results can be obtained.

5. Conclusions

This work focused on the prediction of the adhesive's yield strength and fracture toughness as a function of temperature and environmental moisture. This can be used to predict the shape of the cohesive zone law, which will lead to more accurate numerical simulations of adhesive joints in the long term.

The accuracy of three equations with different complexities was assessed. It was concluded that the complexity of the equations did not influence the results of the prediction significantly and that a very simple equation can be used to obtain good predictions.

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