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New bonded assembly configuration for dynamic mechanical analysis of adhesives

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A B S T R A C T

A new sample configuration has been developed in order to study molecular mobility of an adhesive in a bonded assembly configuration by dynamic mechanical analysis. The torsional rectangular mode is used to provide a shear solicitation all along the adherend/adhesive interface. The initial mechanical properties of each assembly's constituent are first investigated as reference. The modulus of aluminum foils used as substrates exhibits a classic elastic component and a slight viscous part due to microstructural changes or stress relaxation. Four relaxation modes are highlighted and identified for epoxy adhesive tested as a bulk material. Its viscoelastic behavior is compared to the one of adhesive tested in assembly configuration. The relaxation modes of the adhesive remain visible in spite of the sample stiffening by aluminum foils. Relaxation modes comparison shows that the temperature of loss modulus associated with the mechanical manifestation of glass transition slightly increases for the assembly configuration. Energy losses during this relaxation are much higher in the assembly configuration. Influence of rigid aluminum substrates is discussed in terms of the adhesively bonded joint solicitation mode.

Keywords:

Dynamic mechanical analysis
Adhesively bonded joint
Bulk adhesive
Epoxy
Molecular mobility

1. Introduction

Dynamic Mechanical Analysis is a technique commonly used for mechanical characterization of materials [1]. It consists in subjecting a sample to controlled mechanical oscillation and measuring its response. The data collected allow us to determine the viscoelastic properties of bulk polymeric material. Molecular mobility can also be analyzed through primary and secondary relaxations of polymer as temperature is scanned [2]. This technique is particularly suitable to provide information about changes in molecular mobility or in physical properties of a polymeric system due to introduction of fillers [3], ageing [4] or changes in chemical formulation or in manufacturing process [5].

In the past decade, dynamic mechanical analysis has found some applications in the field of adhesion. However, previously reported dynamic mechanical analysis results on adhesives have been focused mainly on the behavior of adhesive resins only as bulk material [6–8]. A few studies are dedicated to adhesive in a configuration of bonded assembly. Most of them use this

technique for evaluating the curing of thermosets [8–10] as an alternative to differential scanning calorimetry. Influence of environmentally induced ageing [11,12] or specific parameters to bonding process, like surface pretreatment of substrates [13,14], is also investigated.

There has been controversy on whether the adhesive properties in the thin film form (adhesive joint) are the same as the corresponding bulk properties. However, in many applications, it is crucial to take into account the intrinsic properties of adhesive joint [15] because it conditions the assembly strength, stiffness and durability [16]. In several mechanical investigations, a good agreement between the two configurations has been found [17–21]. Based on other experiments, some authors highlight differences in the mechanical behavior of adhesive depending on the kind of sample configuration [22–24]. These properties can differ due to changes in chemistry resulting from specific interactions with the adherends during the curing reaction. Existence of a diffused interphase at the boundary substrate/adhesive is mentioned [25–28]. Another explanation can be the complex state of stress in adhesive which affects measurements: test specimen used often presents non-uniform states of stress in the adhesive bond line.

The authors mainly compared static mechanical properties and comparing relevantly to other parameters which characterize

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macromolecular structure of the adhesive. Dynamic mechanical analysis is a relevant technique to examine molecular mobility of adhesive's chain sequences through its relaxation processes. Solid samples can be tested in a torsional analyzer as bars that are twisted about their long axis. Samples are inexpensive and easy to make. This test geometry is expected to provide a shear solicitation all along the interface.

Aim of this study [29] is to explore the feasibility of performing dynamic mechanical testing for adhesively bonded joint. A sample configuration is developed and optimized to be tested in torsion. This configuration is expected to be representative of a usual bonded assembly using aluminum substrate and a commercial epoxy adhesive. Data resulting from this new kind of sample are compared with the ones resulting from the experiment carried out with a bulk configuration.

2. Materials and methods

2.1. Adhesive and substrates

The adhesive is a commercial (3 M) amine-epoxy bi-component adhesive. The two parts are prepared and a nozzle allows us to make and extrude the mix with an accurate repeatability. The hardener (part A) is a mix of several components where aliphatic amine is preponderant. The part B is based on diglycidyl ether of bisphenol-A epoxy resin mixed with other components (fillers, catalyst...). This adhesive is toughened by a blend of polybutadiene and thermoplastic copolymers. Parts A and B are mixed at room temperature (ratio 2:1). The curing process is 7 days at 21 ± 2 °C.

Substrates are aluminum foils (1000 series), provided by Goodfellow in the form of 100 μm thick plates. They are in an annealed state.

2.2. Sample preparation

All experiments are carried out using sample size of 50 mm in length and 10 mm in width.

Adhesively bonded joints were prepared by sandwiching a layer of adhesive between two rectangular aluminum foil strips in a poly(tetrafluoroethylene) (PTFE) mold (Fig. 1). Various assemblies' thicknesses were prepared varying the mold depth. Three assembly configurations were tested and designated by the adhesive thickness of adhesive bond line: 600 μm , 260 μm and 100 μm . A load was applied during 24 h, as recommended by the adhesive manufacturer.

To study mechanical properties of adhesive in a bulk configuration, films of 1.2 mm in thickness were made by casting onto a PTFE mold.

2.3. Dynamic mechanical experiments

The dynamic mechanical analyses (DMA) were performed on a Rheometrics Scientific ARES of TA Instruments. Tests were carried out in the torsional rectangular mode over the linear elasticity range determined in the first part of this work. Samples were tested by applying a sinusoidal deformation at one end and measuring the resultant sinusoidal torque at the other end. This technique allows us to access the shear complex modulus

$$G^*(\omega, T) = G'(\omega, T) + iG''(\omega, T) \quad (1)$$

where G' is the dynamic storage modulus, G'' is the dynamic loss modulus and $\tan \delta = G''/G'$ is the loss factor.

In the case of the dynamic mechanical test upon temperature ramp, the isochronous evolution ($\omega = \omega_0$) of these values is

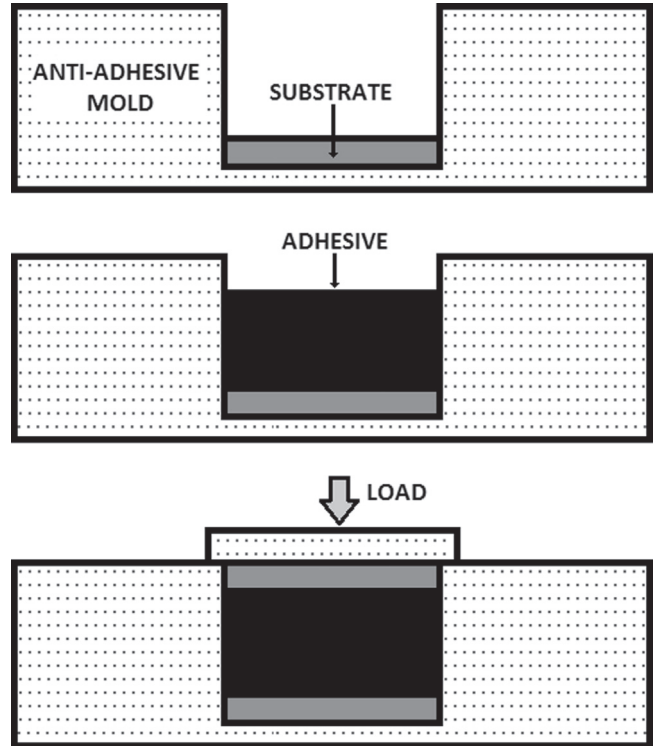


Fig. 1. Preparation of adhesively bonded joints.

recorded as a function of temperature (heating rate: 3 °C/min; ranging from -130 to 150 °C).

Then, G' varies from the glassy value G_g till the rubbery value G_r while G'' passes through a maximum for a temperature T_G^{\max} defined by

$$\omega_0 \tau (T_G^{\max}) = 1 \quad (2)$$

where τ is the anelastic relaxation time.

The temperature variation of $\tan \delta$ is also a bell shaped curve with a maximum at $T_{\tan \delta}^{\max}$ defined by [30]

$$\omega_0 \tau (T_{\tan \delta}^{\max}) = \sqrt{G_r / G_g} \quad (3)$$

3. Results and discussion

3.1. Preliminary experiments

Fig. 2 shows the storage modulus G' as a function of the angular frequency for the three kinds of tested configuration. Measurements have been achieved at room temperature. All the values are not influenced by the frequency rate; the adhesive G' increase (≈ 0.2 GPa) is not significant compared to the high aluminum modulus (≈ 30 GPa). Adhesive is tested as a bulk material. The value of the storage modulus is about 1 GPa. It is consistent with values frequently measured for thermoset polymer. Aluminum foil is also tested as a bulk material. Its modulus is in agreement with shear modulus of aluminum, i.e. 30 GPa [31]. Adhesively bonded joint has an intermediate value of modulus situated between those of its constitutive elements.

The maximal strain amplitude used in DMA experiments has to be well within the linear viscoelasticity range for all the investigated samples. Fig. 3 illustrates the test made to check this hypothesis. It represents the torque measured for each sample as a function of strain. Measurements have been achieved using an angular frequency of 1 rad s^{-1} .

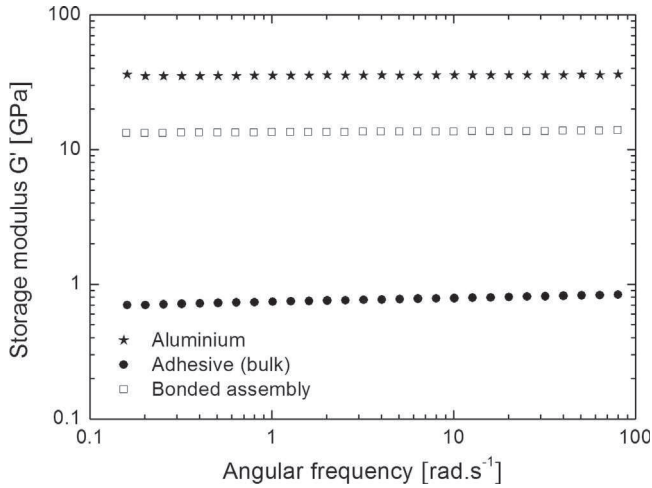


Fig. 2. Shear storage modulus as a function of frequency for the aluminum foil, bulk adhesive and bonded assembly (adhesive thickness: 600 μm).

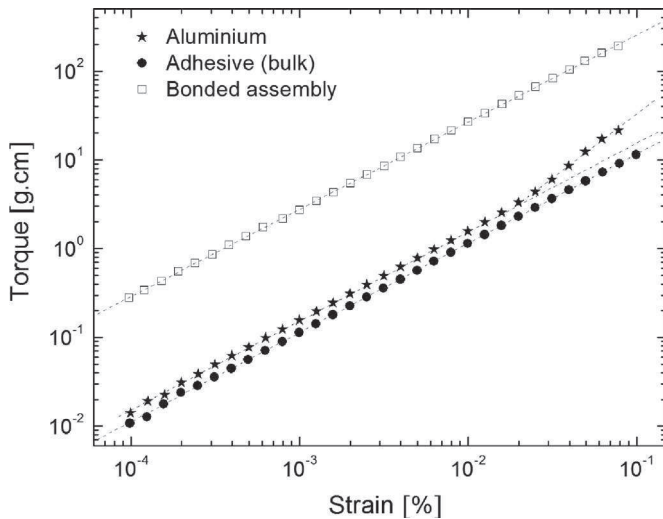


Fig. 3. Measured torque as a function of strain rate for the aluminum foil, bulk adhesive and bonded assembly (600 μm adhesive thickness).

Adhesive and assembly stay in their linear viscoelasticity range whatever the strain rate because the torque is linearly dependent on strain. Aluminum tested as a bulk material is not in its linear range for strain rates higher than $2 \cdot 10^{-2}\%$.

In order to stay within the linear viscoelastic range and to keep a response with enough intensity a $10^{-2}\%$ strain rate and a 1 rad s^{-1} angular frequency have been chosen for this study.

3.2. Intrinsic behavior of aluminum

Aluminum foils have been selected in order to be as thin as possible. The aim was to minimize influence of substrates on adhesive signal. Foils are hardly laminated to obtain a $100 \mu\text{m}$ thickness. They are then annealed to decrease residual stresses. They have been tested as a bulk material to check the temperature stability of the microstructure. The real part of the modulus, $G'(T)$, and the imaginary part $G''(T)$ are reported in Fig. 4.

The storage modulus remains constant (about 30 GPa) between $-130 \text{ }^\circ\text{C}$ and $+150 \text{ }^\circ\text{C}$. On the contrary, the loss modulus increases with temperature:

- G'' does not present any significant evolution for temperature lower than $20 \text{ }^\circ\text{C}$. Values of G'' are of the order of magnitude of

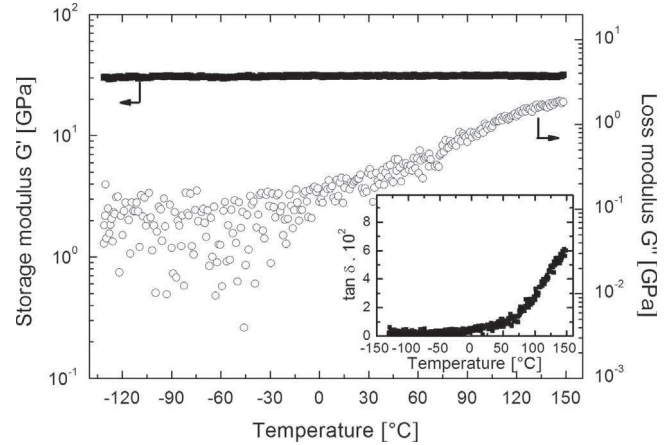


Fig. 4. Shear storage and loss moduli G' (\bullet), G'' (\circ) versus temperature for aluminum foil.

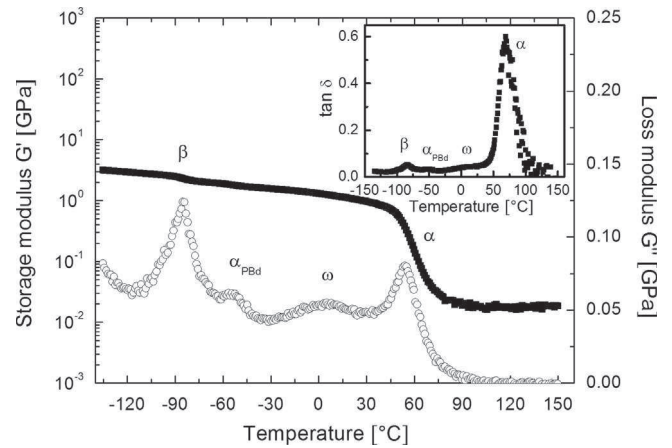


Fig. 5. Shear storage G' (\bullet), loss G'' (\circ) moduli and loss factor versus temperature for the adhesive in the bulk configuration.

noise. Torque values are at the detection limit of the transducer. Aluminum is a pure elastic material and there is no energy dissipation.

- For temperature higher than $20 \text{ }^\circ\text{C}$, aluminum has a viscoelastic behavior. It was already highlighted for pure aluminum [32,33] or aluminum alloys [34,35]. This phenomenon has been assigned to grain boundary dislocations involving a damping effect.

Aluminum foils have a stable elastic modulus but it cannot strictly be consider as an elastic material as expected. There is a loss part in the complex modulus when the temperature is raised above $20 \text{ }^\circ\text{C}$.

3.3. Bulk epoxy adhesive

Bulk epoxy adhesive has been analyzed and results are reported in Fig. 5. It shows the real part of the modulus, G' , the imaginary part G'' and the loss factor $\tan \delta$ versus temperature.

The glassy plateau ($G_g=2 \text{ GPa}$) and the rubbery plateau ($G_r=1.6 \cdot 10^{-2} \text{ GPa}$) are identified on the G' curve. The G' viscoelastic step is about two decades (1 GPa at $20 \text{ }^\circ\text{C}$ and $1.6 \cdot 10^{-2} \text{ GPa}$ at $100 \text{ }^\circ\text{C}$) as frequently observed for polymeric systems. This transition called α is identified as the anelastic relaxation associated with the glass transition of the adhesive.

The molecular origin of relaxations exhibited on G'' and $\tan \delta$ curves has already been discussed in previous works [36,37].

The β , α_{PBd} and ω relaxations are characterized by the maximum of the $\tan \delta$ peak associated with each relaxation. For these relaxations, the maximum of $\tan \delta$ peaks perfectly match with the maximum of G'' peaks. For the α relaxation, both values of maximum will be noticed. The value presented is an average of data on five samples.

- The β peak reaches a maximum at -84 ± 1 °C. It is associated with the mobility of the O-CH₂-CHOH-CH₂ hydroxypropyl-ether units and/or phenyl ring flips [38–41].
- The α_{PBd} peak at $-54 \pm 3 \pm$ C is associated with the anelastic manifestation of the glass transition of the polybutadiene phase dispersed in the epoxy network. It is an amine terminated butadiene–acrylonitrile copolymer.
- The ω peak reaches a maximum at 6 ± 3 °C. This relaxation is associated with heterogeneities in the adhesive network [37,42,43].
- The α peak is associated with the anelastic manifestation of the epoxy glass transition. The maximum of $\tan \delta$ is at 70 ± 1 °C whereas the one of G'' is at 55 ± 1 °C.

3.4. Bulk/assembly comparison

3.4.1. Viscoelastic storage

The adhesive dynamic mechanical response is studied depending on the test configuration.

Fig. 6 shows the storage modulus versus temperature of adhesive tested as a bulk material and the equivalent storage modulus of adhesively bonded joints with various thicknesses.

The glassy and the rubbery plateaus are determined for both configurations. The bonded assembly has a viscoelastic behavior like a polymeric material. The assembly equivalent modulus values are governed by both aluminum foils modulus and bulk adhesive modulus: assemblies have intermediate properties between the two constitutive materials. The assembly glassy plateau (20 GPa) is less temperature dependent than the bulk adhesive one. The adhesive is rigidified and stabilized by the presence of the two aluminum foils. The equivalent G' values are influenced by the adhesive thickness: G' increases for assemblies with a thin adhesive joint.

The evolution of G_g (measured at 10 °C) and G_r (measured at 100 °C) is plotted in Fig. 7 as a function of the adhesive volume

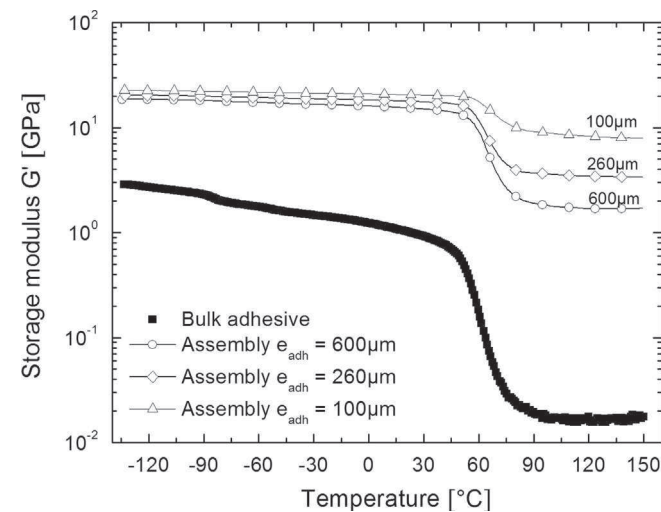


Fig. 6. Storage shear modulus G' versus temperature for bulk adhesive and assembly of various thicknesses.

fraction in the assembly (f_{adh}). The stiffening effect by aluminum foils (increase of both G' values) is enhanced when the adhesive fraction decreases. In Fig. 6, the decrease in G' from 40 °C to 90 °C is associated with the anelastic manifestation of the main glass transition. It is only due to the viscoelasticity of the adhesive in the assembly configuration. The G_g – G_r step (Fig. 7) is independent from the adhesive volume fraction: in other words, the thickness of the joint does not influence the intrinsic viscoelastic response of adhesive. The G' variations on the glassy and rubbery plateaus are only due to the influence of adhesive volume fraction (low modulus) compared to aluminum volume fraction (high modulus).

3.4.2. Anelastic energy dissipation

In order to compare relaxation amplitudes and temperatures, the loss part of the modulus (G'') and the loss factor ($\tan \delta$) have been plotted as a function of adhesive thickness, in Figs. 8 and 9 respectively. The relaxation modes have been identified in the figures. The four relaxations identified for the adhesive in a bulk configuration remain visible in the case of 600 μm and 260 μm assemblies. For the 100 μm assembly, the noise is too important due to the low adhesive fraction that prevents significant observations.

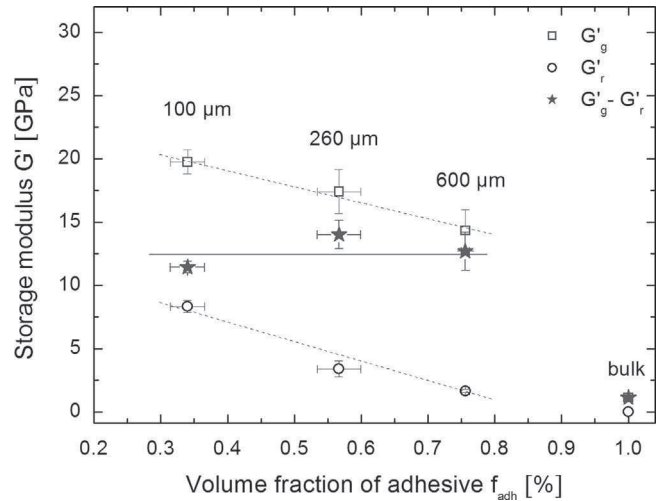


Fig. 7. Storage modulus G' as a function of volume fraction of adhesive in bonded assemblies.

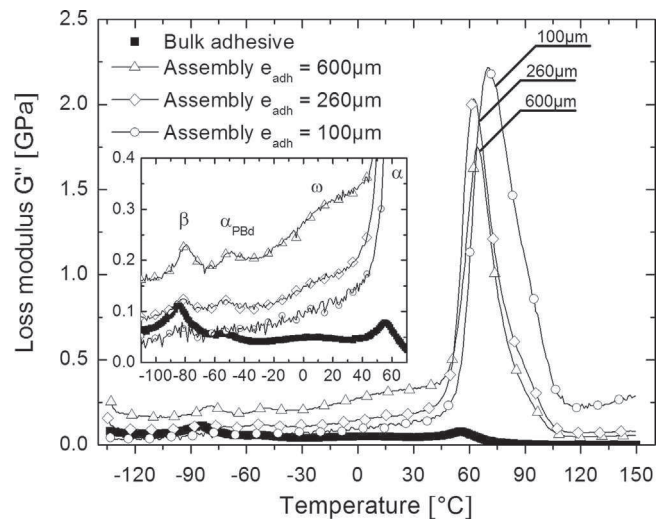


Fig. 8. Shear loss modulus G'' versus temperature for adhesive and assembly.

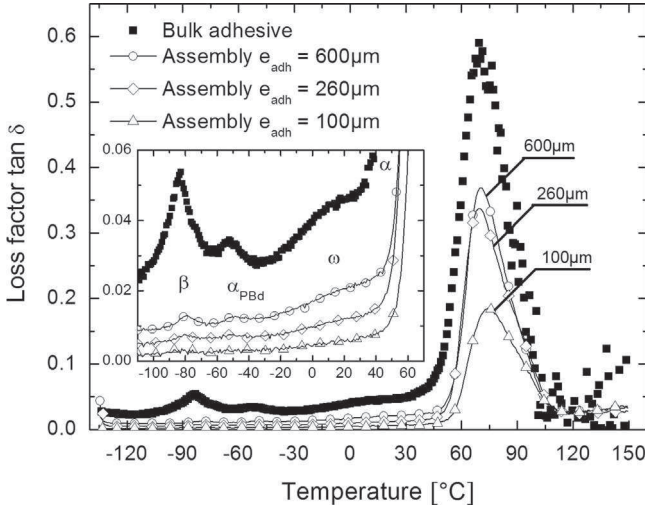


Fig. 9. Loss factor $\tan \delta$ versus temperature for adhesive and assembly of various thicknesses.

The equivalent loss modulus of assemblies G'' (Fig. 8) is higher than for the bulk adhesive. Moreover, G'' decreases with the thickness of assembly and the volume fraction of adhesive that dissipates mechanical energy. Contrarily, the loss factor of assemblies (Fig. 9) is lower than for the bulk adhesive. Values of G'' are of the same order of magnitude for both configurations (≈ 0.1 GPa) whereas G' is two decades higher in the case of assemblies (Fig. 6). Then, as expected, $\tan \delta$ of assemblies is lower than for the bulk adhesive.

Energy dissipated by aluminum is negligible compared to adhesive. Frictional energy dissipation at the bonded interface between adhesive and substrate is considered as negligible too. Consequently, aluminum foils transmit to polymer the whole energy due to torsional strain. The stress generated in adhesive layer is locally raised by the presence of the rigid substrate. When approaching the glass transition, polymeric sequences become mobile and dissipate this anelastic energy. This phenomenon can explain that the loss modulus of assembly is higher than for bulk adhesive.

Such experimental evidence has been previously reported for sandwich structures or constrained viscoelastic layer damping [44].

Areas under the curves cannot be directly compared because the continuum of G'' signals are dependent on configuration. The amplitude of relaxation peaks is then defined by the difference of its maximum and the continuum. Amplitudes and widths of the relaxation peaks are not dependent upon the configuration except for the α -peak. In the case of bulk adhesive, the G'' α peak has the same height as the β peak (Fig. 5). The ratio of amplitude of α and β peaks is about 1. In the case of assemblies, this ratio is 40 whereas the β peak amplitude does not change. In other words, the energy dissipated at the α relaxation is higher when the adhesive is solicited in an assembly configuration due to the rubbery state of adhesive. Accordingly, when adhesive is in the vitreous state, i.e. in the temperature range of the β relaxation, the stress generated by aluminum foils is analogous with the one transmitted by the vitreous. Energy losses during this relaxation are the same, whatever the configuration tested.

3.4.3. Relaxation modes

The β peak reaches its maximum at -80 ± 1 °C whatever the adhesive thickness (the signal of 100 μm assemblies is not sufficient to determine the β peak temperature). It is 4 °C higher than the β peak of bulk adhesive. The area under the G'' curve is also independent from the configuration.

The maximum of α_{PBD} peak is at -50 ± 2 °C. This peak is not influenced by the presence of the substrate.

The ω mode is detectable as a shoulder of the α peak.

Considering the α peak, G'' reaches a maximum at $T_{G''}^{\text{max}} = 55 \pm 1$ °C for the bulk adhesive; the G'' peak is situated at $T_{G''}^{\text{max}} = 63 \pm 1$ °C for 600 μm and 260 μm assemblies. For the 100 μm thick adhesive, this maximum is shifted to higher temperature ($T_{G''}^{\text{max}} = 69 \pm 1$ °C) with a broadening on the high temperature side. Contrarily, the temperature of the $\tan \delta$ maximum is analogous for all configurations and morphologies ($T_{\tan \delta}^{\text{max}} = 70 \pm 1$ °C). This apparent discrepancy is discussed from Eq. (3) where the temperature dependence of the relaxation time is given by

$$\tau = \tau_0 \exp(\Delta H/RT) \quad (4)$$

where τ_0 is the pre-exponential factor, ΔH is the activation enthalpy, and R is the perfect gas constant.

Then, the temperature shift is given by the following equation:

$$T_{\tan \delta}^{\text{max}} - T_{G''}^{\text{max}} = (RT_{\tan \delta}^{\text{max}} T_{G''}^{\text{max}} / \Delta H) \ln(\sqrt{G_g / G_r}) \quad (5)$$

Taking into account the ΔH value of the α relaxation mode (≈ 210 kJ mol $^{-1}$), we obtain a lag that explains the recorded data. Indeed, the ratio G_g / G_r is higher in the case of bulk adhesive (Fig. 6) and it is quite constant whatever the assembly thickness. As a consequence, even if $T_{G''}^{\text{max}}$ is lower for bulk adhesive, values of $T_{\tan \delta}^{\text{max}}$ are comparably independent from configurations and morphologies.

The anelastic manifestation of glass transition can be defined by the temperature of the maximum loss modulus, $T_{G''}^{\text{max}}$ [45]. In the study of bulk adhesive, $T_{G''}^{\text{max}}$ perfectly matches with the calorimetric glass transition temperature measured by differential scanning calorimetry [46]. Moreover, the difference in the temperature of inflection point on G' curves for both configurations corresponds to $T_{G''}^{\text{max}}$ (for example, about 8 °C for a 600 μm assembly).

Using this definition, the epoxy network exhibits a higher temperature of mechanical manifestation of the glass transition, T_g , in an adhesively bonded joint compared to bulk configuration. This result is in agreement with the slight increase of the β peak maximum temperature in the 260 μm and 600 μm assembly configuration. Note that the temperature of the β peak of 100 μm assemblies cannot be discussed. The presence of aluminum substrates decreases the mobility in the network. In the vicinity of metallic substrates, the epoxy network is modified [25,47,48] due to specific interactions between adhesive components and aluminum. They lead to an increase of the crosslinks density. This hypothesis is confirmed by the larger distribution of the α relaxation in high temperature region for the 100 μm assembly: the fraction of polymeric sequences influenced by aluminum substrates increases.

4. Conclusion

A new configuration for dynamic mechanical analysis, in the torsional mode, has been developed and tested in order to study the mechanical behavior of an epoxy adhesive in a bonded assembly configuration i.e. in functional conditions. The anelastic behavior of these bonded joints, mainly governed by the viscoelasticity of adhesive, has been compared with the one of bulk adhesive. The mechanical response of the adhesive in an assembly configuration is different from the one of bulk adhesive. Indeed, in such geometry, elastic aluminum substrates transmit a higher torsional solicitation to the sandwich configuration. The influence of adhesive thickness on the equivalent storage modulus is

explained by the sandwich geometry and the adhesive volume fraction.

For the α relaxation of assemblies, the equivalent loss modulus is 40 times higher than for bulk adhesive. The shear strain in the adhesive layer is considerably increased, since mechanical properties of the rubbery adhesive and adherent become very different. The analysis of the temperature dependence of the loss modulus provides interesting information on the polymeric network of the adhesive. Adhesive in bonded joint presents a difference in molecular mobility compared to the same adhesive tested as a bulk material. The influence of aluminum substrates is evidenced: the epoxy network should be modified due to the presence of aluminum, during the curing reaction.

The main advantage of the sandwich geometry is to offer a configuration that subjects the adhesive/adherent interface to a shear strain, in functional conditions. Then, the dissipation of anelastic energy may be analyzed in great details.

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