MOISTURE ABSORPTION ANALYSIS OF HIGH PERFORMANCE POLYIMIDE ADHESIVE

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ABSTRACT

The high temperature resistant polymers and metal composites are used widely in aviation, space, automotive and electronics industry. The high temperature resistant polymers and metals are joined together using high temperature adhesives. Polyimide and epoxy adhesives that can withstand high temperature (200 °C-300 °C) are commonly used for joining high temperature metals and polymers. The performance of adhesively bonded metals and polymers depends upon physical properties of these high temperature adhesives. The physical properties like modulus, Tg. coefficient of thermal expansion (CTE) etc., are affected by external factors such as force, temperature, humidity etc. The external factors play a vital role in the adhesive bond strength and the durability of bond between metal and polymer. In this investigation moisture absorption analysis of polyimide adhesive is performed using Q5000 moisture absorption analyzer. The moisture absorption data of polyimide at different temperatures and humidity level is obtained. Further, the moisture absorption data is fitted to well known Fickian-fit model to determine the diffusion coefficient (D) and saturated moisture gain Msat. Diffusion coefficient (D) and Msat of polyimide and epoxy adhesive are calculated at different temperature and different humidity level. It is observed that diffusion coefficient changes with the change in temperature and humidity level. The diffusion coefficient (D) and M sat data are used in Fick's second law of diffusion to estimate the time needed for preconditioning of the adhesively bonded titanium samples in humidity chamber at elevated temperature and higher moisture level. After preconditioning of adhesively bonded Titanium samples in moisture chamber for estimated time, samples will be subjected to lap shear tensile test to study the effect of these elevated conditions on adhesive bond strength.

1. INTRODUCTION

Polyimide and Epoxy adhesive are widely used due to their good mechanical properties. However, it is well known that these properties are strongly affected by water sorption[1]. The degradation of adhesively bonded joints through the effects of moisture is one of the major concerns affecting their wide implementation in structure applications. Moisture ingress in an adhesive joint with non-absorbing adherents may occur through the bulk adhesive and in the interfacial region between adhesive and the adherends. [2] .The latter is sometimes referred to as the ‘‘interphase’’. Moisture influences the adhesive by plasticization and swelling[3, 4], which may decrease joint strength[4]. In addition, water can disrupt interfacial bonds in causing non-reversible damage, as predicted by the theories of adhesion, or cause failure by corrosion of the underlying metal substrate[5].

Fickian diffusion has been used by researchers to predict moisture concentration in adhesives. In Fickian diffusion it is assumed that the moisture flux is directly proportional to the concentration gradient in a material. The governing equation for one dimensional diffusion in a polymer sheet of thickness h is give by

$$\frac{dC}{dt}=D\frac{d^2C}{dx^2} \tag{2.1}$$

in which C is the moisture concentration, D is the moisture diffusion, x is spatial coordinate and t is time. A solution to the Eq. 2.1 is given by Crank [6]

$$C=C_0\left[1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\frac{(2n+1)\pi x}{h}\exp\{-(2n+1)^2\pi^2D/h^2\}\right] \tag{2.2}$$

Where C_0 is the boundary condition to the polymer sheet. After integration over thickness, we get measurable weight gain.

$$M_t=M_\infty\left[1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\{-(2n+1)^2\pi^2Dt/h^2\}\right] \tag{2.3}$$

Where $m_\infty=WLh(c_w^{sat}-c_0)$.From the experimental M_t versus time curve both the diffusion coefficient D as well as the final moisture content m_∞ (or M_∞) can be determined. The diffusion coefficient is usually extracted form the initial slope of an M_t versus square root of time plot.

There are many parameters that govern the moisture absorption process. The moisture weight gain, Mt, is determined by:

$$M_t(wt\%)=\frac{m_t-m_0}{m_0}\times 100\% \tag{2.4}$$

Where mt and m_0 are the weights of wet specimen at exposure time t, and of the dried specimen respectively.

Msat is the saturated moisture gain in the sample and is dependent on the temperature. It can be determined by [7]:

$$M_{sat}=k_0\cdot X_{RH}\cdot e^{(-H/RT)} \tag{2.5}$$

where k_0 is the proportional constant, XRH is the relative humidity factor and varies from 0 to 1, i.e. 0 RH% to 100 RH%. H, is the activation energy constant, R is the universal gas constant, 8.314 $JK^{-1}mol^{-1}$, T is the absolute temperature. Msat can be obtained by performing moisture absorption tests at different temperatures and different relative humidity levels. A linear fit of ln(Msat) versus the reciprocal of the absolute temperature 1/T is used to determine the activation energy constant. From the intercept with ln(Msat)-axis, at 1/T = 0, k_0 can be determined.

Diffusion coefficient (D) [8] is supposed to depend on the initial diffusion coefficient (D_0) as follows:

$$D = D_0 \cdot e^{(-E_D / RT)} \tag{2.6}$$

which can be rewritten in the following form:

$$\ln D = \ln D_0 - E_D / RT \tag{2.7}$$

The diffusion activation energy ED can be determined from the slope of the data plot of lnD against 1/T. From the intercept with the lnD-axis, at 1/T = 0, $\ln D_0$ can be formed [5].

Polyimide and Epoxy adhesive are widely used for joining of metal surfaces for high temperature application. In order to calculate the effect of high temperature and moisture, Preconditioning of titanium samples bonded with polyimide and epoxy adhesive respectively need to be done in moisture oven. In moisture oven time require to impregnate the moisture to middle of adhesive layer can be calculated by equation 2.3 .First concentration and mass taken at saturation determined and then time required to reach moisture saturation level to middle of the sample is calculated.

2. EXPERIMENTAL

In order to calculate saturation time for moisture in PI adhesive .PI adhesive sample was exposed to different moisture and temperature conditions in TA instrument Q5000 moisture analyzer. The time calculation from these experiments will be used for preconditioning of adhesively bonded titanium samples in humidity chamber.

3. 2.1 Test Sample Preparation

Test samples must be flat parallel-sided discs or coupons. the linear dimensions must be accurately measured within ±0.02mm.To approximate one dimensional diffusion, for a coupon of length L, width W and thickness h, the following relation must be met:

h<0.05(W x L)/(W+L)

Recommended sample thickness should be in the range from 0.2 to 1.0mm.If samples are too thick, the time to achieve moisture saturation at temperature below 60°C will be excessively long for slowly diffusing compounds. Samples are prepared by using proper processing parameters as recommended by materials suppliers.The preapared samples have been inspected for voids on the surface.

4. 2.2 Test Procedures

The samples are pre dried at 125°C for maximum removal of moisture and volatile material present in sample and weight of sample become stable. Oven pre drying time is optimized at four hours. These pre dried samples are then placed in vacuum chamber for 10 minutes to remove any traces of moisture or volatile material. Moisture weight gain measurements are common experimental technique to investigate the moisture uptake. Usually, specimens are stored in climate chamber which is controlled at constant temperature and relative humidity .The specimens are moved out of the climate chamber in a range of time intervals to measure the weight change. After measuring the weight change, specimens are placed back into climate chamber for further moisture exposure. The disadvantage of this method is the fact that samples have to be removed from the moisture oven for weight measurements. During removing and weighting of the sample, moisture might condense on the sample surface. Furthermore due to the thermal and humidity shock, moisture might suddenly desorb.

A sorption analyzer Q5000 of TA instruments is used to monitor the moisture uptake of Polyimide adhesive in situ. Temperature and relative humidity of climate chamber can be programmed independently. The Q5000 SA is designed for manual or automated sorption analysis of materials under controlled conditions of temperature and relative humidity (RH). Its design integrates latest high sensitivity, temperature-controlled thermobalance with humidity generation system, multi-position autosampler, and Advantage™ software for analysis.It can be used in temperature range of 5°C to 85°C and relatively humidity can v be varied between 0% RH to 98% RH.

5. RESULTS AND DISCUSSION

6. 3.1. Characterisation of Saturated Moisture Content and Diffusion Coefficient

Test are performed at PI adhesive samples at elevated temperatures varying from 20°C to 80°C.The relative humidity is stepwise increased from 0-80%RH. Fig 3.1 gives an illustration of a moisture diffusion experiment. The sample mass changes due to moisture absorption. In the first step, the mass of the sample decreases.This is due to desorption of moisture of moisture which was initially in the sample. weight gain initially increases linearly with respect to time as predicted by Fick's law of diffusion. After the initial fast diffusion, the uptake continues to increase but slowly. The applied relative humidity at start and end is programmed to be 0%RH. The above experiments are repeated at 4 different temprarures.20C,40C,60C,80C

Fig.3.1.Weight change of PI adhesive as function of time at different humidity levels at 60°C

Moisture saturation weight percentage M sat and Diffusion coefficient D is calculated at particular temperature using Fickian fit simulation . and is given Table 3.1

Table 3.1 Calculation of Diffusion coefficient D and Moisture saturation weight gain Msat.

Temperature	D [m2/s]	D [10^{-12}m2/s]	Msat[%]
PI-20°C	2.40E-13	0.24	6.90E-03
PI-40°C	5.38E-13	0.538	7.10E-03
PI-60°C	1.63E-12	1.42	6.90E-03
PI-80°C	2.96E-12	2.96	7.00E-03

It can be seen that the moisture saturation rate are temperature and relative humidity dependent. High temperature and relative humidity will result in fast moisture diffusion and high moisture contents.

Using equation (2.3), combined with tests results of Polyimide adhesive, saturated moisture content at certain temperature and relative humidity can be characterized. A linear fit of lnM_{sat}

versus *1/T* is used to determine the activation energy constant, *H*. From the intercept with lnM_{sat}-axis, at *1/T* = 0, k_0 is obtained (see Fig. 3.2).

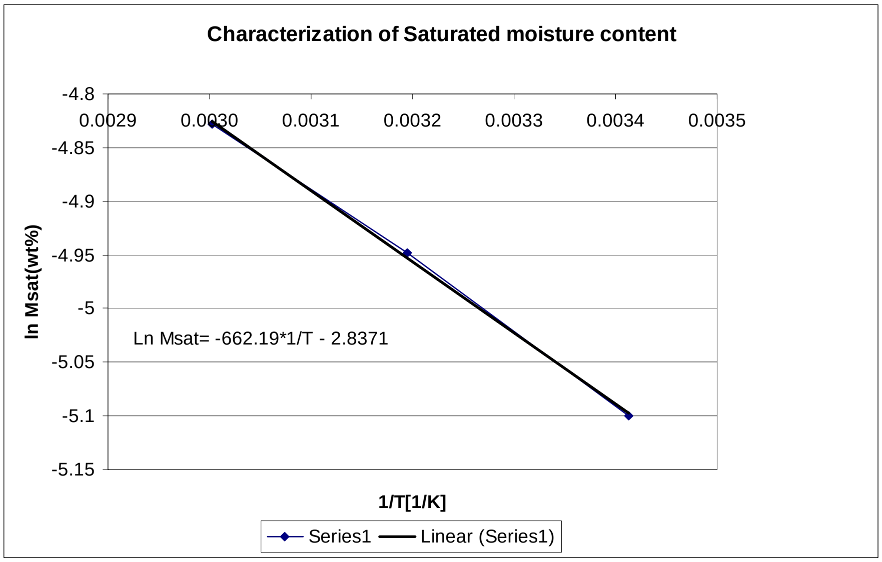

Fig. 3.2 Slope of lnM_{sat} vs *1/T* for Polyimide adhesive

Real line is the three test data fit line and dash line is the linear fit line of lnM_{sat} versus *1/T*. The data obtained from figure 3.2 are *H* = 7.548 kJ/mol, k_0 = 0.0586.The slope of ln*D* versus *1/T* can be used to obtain E_D and D_0, (see Fig. 3.3).

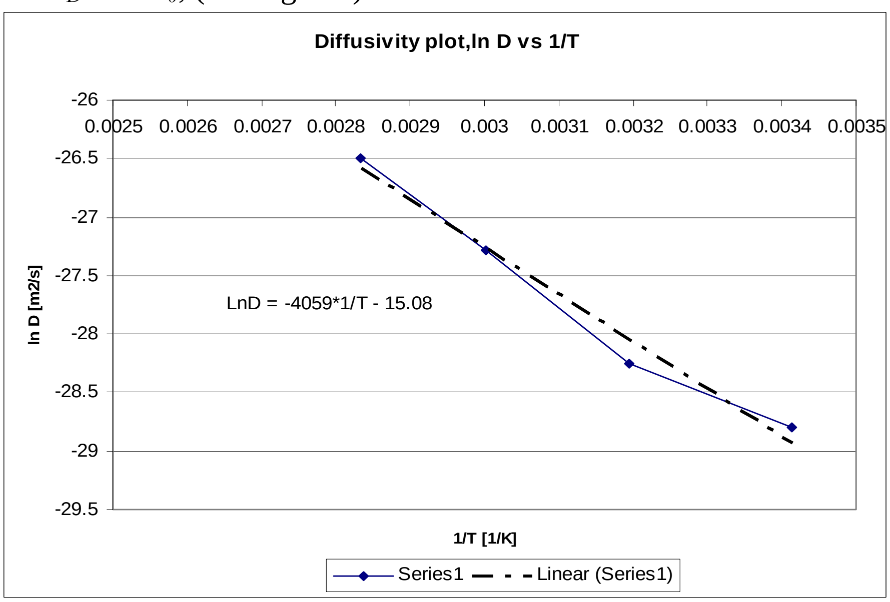

Fig. 3.3 slope of ln*D* vs *1/T* for the Polyimide adhesive.

From data in Fig 3.3 activation energy ED and initial Diffusion coefficient D_0can be calculated .

ED=40.11KJ/mol

D_0 = 2.825 E-7m^2/S

It can be seen that if three moisture absorption tests at different temperature combined with relative humidity stepping are performed then the polyimide adhesive moisture properties can be established.

.Now using equation (2.6) time required to maximum saturation level for PI adhesive of thickness 0.3mm was calculated.

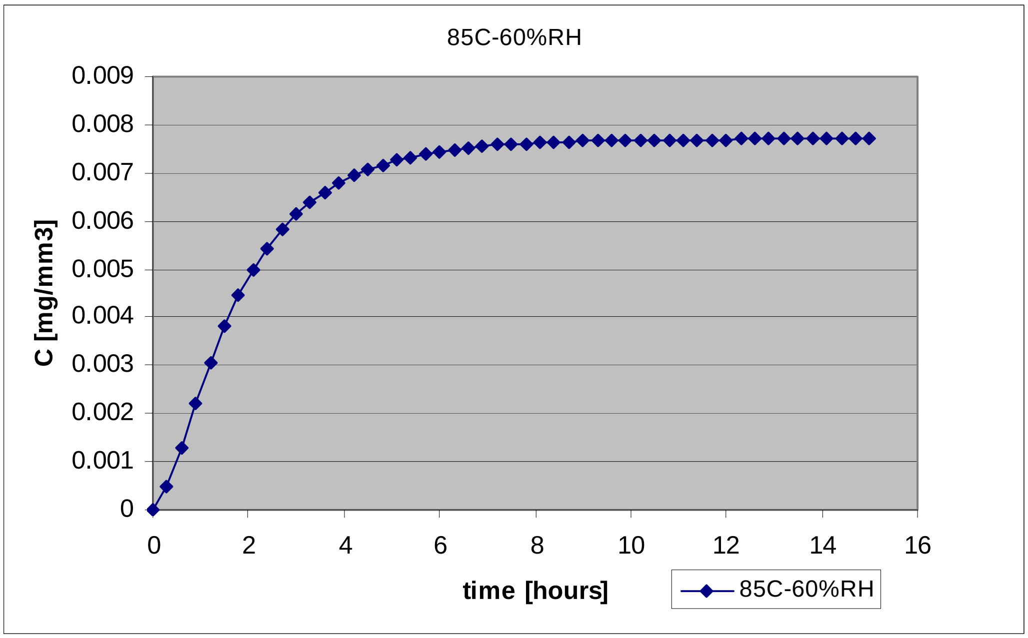

Fig.3.4 Moisture absorption at 80ºC/60%RH for 15 hours.

Fig 3.4 indicates that a PI adhesive sample will reach its saturation level in 12 hrs. Now for calculating preconditioning time of titanium single lap shear samples in moisture oven at 60% RH and 80°C .Time calculation for PI adhesive to reach its saturation level is given in figure 3.4. Now time required in order to reach saturation level in adhesive layer of 12.5X25X0.3mm in single lap shear joint of Titanium samples is calculated using simulation.Single lap shear test sample of Titanium is presented Figure 3.5.

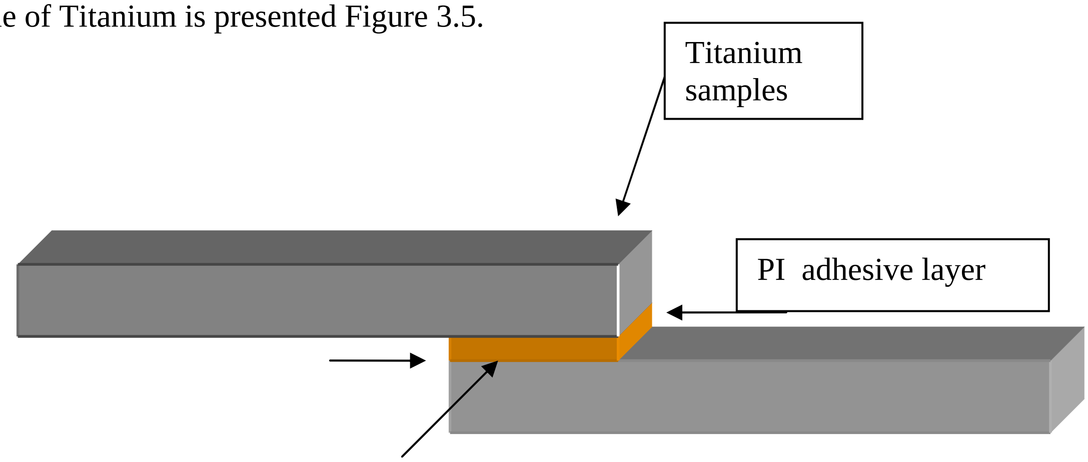

Fig 3.5.single lap shear titanium samples for preconditioning in the moisture oven..

Table 3.2 indicates time calculation made using matlab simulation with fickian model fit for calculating preconditioning time of single lap shear mode (SLS)adhesively bonded titanium samples with Polyimide in the moisture oven.

Table 3.2.moisture saturation time for adhesive layer in SLS Titanium samples.

days	hours	sec	C[mg/mm3 E-3]	(Csat-C)/Csat
60	1440	5184000	7.593	0.01389
70	1680	6048000	7.65	0.00649
80	1920	6912000	7.677	0.00299
90	2160	7776000	7.679	0.00272
120	2880	10368000	7.699	0.00013

This table is based upon simulation presented in figure 3.6.

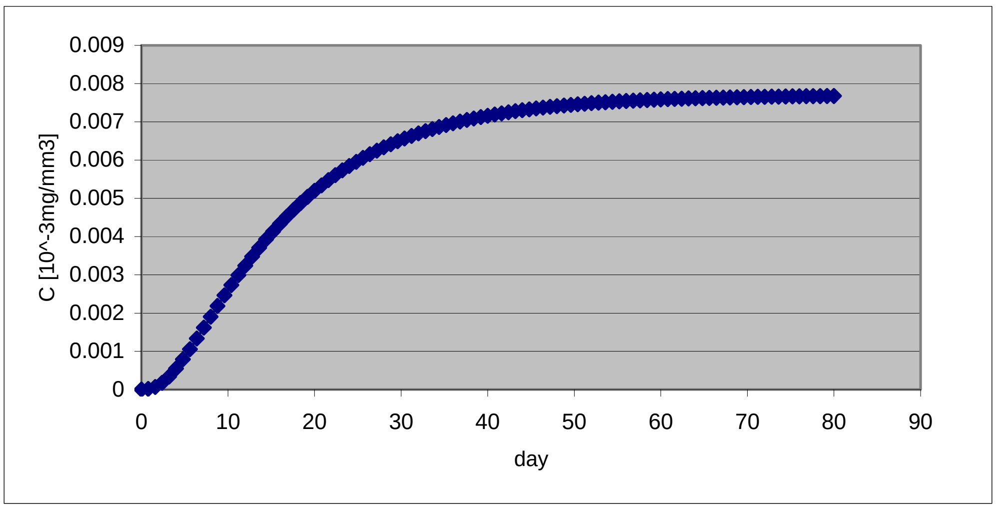

Fig.3.6. Moisture saturation in PI adhesive layer at 60% RH and 80^{o}C.

Table 3.2. indicates that moisture absorption take place at faster rate in first sixty days and then it gradually slows down and it reaches it moisture saturation level in almost 80 days.

7. CONCLUSION

From above tests, simulations and verification in this study, it is found that at the high temperature and high relative humidity acceleration method is suitable for fast moisture sensitivity analysis.

Water absorption experiments of Polyimide adhesive at various temperature and humidity level are performed. Moisture saturation level is temperature and relative humidity dependant. Moisture saturation is difficult to reach at low temperature and low relative humidity. High temperature and relative humidity will result in fast diffusion and High moisture contents. Therefore, low temperature and low relative humidity moisture absorption can be replaced by high temperature and high relative humidity preconditioning and Polyimide adhesive moisture absorption properties can be characterized in short time .With the help of Polyimide adhesive moisture absorption property, moisture diffusion time can be predicted and compared between different conditions.

8. REFERENCES

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