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Nicolas Causse, Eric Dantras, Claire Tonon, Mathieu Chevalier, H el ene Combes, et al.. Environmental ageing of aerospace epoxy adhesive in bonded assembly configuration. *Journal of Thermal Analysis and Calorimetry*, 2013, vol. 114 (n o 2), pp. 621-628. 10.1007/s10973-013-3009-3 . hal-01136617

HAL Id: hal-01136617

<https://hal.science/hal-01136617>

Submitted on 27 Mar 2015

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To link to this article : DOI:10.1007/s10973-013-3009-3

URL : <http://dx.doi.org/10.1007/s10973-013-3009-3>

To cite this version:

Causse, Nicolas and Dantras, Eric and Tonon, Claire and Chevalier, Mathieu and Combes, Hélène and Guigue, Pascale and Lacabanne, Colette *Environmental ageing of aerospace epoxy adhesive in bonded assembly configuration*. (2013) *Journal of Thermal Analysis and Calorimetry*, vol. 114 (n° 2). pp. 621-628. ISSN 1388-6150

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Environmental ageing of aerospace epoxy adhesive in bonded assembly configuration

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Abstract Aerospace epoxy adhesive has been subjected to various environmental ageing processes. A comparative study is performed between ageing under vacuum and atmospheric pressure for various ageing temperatures. The macroscopic behaviour of the assemblies is investigated by single lap shear test. Glass transition temperature of the bulk adhesive is followed by differential scanning calorimetry. Molecular mobility of the adhesive in service configuration is studied by dynamic dielectric spectroscopy. No significant difference is noticed due to an ageing under vacuum. A comparison between test results after each isotherm ageing highlights the temperature influence. For ageing of adhesive in a vitreous state, the crosslink density increases. For ageing of adhesive in a rubbery state, a severe decrease of glass transition is observed. The influence of additives and physical ageing is null. This plasticisation effect might be associated with the homogenisation of the structure of epoxy due to the molecular mobility of loose chains.

Keywords Epoxy adhesive · Ageing · Space environment · Dielectric spectroscopy · Glass transition

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Introduction

Space environment involves specific in-use conditions for materials [1]. On ground or during mission, ageing parameters depend on applications and are not fully understood. Bonded assemblies are widely used for spacecraft conception and require a specific attention. They are notably susceptible to ageing phenomena due to storage on ground during spacecraft integration and thermal cycling under vacuum in orbit [2]. A previous study presented evolution of assemblies' properties depending on simulated hydrothermal ageing conditions (ground ageing) [3]. These modifications were followed in terms of molecular mobility correlated with mechanical behaviour of thermoset bonded structures exposed to moisture. Dielectric spectroscopy showed its ability to analyse adhesive bond in service configuration, thanks to adhesive secondary relaxation modes.

Real ageing after a thermal cycling under vacuum is not accessible (satellites are not returned on Earth). The alternative is to use accelerated testing based on space industry knowledge and ESA normative data [4]. Acceleration laws remain empirical. Simulation parameters' influence and correlations with ageing mechanisms are not clearly defined. Accelerated tests are often designed to be representative of spatial environment, and it is difficult to dissociate ageing parameters and properties evolutions [5–9]. Moreover, thermal cycling studies consider thermal fatigue of composite materials [10, 11]. A few studies are devoted to evolution of polymer properties due to level of temperature reached [12–15]. Oxidative thermal degradation is evidenced by chemical and mechanical characterisation. In some cases, equivalence between real and simulated ageing is explored but ageing processes can differ [16].

The vacuum influence is seldom studied. It does not deal with adhesives but with rubbers used as sealing materials or

thermosets used as matrix in composite materials. Vacuum is often considered as a neutral atmosphere [11]. However, it involves outgassing of volatile substances as moisture, low molecular weight additive, or unreacted species [17]. The expelled gases can be especially detrimental to optical instruments and solar cells on-board the spacecraft. Surfaces may be obscured by condensed outgassing products. The nature and extent of outgassing can lead to serious changes in the basic material properties. Outgassing properties are often tested, thanks to thermogravimetric methods [18, 19]. These phenomena are taken into account, thanks to normalised outgassing test in order to avoid contamination problems [20]. Influence on other properties is quasi non investigated. The aim of this study is to evaluate the influence of vacuum level during thermal ageing on a commercial adhesive. At the same time, it allows us to investigate the evolution of adhesive properties due to temperature. For a better description, ageing has to be achieved avoiding effect of cycling; that is why the thermal ageing is isothermal. The ageing conditions chosen for this study were selected to differentiate thermal effects from thermal spiking effects [15].

In the first part, we will investigate influence of ageing pressure and temperature on the material (mechanical property and physical structure). In the second part, influence of ageing conditions will be evaluated in service configuration at a molecular scale using low frequency chain dynamics.

Experimental

Materials

Initial state

The adhesive was a commercial amine-epoxy bicomposant adhesive. The two parts were prepared and a nozzle allowed to make and extrude the mix with an accurate repeatability. The hardener (part A) was a mix of several components where aliphatic amine is preponderant. The part B was based on diglycidyl ether of bisphenol-A epoxy resin mixed with other components (fillers, catalyst...). This adhesive was toughened by a blend of polybutadiene and thermoplastic copolymers. Parts A and B were mixed at room temperature (ratio 2:1). The curing process occurred in 7 days at 21 ± 2 °C in a clean room. At the end of this cycle, initial state labelled reference was reached.

Ageing procedure

Samples were placed in an isothermal environmental chamber under nitrogen gas (atmospheric pressure) or vacuum ($P < 10^{-5}$ mbar) for 7 days. Selected isotherm temperatures of ageing (T_{ageing}) covered the range used for this kind of adhesive; *i.e.* from -100 to $+150$ °C.

Methods

Single lap shear test

Single lap shear tests were performed at 25 °C using the tensile tension machine Instron 4505 with a 100 kN load cell. The crosshead speed was 1 mm min^{-1} . Five samples were studied for each test. Data were recorded with the Serie IX software. The load at failure was determined, and apparent shear rupture stress was calculated dividing this value by the shear area. The ruptures were analysed visually to determine the percentage of cohesive failure.

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) experiments were performed on a Perkin Elmer Pyris Diamond apparatus. The heat flow between a reference and the sample was measured by power compensation. Bulk adhesive was analysed in sealed aluminium pans during a linear increase of the temperature at a rate of 20 °C min^{-1} between -120 and $+200$ °C. The sample mass was ranging from 5 to 15 mg. For each ageing, the glass transition temperature T_g of five samples was monitored.

Dynamic dielectric spectroscopy

Broadband dynamic dielectric spectroscopy (DDS) was performed using a Novocontrol BDS 4000 covering a frequency range from 10^{-1} to 10^6 Hz with ten points per decade. Experiments were carried out isothermally from -150 to 150 °C by steps of 5 °C. The temperature was controlled with an accuracy of ± 0.5 °C by a nitrogen gas stream heated by a Quatro temperature controller. The samples were round plate assemblies ($\varnothing = 35$ mm). Aluminium alloy substrates were used as electrodes. The real ϵ' and imaginary ϵ'' parts of the relative complex permittivity ϵ^* were measured as a function of frequency f at a given temperature T . The complex dielectric modulus M^* is defined by equation (Eq. 1):

$$M^*(\omega) = \frac{1}{\epsilon^*(\omega)}. \quad (1)$$

Results and discussion

Influence of ageing atmosphere on properties of adhesive

Values of apparent shear strength measured after ageing are shown in Fig. 1. Error bars for samples aged under vacuum at -70 °C are high because of the presence of bubbles in one joint. The failure stress is the same after ageing under atmospheric pressure or under vacuum. For

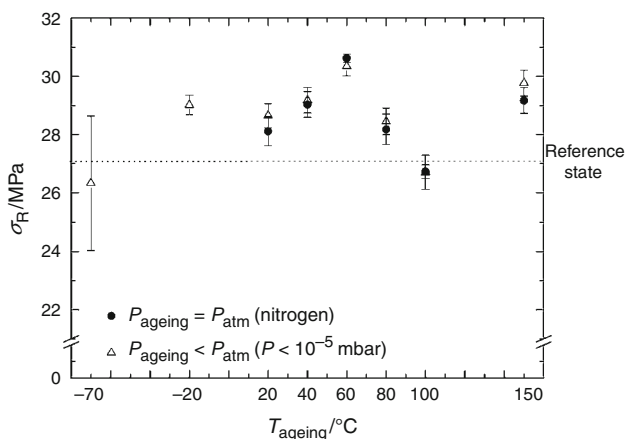


Fig. 1 Influence of pressure and temperature of isothermal ageing on apparent shear failure stress

each isotherm, the difference is lower than dispersion calculated with five samples.

The differential scanning calorimetry data for adhesive at the initial state (after curing) and after ageing (only two ageing temperatures are plotted) are presented in Fig. 2. The adhesive exhibits a glass transition temperature, called T_g at 55 °C (initial state). The endothermic peak at 130 °C is irreversible (not detected during the second scan), and its origin is unknown. For all ageing isotherms, T_g measured during the first scan after ageing under atmospheric pressure is obviously the same as the one measured after ageing under vacuum (Fig. 3). Variations upon environment are lower than uncertainty. Similar observations that are not reported here for the purpose of clarity can be made for T_g measured during the second scan.

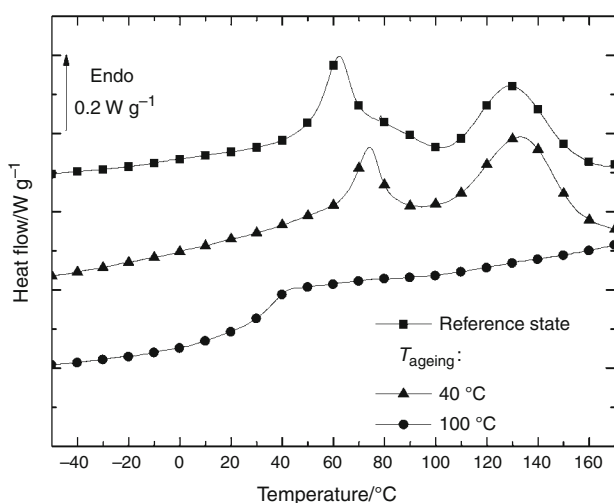


Fig. 2 DSC curves (first scan) obtained on heating (20 °C min^{-1}) after curing (initial state) and after two isothermal ageing processes

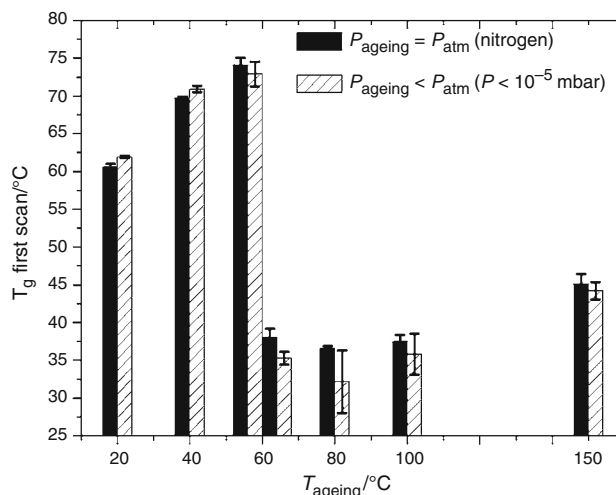


Fig. 3 Influence of ageing pressure on glass transition temperature of adhesive measured during the first scan

Adhesive properties during an isotherm ageing seem to be independent upon vacuum. Even if vacuum level is not the same, it is in agreement with previous studies that report the same thermal behaviour for epoxy, whatever the gaseous environment (nitrogen or vacuum) [19, 21]. This is the reason why ageing temperature influence can be discussed regardless of ageing atmosphere.

Influence of ageing temperature on properties of adhesive

In Fig. 1, stress of aged samples increases in comparison to the initial state. For lowest ageing temperatures (-20 to $+60$ °C), the stress slightly increases with ageing temperature. The highest value (≈ 30.5 MPa) is obtained after an ageing at 60 °C. For higher temperatures, the failure stress decreases to 27 MPa for a 100 °C ageing. The 150 °C ageing temperature leads to a stress equal to 29.5 MPa.

Figure 4 allows us to compare value of T_g depending upon ageing temperature. Results are only presented for ageing under vacuum. T_{g1ref} and T_{g2ref} are the T_g measured for adhesive at the initial state during the first scan and the second scan, respectively. Between the two scans, T_g decreases by 24 °C to reach a value of T_{g2ref} equal to 32 °C.

T_g measured during the first scan (T_{g1}) presents three evolutions with ageing temperature. For coolest ageing at -70 or -20 °C, values are similar to T_{g1ref} . While ageing temperatures are lower than T_{g1ref} , T_{g1} increases with ageing temperature. For example, an ageing at 40 °C leads to T_{g1} equal to 72 °C. We can notice that after 7 days at 60 °C ($\approx T_{g1ref}$), samples present two T_{g1} : the first one equal to 73 °C, the second one to 35 °C. When ageing temperature is above T_{g1ref} , aged adhesive T_{g1} dramatically decreases to values close to 35 °C for an ageing at 80 °C.

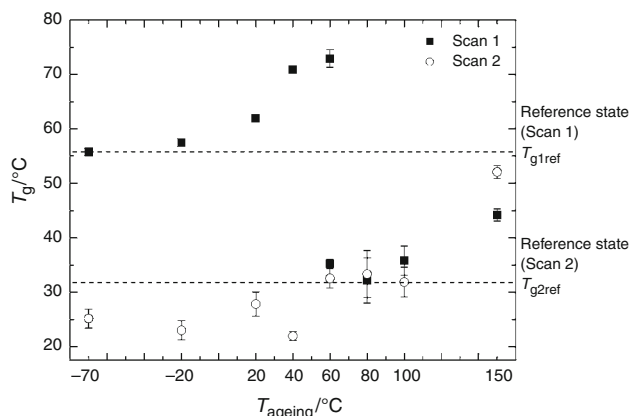


Fig. 4 Influence of ageing temperature on glass transition temperature of adhesive measured during first and second scan (ageing under vacuum)

For the highest ageing temperature, T_{g1} increases with ageing temperature. Value measured after an ageing at 150 °C is enhanced by 10 °C in comparison to an 80 °C ageing temperature.

The evolution of T_g measured during the second scan (T_{g2}) reveals two behaviours. For $T_{\text{ageing}} < T_{g1\text{ref}}$, T_{g2} is constantly close to 25 °C. In these cases, T_{g2} presents a strong decrease in comparison to T_{g1} . This difference is similar to the one observed between $T_{g1\text{ref}}$ and $T_{g2\text{ref}}$. For $T_{\text{ageing}} > T_{g1\text{ref}}$, T_{g2} slightly increases with ageing temperature for higher ageing temperature. The T_{g2} is the same between the two scans (≈ 35 °C), except for an ageing at 150 °C where $T_{g1} = 44$ °C and $T_{g2} = 52$ °C.

The influence of temperature on mechanical properties is not clearly defined as shown in Fig. 1. However, it is highlighted by evolutions of T_g (Fig. 4) values measured after ageing. Two behaviours can be observed.

For the first one, when ageing temperature is lower than adhesive glass transition temperature at the reference state: Values of T_g increase with ageing temperature, and failure stress of assemblies reaches a maximum. DSC curve of the adhesive with the residual endothermic peak at 100 °C (Fig. 2) reveals that after 7 days of curing at 23 °C, cross linking reactions are not fully achieved. Ageing leads to a lengthening of curing duration in comparison to reference state. It can be explained that epoxy network has a higher T_g and higher failure stress after ageing [15]. For ageing at 40 and 60 °C, curing temperature is also raised during the 7 days of ageing. Mobility of unreacted species is then extended, and chemical reactions are thermally activated. In Fig. 2, the exothermic peak at 100 °C disappears after a 40 °C ageing. This is the reason why T_g increases with ageing temperature: this first behaviour is associated with a process of cross linking.

For the second one, when ageing temperature is higher than adhesive glass transition temperature at the reference

state, adhesive glass transition temperature is lower (35 °C) like the failure stress of assemblies. This phenomenon is known as a T_g plasticisation.

An equivalent T_g drop off is noticed between the first ($T_{g1\text{ref}}$) and the second scan ($T_{g2\text{ref}}$) during DSC experiments carried out on reference adhesive. For low ageing temperatures ($T_{\text{ageing}} < T_{g1\text{ref}}$), even if T_{g1} is not plasticised, T_{g2} is also in the vicinity of the lowest values of T_g . In other words, plasticisation occurs when adhesive temperature becomes higher than its T_g at the reference state, through ageing or DSC scan.

In spite of this plasticisation, we note that T_{g1} still increases for high ageing temperatures. It corresponds to a post curing of adhesive with high storage temperature. This is confirmed by the fact that T_{g2} continuously increases with isothermal ageing temperature. Indeed, T_{g2} is not sensitive to plasticisation because it occurred previously during the first scan. It means that curing reactions occur all over the ageing temperature range due to increase of curing duration. These chemical reactions are thermally accelerated. They induce a more stable epoxy network, thanks to a higher crosslink density.

Plasticisation origin

In order to shed some light on the origin of the plasticisation phenomenon, two hypotheses have been proposed.

- The phenomenon may be due to an additive present in the adhesive formulation. This additive could be initially in a liquid state, like polybutadiene–thermoplastic copolymer which is dispersed to toughened epoxy network. When the adhesive temperature becomes higher than its T_g , mobility increased significantly, and the additive could diffuse in the network. Epoxy network is plasticised, and its T_g decreases. In order to check this hypothesis, various solvents have been used to keep DGEBA resin and amines separate from additives. They have been then mixed, optimising stoichiometric ratio, in order to formulate a simpler DGEBA-aminers network. The DSC curve of this simplified network is presented in Fig. 5. It is identical to commercial adhesive signal shown in the same figure. The decrease of T_g noticed between the first and second scan is similar in both cases. Plasticisation phenomenon is analogous without any additives. Additives are not responsible for this decrease.
- The decrease of T_g is then an intrinsic behaviour of DGEBA-aminers network. After a 7 day curing, the DSC curve reveals a huge endothermic peak in the glass transition region (Fig. 2): It is a typical manifestation of physical ageing. This process is characterised by continuous changes in the glassy state properties which are

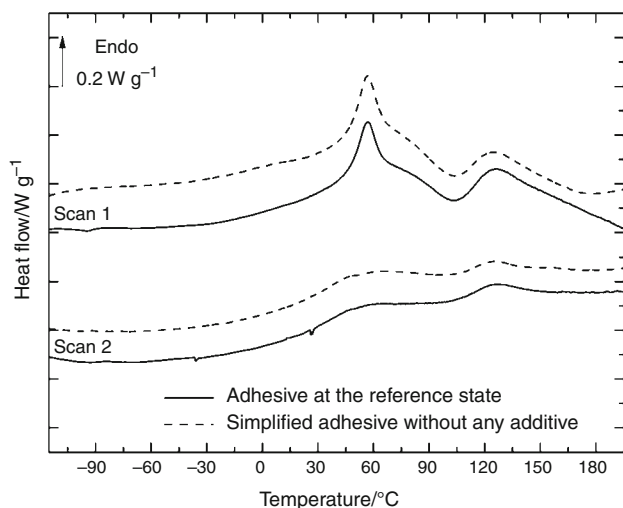


Fig. 5 Comparison of DSC curves monitored during first and second scan for the adhesive at the reference state and a simplified adhesive without any additive

dependent upon chain mobility [22, 23]. Aliphatic amine-cured epoxy systems are amorphous polymers, and they are sensitive to this kind of phenomena [24]. This peak disappears after a first heating above T_{gref} (Fig. 5) and after an ageing above T_{gref} (Fig. 2). This so called rejuvenation process can be accompanied by a decrease of T_{g} [25].

Figure 6 shows experiments carried out to evaluate the influence of physical ageing on T_{g} values. From rejuvenated state (plasticised T_{g}), sample is successively submitted to various annealing processes at 30 °C with increasing duration. This temperature is close to plasticised T_{g} but lower than that. After each annealing, the DSC curve is monitored during sample heating. As expected [26], the longer the annealing, the higher the endothermic peak is. T_{g} measured is not shifted to high temperatures. The onset of the transition is constant, whatever the annealing duration. Experiment conditions are not suitable to return to reference state.

A different but equivalent [27, 28] method to create physical ageing in a controlled way has been carried out, and the results are reported in Fig. 7: It consists in cooling the polymer from a temperature higher than T_{g} (75 °C) to a temperature lower than T_{g} (-50 °C) following various cooling rates (between -40 and -0.25 °C min⁻¹). Physical ageing phenomena are magnified for the slow cooling [29]. As expected, the endothermic peak increases with lowest cooling rate. The glass transition temperature is not modified by physical ageing.

These physical ageing phenomena have been studied in order to understand their kinetics. They do not explain the difference in T_{g} between a sample at the reference state and

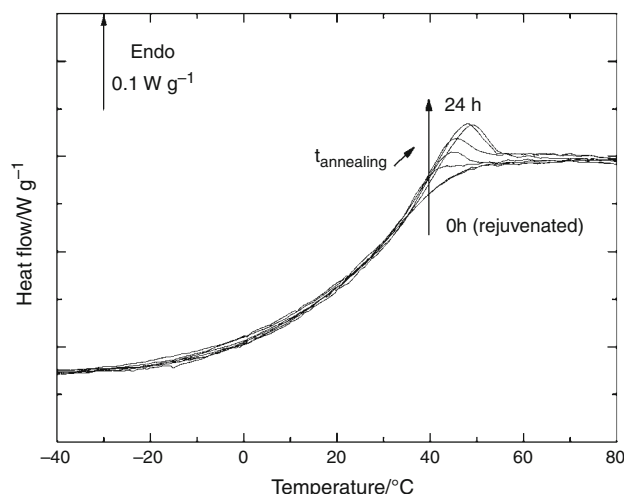


Fig. 6 DSC curves obtained on heating (20 °C min⁻¹) after increasing annealing time at 30 °C

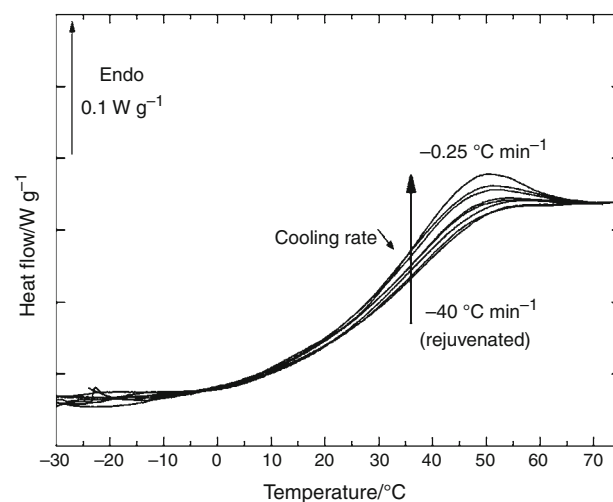


Fig. 7 DSC curves obtained on heating (20 °C min⁻¹) after various slowing cooling rates from 75 to -50 °C

an aged sample ($T_{\text{ageing}} > T_{\text{gref}}$). A controlled physical ageing cannot, fully or partially, simulate this non reversible specific order. It is probably due to the fact that the reference state (7 days of curing at room temperature) is metastable: i.e. it is the result of complex chemical reactions occurring during the curing process. In the reference state, as curing process has been achieved at room temperature, the chemical reactions are not fully completed. Consequently, a significant percentage of dangling chains remains creating a two-phase vitreous state. When the molecular mobility is sufficient, these loose chains might act as a plasticiser [30, 31] of the network in a homogenisation process of the two phases.

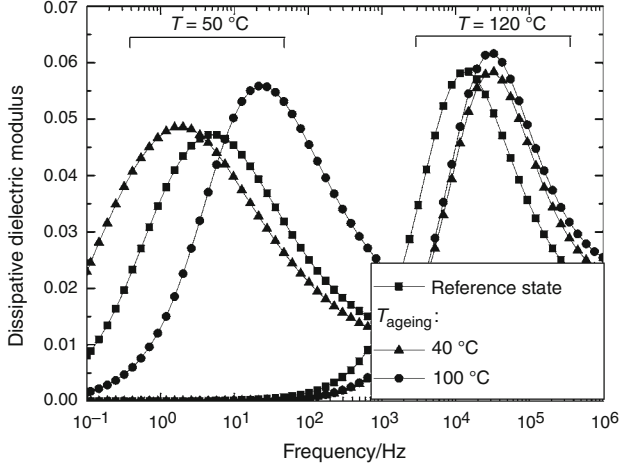


Fig. 8 Evolution of dissipative dielectric modulus measured at 50 and 120 °C after curing (initial state) and after two isothermal ageing (at 40 and 100 °C)

Influence of ageing conditions on adhesive bond in service configuration

Dynamic dielectric spectroscopy gives information about molecular dynamics evolutions of polymeric materials. Adhesive bonds can be tested in service configuration. However, dielectric manifestation of glass transition is often hidden by the contribution of conductivity (high temperature, low frequency). In order to avoid this phenomenon, results are reported considering modulus data (Fig. 8).

Experimental data are fitted by the modified Havriliak–Negami (HN) function [32] (Eq. 2) applied to the electrical modulus.

$$M^*(\omega) = M_\infty - \frac{M_\infty - M_0}{(1 + (i\omega\tau_{\text{HN}})^{\alpha_{\text{HN}}})^{\beta_{\text{HN}}}}, \quad (2)$$

where M_∞ is the real dielectric modulus for high frequencies, M_0 is the real dielectric modulus for low frequencies, α_{HN} and β_{HN} are the HN parameters, τ_{HN} is the relaxation time, ω is the angular frequency. This expression allows us to calculate the relaxation times of chain segments during dielectric manifestation of glass transition. The dependence of the relaxation time as function of temperature is fitted by Vogel–Tammann–Fulcher (VTF) equation (Eq. 3).

$$\tau_{\text{HN}}(T) = \tau_0 \exp\left(\frac{1}{\alpha_f(T - T_\infty)}\right), \quad (3)$$

where τ_0 is the pre-exponential factor, α_f the coefficient of thermal expansion of the free volume, and T_∞ a constant ($T_\infty \approx T_g - 50$ °C). T_∞ is often considered as the temperature for which mobility is frozen.

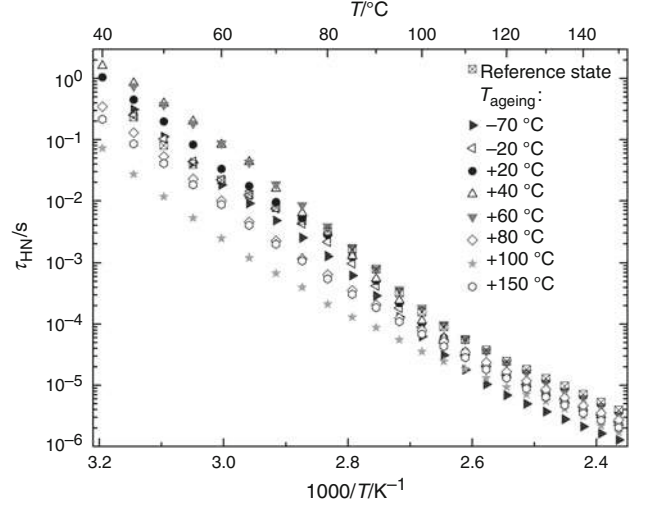


Fig. 9 Arrhenius diagram of relaxation times associated with the α mode as a function of temperature after an ageing under vacuum

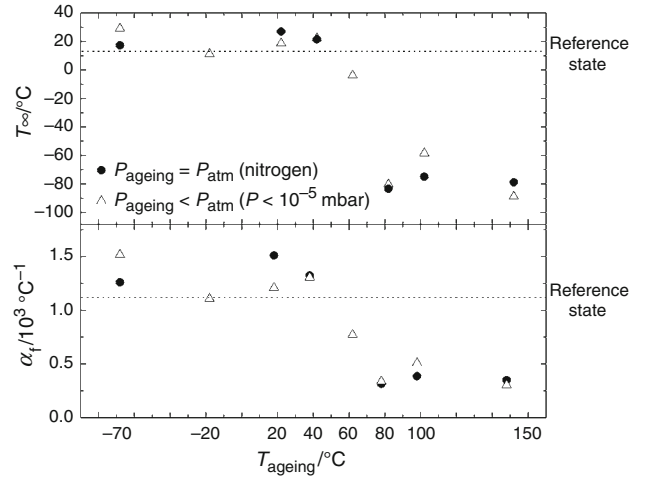


Fig. 10 Parameters of VFT equation depending upon ageing temperature and pressure

The relaxation times associated with the dielectric manifestation of the glass transition labelled α mode are reported in the Fig. 9 as a function of temperature. There is no difference between relaxation times after an ageing under atmospheric pressure (not presented here) and after an ageing under vacuum. This is consistent with parameters extracted from VTF equation (Eq. 3). In Fig. 10, for each ageing isotherm, parameters are not dependent from ageing atmosphere, which is consistent with DSC curves reported in Fig. 3.

The evolution of relaxation times as a function of the ageing temperature is reported in Fig. 9. For lower ageing temperature ($T_{\text{ageing}} < T_{g(\text{ref})}$), relaxation times increase

with ageing temperature. This phenomenon is the result of reduction of chain segments mobility. When ageing temperature is higher than T_{g1ref} , relaxation times decrease to reach a minimum for a 100 °C ageing. For the highest ageing temperature (150 °C), relaxation times increase compared to this minimum. Figure 10 confirms two kinds of VTF parameters value. Low ageing temperatures ($T_{ageing} < T_{g1ref}$) lead to high values of T_{∞} (≈ 20 °C) and α_f ($\approx 1.4 \times 10^{-3}$ °C $^{-1}$). When $T_{ageing} > T_{g1ref}$, VTF parameters are lower ($T_{\infty} \approx -80$ °C and $\alpha_f \approx 0.4 \times 10^{-3}$ °C $^{-1}$).

The increase of relaxation times can be correlated with the end of crosslinking previously revealed by DSC experiments. Cross linking involves a reduction of the chain segment mobility. For ageing temperature higher than T_{g1ref} , the relaxation times decrease as a result of the plasticisation phenomenon previously discussed. It is important to note that loose chains remain even in bonded assembly configuration. The dielectric manifestation of glass transition of the adhesive in service configuration has a similar evolution as a function of ageing temperature to the glass transition in a bulk configuration.

Conclusions

The influence of vacuum and temperature on properties of the adhesive and assemblies has been studied. Concerning adhesive behaviour, a good agreement has been revealed whatever the test configuration (bulk material or in service configuration). The 7 days of ageing are not representative of the life time of a satellite. They have been chosen to be a compromise between a sufficient duration to reach equilibrium and a moderate duration to limit the cost of ageing tests. In the space industry, outgassing tests consist in a 125 °C storage under vacuum during 24 h [20]. It is usually considered as enough to obtain a complete release of gaseous species from a specimen. Polymeric properties do not present any difference after an ageing under vacuum or under atmospheric pressure, whatever the ageing temperature. Consequently, vacuum is not a sensitive ageing parameter, and the 7 days are sufficient to reach equilibrium. Ageing temperature influence is twofold. An increase of ageing temperature below T_{gref} activates curing reactions so that a hardening of the polymeric network is observed. Contrarily, an increase of ageing temperature above T_{gref} involves an intrinsic plasticisation of epoxy network that might be due to the mobility of loose chains. It would be now interesting to vary the ageing duration to reduce tests cost or to establish acceleration laws. It must be recalled here that the classical curing process recommended by the manufacturer for stabilising the structure of such epoxy cannot be done since spacecraft integration in clean room prevents this kind of thermal treatment.

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