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International Journal of Adhesion & Adhesives 22 (2002) 337–346

International Journal of Adhesion & Adhesives

www.elsevier.com/locate/ijadhadh

Curing effects on viscosity and mechanical properties of a commercial epoxy resin adhesive

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Accepted 26 February 2002

Abstract

Before testing the ability of different pre-treatments to promote adhesion, a detailed description of the rheological and mechanical properties of the adhesive is needed. Change of the adhesive properties (due to incomplete curing) can indeed affect the results of the adhesion tests and screen out the effect of the pre-treatment. A two component room temperature curing adhesive paste (Araldite 2014) has been selected. The characterization of the adhesive properties was conducted with respect to the curing temperature and to the elapsed time between the gluing and the testing. It has been shown that any curing temperature increase leads to a more complete curing after a short period of time when the conversion factor reaches a plateau-like regime. In that regime the reaction rate becomes diffusion controlled and the reaction is drastically slowed down. Measurements of the mechanical properties of adhesive samples showed that 28 days are needed at room temperature to complete the curing process (only 4 h at 64°C) and that the properties of the adhesive during that period of time changed drastically. Ageing test (40°C in water vapour) has been conducted on adhesive samples and the adhesives properties recorded over a period of 36 days. It has been shown that the absorbed water works as a plasticizer leading to a softening of the adhesive. The *E*-modulus and the stress at break are lowered while the deformation at break and the plastic contribution to the total deformation are increased.

Keywords: A. Epoxy; D. Cure/hardening; D. Ageing; Mechanical properties

1. Introduction and objectives

The adhesive bonding of aluminium in the aerospace industry [1] has now a successful history spanning several decades. Despite this, engineers and designers are reluctant to design adhesive structural bonding into volume consumer products. The automotive industry is one main target for the advocates of adhesive bonding. Here one can illustrate successful applications of adhesive bonding with examples such as the Lotus Elise and Aston Martin Vanquish, but there is still a long step forward to a large volume production vehicle. Both of these cars utilize adhesive bonding and extruded aluminium components in the main load bearing construction of the vehicle. Even where adhesive bonding is applied there is a tendency to over dimension and/or add an insurance policy in the form of screws or rivets.

The competing technologies of welding or riveting are not without problems. Welding results in the formation of structural heterogeneities that can often give rise to technological difficulties. Hardenable grades of aluminium will, as a result of the local thermal history of the weld, tend to have significantly reduced mechanical properties at and around the weld. There are also potential corrosion problems related to the local compositional inhomogeneities. Welding of aluminium is not as straightforward as welding of steel. Riveting and bolting as techniques are not foolproof. The correct selection of alloy and the correct mechanical treatment of the rivet are important to ensure success.

One of the limiting factors restricting the increased application of structural bonding is the inadequacy of screening, testing and qualification procedures. Before test procedures for adhesive joints can be designed a comprehensive understanding of the adhesive as a material is required. This is particularly poignant where

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0143-7496/02/$ - see front matter
PII: S0143-7496(02)00013-1

accelerated testing is considered. The test must model the conditions expected during the real application of the adhesive. The adhesive must be in the same condition as it would be found in the field after extended time. The adhesive, as a thermoset polymer, is a material that has properties that are dependent not only on the test environment but that also on its thermal and environmental history. A thermoset adhesive has a glass transition temperature (T_g) that varies due to degree of cure and water content. Other mechanical properties vary in step with these changes in degree of cure and plastification. Results from the testing of a newly formed joint cannot be easily compared with tests of an aged sample. Not only can the interface between the substrate and the adhesive change, but because of changes in the mechanical behaviour of the adhesive, the loading of the interface in the test can also vary significantly.

This paper looks at the development of properties of a commercial constructional adhesive as it is cured under different conditions. Firstly we consider the process of curing and explore the rheology of the adhesive at different temperatures. We study the degree of cure and the time required to attain a satisfactory degree of cure. We then look at the consequence of ageing the cured adhesive in a humid environment.

2. Curing kinetics

Araldite 2014 is an adhesive paste that can be cured at room temperature. This can be important in commercial applications where the substrates to be joined do not tolerate high temperature. The temperature at which they are cured determines many properties of epoxy adhesives. It has been shown [2–5] that for curing temperatures less than the ultimate glass transition of the completely cross-linked resin, the network will vitrify. The resin will then be in a glassy but undercured state. In the glassy state the cross-linking reaction slows dramatically and it may take a long time before the ultimate properties of the adhesive are reached.

The temperature dependence of the curing was studied by differential scanning calorimetry (DSC). Fig. 1 shows a DSC scan of an uncured sample (just after the mixing of the two components). The DSC curve for the unreacted epoxy shows an exotherm peak representing 197 J/g. This area is defined as A_0 and will be used as reference. A_0 is directly related to the amount on unreacted reactants. As the curing progresses the amplitude of the peak decreases and the area $A(t, T)$ was measured. The ratio $[1 - (A_0/A(t, T))]$ was defined as the conversion factor. According to that definition, a conversion factor of 1 (or 100%) was related to a fully cured epoxy. Samples were cured at different temperatures (23°C, 45°C and 64°C) and the conversion factor determined (see Fig. 2). The curing temperature of 64°C was recommended by the adhesive producer and was believed to give the most efficient curing. Fig. 2 shows that the curing state can be characterized by three different conversion factors (once the plateau-like regime is reached) varying from 74% at 23°C to 99% at 64°C. The plateau-like regime was reached after only 4 h at 64°C and the curing can be considered as complete. At lower curing temperatures, the adhesive is not fully cured when the plateau-like regime is reached. This suggests that in that regime the glass transition temperature T_g of the adhesive exceeds the curing temperature leading to vitrification. The mobility of the unreacted molecules is then drastically reduced and it will be shown in the next section that for a curing temperature of 23°C, 28 days are needed to reach a fully

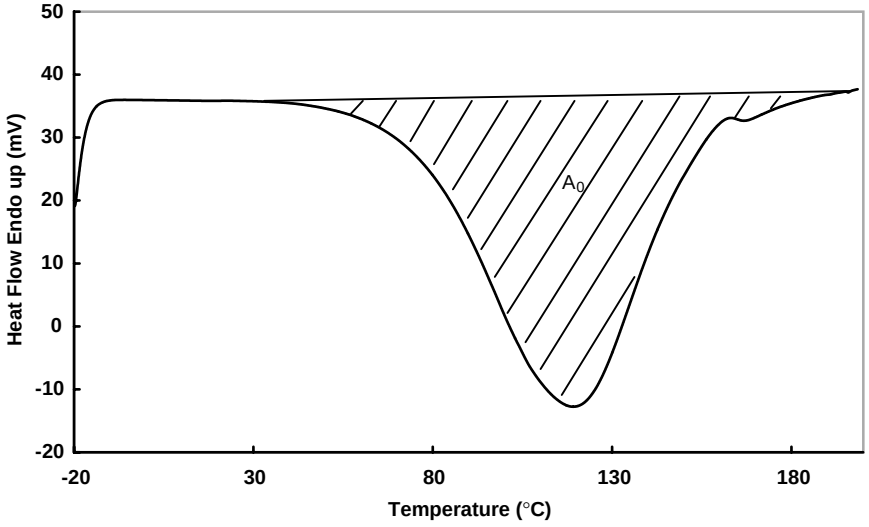

Fig. 1. DSC scan of an uncured sample.

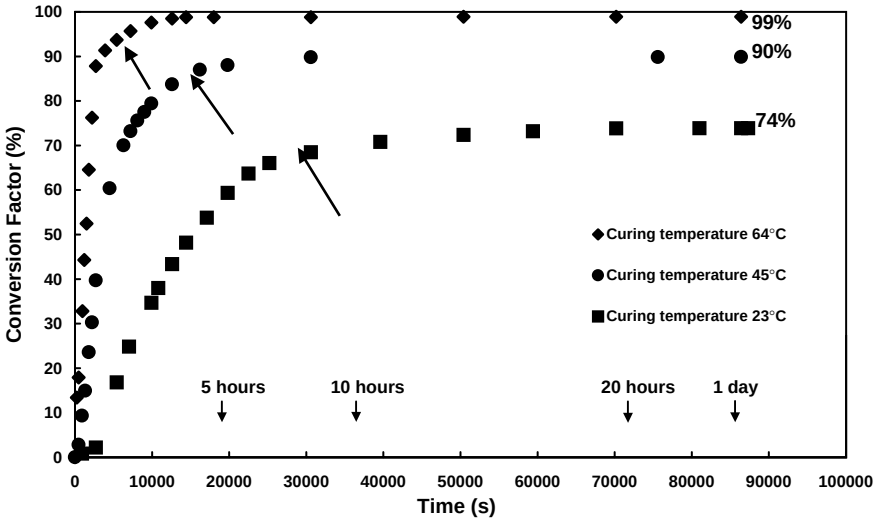

Fig. 2. Curing of Araldite 2014 at different temperatures.

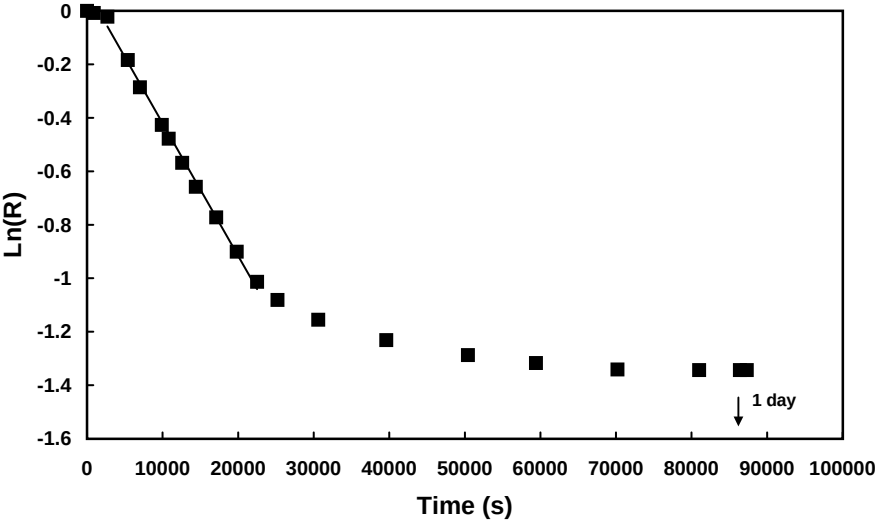

Fig. 3. Plot of the fraction remaining epoxy $R = A_0/A(t)$ with time of curing at 23°C. The linear behaviour indicates a first-order reaction.

cured state. In the mean time, the mechanical properties of the adhesive evolve and any testing of the bonded joint should be avoided.

The kinetics of the curing reaction has been studied. A plot of the fraction of epoxy remaining with time (see Fig. 3) shows that the reaction follows a first order law [2,6] at all curing temperatures until the transition to the plateau-like regime (see Fig. 2) is reached. From the Arrhenius plot of the rate coefficient with the inverse of the temperature, the activation energy was determined to be 34.6 kJ/mol (see Fig. 4). After a temperature dependent curing time, the first order law is no longer valid. As mentioned earlier the T_g of the adhesive is believed to be higher than the curing temperature. The diffusion of the unreacted components through the network is then limited and the reaction becomes diffusion controlled and hence very slow.

In order to determine when the T_g of the adhesive overcomes the curing temperature, dynamic differential scanning calorimetry (DDSC) has been used (Perkin-Elmer Pyris 1 DDSC). Dynamic differential scanning calorimetry is a relatively new thermal analysis procedure. The particular technique used to conduct the experiments is designed to facilitate the separation of overlapping events in a material such as melting and recrystallization or to isolate the specific heat change of a glass transition from non-reproducible events, such as reactions, moisture loss, decomposition and crystallization. The DSC typically ramps the temperature in a linear fashion. The rate is chosen depending on the

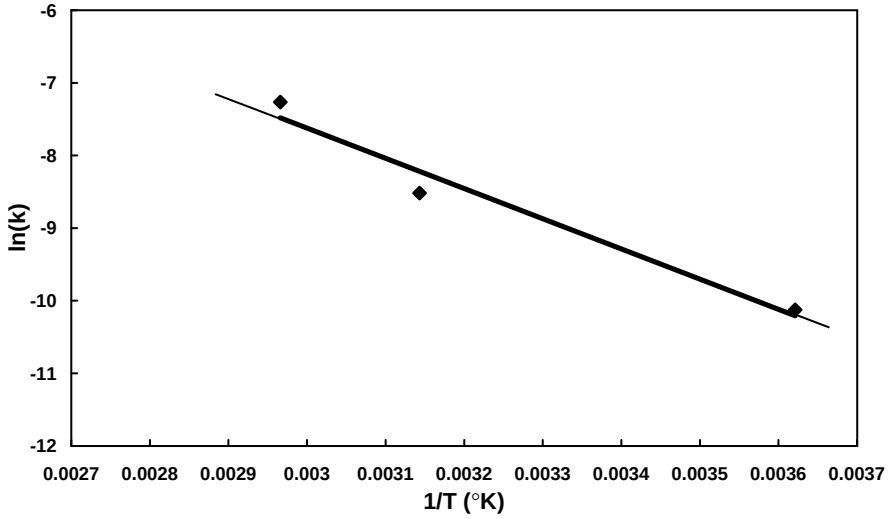

Fig. 4. Arrhenius plot of rate coefficient. The activation energy was determined to be 34.6 kJ/mol.

phenomena of interest. In the case of T_g measurement, the rate is high, typically 20°C/min, in order to avoid an increase of the T_g during the measurement. In practise that cannot be avoided but a high rate reduces the shift of the T_g towards higher temperatures. The DDSC, on the other hand, applies a modulation to the temperature change. The temperature change is altered to follow a sinusoidal or a saw tooth ramp. The parameters required for DDSC are the amplitude and the frequency of temperature modulation which have to be adjusted to get a proper equilibration. The primary calculation that results from the DDSC analysis is that of separating the in-phase (storage) specific heat from the out-of-phase (loss) specific heat.

The storage specific heat is the simple linear specific heat that results from the uptake of energy into various atomic and molecular mechanisms of energy storage as the sample is heated. In the absence of structural changes, and with no other reactions or processes taking place, the storage C_p is exactly equal to the equilibrium C_p as measured by standard DSC. When a physical or chemical process is taking place, the storage specific heat is that component of the specific heat that acts in the simple linear fashion. When a material is heated through the glass transition region, there is an increase in the storage C_p due to the increase in the degrees of freedom necessary for energy storage. This makes T_g assignment particularly straightforward. Compared to T_g measured with dynamic mechanical analysis (DMA), DSC values are lower. The difference depends on the excitation frequency used for the mechanical measurements. DSC gives a T_g similar to a very low frequency DMA experiment.

The loss C_p is the component of the dynamic specific heat which is out of phase with the temperature change because the heat flow has resulted in a structural change in the sample material rather than merely raising the temperature. The loss C_p curve is zero in temperature regions where little structural change is expected. In the region of the glass transition, this curve quantifies the change taking place.

In the DDSC experiment performed to follow the curing process of the adhesive, the temperature was held constant and small amplitude perturbations ($\Delta T = \pm 0.4$°C) were superposed on top of it. The period of the cyclic perturbation was set to 100 s. When the T_g of the curing adhesive overcomes the experimental temperature, a peak on loss C_p curve and a progressive decrease of the storage C_p were expected. Results of a curing experiment at 23°C are shown in Fig. 5.

The progressive decrease of the storage C_p indicates a reduction of the degrees of freedom related to the glass transition. The same glass transition is also revealed on the loss C_p curve by the presence of a peak. During the curing process of the adhesive, a network is slowly built up and the T_g of the material increases. At some time, the T_g will exceed the curing temperature. The time at which this transition occurs can be read on the time axis of the DDSC measurements. These times are indicated in Fig. 2 by the arrows. There is a strong correlation between the change of the curing kinetics and the transition to the glassy state. This confirms that the slowing down of the curing reaction is due to the material vitrification as proposed earlier.

There is a strong correlation between the degree of conversion and the viscosity of the epoxy adhesive [7]. The viscosity has been recorded (using a Dynamic Stress Rheometer, Rheometrics) over six orders of magnitude during curing and the results are shown in Fig. 6. The dramatic increase of viscosity is associated with gelation. From a molecular point of view, this process is associated with both an increase of the molecular weight and an incipient creation of molecules with finite

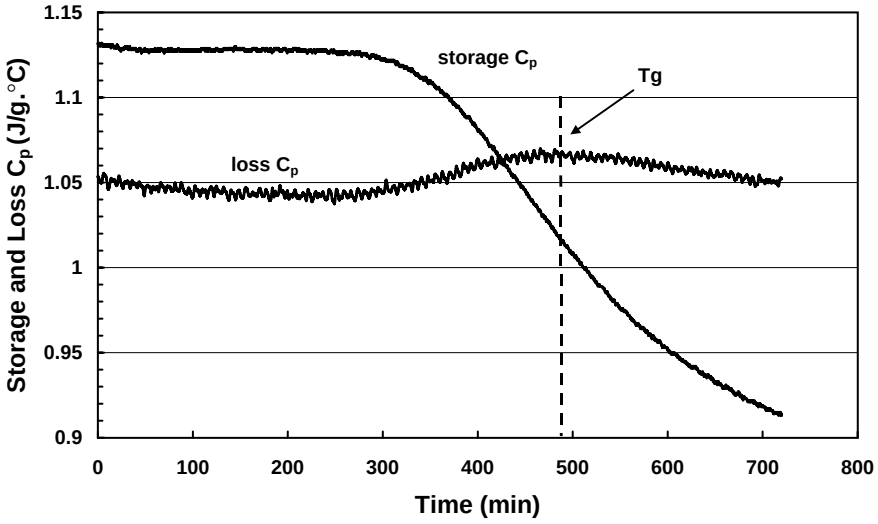

Fig. 5. Dynamic differential scanning calorimetry. Measurements of the storage and loss specific heat C_p during the curing of the adhesive at 23°C.

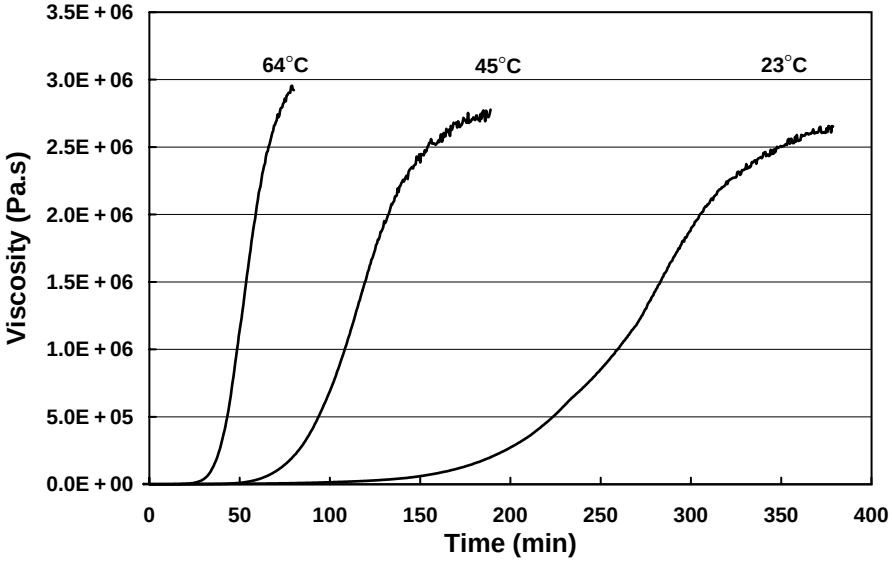

Fig. 6. Viscosity measurement during curing.

branches until a cross-linked structure is obtained. Measurements show that the relationship between the conversion factor β and the viscosity η can be described by (see Fig. 7)

$$\beta \propto k(T) \ln\left(\frac{\eta - \eta_0}{\eta_0}\right),$$

where η_0 is the initial viscosity before the curing reaction starts.

3. Mechanical properties

In order to study how the curing process affects the mechanical properties of the adhesive, samples were moulded and cured at different temperatures (23°C, 45°C and 64°C). The samples were moulded in a multi-cavity silicon mould covered by a 10 mm thick glass plate (see Fig. 8). A vacuum was created in the cavities to help the mould filling of the high viscosity adhesive ($\eta \approx 300\,\text{Pa}\cdot\text{s}$ at room temperature) and to avoid air bubbles in the specimen. After curing the samples were tested in tension and flexion (3 point bending) at room temperature. Results are shown in Figs. 9–11.

According to the DSC measurements (see Fig. 2) the curing of the adhesive is completed after 4 h at 64°C. The measurement of the mechanical properties shows (see Fig. 9) that 28 days at 23°C are needed to reach the same level of cure. This confirms the assumption that the curing process is not stopped once the plateau-like regime is reached in Fig. 1 but only slowed down. The measurements made in tension and in flexion (see

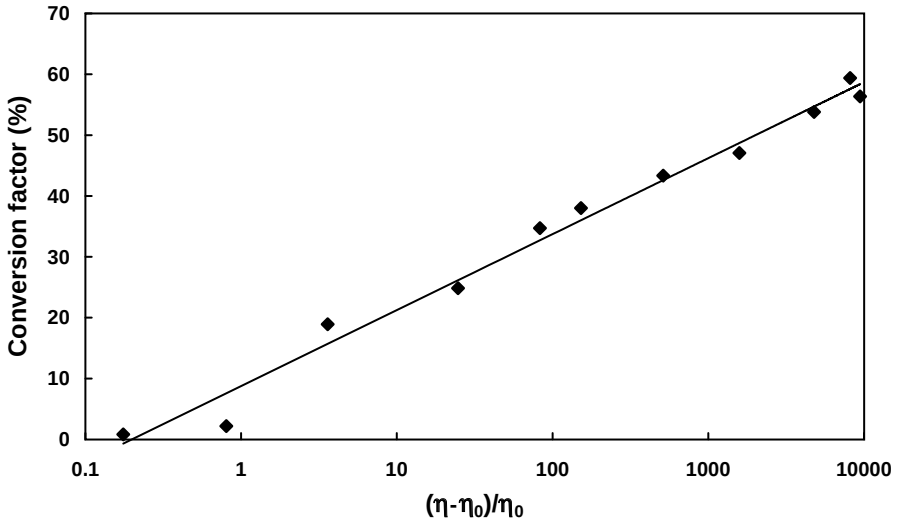

Fig. 7. Conversion factor vs. viscosity (log scale) for a sample cured at 23°C.

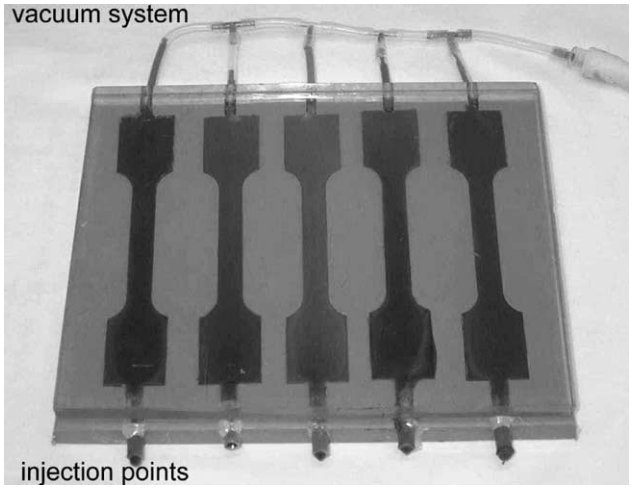

Fig. 8. Set-up used to mould adhesive samples for mechanical testing.

Fig. 10) are in perfect accordance. This may have implications in the testing of adhesive joints cured at room temperature. That shows that great care should be taken in industrial applications where the adhesive is cured at room temperature.

The inaccuracy of testing adhesively bonded structures while in the undercured state is shown in Fig. 11. Araldite 2014 sample were tested in tension at different stage of the curing process and the deformation at break and the plastic deformation were recorded. The total deformation was the deformation at failure, whereas the plastic deformation was defined as the difference between the deformation at breaking if the material had behaved elastically and the measured deformation at breaking (see Fig. 12).

Fig. 9 showed that the stress at break and the elastic modulus were increasing with time. Figs. 10 and 11 show that the adhesive becomes stiffer and stiffer as the process continues and that it behaves more and more elastically. The plastic deformation is reduced to $<0.1\%$ during the first 4 weeks. In the same time the deformation at break is reduced by almost 50%. This will affect the adhesive joint ability to absorb energy during testing and also the stress distribution across the joint.

By measuring the mechanical properties of adhesive samples it has been observed that the cure can be re-activated after vitrification. Samples cured at room temperature until the plateau-like regime is reached have been subsequently heated to 64°C for 2 h. The measurement of the *E*-modulus, deformation and stress at failure showed that the samples were fully cured.

4. Ageing properties

To study the ability of surface pre-treatments to promote adhesion and to protect the surface against corrosion, it is usually necessary to run accelerated ageing test to differentiate the surface treatment quality. Tests run under normal conditions of temperature and humidity after the curing of the adhesive may not provide results allowing a clear ranking of different surface pre-treatments adhesion promoter, and anti-corrosion protector abilities. To do so, adhesively bonded samples have to be exposed to severe conditions of temperature and humidity. When ageing tests are run to evaluate the quality of surface pre-treatments, changes in the mechanical properties of the adhesive should also be taken into account. They may affect the stress transfer from the adhesive layer to the interface and modify the results of the mechanical testing. In order to analyse correctly such experiments, the behaviour of the adhesive should be studied under

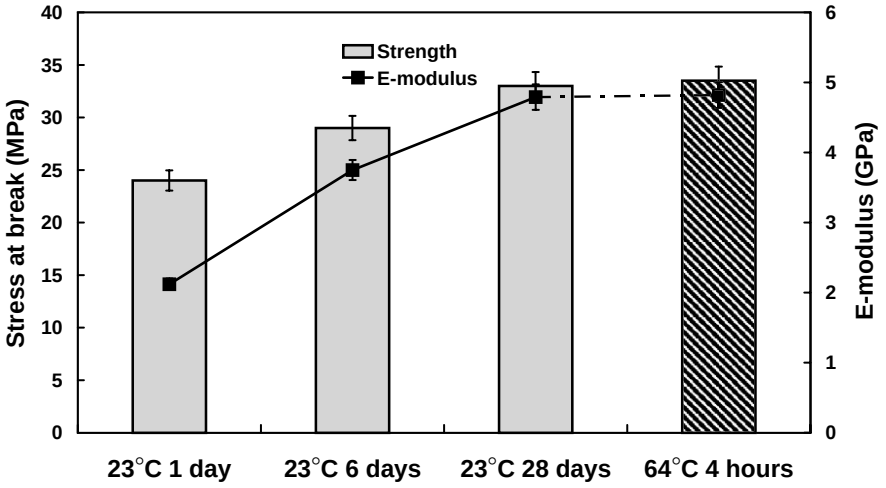

Fig. 9. Tensile testing of Araldite 2014 samples. The stress and *E*-modulus are measured from the stress–strain curves.

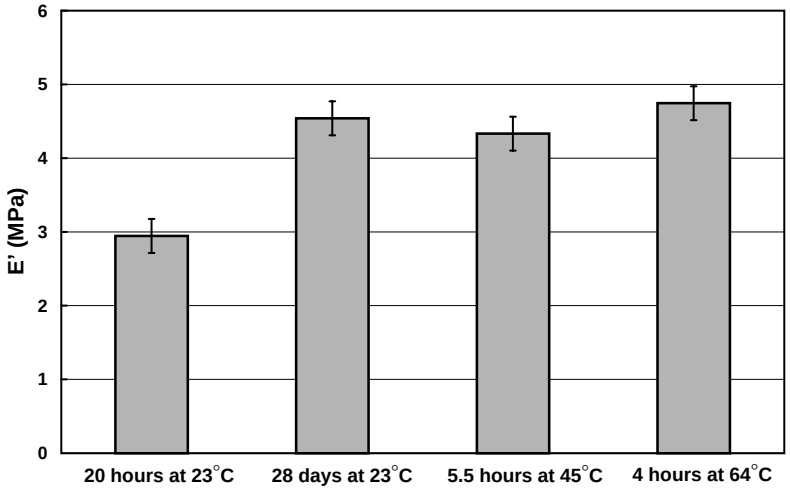

Fig. 10. Real part E' of the complex elastic modulus E^* measured in 3 point bending testing.

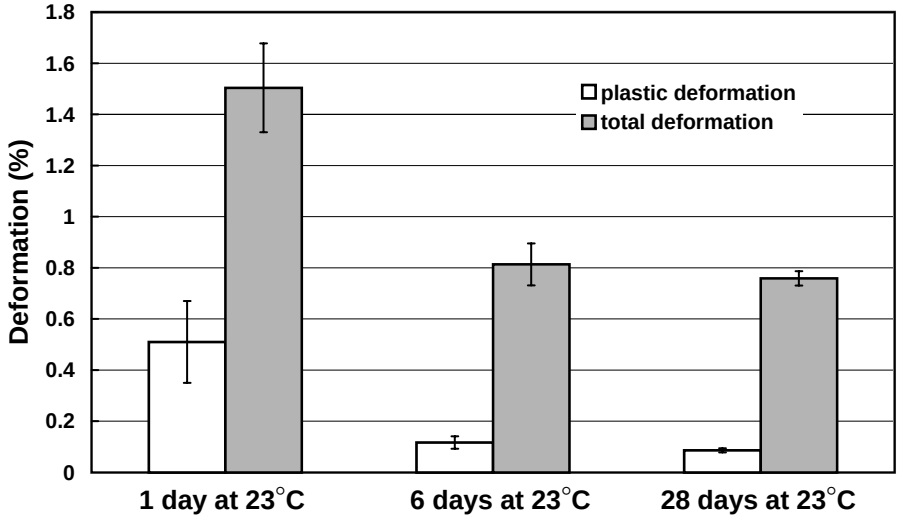

Fig. 11. Curing effect on Araldite 2014 samples tested in tension and cured at room temperature.

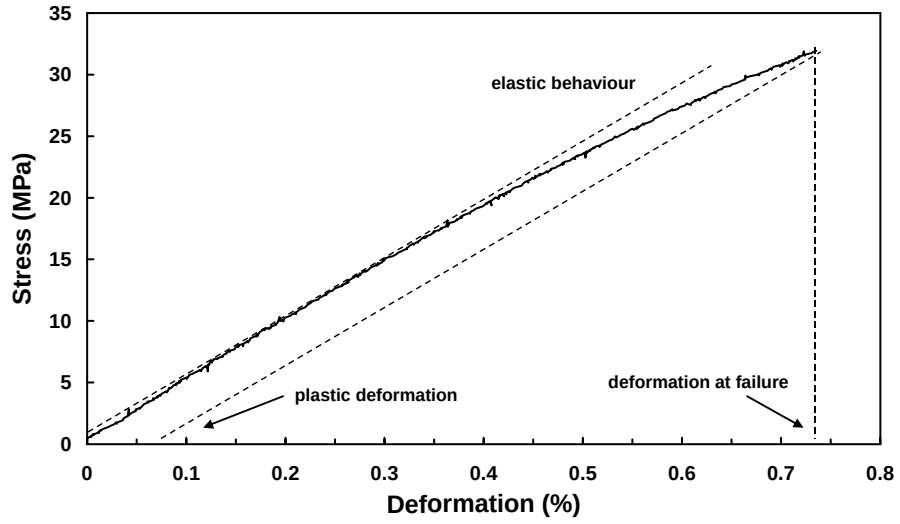

Fig. 12. Tensile testing of an Araldite 2014 sample cured for 28 days at 23°C. The results reported in Figs. 9 and 11 are an average over five samples.

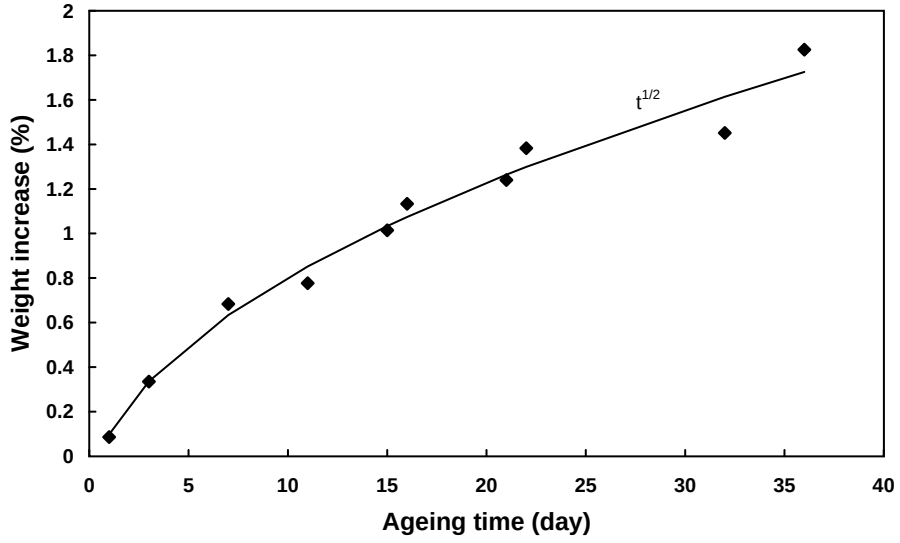

Fig. 13. Weight vs. time during ageing test for samples with a thickness of 1.5 mm. The weight increased follows a $t^{1/2}$ law.

ageing test conditions. Samples (1.5 mm thick) of Araldite 2014 were moulded at room temperature and subsequently cured at 64°C. The samples were then believed to be fully cured and they were exposed to 40°C and water vapour. The relative humidity was not measured but it was assumed to be between 90% and 100%. The weight of the samples and their tensile mechanical properties at room temperature were measured over a 36-day period (see Figs. 13–16).

The measurement of the weight of the samples (see Fig. 13) shows a weight increase due to an increasing water content in the epoxy with the exposure time. The weight increases with the square root of time in agreement with the standard Fickian diffusion. According to Fig. 13 the water diffusion continues even after 36 days and no equilibrium state is reached during that period of time. Water works usually as plasticizer leading to a softening of the material. This is also the case for the epoxy adhesive Araldite 2014. Figs. 14 and 15 show how the mechanical properties (stress at break, *E*-modulus and deformation at break) are affected by the exposure time and thus by the water content.

The plasticizing effect of the water is apparent from the curves in Fig. 15. The deformation at break and the plastic contribution to the total deformation are shown to increase. As mentioned previously, the Araldite 2014 was very stiff before exposure to ageing, with a plastic deformation (0.06%) representing 10% of the total deformation. After 1 month in water vapour at 40°C, the adhesive is not so stiff (*E*-modulus decrease of 35%), the deformation at break has been increased by 70% and the ratio plastic deformation/total deformation

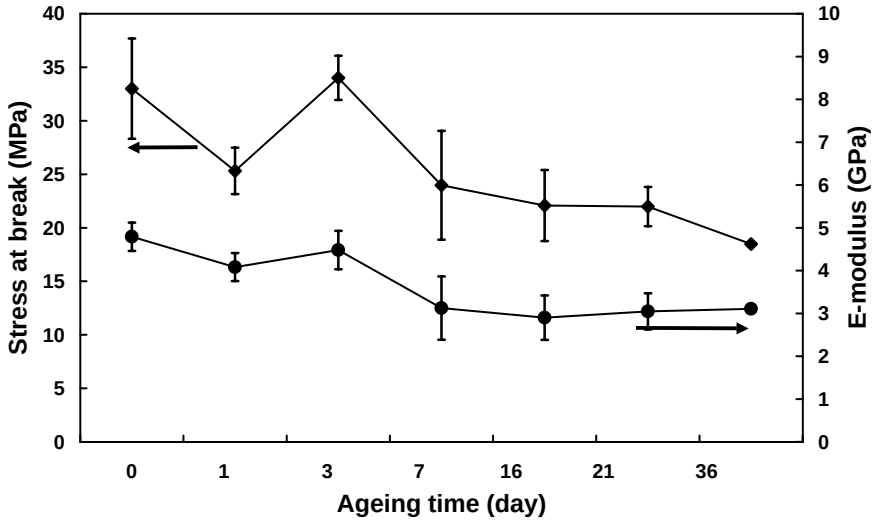

Fig. 14. Mechanical properties during ageing test measured in tension. Each point is the average of measurements performed on five samples.

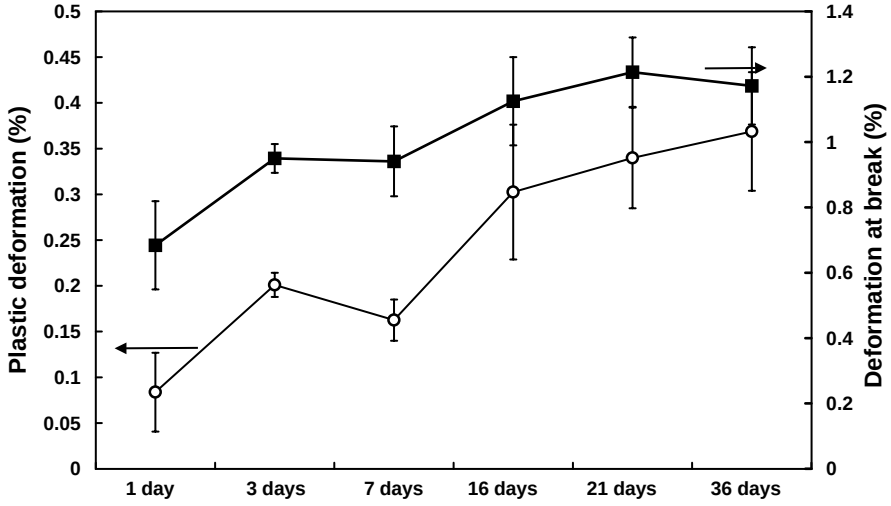

Fig. 15. Deformation at break and plastic deformation (tensile test) of Araldite 2014 during ageing test.

went from 10% (unexposed adhesive) to 32% after 36 days of exposure. These results show that the study of the behaviour of an adhesive under different conditions is necessary for a good interpretation of ageing tests conducted on glued samples. The results are quantitatively dependent on the sample geometry (ratio volume/surface area). The geometry dependence of the moisture absorption will be addressed in a further work.

5. Conclusions

The curing process of a room temperature curing epoxy adhesive paste (Araldite 2014) has been studied. It has been shown that any curing temperature increase leads to a more complete curing after a short period of time when the conversion factor reaches a plateau-like regime. In that regime the reaction rate becomes diffusion controlled and the reaction is drastically slowed down. Measurements of the mechanical properties of adhesive samples showed that 28 days are needed at room temperature to complete the curing process (only 4 h at 64°C) and that the properties of the adhesive during that period of time changed drastically.

Ageing test (40°C in water vapour) has been conducted on adhesive samples and the adhesives properties recorded over a 36 days long period of time. It has been shown that the absorbed water works as a plasticizer leading to a softening of the adhesive. The *E*-modulus and the stress at break are lowered while the

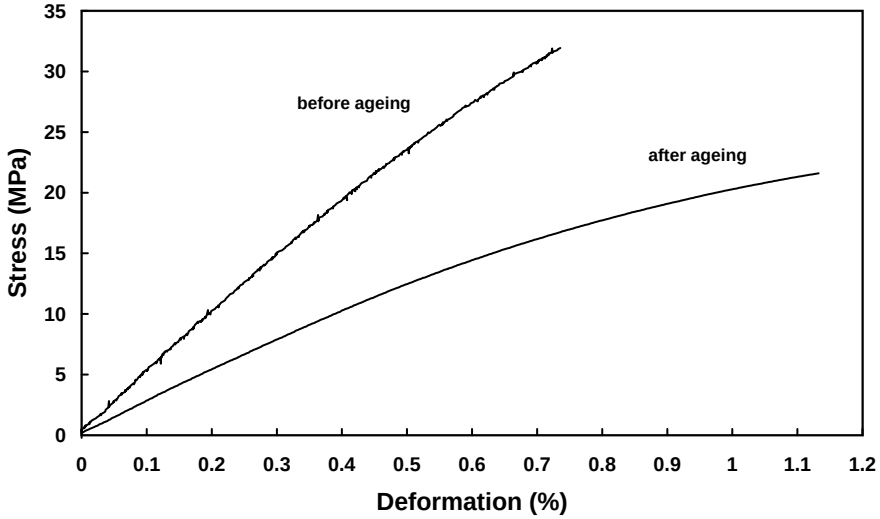

Fig. 16. Stress-deformation curves before and after ageing test. An increase of the deformation at break and of its plastic component is observed. In the same time a softening of the material is measured.

deformation at break and the plastic contribution to the total deformation are increased.

Acknowledgements

The authors acknowledge the financial support of the Norwegian Research Council.

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