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TITLE:

Evaluation of the Curing of Adhesive Systems by Rheological and Thermal Testing

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SUMMARY:

An experimental methodology based on thermal and rheological measurements is proposed to characterize the curing process of adhesives with to obtain useful information for industrial adhesive selection.

ABSTRACT:

The analysis of thermal processes associated to the curing of adhesives and the study of mechanical behavior once cured, provide key information to choose the best option for any specific application. The proposed methodology for the curing characterization, based on thermal analysis and rheology, is described through the comparison of three commercial adhesives. The experimental techniques used here are Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Rheology. TGA provides information about the thermal stability and filler content, DSC allows the evaluation of some thermal events associated to the cure reaction and to thermal changes of the cured material when subjected to temperature changes. Rheology complements the information of the thermal transformations from a mechanical point of view. Thus, the curing reaction can be tracked through the elastic modulus (mainly the storage modulus), the phase angle and the gap. In addition, it is also shown that although DSC is of no use to study the curing of moisture curable adhesives, it is a very convenient method to evaluate the low temperature glass transition of amorphous systems.

INTRODUCTION:

Nowadays there is an increasing demand of adhesives. Today's industry demands that adhesives have increasingly varied properties, adapted to the growing diversity of possible new applications. It makes the selection of the most suitable option for each specific case a difficult task. Therefore, creating a standard methodology to characterize the adhesives according to their properties would facilitate the selection process. The analysis of the adhesive during the curing process and the final properties of the cured system are crucial to decide whether an adhesive is valid or not for a certain application.

Two of the most commonly used experimental techniques to study the behavior of adhesives are Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). Rheological measurements and thermogravimetric tests are also widely used. Through them, the glass transition temperature (Tg) and the residual heat of curing, which are related to the degree of cure[1,2], can be determined.

TGA provides information about the thermal stability of the adhesives[3,4], which is very useful to establish further process conditions, on the other hand rheological measurements allows the determination of the gel time of the adhesive, analysis of the curing shrinkage, and the definition of the viscoelastic properties of a cured sample[5-7], while the DSC technique allows measurement of the residual heat of curing, and discernment between one or more thermal processes that can take place simultaneously during the curing[8,9]. Therefore, the combination of DSC, TGA and rheological methodologies provide detailed and reliable information to develop a complete characterization of adhesives.

There is a number of studies of adhesives where DSC and TGA are applied together[10–12]. There are also some studies that complement the DSC with rheological measurements[13–15]. However, there is not a standardized protocol to address the comparison of adhesives in a systematic way. That comparison would all to better choose the right adhesives in different contexts. In this work, an experimental methodology is proposed for doing a characterization of the curing process through the combined use of the thermal analysis and rheology. Applying these techniques as an ensemble allows to gather information about the adhesive behavior during and after the curing process, also the thermal stability and the Tg of the material[16].

The proposed methodology involving the three techniques, DSC, TGA and rheology is described in this work using three commercial adhesives as an example. One of the adhesives, hereinafter referred to as S2c, is a two-component adhesive: component A contains tetrahydrofurfuryl methacrylate and component B contains benzoyl peroxide. The component B acts as an initiator of the curing reaction by causing the tetrahydrofurfuryl methacrylate rings to open. Through a free radical polymerization mechanism, the C=C bond of the monomer reacts with the growing radical to form a chain with tetrahydrofurfuryl side groups[17]. The other adhesives, T1c and T2c, are the one- and two-component versions from the same commercial house of a modified silane polymer adhesive. The curing process begins by the hydrolysis of the silane group[18], which can be initiated by ambient humidity (as in the case of T1c) or by the addition of a second component (as in the case of T2c).

Concerning the application areas of these three different systems: the adhesive S2c was designed to substitute, in some cases, welding, riveting, clinching and other mechanical fastening techniques and it is suitable for high strength fastening of concealed joints on different types of substrates including top coats, plastics, glass, etc. The T1c and T2c adhesives are used for elastic bonding of metals and plastics: in caravan manufacturing, in the railroad vehicle industry or in shipbuilding.

PROTOCOL:

1. Checking the manufacturer curing conditions

1.1. Cure the adhesive sample following the manufacturer recommendations, and then evaluate it by a TGA and a DSC test. Record the specific curing conditions.

1.2. TGA test of cured sample

1.2.1. Perform thermogravimetric tests in a TGA or in a simultaneous DSC+TGA equipment (SDT).

1.2.2. Carry out a thermogravimetric test of the cured sample to determine the inorganic filler content and the temperature at which the material starts to degrade. Do not exceed that temperature in further tests.

1.2.3. Open the air stopcock. Switch on the SDT (or TGA) apparatus. Open the SDT control software.

1.2.4. Open the furnace of the SDT and place two empty capsules: one will be the reference capsule and the other will contain the sample.

1.2.5. Close the furnace and press the bottom **Tare**.

1.2.6. Open the furnace and place a sample size of 10-20 mg in the sample capsule.

1.2.7. Fill the information about the sample in the tab **Summary**.

1.2.8. Open the tab **Procedure** and click **Editor**. Drag the segment type **Ramp** to the **Editor** screen. Establish the ramp as 10 or 20 °C/min to 900 °C. Click **OK**.

1.2.9. Open the tab **Notes**. Choose **Air** as the purge gas and establish a flow rate of 100 mL/min. Click **Apply**.

NOTE: TGA test has two objectives: 1) to determine the inorganic filler content and 2) to determine the temperature at which the material starts to degrade. For the first objective the

test has to be performed in an air atmosphere. For the second one, an air atmosphere represents the most common situation in normal use.

1.2.10. Close the furnace.

1.2.11. Start the experiment.

1.3. DSC test of cured sample

1.3.1. Carry out the DSC tests on a standard DSC or on a modulated temperature DSC (MTDSC) instrument working in standard mode, use aluminum crucibles. Carry out a DSC test of the cured sample to study the following parameters: the Tg of the material, a possible residual curing and the Tg_{∞} of the sample.

1.3.2. Open the nitrogen stopcock. Switch on the DSC apparatus. Open the control software of the DSC instrument.

1.3.3. Click **Control | Event | On**. Then click the tab **Tool | Instrument Preferences**, choose **DSC** and establish a standby temperature of 30 °C.

1.3.4. Click **Apply**. Click the tab **Control** | **Go to Standby Temperature** and wait for at least 45 min before starting any experiment.

1.3.5. Open the tab **Summary**. Click **Mode** and choose **Standard**.

1.3.6. Open the tab **Procedure**, click **Test** and choose **Custom**. Click **Editor**.

1.3.7. Drag an **Equilibrate** segment indicating the temperature at which to start the experiment (that temperature should be relatively low, for example -80 or -60 °C).

1.3.8. Drag the segment type **Ramp** to the Editor screen. Introduce a heating rate of 10 or 20 °C/min and the final temperature into the command editor window. The final temperature is tentatively chosen to allow for a complete cure and must be lower than the degradation temperature obtained from the previous TGA test. Click **Apply**.

NOTE: These recommended heating rates are proposed as a starting point that will probably work fine in most cases. However, these heating rates can be modified to improve sensitivity or resolution.

1.3.9. Drag the segment type **Ramp** to the Editor screen. Similarly, to the previous step, introduce a 10 or 20 °C/min cooling rate to a temperature tentatively below the glass transition.

1.3.10. Drag the segment type **Ramp** to the Editor screen. Introduce a 10 or 20 °C/min heating rate to a temperature slightly below the degradation temperature.

1.3.11. Open the tab **Notes**. Choose **Nitrogen** as the flow gas and establish a flow rate of 50 mL/min. Click **Apply**.

1.3.12. Fill the information about the sample in the tab **Summary**.

1.3.13. Click **Control | Lid | Open**. Place a reference pan and a pan with a sample of 10-20 mg weight inside the DSC cell.

1.3.14. Launch the experiment by clicking **Start**.

2. DSC analysis of a fresh sample

2.1. Prepare a fresh sample of the adhesive using the ratios and procedures recommended by manufacturer and immediately subject it to the following tests.

2.2. Ramp curing test

2.2.1. Perform a heating-cooling-heating test to obtain the curing enthalpy of the adhesive, the final glass transition on heating and to establish the range of temperatures where the curing process starts.

2.2.2. Open the tab **Summary**. Click **Mode** and choose **Standard**.

2.2.3. Click the tab **Tool | Instrument Preferences**, choose **DSC** and establish a standby temperature of 10 °C. Click **Apply**. Click the tab **Control | Go to Standby Temperature**,

2.2.4. Open the tab **Procedure**, click **Test** and choose **Custom**. Click **Editor**. Drag the segment type **Equilibrate** at -80 °C to the Editor screen. Drag the segment **Ramp** and establish 10 or 20 °C/min to (a temperature slightly below the degradation temperature obtained from the TGA test).

2.2.5. Insert the segment **Equilibrate** at -80 °C. Then drag the segment **Ramp**, establish 10 or 20 °C/min to (the same temperature as before). Click **Apply**.

2.2.6. Fill the information about the sample in the tab **Summary**.

2.2.7. Click **Control | Lid | Open**. Place a reference pan and a pan with the freshly prepared sample of 10-20 mg weight inside the furnace.

2.2.8. Start the experiment.

2.3. Isothermal curing test

2.3.1. Taking into account the DSC plot of the curing in ramp, choose several temperatures at the beginning of the exotherm to execute the isothermal experiments.

NOTE: The isothermal experiments will allow to evaluate the maximum degree of curing that can be obtained at each temperature.

2.3.2. Open the **Summary** tab. Click **Mode** and choose **Standard**.

2.3.3. Open the **Procedure** tab, click **Test** and choose **Custom**. Click **Editor**. Drag the segment type **Ramp** to the Editor screen. Introduce a 20 °C/min to the chosen isothermal temperature.

2.3.4. Introduce an **Isothermal** segment for time enough to complete the cure at this temperature. It is possible, for example, to establish 300 min, but the test can be stopped when the heat flow curve is flat.

2.3.5. Introduce a command segment **Equilibrate at 0 °C**. Add a **Ramp** segment, establish a heating rate between 2 and 20 °C/min (in the example 2.5 °C/min was chosen) to the maximum temperature, which was chosen from the TGA test in order not to compromise the thermal stability of the adhesive.

2.3.6. Drag the **Mark end of cycle** segment to the editor window. Insert another **Equilibrate** segment, this time with a temperature of -80 °C. Add another **Ramp** segment with a heating rate between 2 and 20 °C/min (in the example 2.5 °C/min was chosen) to the same temperature indicated before. Click **Apply**.

NOTE: A set of heating rates are suggested. Probably, most of them work correctly and depending of the nature of the curing process, mainly its kinetics, and the sensitivity and resolution required, some of these heating rates could be better. If the evaluation is done with comparative purposes the same conditions should be used for each studied adhesive system. In order to minimize the time elapsed from mixing the components to the beginning of the isothermal experiments, the temperature of the DSC cell should be adjusted to a temperature lower than the isothermal temperature before mixing both components.

2.3.7. Click the tab **Tool | Instrument Preferences**, choose **DSC** and establish a temperature lower than the isotherm temperature of the experiment. Click **Apply**. Click the tab **Control | Go to Standby Temperature**.

2.3.8. Fill the information about the sample in the tab **Summary**.

2.3.9. Click **Control | Lid | Open**. Place a reference pan and a pan with the sample of 10-20 mg weight inside the furnace.

2.3.10. Start the experiment.

3. Rheological analysis

3.1. Perform the rheological tests on a rheometer, using a 25 mm parallel plate geometry.

3.2. Logarithmic strain sweep test

3.2.1. Do an exploratory logarithmic strain sweep test to set up the strain amplitude to be used in the curing study of the adhesive in the rheometer. Perform the test with a fresh sample (before curing).

3.2.2. Open the air stopcock. Switch on the rheometer apparatus. Open the rheometer control software.

3.2.3. Place the specific geometry on the rheometer.

3.2.4. Click **Zero Gap**.

3.2.5. Click the tab **Geometry**. Choose the specific geometry.

3.2.6. Open the tab **Experiment**.

3.2.7. Fill the information about the sample in the tab **Sample**.

3.2.8. Click the tab **Procedure**. Choose **Oscillation Amplitude**. This experiment can be performed at room temperature (the actual temperature is annotated), and with a frequency of 1 Hz and a logarithmic sweep from 10^{-3} to 100% of strain.

NOTE: To prepare a sample of the two-component system, weigh components at room temperature, about 20 °C to the exact proportions recommended by the manufacturer. Then mix both components.

3.2.9. Place the sample on the bottom plate with the upper plate separated about 40 mm from the lower plate. Lower the upper plate until a gap of about 2 mm is observed between both plates. Trim off the excess adhesive.

3.2.10. Start the experiment.

3.3. Isothermal multifrequency curing test

NOTE: This test shows if there is or not gelation and, in case of gelation, it provides the gelation time. In addition, the contraction and the evolution of G' and G'' can be observed along the curing process.

3.3.1. Follow the subsequent procedure to monitor the curing of the adhesive.

3.3.2. Click the tab **Procedure**. Choose **Conditioning Options**. Establish the Mode Compression, Axial Force 0 N and Sensitivity of 0.1 N. Click **Advance** and establish a Gap change limit of 2000 µm in the up and down directions.

3.3.3. Insert a new step of an oscillatory time sweep. This experiment can be performed at room temperature (the actual temperature is annotated), the duration of the test as a function of the estimated curing time based on the Data Sheet of the adhesive, and the percentage of Strain which is chosen from the result of the previous logarithmic strain sweep test. Choose **Discrete** and then set the frequencies 1, 3 and 10 Hz for all samples.

3.3.4. Remove the previous sample, do the **Zero Gap** and place a new sample. Then proceed as in step 3.2.9.

3.3.5. Start the experiment.

NOTE: Do not remove the sample at the end of experiment. It will be used in the next experiment.

3.4. Torque sweep test

3.4.1. Once the curing test ends, proceed to the torque sweep test to find out the linear viscoelastic range for the previously cured material.

NOTE: The extension of LVR can be determined either by applying strain sweep test, mostly in controlled-strain rheometers, or torque or stress sweep test, mostly in controlled-stress rheometer. However, in some rheometers both methods can be used.

3.4.2. Click the tab **Procedure**. Choose the Oscillation Amplitude. This experiment can be performed at room temperature (the actual temperature is annotated), with a frequency of 1 Hz and a logarithmic sweep from 10 to 10000 µNm of torque.

NOTE: Use the same sample that was left in the instrument from the previous experiment.

3.4.3. Start the experiment.

NOTE: Do not remove the sample at the end of experiment. It will be used in the next experiment.

3.5. Temperature scan test

3.5.1. Perform a temperature scan test to verify the cure is complete.

3.5.2. Click the tab **Procedure**. Choose **Temperature Ramp**. Initiate the experiment from room temperature, establish a ramp rate of 1 °C/min, which ensure a uniform distribution of temperature into the sample without consuming too excessive time, a frequency of 1 Hz and a

given Torque amplitude, which is chosen from the previous Torque sweep test.

NOTE: Use the same sample that was left in the instrument from the previous experiment.

3.5.3. Close the furnace of the rheometer. Open the air stopcock of the furnace.

3.5.4. Start the experiment.

NOTE: If the next experiment is needed, do not remove the sample at the end of experiment. In that case it would be used for the next experiment.

REPRESENTATIVE RESULTS:

In order to show the application of the proposed method three adhesive systems are used (**Table of Materials**):

- S2c, a two-component system.
- T1c, a one-component silane-modified-polymer, whose cure reaction is triggered by moisture.
- T2c, a two-component system. It is a silane-modified-polymer too, but the second component is aimed to make the curing rate a little more independent from the moisture content of air.

The thermal stability and the amount of filler of the cured adhesives are analyzed by TGA. **Figure 1** shows the thermogravimetric plots obtained in air from the three adhesives. In the case of S2c a slight mass loss is observed from about 50 °C, which is probably related to moisture volatilization. The onset of the main degradation process appears at 196 °C. For T1c and T2c, the degradation onsets appear at slightly higher temperatures: 236 °C and 210 °C, respectively. These degradation temperatures should be not reached in further DSC or rheology experiments. The residue at 600 °C probably corresponds to inorganic fillers. It amounts 37.5% for T1c, 36.9% for T2c, and 24.6% for S2c. In the case of S2c an important mass loss is observed in the 600-800 °C range which suggests that $CaCO_3$ is the main filler component since it is a typical filler which decomposes in that range of temperature in air. A mass loss of 10.32% was observed what corresponds to a 23.5% of $CaCO_3$ in the cured sample.

[Place **Figure 1** here]

Following the procedure, the next step consists of performing DSC tests of cured samples. **Figure 2** shows the heat flow curves obtained. The S2c was previously cured at room temperature (approx. 20 °C) during 95 min. The T1c (moisture curing system) and T2c were previously cured at room temperature for 48 h.

[Place **Figure 2** here]

Figure 2A shows no evidence of residual cure. A small deviation from the baseline is observed at about 60 °C during the first heating ramp. It could be considered a manifestation of a glass

transition, but it is practically negligible, and it would be better to wait for the rheological test to confirm. A glass transition temperature at 60 °C was specified by the manufacturer but it is not observed in this DSC plot. At -67 °C, there is a tiny drop in the heat flow signal that suggest a possible glass transition of a component of the adhesive. **Figure 2B** shows a clear glass transition at -66 °C. There is also an endothermic peak between 65 °C and 85 °C on heating and the corresponding exotherm on cooling at 53 °C. The shape and size of these peaks suggest possible melting and crystallization processes of a polymeric compound and will be discussed in the scope of additional results. The only important event in **Figure 2C** is a glass transition at -64 °C.

The next results are also related to DSC tests. **Figure 3** shows the curing plot of a S2c sample at 20 °C/min in a heating ramp. That ramp will be followed by a cooling and heating ramps not displayed in this Figure. The curing enthalpy of the adhesive, 171.5 J/g, is obtained by integration of the peak. The shape of the exotherm suggests an autocatalytic curing reaction[19–21], which would correspond to the methyl methacrylate free radical polymerization of the S2c adhesive[22].

[Place **Figure 3** here]

In the case of T1c and T2c no curing exotherm was observed by DSC, as expected for moisture curing adhesives. Rheology studies of the curing will be of highest interest for these systems.

In order to evaluate the degree of curing that can be achieved at different temperatures isothermal DSC experiments were performed only for S2c, since the moisture curable systems cannot be tracked by DSC. For T1c and T2c samples, rheological measurements such as G' or the gap can be used to track the advancement of the curing reaction at any temperature at which the experiment is performed. **Table 1** shows the curing enthalpy values obtained at three temperatures. The degree of curing is calculated by comparing the curing enthalpy obtained at each temperature to that obtained in a heating ramp. The one used to calculate the values displayed on **Table 1** was obtained at 20 °C/min.

[Place **Table 1** here]

Figure 4 shows how the residual cure is much smaller in the case of the sample cured at the higher temperature. That is so because the degree of curing achieved at 20 °C is higher than that obtained at 10 °C, as it can be observed in **Table 1**.

[Place **Figure 4** here]

Important features of a curing process that were not observed by DSC are the gelation, the shrinkage produced by the curing and the change of the moduli along the cure process. The latter is especially important in the case of moisture triggered curing, since in these systems the conversion of the curing process cannot be tracked by DSC. These missing features can be evaluated by rheology.

The first rheological test performed with each sample consists of a strain sweep that allows to

see the linear viscoelastic range from which a strain value will be chosen for the next experiment, an isothermal multifrequency test with the following frequencies: 1, 3 and 10 Hz. (6.28, 18.85 and 62.83 rad/s). **Figure 5** corresponds to the cure of a fresh S2c sample that is placed between the parallel plates of the rheometer. The gelation time of the material can be observed as the point where the phase angle, δ, becomes frequency independent, according to the Winter and Chambon criterion[23,24]. The gelation time is the time from mixing the two components to the instant when the phase angle curves obtained at different frequencies cross. After the gelation, the Tg continues to increase until a value somewhat above the cure temperature. The high filler content of this sample, about 23%, is the reason why a higher value of G' than of G" is obtained throughout the test. **Figure 5** also gives information about the shrinkage of the adhesive along the curing, that is about 6.5% in 10 minutes. A value of 20.5 MPa the modulus is obtained after about 11 minutes from mixing the components. After that instant, the moduli and the gap change only very little.

[Place **Figure 5** here]

Performing the isothermal multifrequency test at different temperatures, it would be possible to evaluate how the gel time varies with the curing temperature. In the case of the T1c and T2c systems, **Figure 6** and **Figure 7**, there is no sign of gelation of the adhesives. A comparison of the slopes of the moduli of both adhesives reveals that T2c cures faster than T1c, which is normal since T2c has an additional compound to accelerate the curing reaction. An important increase of the storage modulus is observed in both cases, reaching an almost constant value after 24 h. A value of 0.94 MPa is observed for T1c and 1.2 MPa for T2c, which are much smaller than that observed for S2c.

Again, a high filler explains that G' is consistently higher than G" along the test. The behavior of tan δ in both cases, seems to be related to the shear that those thixotropic materials undergo between the plates of the rheometer and also because of the curing process.

On the other hand, the contraction observed for both T1c and T2c systems in 24 h, 0.65% and 0.89%, respectively, are very little in comparison to that observed for S2c in 15 minutes, 5.7%.

[Place **Figure 6** here]

[Place **Figure 7** here]

The temperature scan tests of the cured samples are needed to evaluate the linear viscoelastic range (LVR) of the cured samples. The LVR is usually determined either by applying strain sweep test, in controlled-strain rheometers, or stress or torque sweep test, in controlled-stress rheometer. However, in some rheometers both methods can be used. On this occasion torque sweeps were done.

Figure 8 shows the results of a temperature scan of the S2c sample that was cured for one hour in the rheometer. The glass transition can be easily identified as a drop in G', and as broad peaks

in G'' and in the phase angle, δ. The value of Tg, measured as the δ peak, is 60.2 °C.

[Place **Figure 8** here]

Temperature scans of fully cured T1c and T2c adhesives are reflected in **Figure 9**. The scan of T2c does not shows any relaxation in all temperature range. That can be of interest in case a consistent behavior is sought in that range of temperature. On the other hand, the moduli of the scan of T1c show a slow decrease until up to 60 °C, and then a more intense decline between 60 °C and 80 °C to then persist constant until the end of test.

[Place **Figure 9** here]

Figure 1: TGA curves of the three adhesives. The curves were obtained from cured samples using air as the purge gas.

Figure 2: DSC heat flow curves obtained from cured samples of the three adhesives: S2c **(A),** T1c **(B),** T2c **(C)**

Figure 3: DSC heat flow curves obtained from a fresh sample of the S2c adhesive system

Table 1. Curing enthalpy and the degree of curing values resulting from the isothermal cure of S2c samples at different temperatures.

Figure 4. Specific heat flow plots obtained in the first and second heating scans from S2c samples isothermally cured at the indicated temperatures

Figure 5: Plots resulting from the isothermal curing of a S2c sample in the rheometer at room temperature.

Figure 6: Plots resulting from the isothermal curing of a T1c sample in the rheometer at room temperature.

Figure 7: Plots resulting from the isothermal curing of a T2c sample in the rheometer at room temperature.

Figure 8: Temperature scan test performed in the rheometer with a cured S2c sample.

Figure 9: Temperature scan tests of the cured adhesives T1c and T2c. Values of G', G'' and δ were obtained from a 1°C /min temperature scan.

DISCUSSION:

A preliminary TGA test of each adhesive is always a fundamental step as it gives information about the temperature range at which the material is stable. That information is crucial to correctly setting up further experiments. In addition, TGA may also inform about the filler

content, which can be very insightful to understand that storage and loss modulus may not to cross along the cure.

On the other hand, DSC allows to study the cure of most thermosetting systems but not of those whose cure reaction is moisture triggered. Rheology allows to track the cure of any system, moisture triggered or not and is the right technique to compare them. However, it must be taken into account that a typical limitation of rheometers is the minimum temperature at which a curing test can be performed. Fortunately, most adhesives are intended to be used at room temperature or higher.

Most flexible adhesives have a glass transition temperature at sub ambient temperatures. Some components of semi-rigid systems may have a low Tg too but it is frequent that common rheometers cannot reach that low temperature. Many commercial DSC can easily reach -80 °C and thus can be used to determine that low Tg.

An interesting feature of some rheometers is the possibility of applying an almost null axial force, which allows to track the gap changes due to the adhesive contraction along the cure. That feature was not common in the past but nowadays many rheometers incorporate that feature. Another interesting advantage of rheology respect to DSC is the possibility of identifying the gel point through the phase angle at different frequencies. That is useful to see it the adhesive is a thermoset or not and, if so, to measure the gel time, a critical factor that is directly related to the working time at a given temperature.

A critical step within the protocol is the use of appropriate ratios and procedures recommended by manufacturer with two component systems, as well as adjusting both DSC temperature and time expended to launch experiment for freshly prepared samples. In relation to the rheological test, it is important to keep the heating rate at low values to ensure a uniform distribution of temperature, also for DSC test the chosen heating rate should take into account aspects such as sensitivity and resolution.

The experimental results that can be obtained by the proposed methodology allow to better understand how time and temperature parameters involved in the preparation of any adhesive joint may affect the technological properties of the adhesives. For example, in the case of thermosets, it is important to complete the application of the different elements of a joint before gelation occurs, and it is also important to keep the elements in their place until about a 90% of the maximum modulus is reached. This methodology can help to choose between adhesives with different reactivity, modulus, or contraction in the curing.

From all the above, it can be deduced that the convenience of the elaboration of a methodology for the systematic study of the cure of adhesive systems through two techniques, thermal analysis and rheology, which complement each other efficiently to achieve a complete characterization of the cure for very different systems.

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DISCLOSURES:

The authors have nothing to disclose.

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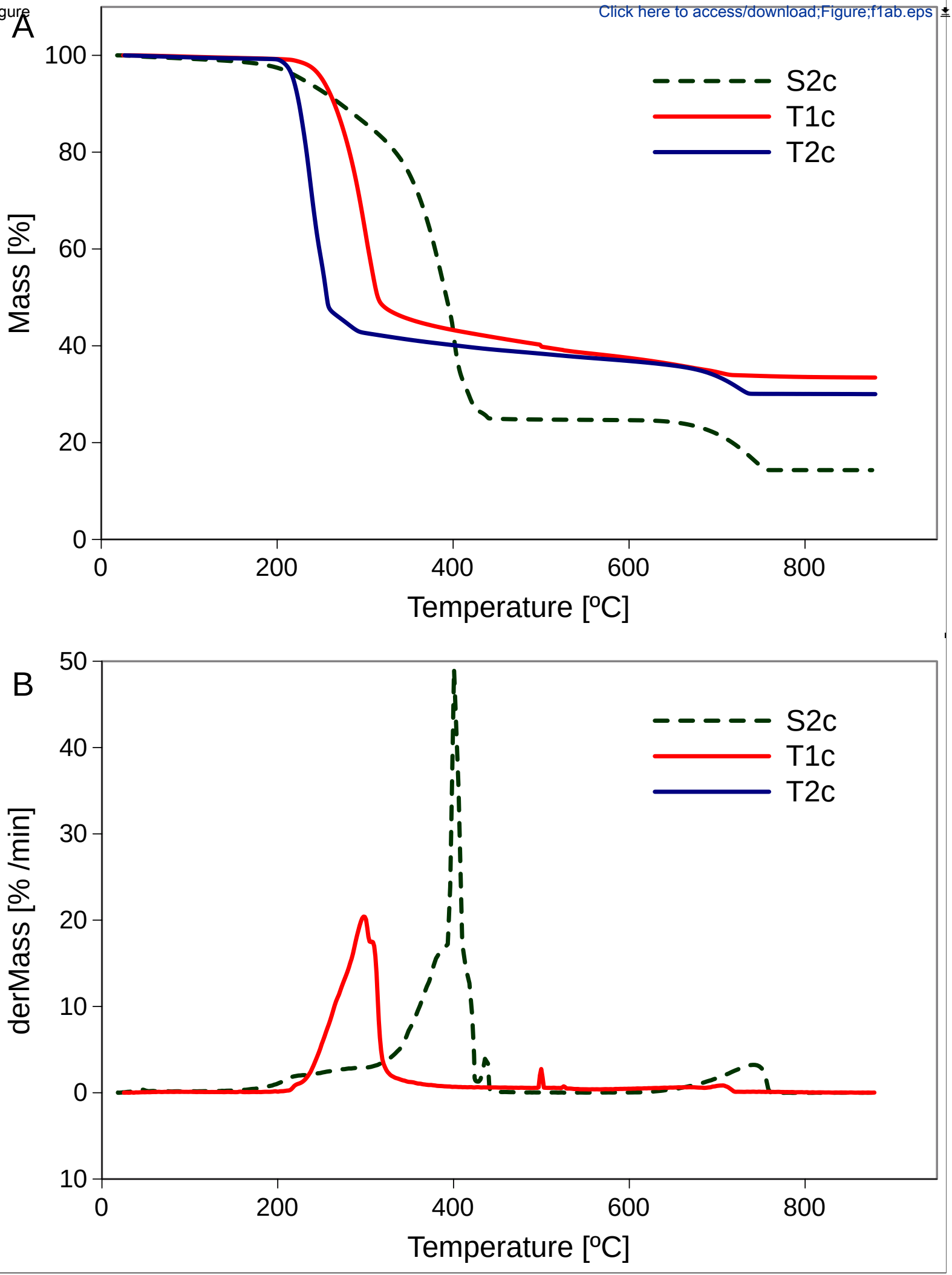
Figure



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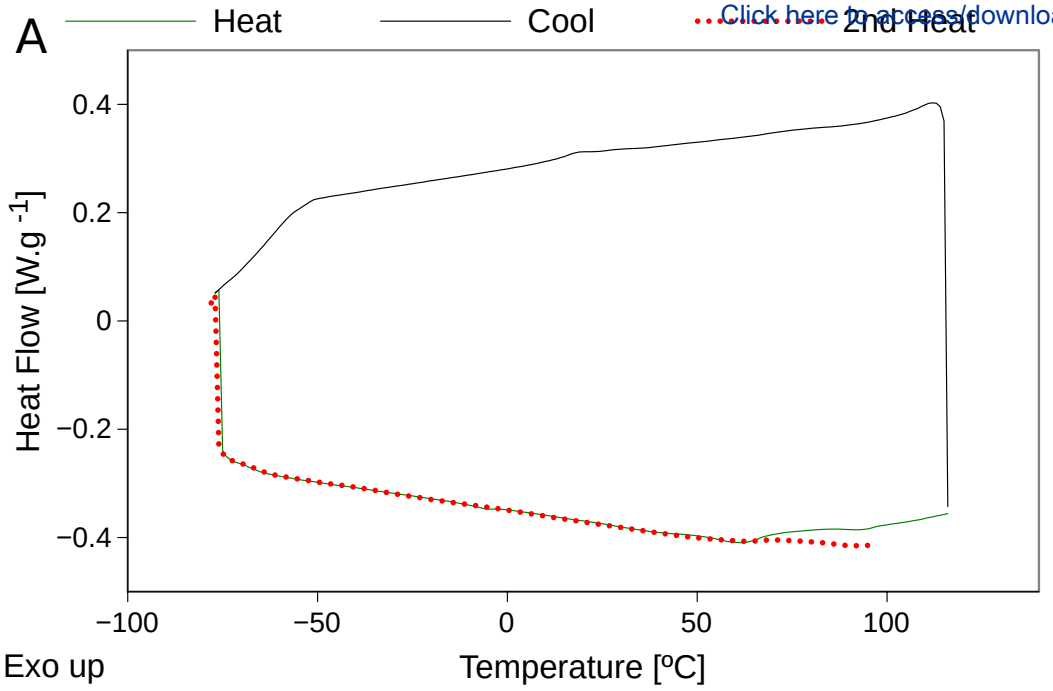

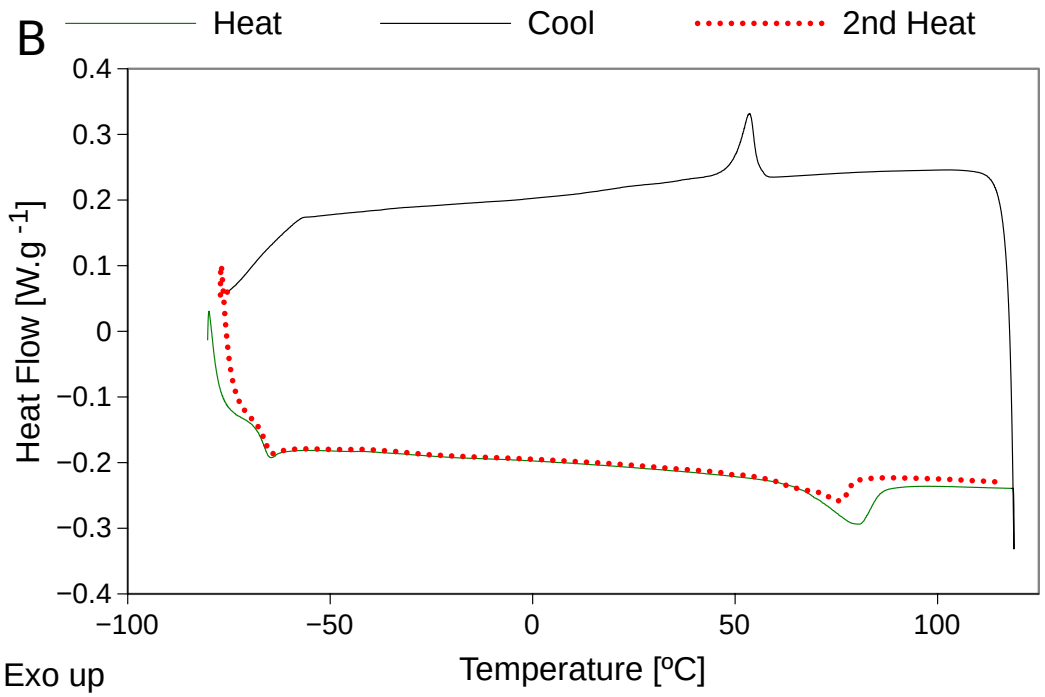

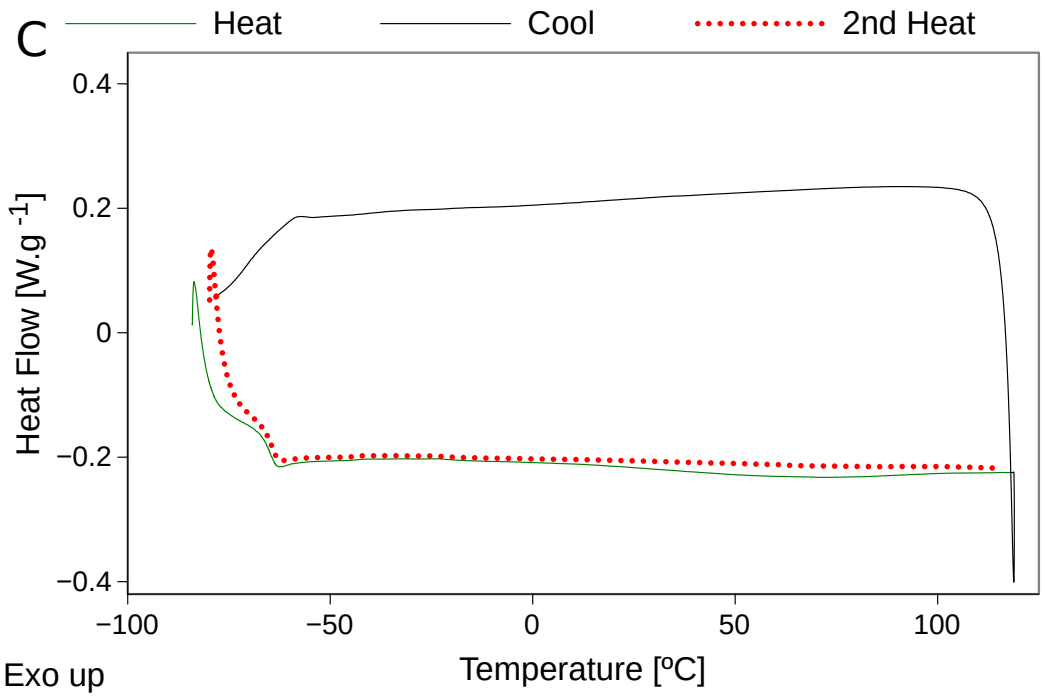

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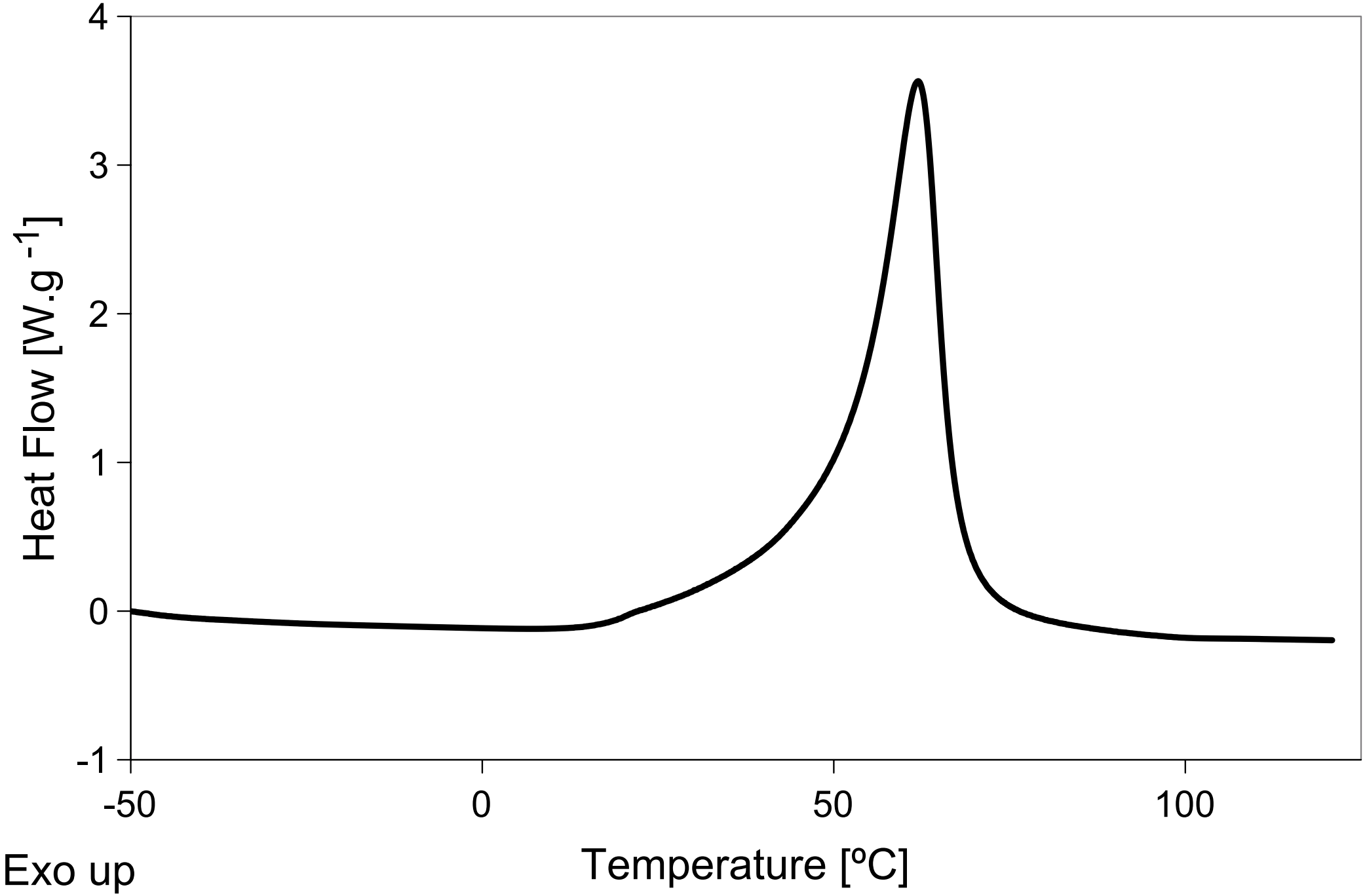

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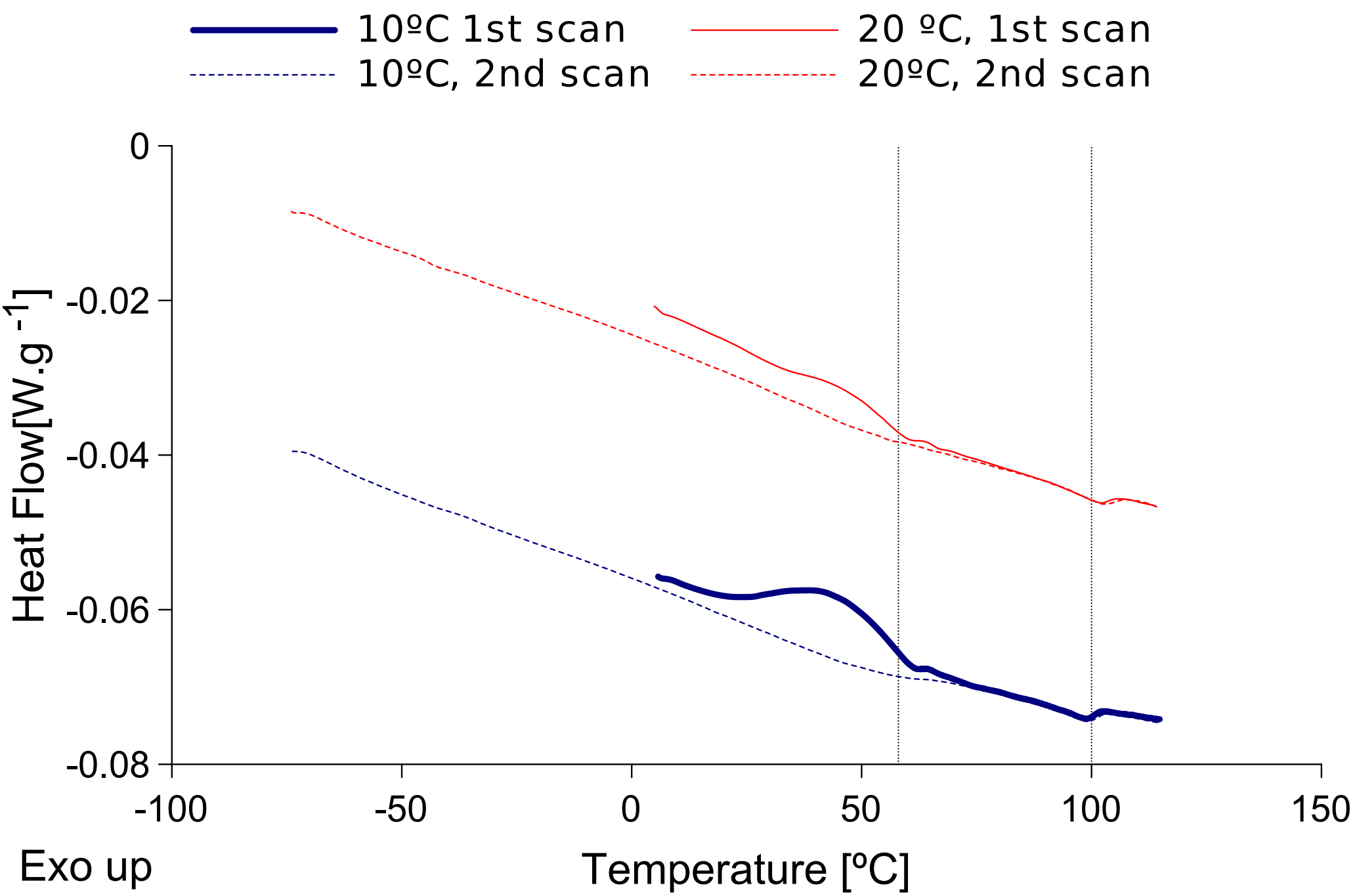

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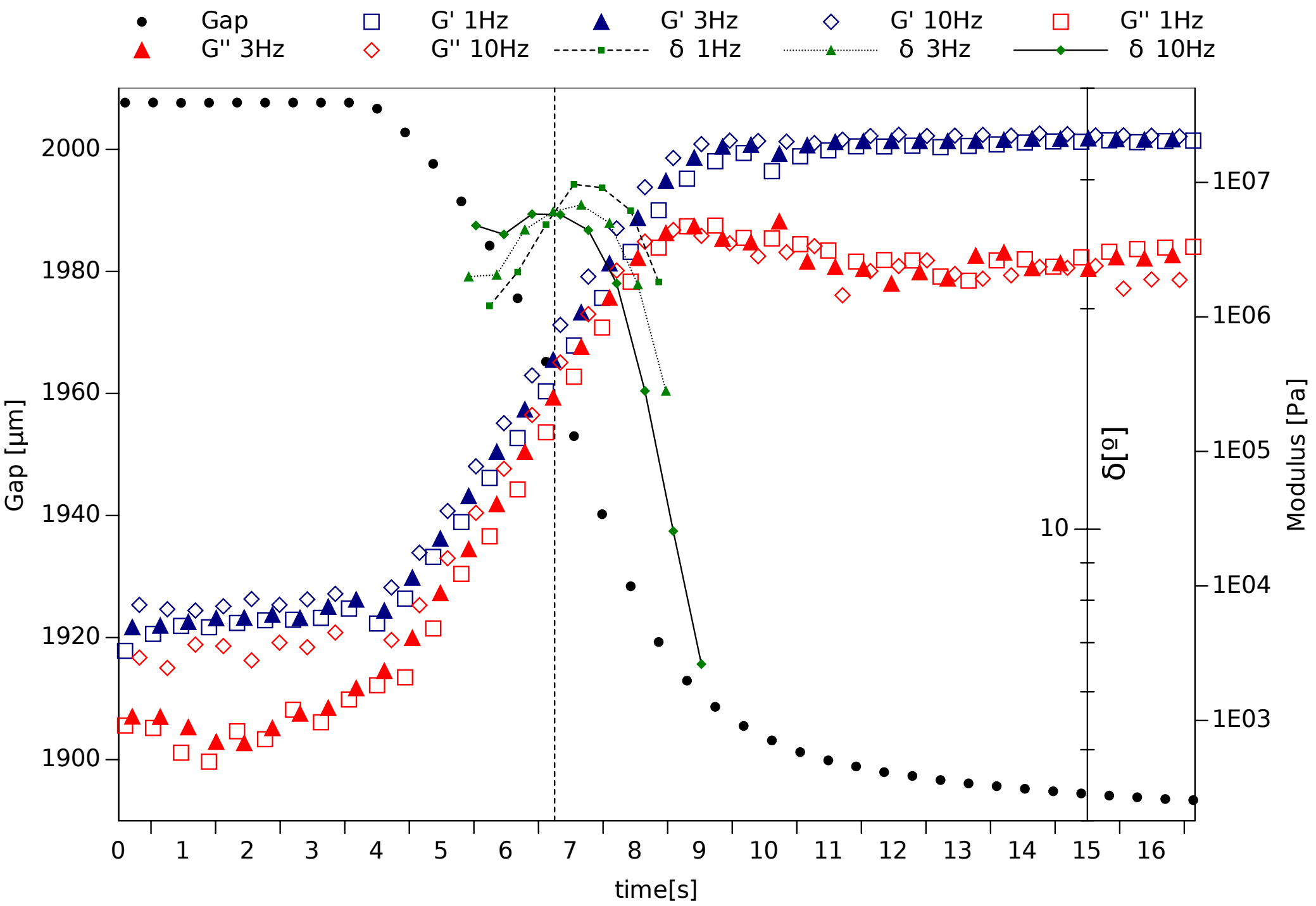

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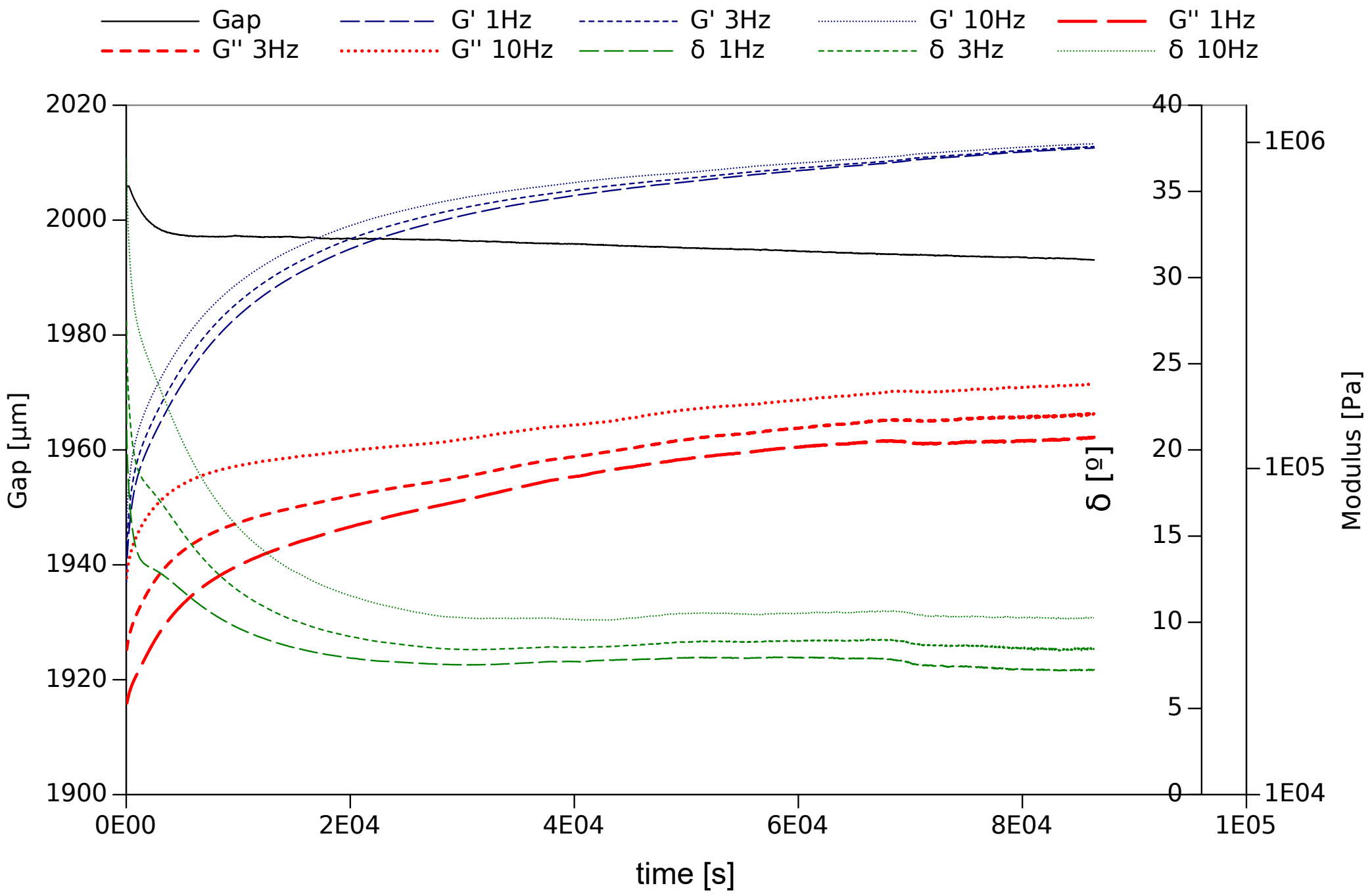

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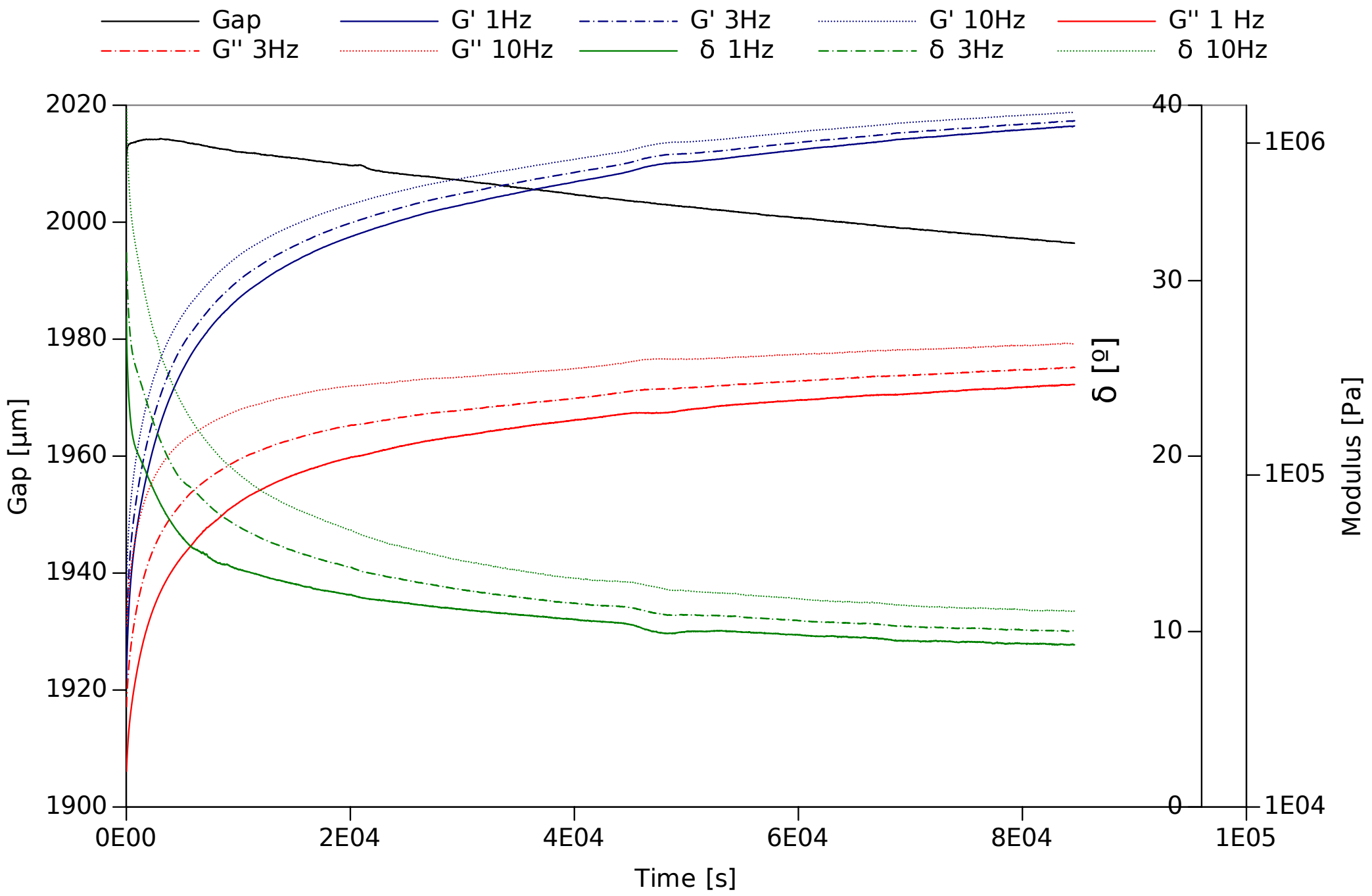

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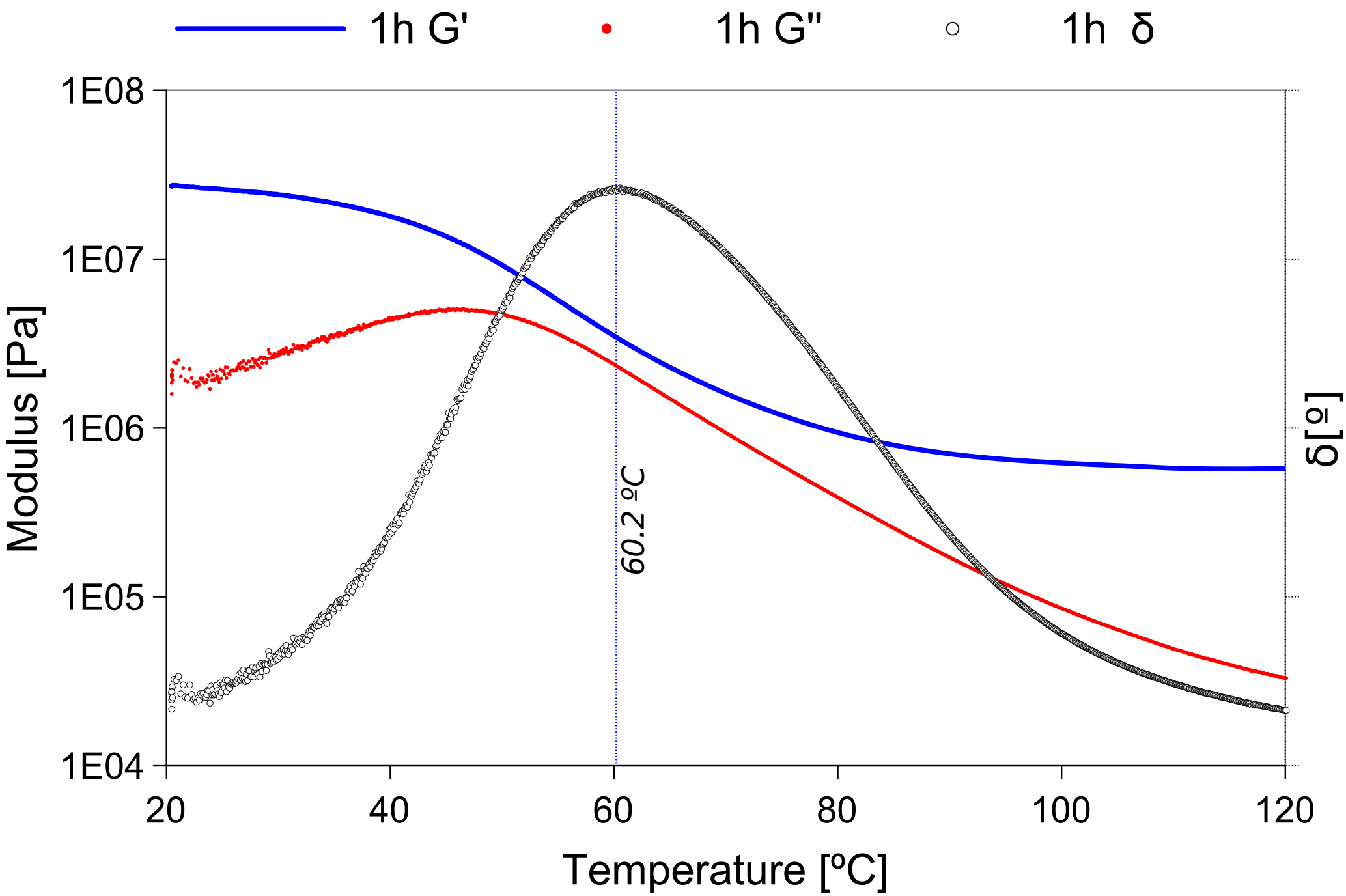

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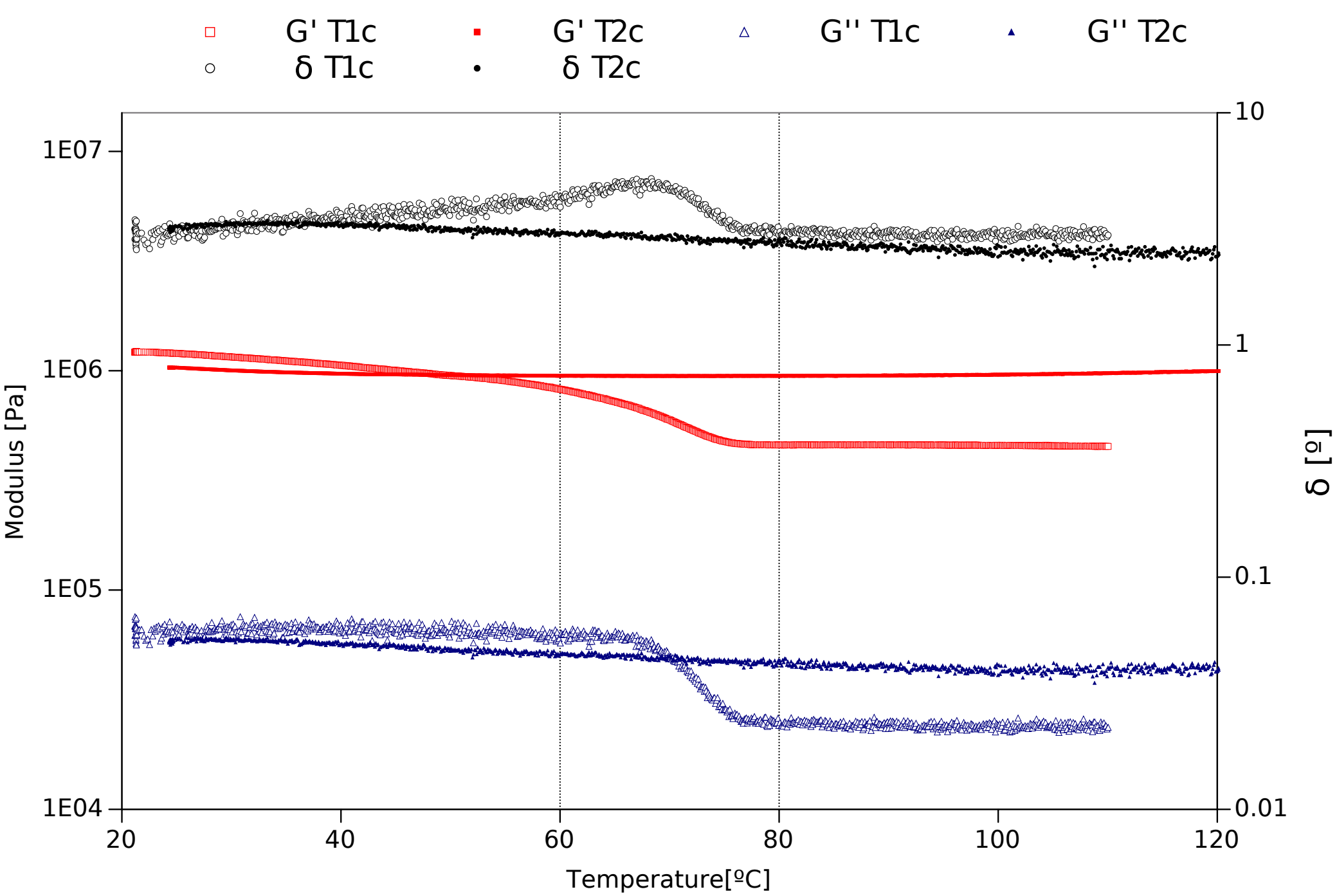


Table

Temperature	Curing enthal	Degree of curing (%)
10	162.1	94.5
15	166.0	96.8
20	169.5	98.8

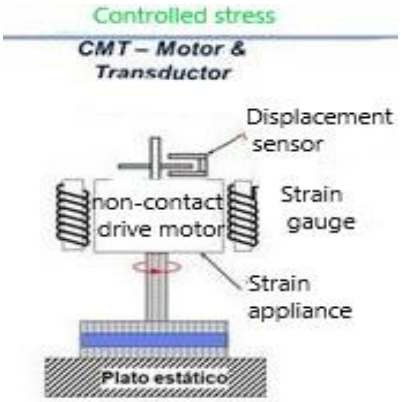
Table of Materials

Click here to access/download;Table of Materials;JoVE_Table_of_Materials.xlsx

Name of Material/Equipment	Company	Catalog Number
2960 SDT	TA Instruments	
Discovery HR-2	TA Instruments	
MDSC Q2000	TA Instruments	
Sikafast 5211NT	Sika	
Teroson MS 939 FR	Henkel	
Teroson MS 9399	Henkel	
TRIOS	TA Instruments	

Comments/Description

Simultaneous DSC/TGA device: Used to perform thermogravimetric tests.



Rheometer to perform rheological test.
Differential Scanning Calorimeter with optional temperature modulation. Used to peform DSC and MDSC tests.
S2c: a two component system manufactured by Sika. It is based on tetrahydrofurfuryl methacrylate and contains an ethoxylated aromatic amine.
The second component contains benzoyl peroxide as the initiator for the crosslinking reaction.
T1c: manufactured by Henkel, which is a one component sylil-modified-polymer, whose cure reaction is triggered by moisture.
T2c: a two component system manufactured by Henkel. It is a sylil-modified-polymer too but the second component is aimed to make the curing rate a little more independent from the moisture content of air.
Control Software for the rheometer. Version 4.4.0.41651

JoVE61468 "Evaluation of adhesive systems by rheological and thermal testing"

You will find Editorial comments and Peer-Review comments listed below. Please read this entire email before making edits to your manuscript.
NOTE: Please include a line-by-line response to each of the editorial and reviewer comments in the form of a letter along with the resubmission.

Editorial Comments:

• The manuscript will benefit from thorough language revision as there are a number of grammatical errors throughout. Please thoroughly review the manuscript and edit any errors. Examples:
1) "Open the air out"
2) "Open the air out of the Furnace"
3) "Insert a new step of Oscillation Time"

A language revision was done and some errors and mistakes were corrected.

• **Introduction:** Please expand your Introduction to include the following:

The advantages over alternative techniques with applicable references to previous studies; Description of the context of the technique in the wider body of literature; Information that can help readers to determine if the method is appropriate for their application.

The introduction section was rewritten and a better contextualization of the work was done.

• **Protocol Language:** Please ensure that ALL text in the protocol section is written in the imperative voice/tense as if you are telling someone how to do the technique (i.e. "Do this", "Measure that" etc.) Any text that cannot be written in the imperative tense may be added as a "Note", however, notes should be used sparingly and actions should be described in the imperative tense wherever possible.
1) Examples NOT in the imperative: Lines 96-103, 174-176, 244-251, etc.

The text in the protocol was revised and rewritten in the imperative voice.

• **Protocol Detail:** Please note that your protocol will be used to generate the script for the video, and must contain everything that you would like shown in the video. There should be enough detail in each step to supplement the actions seen in the video so that viewers can easily replicate the protocol.

The protocol was revised accordingly.

• **Discussion:** JoVE articles are focused on the methods and the protocol, thus the discussion should be similarly focused. Please ensure that the discussion covers the

following in detail and in paragraph form (3-6 paragraphs): 1) modifications and troubleshooting, 2) limitations of the technique, 3) significance with respect to existing methods, 4) future applications and 5) critical steps within the protocol.

The discussion was also modified.

• **Figures:** Please remove the embedded figures from the manuscript. Figure legends, however, should remain within the manuscript text, directly below the Representative Results text.

It was done.

• **Tables:** Please remove the embedded Table from the manuscript. All tables should be uploaded to the Editorial Manager site in the form of Excel files. A description of the table should be included with the Figure legends.

It was done.

• **Commercial Language:**JoVE is unable to publish manuscripts containing commercial sounding language, including trademark or registered trademark symbols (TM/R) and the mention of company brand names before an instrument or reagent. Examples of commercial sounding language in your manuscript are TA Instruments Rheometer HR-2, TRIOS, items on Lines 401-404
1) Please use MS Word's find function (Ctrl+F), to locate and replace all commercial sounding language in your manuscript with generic names that are not company-specific. All commercial products should be sufficiently referenced in the table of materials/reagents. You may use the generic term followed by "(see table of materials)" to draw the readers' attention to specific commercial names.

The manuscript was modified to avoid commercial sounding language. Specific commercial names are now included in the Table of Materials.

• **Table of Materials:**Please revise the table of the essential supplies, reagents, and equipment. The table should include the name, company, and catalog number of all relevant materials/software in separate columns in an xls/xlsx file. Please include items such as software, reagents, etc.

The table was revised and updated.

• If your figures and tables are original and not published previously or you have already obtained figure permissions, please ignore this comment. If you are re-using figures from a previous publication, you must obtain explicit permission to re-use the figure from the previous publisher (this can be in the form of a letter from an editor or a link to the editorial policies that allows you to re-publish the figure). Please upload the text of the re-print permission (may be copied and pasted from an email/website) as a Word document to the Editorial Manager site in the "Supplemental files (as requested by JoVE)" section. Please also cite the figure appropriately in the figure legend, i.e.

"This figure has been modified from [citation]."

Comments from Peer-Reviewers:

Reviewer #1:
Manuscript Summary:
This paper presents suitable and convenient thermal and rheological methods to evaluate and discriminate the different possible thermal events associated to curing phenomena in adhesives. The different tests are well described and set out in the right order. I recommend the publication/visualization of this methodology in JoVE.
Some minor points need a certain degree of clarification and/or justification.

Major Concerns:
None

Minor Concerns:
* Abstract. Line 46. Please, specify here what viscoelastic moduli should be evaluated.

The related sentence has been rewritten as follows: "…Thus, the curing reaction can be tracked through the elastic modulus (mainly the storage modulus), the phase angle and the gap. …"

* Please, briefly justify why TGA test must be performed under air purge and DSC test under N2 purge.

TGA test has two objectives: 1) to determine the inorganic filler content and 2) to determine the temperature at which the material starts to degrade. For the first objective the test has to be performed in an air atmosphere. For the second one, an air atmosphere represents the most common situation in normal use. Also, the temperature at which the material starts to degrade represents a limit that should not be reached in the DSC experiments. This explanation is now included in the manuscript.

* Justify why a 10 or 20 °C/min heating or cooling rate ramps are proposed in TGA and DSC tests for cured and fresh samples and discuss the appropriateness. Also, why a heating rate between 2 and 20°C/min were proposed in isothermal curing tests (pages 218 and 224).

10 ºC/min is the most frequently used heating rate. 20 ºC/min is also very common and allows to save time. These recommended heating rates are proposed as a starting point that will probably work fine in most cases. However, these heating rates can be modified to improve sensitivity or resolution.

For the first and second heating scans after isothermal curing, a set of heating rates was suggested. Probably, most of them work correctly and depending of the nature of the

curing process, mainly its kinetics, and the sensitivity and resolution required, some of these heating rates could be better.

If the evaluation is done with comparative purposes the same conditions should be used for each studied adhesive system.

* There is no reason to propose performing strain sweep tests and torque sweep tests in two different places (sections 3.1 and 3.3) for the same purpose, i.e. to determine the linear viscoelastic range (LVR). The extension of LVR can be determined either by applying strain sweep tests, in controlled-strain rheometers, or stress (better than torque) sweep tests, in controlled-stress rheometer. This issue must be unified and mentioned.

It is now better explained that in section 3.1 the extension of LVR is determined from a fresh sample (before curing), and in section 3.2, is obtained for a cured sample.

We agree with reviewer 1 that the extension of LVR can be determined either by applying strain sweep test, mostly in controlled-strain rheometers, or torque or stress sweep test, mostly in controlled-stress rheometer. However, in some rheometers both methods can be used. In this work a stress controlled rheometer was used and torque and strain sweep tests were used to evaluate the extension of the LVR. This is now mentioned in the manuscript.

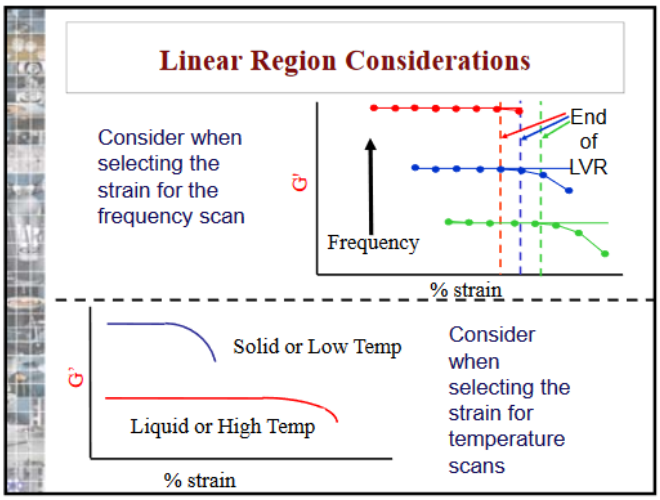
* Lines 503-504. To apply the Chambon-Winter criterion, a broader range of frequencies should be considered.

The following frequencies were used: 1, 3 and 10 Hz. (6.28, 18.85 y 62.83 rad/s)

Of course, a broader range of frequencies would be nice. These frequencies were chosen in accordance to the limitations of the instrument and recommendations from the manufacturer. Not many instruments allow to apply simultaneous oscillations at different frequencies. However, the results were clear and the gelation was observed. The possibility of a frequency in each separated test or successive frequencies in a single test would not ensure simultaneity of the measurements, what we think is important to apply the Chambon-Winter criterion.

* If the reason for performing torque sweep tests in section 3.3 is delimiting the LVR in the subsequent temperature scan test, the temperature applied should be the maximum reached in the latter, since temperature will affect the limits of the LVR.

It is generally accepted that for a cured sample the limit of LVR is lower for the minimum temperature, as it can be observed in this picture from the manufacturer of the rheometer. We understand the reviewer’s concern because sometimes the LVR obtained at low temperature is not valid for higher temperatures. However, on this occasion, in addition of determining the glass transition temperature we wanted to see if the material experiences some residual curing along the heating ramp. Thus, the amplitude had to be chosen before starting the first heating ramp.



At the minimum temperature the sample is below its glass transition and even taking into account a possible small residual cure, surely the LVR is thinner at the initial temperature.

* Again, justify why a 1°C/min heating rate ramps is proposed in the temperature scan tests and discuss the appropriateness. It's well known that Tg may be influenced by the heating ramp.

According to the manufacturers, the recommended heating rate is between 2 and 5 ºC/min. But, the lower the heating rate, the lower the temperature gradient into the sample. A 1ºC/min heating rate ramp is proposed in the temperature scan tests because it is a convenient value to ensure a uniform distribution of temperature into the sample without consuming too excessive time.

Reviewer #2:
Minor Concerns:
Comment to the paper "Evaluation of adhesive systems by rheological and thermal testing" by A. Díaz-Díaz et al.
1. The title will expand, specify "adhesive systems"?

As results of the reviewers' comments and the corresponding modifications of the manuscript the new title is: "Evaluation of the curing of adhesive systems by rheological and thermal testing"

The aim is that the method can be applied to different systems. Two very different systems were chosen as an example.

2. Introduction section is poor references (6 references), please add other references.

The introduction section was improved. The total number of references is now 18.

3. Talk a little bit about polymer materials used in this study (Introduction).

More information about the materials used was added at the Introduction section.

4. The experimental section is very big? it must be summarized.

Taking into account this comment and the comments of other reviewers the scope of the article and also the experimental section were reduced.

5. All figures have inhomogeneous? axes X and Y for example 1.103 not 1E3…

Figures were modified accordingly to the recommendations.

6. About methodology, how authors guarantee that curing was complete? The number of formulations they used is not adequate for drawing a conclusion on rheological properties. Even in the conclusion, no values are compared and discussed.
In the next lines we discuss about how guarantee a complete curing for the different test performed in the different sections of the Protocol:

Section 1. Analysis of a cured sample.

The sample was cured according to the manufacturer recommendations and then tested. The DSC test (section 1.2) includes two heating: the first one allows us to check if there is a residual cure, if yes, the second scan allow us to find out the glass transition temperature of the fully cured sample; if not, first and second scan should be identical. Of course, if we observe a residual cure we can conclude that the recommended curing conditions are not enough for getting the total cure of the adhesive system.

Section 2. DSC analysis of a fresh sample.

For a ramp curing test, typically an exothermic peak is observed by DSC and if the exothermic peak ends, this means that the curing reaction was completed.

For the isothermal curing test, after them, the sample is cooled and then heating to quantify the residual cure. And finally, it is cooled and heating again to verify there is not residual cure and find out the glass transition of total cured sample.

Section 3. Rheological test

The samples were cured isothermally into the rheometer until the storage modulus signal was flat of practically flat. And then, the samples were submitted an oscillatory temperature sweep test to check it there was residual cure or not.

On the other hand, it is now better explained that the aim is not focused on the adhesives properties but on the method.

Reviewer #3:
Manuscript Summary:

The methods are helpful. However, the manuscript needs to be well revised before acceptance

Minor Concerns:
The detailed comments are as follows:
1. The abbreviation of thermogravimetry is TG, not TGA (thermogravimetric analysis). Please unify TG or TGA in the manuscript.

Now, we use always the abbreviation of thermogravimetric analysis (TGA).

2. In the Protocol section, the manufactures, models and software version of all instruments, such as TG and DSC used in this paper should be provided, since different instruments have different operations.

In this issue, we will follow the Editorial recommendations: "*JoVE is unable to publish manuscripts containing commercial sounding language, including trademark or registered trademark symbols (TM/R) and the mention of company brand names before an instrument or reagent. Examples of commercial sounding language in your manuscript are TA Instruments Rheometer HR-2, TRIOS, items on Lines 401-404 1) Please use MS Word's find function (Ctrl+F), to locate and replace all commercial sounding language in your manuscript with generic names that are not company-specific. All commercial products should be sufficiently referenced in the table of materials/reagents. You may use the generic term followed by "(see table of materials)" to draw the readers' attention to specific commercial names.*"

3. In DSC measurement, the objective of the second heating run for removing the thermal history should be mentioned in the manuscript.

Related to the section 1.2 DSC test of cured sample, the second heating is not for removing the thermal history. In this is case, the comparison between first and second heating allow us quantify the possible residual cure in the first one.

For section 2.1. Ramp curing test, again, it is not a question of erasing the thermal history. Here, during the first heating the curing should be observed and the second heating allows to observe the glass transition of fully cured sample and the heat flow curve obtained could be used as baseline for making the integration of exothermic peak obtained in the first one.

In this work, the second heating is not used for removing thermal history.

4. The full name of MTDSC should be given once where it first appears. In the following section, please only use the abbreviation.

It was done.

5. Detailed information, like polymer type and components of three adhesive systems will be helpful for the readers to understand the results.

More information about the three adhesive system is now provided in the manuscript.

6. In Line 415-47, "In the case of S2c an important mass loss is observed in the 60-800 ºC range which suggests that CaCO3 is the main filler component since it is a typical filler which decomposes in that range of temperature in air." Why not other fillers? More other measurements are needed to determine the filler is CaCO3.

We agree with the reviewer that more other measurements are needed to determine the filler is $CaCO_3$. The mass loss observed for S2c in the 600-800ºC matches with the thermal decomposition of calcium carbonate according to the following chemical reaction: $CaCO_3 \rightarrow CaO + CO_2$ and the calcium carbonate it is most commonly used extender for adhesive formulations. Taking these two things into account, we dare to suggest the presence of $CaCO_3$.

7. In Fig. 1, derivative TG (TGA) should be added.

Derivative TG (TGA) was added to Figure 1.

8. In Fig. 2 and 3, the endothermal or exothermal direction should be marked in every DSC thermogram.

It was done.

9. In Fig. 4-6, sample names should be included in the figure captions.

Old Figures 4 and 5 are not present in the current version of the manuscript. The caption of the old Fig. 6 (now renamed as Fig. 4) includes the sample name.

10. In Line 487-488, 20 oC and 10 oC should be 20 oC/min and 10 oC/min.

No. 20ºC and 10ºC are the isothermal temperatures used to cure the samples.

11. In Fig. 7-11, Moduli should be Modulus.

It was done. Although the figures numeration has changed.

12. In Line 577, I think Discussion should be Conclusions.

There is no Conclusions section according to the Jove template.

Reviewer #4:
Manuscript Summary:
The manuscript describes thermal analysis and rheological characterization of adhesive

systems. Analysis during cure, and properties of the cured adhesives are discussed.

Major Concerns:
If this is meant for an industry protocol, I am concerned about lack of clear emphasis. Characterization of the curing is generally relevant from one point of view, while characterization of cured adhesive is from another point of view. Of course, they are related to each other, but my opinion is that a manuscript should focus on one aspect or the other.

We agree that the detailed explanation of both the characterization of the cure and the characterization of the cured material may cause some confusion. Thus, we chose to minimize the characterization of the cured material.

If curing is the main emphasis, gel time at different temperature and / or heating rates is most important. Since the authors take the gel time to be at crossover between G' and G", does it mean that rheology offers no help to industrial user in terms of time required for gelation? Surely, crosslinked network increases and undergoes percolation as the cure proceeds, then what is the procedure to detect the gel time?

Of course, a crossing of G’ and G’’ is observed during the curing of many adhesive systems, being the cross-over point of G' and G" often taken as the gel time. However, that cross-over point is frequency dependent and the phase angle cross-over obtained at different frequencies can be used as a more accurate measurement of the gel time (ref. Chambon and Winter). In addition, A crossing of G’ and G’’ may not occur at the gelation. The case presented in Figure 7 is a clear example of that behavior: there is no cross-over of G’ and G’’ but the gelation can be clearly observed through the crossing of the phase angle at three different frequencies.

In relation to the comment related to the gel time, gel time was evaluated only at room temperature because the aim of this work is to show the procedure. On the other hand, the systems used in this work are normally used at room temperature.

If cured adhesive is the emphasis, then mechanical properties of cured adhesive are most important. The manuscript does not claim to do this.

As commented above, in order to improve the clarity, we chose to minimize the characterization of the cured material.

Discussion section of the manuscript is very general, and does not seem to specifically talk about protocols/results of the manuscript.

Discussion section was improved through comments on results and protocols.

Minor Concerns:
1. Not sure about the relevance of TGA as presented. Maybe, more focus on weight loss below 150 C might help connection with rest of the analysis.

TGA test has two objectives: 1) to determine the inorganic filler content and 2) to determine the temperature at which the material starts to degrade. For the first objective the test has to be performed in an air atmosphere. For the second one, an air atmosphere represents the most common situation in normal use. The temperature at which the material starts to degrade represents a limit that should not be reached in the DSC experiments. This explanation is now included in the manuscript.

2. DSC curing is done at several temperatures, but rheometer curing only at room temperature. Why?

It is now better explained that isothermal curing DSC tests of one adhesive system were performed at different temperatures to demonstrate how the temperature effect on the curing rate can be evaluated by any method that can "see" the curing reaction. It is also commented in the rheological section how the G' or the gap can be used to track the advancement of the curing reaction at any temperature at which the experiment is performed. In addition, it is also commented how the multifrequency setup can be applied for curing at different temperatures to evaluate how the gel time varies with the curing temperature.

3. "which is incompatible with the fact that a glass transition occurs, since the temperature changes near the Tg typically modify the relaxation time by decades". Based on DSC, it is already concluded that it is "smaller ingradient" undergoing transformation: either Tg or Tm. Since the ingredient is known to be very small, and its effect of moduli decrease is also small, relaxation time of the overall sample will not be influenced significantly. Therefore, from stress relaxation, one cannot conclude that it is not Tg. The relaxation time of ingredient undergoing Tg will change by decades, however the overall relaxation time of the sample depends on all the ingredients.

As the reviewer points, the relaxation experiment may admit differnt interpretations. As commented above, in order to improve the clarity, we remove most of the characterization of the cured material.

Reviewer #5:

Manuscript Summary:

The paper deals with the measurement of thermodynamic and thermomechanical effects in the curing of adhesives formed by a filler containing thermoset. Although these are industrial adhesives, this experimental investigation can be of benefit to both education and science and engineering experts. Understanding and discussion of individual results are generally correct.

Major Concerns:

1) The biggest drawback of the work is the absence of experiments investigating the chemical structure of adhesives. Therefore, some conclusions should be taken only as speculative. Although curing reactions are often difficult to detect for conventional experimental methods (FTIR), at least basic information about the chemical structure of the system would be very useful to better understand the results obtained.

The work is focus on the proposal of a method for the evaluation of the curing of adhesive systems by rheological and thermal testing. Now some basic information about the

chemistry was included to help to understand the curing processes. The chemical explanations were not very long because other reviewers recommended to focus only on the experimental part of the curing.

2) The aims of this study should be formulated more precisely.

The aim of the study is now better explained: it is focusing on the proposal of a method for the evaluation of the curing of adhesive systems by rheological and thermal testing.

3) The adhesives under investigation should be described in more detail (using at least the manufacturer's material sheets) and their primary use should be stated.

It was done.

4) The authors do not state how the obtained results relate to the utility and technological properties of the investigated adhesives.

The work is aimed to provide a method to study the curing. The experimental results that can be obtained by the method allow to better understand how time and temperature parameters involved in the preparation of any adhesive joint may affect the technological properties of the adhesives. For example, in the case of thermosets, it is important to complete the application of the different elements of a joint before gelation occurs, and it is also important to keep the elements in their place until about a 90% of the maximum modulus is reached. This method can help to choose between adhesives with different reactivity, modulus, or contraction in the curing. This explanation was included in the text.

5) Conclusion of the thesis is missing

According to the JOVE template there is not a Conclusions section. The journal is focused in demonstrating the methodology of experimental methods.

6) The experiment in Fig. 1 is pyrolysis or oxidation? Both of these experiments would be interesting.

The experiment in Fig 1 is oxidation. In this case, TGA test has two objectives: 1) to determine the inorganic filler content and 2) to determine the temperature at which the material starts to degrade. For the first objective the test has to be performed in an air atmosphere. For the second one, an air atmosphere represents the most common situation in normal use. The temperature at which the material starts to degrade represents a limit that should not be reached in the DSC experiments. This explanation is now included in the manuscript.

Minor Concerns:

7) FIG. 2A - Why cannot a breaking at 60 ° C be considered a manifestation of a glass transition? (and the one at 20 ° C as hysteresis on cooling)

We agree with the reviewer. But the transitions are very smooth and should be confirmed by other techniques. The glass transition is clearly observed at 60ºC in the rheological temperature ramp test. This is a clear example of how rheology and calorimetry can be complementary.

8) For the sake of clarity, it would be a good idea to show the records of all three adhesives examined in the diagram in FIG. 3

It is explained in the manuscript, that “In the case of the T1c and T2c no curing exotherm was observed by DSC, as expected for moisture curing adhesives. Rheology studies of the curing will be of highest interest for these systems” (line 472 of the original manuscript).

9) For Figures 7, 8 and 9 I recommend to unify the unit of time.

It was done.

10) The design of rheometers is more variable than TGA or DSC. It would be appropriate to give a scheme of the used rheometer.

The design (scheme) of the used rheometer is included in the Table of Materials of the article.

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TITLE:

Evaluation of the curing of adhesive systems by rheological and thermal testing

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KEYWORDS:

Adhesives, rheology, DSC, curing, polymers, glass transition

SUMMARY:

An experimental methodology based on thermal and rheological measurements is proposed to characterize the curing process of adhesives with the aim of obtaining useful information for industrial adhesive selection.

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ABSTRACT:

The analysis of thermal processes associated to the curing of adhesives and the study of mechanical behavior once cured, provide key information to choose the best option for any specific application. The proposed methodology for the curing characterization, based on thermal analysis and rheology, is described through the comparison of three commercial adhesives. The experimental techniques used here are Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Rheology. TGA provides information about the thermal stability and filler content, DSC allows the evaluation of some thermal events associated to the cure reaction and to thermal changes of the cured material when subjected to temperature changes. Rheology complements the information of the thermal transformations from a mechanical point of view. Thus, the curing reaction can be tracked through the elastic modulus (mainly the storage modulus), the phase angle and the gap. In addition, it is also shown that although DSC is of no use to study the curing of moisture curable adhesives, it is a very convenient method to evaluate the low temperature glass transition of amorphous systems.

INTRODUCTION:

Nowadays there is an increasing demand of adhesives. Today's industry demands that adhesives have increasingly varied properties, adapted to the growing diversity of possible new applications. It makes the selection of the most suitable option for each specific case a difficult task. Therefore, creating a standard methodology to characterize the adhesives according to their properties would facilitate the selection process.

The analysis of the adhesive during the curing process and the final properties of the cured system are crucial to decide whether an adhesive is valid or not for a certain application.

Two of the most commonly used experimental techniques to study the behavior of adhesives are Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). Also rheological measurements and Thermogravimetric tests are widely used. Through them, the glass transition temperature (Tg) and the residual heat of curing, which are related to the degree of cure[1,2], can be determined.

TGA provides information about the thermal stability of the adhesives[3,4], which is very useful to establish further process conditions, on the other hand rheological measurements allows to determine the gel time of the adhesive, to analyze the curing shrinkage, and to define the viscoelastic properties of a cured sample[5–7], while the DSC technique allows to measure the residual heat of curing, and discern between one or more thermal processes that can take place simultaneously during the curing[8,9]. Therefore, the combination of DSC, TGA and rheological methodologies provide detailed and reliable information to develop a complete characterization of adhesives.

There is a number of studies of adhesives where DSC and TGA are applied together[10–12]. There are also some studies that complement the DSC with rheological measurements[13–15]. However,

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Eliminado: These variables can provide an additional insight for some thermal events observed in the cured material too. As a result, Modulated Temperature Differential Scanning Calorimetry (MTDSC) and Rheology allow to elucidate the nature of some processes which are not clear for DSC.
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there is not a standardized protocol to address the comparison of adhesives in a systematic way. That comparison would all to better choose the right adhesives in different contexts. In this work, an experimental methodology is proposed for doing a characterization of the curing process through the combined use of the thermal analysis and rheology.

Applying these techniques as an ensemble allows to gather information about the adhesive behavior during and after the curing process, also the thermal stability and the Tg of the material[16].

The proposed methodology, involving the three techniques, DSC, TGA and rheology, is described in this work using, as an example, three commercial adhesives. One of the adhesives, hereinafter referred to as S2c, is a two-component adhesive: component A contains tetrahydrofurfuryl methacrylate and component B contains benzoyl peroxide, the component B acts as an initiator of the curing reaction by causing the tetrahydrofurfuryl methacrylate rings to open, through a free radical polymerization mechanism, the C=C bond of the monomer reacts with the growing radical to form a chain with tetrahydrofurfuryl side groups[17]. The other adhesives, T1c and T2c, are the one- and two-component versions from the same commercial house of a modified silane polymer adhesive, the curing process begin by the hydrolysis of the silane group[18] which can be initiated by ambient humidity, this is the case of T1c, or either by the addition of a second component, as in the case of the adhesive T2c.
Concerning the application areas of these three different sytems: the adhesive S2c was designed to substitute, in some cases, welding, riveting, clinching and other mechanical fastening technicques and it is suitable for high strength fastening of concealed joints on different types of substrates including top coats, plastics, glass, etc; the T1c and T2c adhesives are used for elastic bonding of metals and plastics, for example in the caravan manufacture, in the railroad vehicule industry or in shipbuilding.

PROTOCOL:

1 Checking the manufacturer curing conditions

Cure the adhesive sample following the manufacturer recommendations, and then evaluate it by a TGA and a DSC test. Record the specific curing conditions.

1.1 TGA test of cured sample

Perform Thermogravimetric tests in a TGA or in a simultaneous DSC+TGA equipment (SDT).

Carry out a thermogravimetric test of the cured sample in order to determine the inorganic filler content and the temperature at which the material starts to degrade. Do not exceed that temperature in further tests.

Follow the procedure explained below:

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1.1.1. Open the air stopcock. Switch on the SDT (or TGA) apparatus. Open the SDT control software.

1.1.2. Open the FURNACE of the SDT and place two empty capsules. One will be the reference capsule and the other will contain the sample.

1.1.3. Close the FURNACE and press the bottom TARE.

1.1.4. Open the Furnace and place a sample size of 10 – 20 mg in the sample capsule.

1.1.5. Fill the information about the sample in the tab "Summary".

1.1.6. Open the tab "Procedure" and click EDITOR. Drag the segment type "Ramp" to the Editor screen. Establish 10 or 20 °C/min to 900 °C. Click Ok.

1.1.7 Open the tab "Notes". Choose Air as the purge gas and establish a flow rate of 100 mL/min. Click Apply.

Note: TGA test has two objectives: 1) to determine the inorganic filler content and 2) to determine the temperature at which the material starts to degrade. For the first objective the test has to be performed in an air atmosphere. For the second one, an air atmosphere represents the most common situation in normal use.

1.1.8 Close the Furnace.

1.1.9 Start the experiment.

1.2 DSC test of cured sample

Carry out the DSC tests on a standard DSC or on a Modulated temperature DSC (MTDSC) instrument working in standard mode, use aluminum crucibles. Carry out a DSC test of the cured sample to study the following parameters: the Tg of the material, a possible residual curing and the Tg_∞ of the sample. Follow the procedure below:

1.2.1. Open the nitrogen stopcock. Switch on the DSC apparatus. Open the control software of the DSC instrument.

1.2.2. Click "Control" → Event → On. Then click the tab "Tool" → Instrument Preferences, choose DSC and establish a standby temperature of 30 °C. Click "Apply". Click the tab "Control" → Go to Standby Temperature, and wait for at least 45 min before starting any experiment.

1.2.3. Open the tab "Summary". Click Mode, choose Standard.

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1.2.4. Open the tab “Procedure”, click “Test” and choose Custom. Click EDITOR.
- Drag an “Equilibrate” segment indicating the temperature at which you want to start the experiment (that temperature should be relatively low, for example -80 or -60 ºC).

- Drag the segment type “Ramp” to the Editor screen. Introduce a heating rate of 10 or 20 °C/min and the final temperature into the command editor window. The final temperature is tentatively chosen to allow for a complete cure and has to be lower than the degradation temperature obtained from the previous TGA test. Click Apply.

Note: These recommended heating rates are proposed as a starting point that will probably work fine in most cases. However, these heating rates can be modified to improve sensitivity or resolution.

- Drag the segment type “Ramp” to the Editor screen. Similarly, to the previous step, introduce a 10 or 20 °C/min cooling rate to a temperature tentatively below the glass transition.

- Drag the segment type “Ramp” to the Editor screen. Introduce a 10 or 20 °C/min heating rate to a temperature slightly below the degradation temperature.

1.2.5. Open the tab “Notes”. Choose Nitrogen as the flow gas and establish a flow rate of 50 mL/min. Click Apply.

1.2.6. Fill the information about the sample in the tab “Summary”.

1.2.7. Click “Control” → Lid → Open. Place a reference pan and a pan with a sample of 10-20 mg weight inside the DSC cell.

1.2.8. Launch the experiment by clicking Start.

2 DSC analysis of a fresh sample

Prepare a fresh sample of the adhesive using the ratios and procedures recommended by manufacturer and immediately subject it to the following test:

2.1. Ramp curing test

Perform a Heating-Cooling-Heating test, in order to obtain the curing enthalpy of the adhesive, the final glass transition on heating and to establish the range of temperatures where the curing process starts. Follow the steps below:

2.1.1. Open the tab “Summary”. Click Mode, choose Standard.

2.1.2 Click the tab “Tool” → Instrument Preferences, choose DSC and establish a standby

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temperature of 10 °C. Click “Apply”. Click the tab “Control” → Go to Standby Temperature,

2.1.3 Open the tab “Procedure”, click “Test” and choose Custom. Click EDITOR. Drag the segment type “Equilibrate” at -80 °C to the Editor screen. Drag the segment Ramp and establish 10 or 20 °C/min to (a temperature slightly below the degradation temperature obtained from the TGA test).

2.1.4 Insert the segment Equilibrate at -80 °C. Then drag the segment Ramp, establish 10 or 20 °C/min to (the same temperature as before). Click “Apply”.

2.1.4. Fill the information about the sample in the tab “Summary”.

2.1.5. Click “Control” → Lid → Open. Place a reference pan and a pan with the freshly prepared sample of 10-20 mg weight inside the Furnace.

2.1.6. Start the experiment.

2.2 Isothermal curing test

Taking into account the DSC plot of the curing in ramp, choose several temperatures at the beginning of the exotherm to execute the isothermal experiments.

Note: The isothermal experiments will allow to evaluate the maximum degree of curing that can be obtained at each temperature.

Follow the steps explained below:

2.2.1. Open the “Summary” tab. Click Mode, choose Standard.

2.2.2. Open the “Procedure” tab, click “Test” and choose Custom. Click EDITOR. Drag the segment type “Ramp” to the Editor screen. Introduce a 20 °C/min to the chosen isothermal temperature.

2.2.3. Introduce an Isothermal segment for time enough to complete the cure at this temperature (It is possible, for example, to establish 300 min, but the test can be stopped when the Heat Flow curve is flat).

2.2.4. Introduce a command segment “Equilibrate at 0 °C”. Add a Ramp segment, establish a heating rate between 2 and 20 °C/min (in the example 2.5 ºC/min was chosen) to the maximum temperature, which was chosen from the TGA test in order not to compromise the thermal stability of the adhesive.

2.2.5 Drag the “Mark end of cycle” segment to the editor window. Insert another Equilibrate segment, this time with a temperature of -80 °C. Add another Ramp segment with a heating rate between 2 and 20 °C/min (in the example 2.5 ºC/min was chosen) to the same temperature

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Bajado hacia abajo[1]: The isothermal experiments will allow to evaluate the maximum degree of curing that can be obtained at each temperature. The residual cure and the glass transition obtained are evaluated by MDSC after the isothermal step

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The experimental setup consists of these steps:

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indicated before. Click “Apply”.

NOTE: A set of heating rates are suggested. Probably, most of them work correctly and depending of the nature of the curing process, mainly its kinetics, and the sensitivity and resolution required, some of these heating rates could be better. If the evaluation is done with comparative purposes the same conditions should be used for each studied adhesive system.

NOTE: In order to minimize the time elapsed from mixing the components to the beginning of the isothermal experiments, the temperature of the DSC cell should be adjusted to a temperature lower than the isothermal temperature before mixing both components.

2.2.6. Click the tab “Tool” → Instrument Preferences, choose DSC and establish a temperature lower than the isotherm temperature of the experiment. Click “Apply”. Click the tab “Control” → Go to Standby Temperature.

2.2.7. Fill the information about the sample in the tab “Summary”.

2.2.8. Click “Control” → Lid → Open. Place a reference pan and a pan with the sample of 10-20 mg weight inside the Furnace.

2.2.9. Start the experiment.

3 Rheological analysis

Perform the rheological tests on a Hybrid rheometer, using a 25 mm parallel plate geometry.

3.1. Logarithmic strain sweep test

Do an exploratory logarithmic strain sweep test in order to set-up the strain amplitude to be used in the curing study of the adhesive in the rheometer. This test is performed with a fresh sample (before curing). Follow the procedure below:

3.1.1. Open the air stopcock. Switch on the Rheometer apparatus. Open the Rheometer control software.

3.1.2. Place the specific geometry on the Rheometer.

3.1.3. Click “Zero Gap”.

3.1.4. Click the tab “Geometry” Choose the specific geometry.

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If in the previous experiments some peaks apart from the curing one appear, then carry out then additional tests at different heating rates can be performed to clarify if some of the events observed correspond to crystallization or other non-reversible events. Moreover, cyclic tests provide information about the reversibility of the process. ¶
¶
Increase the sample size, or either the heating or cooling rate, Iif the heat involved in a process is too small (relatively to the device sensitivity), the sample size should be increased. Another possibility to increase sensitivity consists of increasing the heating or cooling rate. Be carefull, becauseHowever, a too fast cooling scan would hide the crystallization process if the sample does not stay enough time at the temperatures at which crystallization can proceed.¶

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3.1.5. Open the tab “Experiment”.

3.1.6. Fill the information about the sample in the tab “Sample”.

3.1.7. Click the tab “Procedure”. Choose Oscillation Amplitude. This experiment can be performed at room temperature (the actual temperature is annotated), and with a frequency of 1 Hz and a logarithmic sweep from 10^{-3} to 100 % of Strain.

NOTE: To prepare a sample of the two component system, weight components at room temperature, about 20 °C to the exact proportions recommended by the manufacturer. Then mix both components.

3.1.8. Place the sample on the bottom plate with the upper plate separated about 40 mm from the lower plate. Lower the upper plate until a gap of about 2 mm is observed between both plates. Trim off the excess of adhesive.

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3.1.9. Start the experiment.

3.2. Isothermal multifrequency curing test

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The subsequent procedure explains the steps to be followed to monitor the curing of the adhesive. This test shows if there is or not gelation and, in case of gelation, it provides the gelation time. In addition, the contraction and the evolution of G’ and G’’ can be observed along the curing process.

Note: This test shows if there is or not gelation and, in case of gelation, it provides the gelation time. In addition, the contraction and the evolution of G’ and G’’ can be observed along the curing process.

Bajado hacia abajo[2]: This test shows if there is or not gelation and, in case of gelation, it provides the gelation time. In addition, the contraction and the evolution of G’ and G’’ can be observed along the curing process.

Follow the subsequent procedure to monitor the curing of the adhesive.

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3.2.1. Click the tab “Procedure”. Choose Conditioning Options. Establish the Mode Compression, Axial Force 0 N and Sensitivity of 0,1 N. Click “Advance” and establish a Gap change limit of 2000 µm in the up and down directions.

3.2.2. Insert a new step of an oscillatory time sweep. This experiment can be performed at room temperature (the actual temperature is annotated), the duration of the test as a function of the estimated curing time based on the Data Sheet of the adhesive, and the percentage of Strain which is chosen from the result of the previous logarithmic strain sweep test. Choose Discrete and then set the frequencies 1, 3 and 10 Hz for all samples.

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3.2.3. Remove the previous sample, do the Zero Gap and place a new sample. Then proceed as in the 3.1.8 subsection.

3.2.4. Start the experiment.

Note: Do not remove the sample at the end of experiment. It will be used in the next experiment.

3.3 Torque sweep test

Once the curing test ends, proceed to the torque sweep test in order to find out the linear viscoelastic range for the previously cured material.

Note: the extension of LVR can be determined either by applying strain sweep test, mostly in controlled-strain rheometers, or torque or stress sweep test, mostly in controlled-stress rheometer. However, in some rheometers both methods can be used.

3.3.1. Click the tab "Procedure". Choose Oscillation Amplitude. This experiment can be performed at room temperature (the actual temperature is annotated), with a frequency of 1 Hz and a logarithmic sweep from 10 to 10000 µNm of Torque.

Note: Use the same sample that was left in the instrument from the previous experiment.

3.3.2. Start the experiment.

Note: Do not remove the sample at the end of experiment. It will be used in the next experiment.

3.4 Temperature scan test

Perform a temperature scan test to verify the cure is complete, Follow the procedure below:

3.4.1. Click the tab "Procedure". Choose Temperature Ramp. Initiate the experiment from room temperature, establish a ramp rate of 1 °C/min, which ensure a uniform distribution of temperature into the sample without consuming too excessive time, a frequency of 1 Hz and a given Torque amplitude, which is chosen from the previous Torque sweep test.

Note: Use the same sample that was left in the instrument from the previous experiment.

3.4.2. Close the Furnace of the Rheometer. Open the air stopcock of the furnace.

3.4.3. Start the experiment.

Note: If the next experiment is needed, do not remove the sample at the end of experiment. In that case it would be used for the next experiment.

REPRESENTATIVE RESULTS:

In order to show the application of the proposed method three adhesive systems are used:

- S2c, a two component system.
- T1c, a one component silane-modified-polymer, whose cure reaction is triggered by moisture.

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Relaxation stress and Modulated Temperature DSC tests can be of interest in order to determine if a process which was initially identified by a moderate drop of the storage modulus in the rheometer or by a little endotherm on heating in DSC correspond to a single process or overlapping relaxation and melting processes may exist. The values of the relaxation times obtained by the relaxation stress tests performed before and after the event provide information about the event. Thus, if the event was a glass transition, the difference between the relaxation times should be of very different order. Also, MTDSC allows to distinguish between glass transitions and melting processes. For instances, a cooling MTDSC tests will show the glass transition on the reversing signal (if in case) and crystallization processes on the non-reversing signal (if in case). ¶
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- T2c, a two component system. It is a silane-modified-polymer too but the second component is aimed to make the curing rate a little more independent from the moisture content of air. (see table of materials for more information)

The thermal stability and the amount of filler of the cured adhesives are analyzed by TGA. Figure 1 shows the thermogravimetric plots obtained in air from the three adhesives. In the case of S2c a slight mass loss is observed from about 50 °C which is probably related to moisture volatilization. The onset of the main degradation process appears at 196 °C. For T1c and T2c the degradation onsets appear at slight higher temperatures: 236 °C and 210 °C, respectively. These degradation temperatures should be not reached in further DSC or rheology experiments. The residue at 600 °C probably corresponds to inorganic fillers. It amounts 37.5% for T1c, 36.9% for T2c, and 24.6% for S2c. In the case of S2c an important mass loss is observed in the 600-800 °C range which suggests that $CaCO_3$ is the main filler component since it is a typical filler which decomposes in that range of temperature in air. A mass loss of 10.32% was observed what corresponds to a 23.5% of $CaCO_3$ in the cured sample.

[Place **Figure 1** here]

Figure 1: TGA curves of the three adhesives. The curves were obtained from cured samples using air as the purge gas.

Following the procedure, the next step consists of performing DSC tests of cured samples. Figure 2 shows the heat flow curves obtained. The S2c was previously cured at room temperature (aprox. 20°C) during 95 min. The T1c (moisture curing system) and T2c were previously cured at room temperature for 48 h.

[Place **Figure 2** here]

Figure 2: DSC heat flow curves obtained from cured samples of the three adhesives: S2c **(A),** T1c **(B),** T2c **(C)**

Figure 2a shows no evidence of residual cure. A small deviation from the baseline is observed at about 60 °C during the first heating ramp. It could be considered a manifestation of a glass transition, but it is practically negligible and it would be better to wait for the rheological test to confirm. A glass transition temperature at 60°C was specified by the manufacturer but it is not observed in this DSC plot. At -67 °C there is a tiny drop in the heat flow signal that suggest a possible glass transition of a component of the adhesive.
Figure 2b shows a clear glass transition at -66 °C. There is also an endothermic peak between 65 °C and 85 °C on heating and the corresponding exotherm on cooling at 53 °C. The shape and size of these peaks suggest possible melting and crystallization processes of a polymeric compound and will be discussed in the scope of additional results. The only important event in Figure 2c is a glass transition at -64 °C.

The next results are also related to DSC tests. Figure 3 shows the curing plot of a S2c sample at

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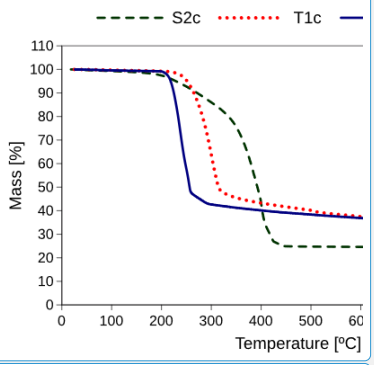

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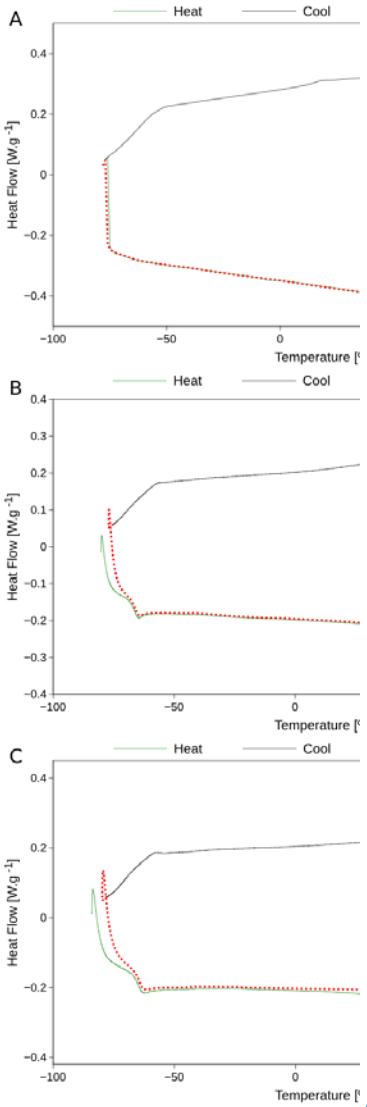

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20 °C/min in a heating ramp. That ramp will be followed by a cooling and heating ramps not displayed in this Figure. The curing enthalpy of the adhesive, 171.5 J/g, is obtained by integration of the peak. The shape of the exotherm suggests an autocatalytic curing reaction[19–21], which would correspond to the methyl methacrylate free radical polymerization of the S2c adhesive[22].

[Place **Figure 3** here]

Figure 3: DSC heat flow curves obtained from a fresh sample of the S2c adhesive system

In the case of T1c and T2c no curing exotherm was observed by DSC, as expected for moisture curing adhesives. Rheology studies of the curing will be of highest interest for these systems.

In order to evaluate the degree of curing that can be achieved at different temperatures isothermal DSC experiments were performed only for S2c, since the moisture curable systems cannot be tracked by DSC. For T1c and T2c samples, rheological measurements such as G' or the gap can be used to track the advancement of the curing reaction at any temperature at which the experiment is performed. Table 1 shows the curing enthalpy values obtained at three temperatures. The degree of curing is calculated by comparing the curing enthalpy obtained at each temperature to that obtained in a heating ramp. The one used to calculate the values displayed on Table 1 was obtained at 20 °C/min.

Table 1. Curing enthalpy and the degree of curing values resulting from the isothermal cure of S2c samples at different temperatures.

[Place **Table 1** here]

Figure 4 shows how the residual cure is much smaller in the case of the sample cured at the higher temperature. That is so because the degree of curing achieved at 20 °C is higher than that obtained at 10 °C, as it can be observed in Table 1.

[Place **Figure 4** here]

Figure 4. Specific heat flow plots obtained in the first and second heating scans from S2c samples isothermally cured at the indicated temperatures

Important features of a curing process that were not observed by DSC are the gelation, the shrinkage produced by the curing and the change of the moduli along the cure process. The latter is especially important in the case of moisture triggered curing, since in these systems the conversion of the curing process cannot be tracked by DSC. These missing features can be evaluated by rheology.
The first rheological test performed with each sample consists of a strain sweep that allows to see the linear viscoelastic range from which a strain value will be chosen for the next experiment,

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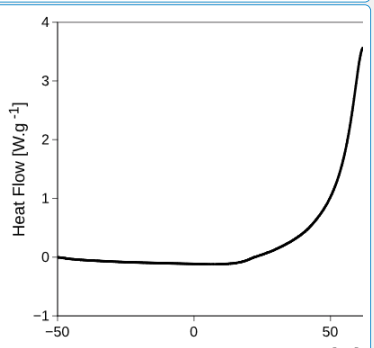

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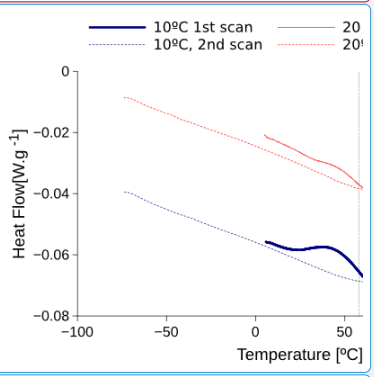

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an isothermal multifrequency test with the following frequencies: 1, 3 and 10 Hz. (6.28, 18.85 and 62.83 rad/s). Figure 5, corresponds to the cure of a fresh S2c sample that is placed between the parallel plates of the rheometer. The gelation time of the material can be observed as the point where the phase angle, δ, becomes frequency independent, according to the Winter and Chambon criterion[23, 24]. The gelation time is the time from mixing the two components to the instant when the phase angle curves obtained at different frequencies cross. After the gelation, the Tg continues to increase until a value somewhat above the cure temperature. The high filler content of this sample, about 23 %, is the reason why a higher value of G' than of G" is obtained throughout the test. Figure 5 gives also information about the shrinkage of the adhesive along the curing, that is about 6,5 % in 10 minutes. A value of 20.5 MPa the modulus is obtained after about 11 minutes from mixing the components. After that instant the moduli and the gap change only very little.

[Place **Figure 5** here]

Figure 5: Plots resulting from the isothermal curing of a S2c sample in the rheometer at room temperature.

Performing the isothermal multifrequency test at different temperatures, it would be possible to evaluate how the gel time varies with the curing temperature.

In the case of the T1c and T2c systems, Figures 6 and 7, there is no sign of gelation of the adhesives. A comparison of the slopes of the moduli of both adhesives reveals that T2c cures faster than T1c, which is normal since T2c has an additional compound to accelerate the curing reaction. An important increase of the storage modulus is observed in both cases, reaching an almost constant value after 24 h. A value of 0.94 MPa is observed for T1c and 1.2 MPa for T2c, which are much smaller than that observed for S2c.
Again, a high filler explains that G' is consistently higher than G" along the test. The behavior of tan δ in both cases, seems to be related to the shear that those thixotropic materials undergo between the plates of the rheometer and also because of the curing process.
On the other hand, the contraction observed for both T1c and T2c systems in 24 h, 0.65 % and 0.89 %, respectively, are very little in comparison to that observed for S2c in 15 minutes, 5.7 %.

[Place **Figure 6** here]

Figure 6: Plots resulting from the isothermal curing of a T1c sample in the rheometer at room temperature.

[Place **Figure 7** here]

Figure 7: Plots resulting from the isothermal curing of a T2c sample in the rheometer at room temperature.

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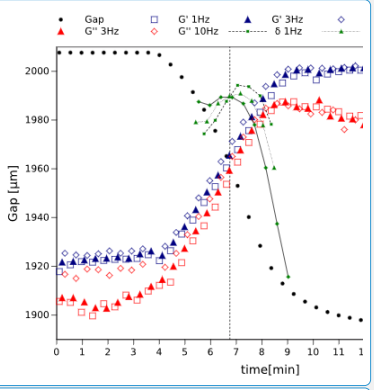

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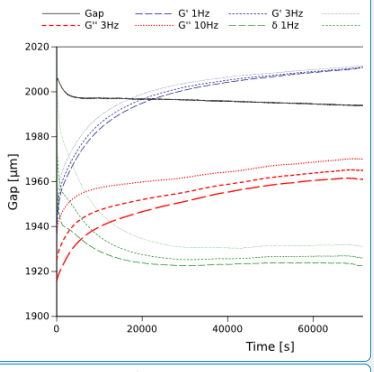

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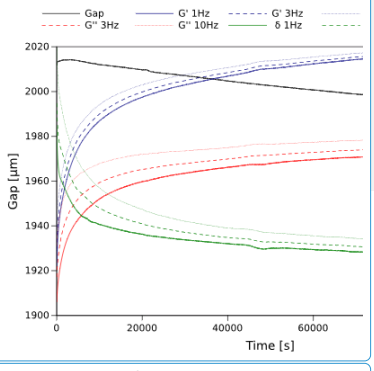

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In advance to perform the temperature scan tests of the cured samples, it is needed to evaluate the linear viscoelastic range (LVR) of the cured samples. The LVR is usually determined either by applying strain sweep test, in controlled-strain rheometers, or stress or torque sweep test, in controlled-stress rheometer. However, in some rheometers both methods can be used. On this occasion torque sweeps were done.

Figure 8 shows the results of a temperature scan of the S2c sample that was cured for one hour in the rheometer. The glass transition can be easily identified as a drop in G', and as broad peaks in G'' and in the phase angle, δ. The value of Tg, measured as the δ peak, is 60.2 °C.

[Place **Figure 8** here]

Figure 8: Temperature scan test performed in the rheometer with a cured S2c sample.

Temperature scans of fully cured T1c and T2c adhesives are reflected in Figure 9. The scan of T2c does not shows any relaxation in all temperature range. That can be of interest in case a consistent behavior is sought in that range of temperature.

[Place **Figure 9** here]

Figure 9: Temperature scan tests of the cured adhesives T1c and T2c. Values of G', G'' and δ were obtained from a 1°C/min temperature scan.

On the other hand, the moduli of the scan of T1c show a slow decrease until up to 60 °C, and then a more intense decline between 60 °C and 80 °C to then persist constant until the end of test.

DISCUSSION:

A preliminary TGA test of each adhesive is always a fundamental step as it gives information about the temperature range at which the material is stable. That information is crucial to correctly setting-up further experiments. In addition, TGA may also inform about the filler content, which can be very insightful to understand that storage and loss modulus may not to cross along the cure.

On the other hand, DSC allows to study the cure of most thermosetting systems but not of those whose cure reaction is moisture triggered. Rheology allows to track the cure of any system, moisture triggered or not and is the right technique to compare them. However, it has to be taken into account that a typical limitation of rheometers is the minimum temperature at which a curing test can be performed. Fortunately, most adhesives are intended to be used at room or higher temperatures.

Most flexible adhesives have a glass transition temperature at sub ambient temperatures. Some components of semi-rigid systems may have a low Tg too but it is frequent that common rheometers cannot reach that low temperature. But many commercial DSC can easily reach -80 ºC and thus can be used to determine that low Tg.

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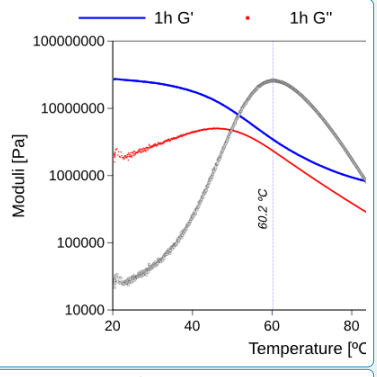

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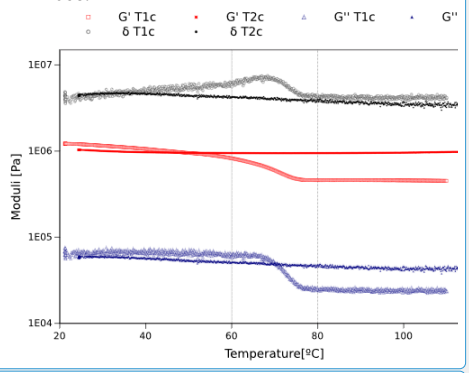

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An interesting feature of some rheometers is the possibility of applying an almost null axial force, which allows to track the gap changes due to the adhesive contraction along the cure. That feature was not common in the past but nowadays many rheometers incorporate that feature.
Another interesting advantage of rheology respect to DSC is the possibility of identifying the gel point through the phase angle at different frequencies. That is useful to see it the adhesive is a thermoset or not and, if so, to measure the gel time, a critical factor that is directly related to the working time at a given temperature.
A critical step within the protocol is the use of appropriate ratios and procedures recommended by manufacturer with two component systems, as well as adjusting both DSC temperature and time expended to launch experiment for freshly prepared samples. In relation to the rheological test, it is important to keep the heating rate at low values to ensure a uniform distribution of temperature, also for DSC test the chosen heating rate should take into account aspects such as sensitivity and resolution.
The experimental results that can be obtained by the proposed methodology allow to better understand how time and temperature parameters involved in the preparation of any adhesive joint may affect the technological properties of the adhesives. For example, in the case of thermosets, it is important to complete the application of the different elements of a joint before gelation occurs, and it is also important to keep the elements in their place until about a 90% of the maximum modulus is reached. This methodology can help to choose between adhesives with different reactivity, modulus, or contraction in the curing.
From all the above, it can be deduced that the convenience of the elaboration of a methodology for the systematic study of the cure of adhesive systems through two techniques, thermal analysis and rheology, which complement each other efficiently to achieve a complete characterization of the cure for very different systems.

ACKNOWLEDGMENTS:

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DISCLOSURES:

The authors have nothing to disclose.

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It is the aim of the authors to extend this method to other adhesive systems in order to refine it and to develop an standard of more general application for industrial adhesive selection.¶
A critical step within the protocol is the use of appropiate¶ ratios and procedures recommended by manufacturer with two component systems, as well as adjusting both DSC temperature and time expended to launch experiment for freshly prepared samples. Related to heating rate values (see section 3.4), ensure a uniform distribution of temperature into the sample without consuming too excessive time can justify lower heating rates than proposed ones.¶

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