

Thermal and rheological comparison of adhesives

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Abstract

In some industrial sectors such as naval construction, the use of adhesives is still limited to some specific applications. However, shipbuilders, academia and classification societies are cooperating to expand the field of certificated applications of adhesive joints. As apart of a validation study, thermal and rheological studies of the curing process and of the cured adhesives should be included. While a neat glass transition and other relaxation processes can be normally identified by ramp temperature tests performed both on a differential scanning calorimeter or on a rheometer, there are some adhesive systems in which several glass transitions or melting or crystallization processes overlap. Applying a thermal treatment to delete the thermal history and conditioning are common practices to clarify what happens in complex systems. However, although that practices usually help, there are still some complexities due to overlapping processes that cannot be easily understood. An important point of this work is to show how differential scanning calorimetry (DSC) and rheology complement to each other in order to demonstrate several thermal relaxations and to obtain a better understanding of the cure process. The use of two different techniques along with a careful election of the setup parameter values allows to better interpret the thermal events. In addition, thermogravimetry (TG) helps to understand some rheological behaviors.

In the end, this work shows how a good insight of the adhesive properties can be obtained by means of the combined use of DSC, rheology and TG.

Keywords: adhesives, DSC, rheology, TG

Introduction

The use of adhesives in industry has been constantly increasing during the last decades, substituting in many cases more complex, invasive and expensive join techniques such as welding in shipbuilding [1]. In addition, new adhesives are now needed for new applications in medicine and dentistry such as those related to drug delivery and tissue engineering [2]. Thus, taking into account the expanded fields of applications, the number of studies devoted to synthesis and characterization are also growing. On the other hand, the experimental procedures that provide tools to develop selection criteria are increasing too [1–4]. Thermal analysis techniques such as differential scanning calorimetry (DSC) and dynamical mechanical analysis

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4 (DMA) are two of the most popular experimental techniques used to analyze adhesives, among
5 others such as gel permeation chromatography, Fourier transform infrared, Raman spectroscopy
6 and nuclear magnetic resonance [1,2,4,5]. DSC and DMA are profusely applied to study the
7 curing and the degradation reactions, in addition to analyze other transitions such as
8 crystallization, melting, and enthalpy relaxation [6]. The combining use of different experimental
9 techniques is advised in order to obtain reliable, detailed and unambiguous information about the
10 adhesives properties [3]. In fact, in the majority of the cases the use of at least two techniques is
11 mandatory. That is the case of the combined application of DSC and DMA, or even DSC and
12 rheological measurements, as is the present case. In fact, classical studies of adhesives include
13 thermal and rheological testing [7–9]. Thermogravimetry (TG) is normally used to study thermal
14 degradation and to evaluate fire retardants [10–12].

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21 Glass transition temperature and residual heat of curing are related to the degree of cure. Both
22 can be determined by DSC, which is also frequently used to study the kinetics of the curing
23 reactions. However, DMA and rheological measurements can be more adequate for the study of
24 the glass transition, especially for highly crystalline polymers. There are an enormous amount of
25 works where DSC, rheological testing, or combinations of both are used to evaluate the degree of
26 curing and the properties of the cured material. For example, the glass transition temperature
27 (T_g) and residual heat of curing are related to the degree of cure and both can be determined by
28 DSC and rheological tests [13–16]. When comparing the results obtained by dynamic and non-
29 dynamic methods, it has to be taken into account that the dynamic glass transition (T_{gd}) is
30 frequency dependent [6,17,18].

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36 In this work, an experimental methodology based on the application of thermal and rheological
37 measurements is proposed and illustrated by the analysis of three commercial adhesives, one
38 based on methacrylic polymers and the other two on silyl-modified polymer. The aim is to show
39 how the combined use of DSC and rheology can provide a very significant and useful
40 information to develop selection criteria for specific technological requirements.

41 42 43 44 **Experimental**

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46 Three adhesive systems were used in this study. The first one is Sikafast 5211NT (S2c), a two
47 component system manufactured by Sika. The resin is based on tetrahydrofurfuryl methacrylate
48 and contains an ethoxylated aromatic amine. The second component contains benzoyl peroxide
49 as the initiator for the crosslinking reaction. The other two adhesives are Teroson MS 939FR
50 (T1c), and Teroson MS 9399 (T2c) from Henkel. It is a one part silyl-modified polymer.
51 Crosslinking to form a rubber-elastic final product is triggered by the penetration of water in the
52 form of atmospheric moisture. Both T1c and T2c are thixotropic, of the silane modified polymer
53 (SMP) type, which undergo moisture curing and react to form high performance elastomers. T1c
54 is a fire resistant adhesive and comes as a one component system. T2c comes in two components.
55 The second component, a booster, is mixed to uniformly ensure the curing with some
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4 independence from atmospheric moisture. Apart from these details, both adhesives are basically
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6 of the same type and share the same cure chemistry.

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8 The three adhesive systems were evaluated by DSC and rheology. Thermogravimetric analysis
9 of cured samples was also done.

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11 DSC tests were performed on a TA Instruments MDSC Q2000, using aluminum Tzero crucibles.
12 In the case of two-component systems, the two components were precisely weighed at room
13 temperature, about 20 °C, to the exact proportions recommended by the manufacturer. Then, the
14 two components were manually mixed for 25 s and immediately placed on the crucibles and into
15 the instrument to launch the experiment. For the one component system a similar procedure was
16 applied except for mixing the components. Sample size was in the 8 mg to 14 mg range. Four
17 types of test were used:

- 18 • Isothermal curing at 10, 12, 13.5, 15 and 20 °C. In order to minimize the time elapsed from
19 mixing the components to the beginning of the isothermal experiments, the temperature of
20 the DSC cell was adjusted to that isothermal temperature before mixing both components.
21 That time was about 25 s.
- 22 • Temperature ramps of isothermally cured samples. Some of the isothermally cured samples
23 were subjected to a 20 °C/min heating ramp from the curing temperature to 120°C, followed
24 by equilibration at -80°C and a new heating ramp to 120°C. Other samples, were cooled after
25 the isothermal curing and then a heating ramp was applied.
- 26 • Temperature ramps of unreacted samples. The experiments consisted of a cooling step to -
27 85°C or -60°C, followed by heating to 150°C or 200°C, and then cooling and heating again.
28 The programmed heating and cooling rates were 5, 10, 20, and 30°C/min. For these
29 experiments the cell was equilibrated at 15°C before loading the samples.
- 30 • Modulated temperature DSC (MTDSC) ramp from 100°C to -10°C at 1°C/min with an
31 amplitude of 0.11°C in both positive and negative directions and a period of 40 s. This
32 method was only applied on a cured T1c sample. Sample size was 5.52 mg.

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34 Rheological tests were performed on a TA Instruments HR-2, using a 25 mm parallel plate
35 geometry. The relative humidity was 70 %. The samples were put between the parallel plates for
36 the preliminary tests, then removed and new samples were placed for the curing and the
37 subsequent tests. The preliminary tests consisted of logarithmic sweeps from 10⁻³ % to 100%
38 strain at room temperature, 21 °C, using a 1 Hz frequency. After mixing the components, in the
39 case of the two component systems, the samples were put between the plates and the experiment
40 was immediately launched. About 72 s were needed, after mixing, to place the sample between
41 the parallel plates and launch the experiment. For the curing tests, a multi-frequency setup was
42 used with a 2 mm gap and frequencies of 1, 3 and 10 Hz for all samples. The strain was chosen
43 in each case from the preliminary strain sweep tests. A strain of 0.04% was chosen for S2c,
44 0.42% for T1c and 0.15% for T2c. Axial force adjustment was set to 0 N in compression mode
45 and sensitivity to 0.1 N. A gap change limit was set to 2000 µm in the up and down directions.
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4 The tests were done at room temperature. For S2c and T2c the temperature was 21.0 °C, while
5 for T1c it was 18.6 °C. Once each curing test ended, the cured sample was let in the rheometer
6 for additional testing. Each cured sample was subjected to a temperature scan, but previously a
7 torque sweep was done to identify the viscoelastic linear region and choose a torque amplitude
8 into that region for each temperature scan test. Torque sweep tests consisted of a logarithmic
9 sweep from 10 to 10000 $\mu\text{N}\cdot\text{m}$ at room temperature and using a 1 Hz frequency.
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11 Temperature scan tests consisted of a 1 °C/min heating ramp from room temperature to 110 °C
12 using 1 Hz frequency and the torque amplitude chosen in each case from the torque sweep test.
13 For S2c the torque amplitude was 4000 $\mu\text{N}\cdot\text{m}$. For T1c 1500 $\mu\text{N}\cdot\text{m}$ and for T2c 1600 $\mu\text{N}\cdot\text{m}$. In
14 addition, stress relaxation tests were performed with cured T2c samples at 40 °C and at 90 °C
15 using the rheometer double plate geometry in compression. An axial force of 10 N and a strain of
16 0.18% were applied in both cases.
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20 The thermogravimetric tests were performed on a TA Instruments 2960 SDT apparatus and
21 consisted of 20 °C/min heating ramps from room temperature to 900 °C, using a 100 mL/min
22 purge of air. The samples were allowed to cure at room temperature for 24 h before starting the
23 experiments. Sample sizes were in the 10 to 12 mg range.
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28 **Results and discussion**

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30 Figure 1 shows the heat flow curves obtained isothermally at three different temperatures from
31 sample S2c. These plots resemble the cure behavior of an autocatalytic curing reaction [19–21].
32 That is not strange since strong evidence for the intervention of an autocatalytic reaction was
33 reported for Methyl Methacrylate free radical polymerization [22]. It can be observed how the
34 height of the curing peak increases and the peak time decreases as the curing temperature
35 increases. However, for a fast curing system like this, the peak time can be significantly affected,
36 in a non-controlled way, by the time elapsed from the instant when the two components were
37 mixed to the beginning of the isothermal step into the DSC.
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44 Figure 2a shows the DSC plots corresponding to three heating ramps applied on the isothermally
45 cured samples of S2c. It can be observed a glass transition process followed by an exotherm that
46 corresponds to the residual curing. Table 1 shows how the curing areas, the conversions and the
47 T_g of the resulting material increase with the curing temperature. Additional experiments show,
48 Figure 2b, that the only changes observed in the second scan of isothermally cured samples are a
49 change of slope near 50 °C, which corresponds to the end of the glass transition of the fully cured
50 sample, and a small endothermic peak at about 100 °C, which will be commented below.
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54 Figure 3a shows how, as expected, the curing reaction shifts to higher temperature as the heating
55 rate increases. Figure 3b shows change of slope related to the glass transition is observed at
56 about 50 °C. The glass transition seems to cover a broad range of temperature with a moderate
57 change in the heat flow and, as expected, there is no trace of any residual curing. A segment of
58 the cooling step at 20 C/min was included in Figure 3b to show the reversibility of the
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4 endothermic peak at 100 C, which seems to correspond to a melting process. It is very difficult to
5 observe that peak at a lower heating rate because it is very small and sensitivity decreases when
6 decreasing the heating rate. A trial was done in heat only modulated mode on cooling to
7 demonstrate that it corresponds to a crystallization process. However the intensity of the peak is
8 too weak to be detected in modulated mode, even when using a heating rate of 5 C/min, which is
9 high for modulation. Finally, another experiment was done with a bigger sample at different
10 cooling rates, Figure 3c. It was observed that the size of the peak is maximum at 20 C/min and
11 decreases when increasing or decreasing the cooling rate. That is so because at low cooling
12 rates the process is too slow to be detected by the instrument and at higher cooling rates there is
13 no enough time to crystallize. That melting peak may correspond to any filler or additive which
14 melts around 100 C.
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21 On the other hand, no curing peak was observed in isothermal or on heating with the T1c and
22 T2c adhesives. Figure 4 shows no thermal evidence of the curing reaction for a fresh T1c sample.
23 That is probably so because these adhesives are very slow cure systems. One of them undergoes
24 moisture curing and and, thus, curing is not likely to occur into the DSC cell. The other one
25 contains a booster, which should ensure the curing with some independence of the atmospheric
26 moisture. However, it seems that the the curing heat is released at a very low rate, falling below
27 the sensitivity of the instrument. In SMP adhesives the curing process goes outside inside [23].
28 The type of curing reaction which takes place in the modified silanes involves hydrolysis of the
29 silyl alkoxide which then results in the formation of cohesive siloxane bonds. It is a two-
30 step process. The first step consists of the conversion of alkoxysilane to silanol. The second step
31 may consist of the condensation of -Si-OH and -Si-OR to form siloxane bonds with
32 elimination of ROH, or of the condensation of two -Si-OH with H₂O abstraction. The
33 condensation process is promoted by the surrounding moisture arising from the environment or
34 the substrate onto which the adhesive is applied [24]. However, Figure 4 also shows a melting
35 peak on heating at about 77 °C and its corresponding crystallization exotherm on cooling at 57
36 °C. On the other hand, the T_g is observed at about -67 °C which is an indication of the lowest
37 limit for the rubber-like behavior. The C_p change observed at the glass transition, of about 0.44
38 J/(g °C), corresponds to an amorphous polymer and the melting-crystallization peak probably
39 corresponds to a fire retardant. This kind of experiments were repeated with samples that were
40 previously cured at 40, 45 and 60 % of relative humidity at room temperature for times ranging
41 from 1 to 4 h. But no important change was observed on the glass transition or in the melting
42 process.
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54 Similar experiments to that showed in Figure 4 for T1c, with heating ramps between -85°C and
55 150°C, were done with T2c. No evidence of the curing reaction was observed, what is consistent
56 with being this adhesive moisture curing system. Differently than for T1c, this sample does not
57 show any melting or crystallization process. No glass transition was observed, what, considering
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4 that it is a flexible adhesive with mechanical properties similar to those of T1c, is an indication
5 that its Tg is below -70°C.
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8 Figure 5 shows the rheological signals obtained from the curing of S2c. Gelation was determined
9 making use of the Winter and Chambon criterion [25,26]. Accordingly, gelation is detected as the
10 point where $\tan \delta$ becomes frequency independent. The gelation is observed at 405 s. Since
11 another additional 72 s were needed to place the sample and launch the experiment, the gelation
12 time was about 477 s. Vitrification is observed as a peak of $\tan \delta$ after the gelation. Vitrification
13 is associated to the glass transition due to reaction and occurs when the increasing Tg becomes
14 equal to the cure temperature [27]. On the other hand, the fact that G' is higher than G'' at all
15 times can be related to an important amount of filler. Effectively, a 25% of inorganic filler was
16 determined by TGA, as it can be observed on Fig. 6. It decomposes in the 600-800 °C range with
17 a 42.1 % mass loss, which points to CaCO₃ as a main component of the filler.
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23 Figures 7 and 8 show no trace of gelation for the samples T1c and T2c during the experiment of
24 about 24 hours. However the storage modulus increases up to 0.96 MPa in the case of T1c and
25 up to 1.2 MPa in the case of T2c. The S2c is a more rigid adhesive reaching a storage modulus of
26 4.3 MPa in about 13 minutes. Also, looking at the slopes of the moduli, it is observed that the
27 curing is initially faster for the T2c than for the T1c system. Even more noticeably than in case of
28 S2c, G' is higher than G'' at all times and it can also be related to an important amount of filler.
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32 Fig. 6 shows about a 37.0 % residue at 600 °C for both T1c and T2c. In can be also observed the
33 important effect of the fire retardant on T1c, being the extrapolated degradation onset
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35 temperature 207.6 °C for S2c, 217.7 °C for T2c, and 251.5 °C for T1c. On the other hand, the
36 high starting values of $\tan \delta$, which are decreasing with time, are associated to a continuous
37 increase of viscosity that may come from the fact that this thixotropic material was subjected to
38 shear when applying it between the plates of the rheometer and also from the curing reaction.
39 The relative values of $\tan \delta$ at the three 1, 3, and 10 Hz follow the same order than in the S2c
40 case, Figure 5, before the gelation: $\tan \delta$ at 10Hz > $\tan \delta$ at 3Hz > $\tan \delta$ at 1Hz. In addition, no
41 gelation was observed when manually stirring the system for several minutes open to the air.
42 These two facts together make us think that there is no gelation in these systems.
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47 The thickness contraction along the curing is about 6.5 % for S2c, 0.60 % for T1c and 0.75 % for
48 T2c. Most of the little contraction of T1c took place during the first hour after application while
49 the contraction of T2c is during the curing time and did not stop after 24 h. In about 10 minute,
50 S2c reaches a constant gap but T1c and T2c do not reach a stable thickness in 24 h.
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53 Once the curing experiments ended, the samples were allowed to cool in the rheometer and then,
54 after a torque scan to choose the right torque amplitude in each case, the cured samples were
55 subjected to a temperature scan. Figure 9 shows a clear relaxation for the S2c system in the range
56 from room temperature to 120 °C. That relaxation corresponds to the glass transition and can be
57 observed in G', G'', and $\tan \delta$. It is observed how the Tg changes slightly depending on the
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4 degree of curing. A T_g of 60.2 °C is measured, as the $\tan \delta$ peak, after curing for one hour at
5 room temperature. After 24 h curing at the same temperature that value increases to 62.6 °C,
6 which is very close to that of a fully cured material measured on a second heating scan. It is also
7 observed that the modulus G' practically does not change from the first to the second scan. This
8 indicates that even the material is not fully cured after one hour at room temperature, its
9 mechanical performance as an adhesive is practically the same as if it was fully cured.
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13 Figure 10 shows the storage and loss moduli and $\tan \delta$ of cured T1c and T2c samples. In case of
14 the T2c sample, both the storage and loss moduli are very stable in the range from room
15 temperature to 110 °C. There is no evidence of any important relaxation in that range. This is of
16 interest for applications where changes of temperature are possible. For T1c it can be observed a
17 slow decrease down to 60 °C. A more intense drop of G' is observed from 60 °C to 75 °C. Then,
18 G' remains almost constant. In order to confirm that the relaxation in the 60-75 °C range
19 corresponds to the small melting process and there is no glass transition of some of the
20 components, a modulated temperature DSC (MTDSC) and two relaxation tests were done. The
21 MTDSC experiment was conducted on cooling. Fig. 11 shows that there is an exotherm on
22 cooling corresponding to the crystallization, what is the same observed in standard DSC. But, in
23 addition, we can see that there is practically no change on the reversing heat flow signal. If there
24 was a glass transition, then a change should be observed on the reversing signal as a consequence
25 of the change in heat capacity associated to the glass transition. What we can see is practically no
26 change in heat capacity, and that is compatible with a crystallization process but not with a glass
27 transition. It confirms not only that the peaks on heating and cooling correspond to a melting and
28 crystallization process but also that there is no glass transition in the observed range of
29 temperature.
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34 Fig. 12 shows the plots of G' versus time obtained at 40 °C and 90 °C. It is observed that the
35 relaxation times at temperatures just below and above the transition is about one order of
36 magnitude. However, temperature changes near the glass transition temperature of one degree
37 can shift the relaxation time by decades, corresponding to apparent activation energies that are
38 two or more orders of magnitude larger than the van der Waals bond energy between molecules
39 [28]. Thus, if the transition was a glass transition, the relaxation times should be of very different
40 order.
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50 **Conclusions**

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52 In view of the results obtained with three different adhesives, it seems that in some cases it is
53 very difficult to precisely interpret some rheological events without the complement of DSC
54 data, an also, rheological data are needed to better interpret DSC events. On the other hand, TG
55 informs about thermal stability and complements the other two techniques, which are not needed
56 to interpret the TG data. Thus, in order to address a characterization study of other adhesives,
57 preliminary routine TG test is advisable since it provides the range of temperature at which the
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4 material is stable and the filler content, which is a key factor to understand further thermal and
5 rheological tests. From a practical point of view, when focusing on applications where
6 mechanical performance is a main concern, rheology is indoubtably the key tool for any kind of
7 adhesives. It allows to track the thickness of the adhesive layer and the moduli along the curing
8 reaction, and identifying the the gel point too. It also allows to see the temperature effects on the
9 mechanical properties of the cured material and clearly identify its glass transition. The later is
10 particularly important because some adhesive systems are complex and do not exhibit a clear
11 glass transition in DSC. However, there are some limitations that depend on the rheometer model
12 and options. In this study, it was not possible to perform rheological tests at low temperature with
13 disposable platens. In other cases, measurements of the gap as presented here are not available.

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19 On the other hand, DSC is a more affordable technique that allows to easily reach low
20 temperatures. This is of high interest for flexible adhesives with glass transition far below room
21 temperature. Adhesive systems may contain a number of minor crystalline components.
22 Observed by rheology, the melting of that minor components can produce a drop of the modulus
23 similar to that of a glass transition. In that context, a DSC heat-cool cycle allows to clearly
24 identify a melting-crystallization process. In principle MTDSC can provide an additional insight
25 on cooling, since it allows for separation of the heat flow in its reversing and non-reversing
26 signals. However, the sensitivity associated to the relatively low heating rates required in
27 MTDSC can be too low for minority components. It is clear that DSC is the best way to see the
28 effect of temperature on the reaction rate for exothermic reactions. But that is useless for
29 moisture cure systems like some of the silane modified polymer type where no exotherms are
30 observed.

31 32 33 34 35 36 37 38 **Acknowledgment**

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Table captions

Table 1. Area under the curing peaks displayed on Figure 1. The conversion is calculated by comparing the isothermal areas with that obtained from a 5 °C/min heating ramp. The Tg values were calculated from the curves in Figure 2

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4 **Figure captions**
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7 Fig. 1. Overlay of the DSC plots obtained from S2c at 10, 15, and 20 °C. The curves were
8 horizontally shifted to match the beginnings of the isothermal steps
9

10 Fig. 2. DSC plots obtained in the first scan of temperature of the S2c isothermally cured samples
11 (a). DSC curves obtained in the first and second scans of S2c samples cured at the indicated
12 temperatures (b)
13

14 Fig. 3. DSC plots corresponding to the first linear heating ramp of fresh S2c samples (a), to the
15 second heating of the same samples at the indicated heating rates (b), and to several ramps
16 obtained from a 35.5 mg sample at the indicated cooling or heating rates (c)
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18

19 Fig. 4. DSC plots corresponding to the heat-cool-heat cycle of a fresh T1c sample
20

21 Fig. 5. Isothermal curing of S2c at 21 °C
22

23 Fig. 6. TG curves obtained from cured samples of the three adhesives in air
24

25 Fig. 7. Isothermal curing of T1c at 18.6 °C
26

27 Fig. 8. Isothermal curing of T2c at 21 °C
28

29 Fig. 9. Temperature scan tests performed in the rheometer with S2c samples cured in different
30 conditions: 1 h at room temperature, the same sample after the first temperature scan, and
31 another sample cured at room temperature for 24 h
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33 Fig. 10. G' , G'' and $\tan \delta$ plots obtained in a 1°C/min temperature scan from T1c and T2c cured
34 samples
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36 Fig. 11. MTDSC plots obtained from the T1c sample on cooling
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38 Fig. 12. Relaxation curves obtained from the T1c sample at 40 and 90°C
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Figure 1

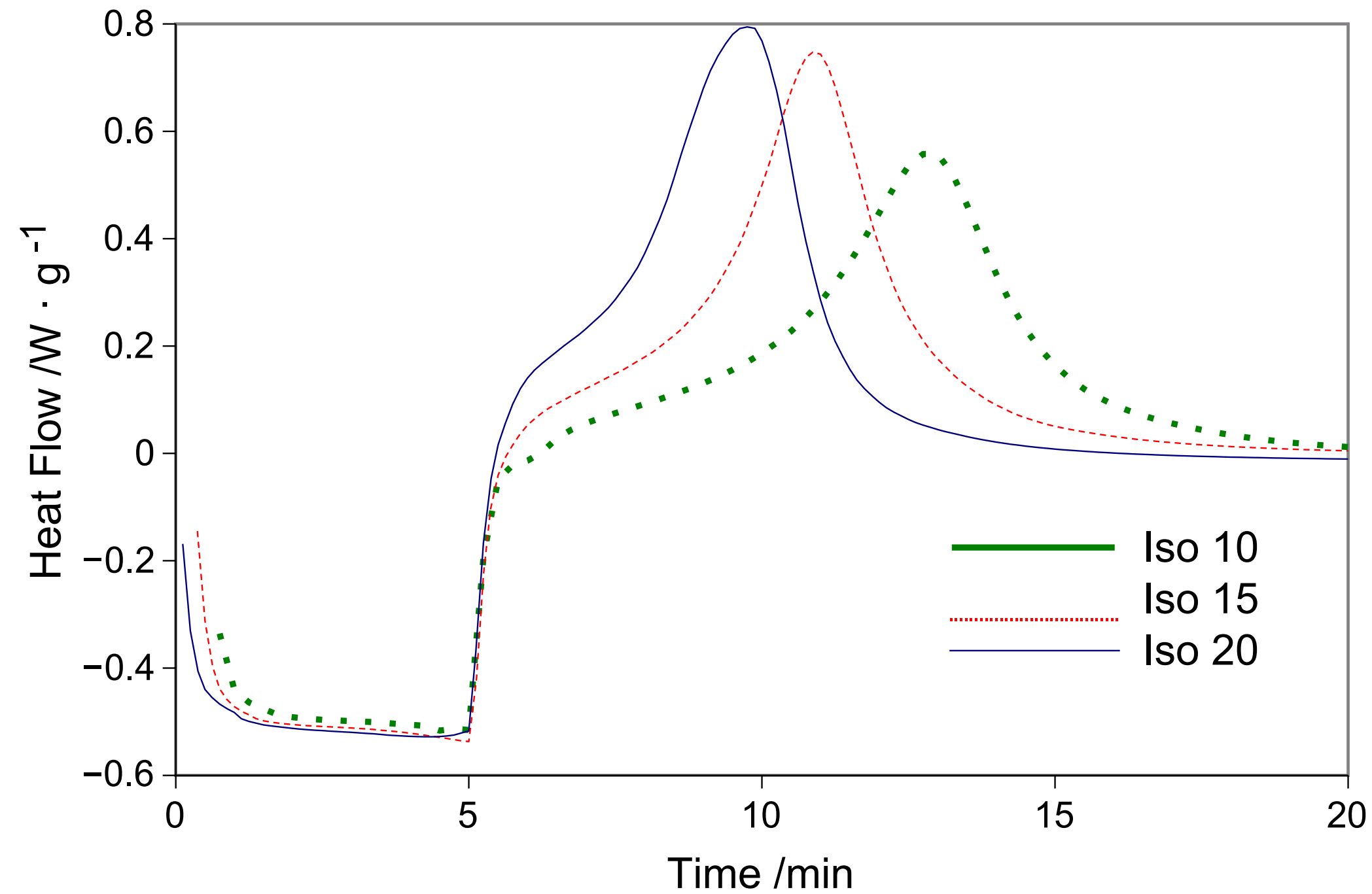


Figure 2a

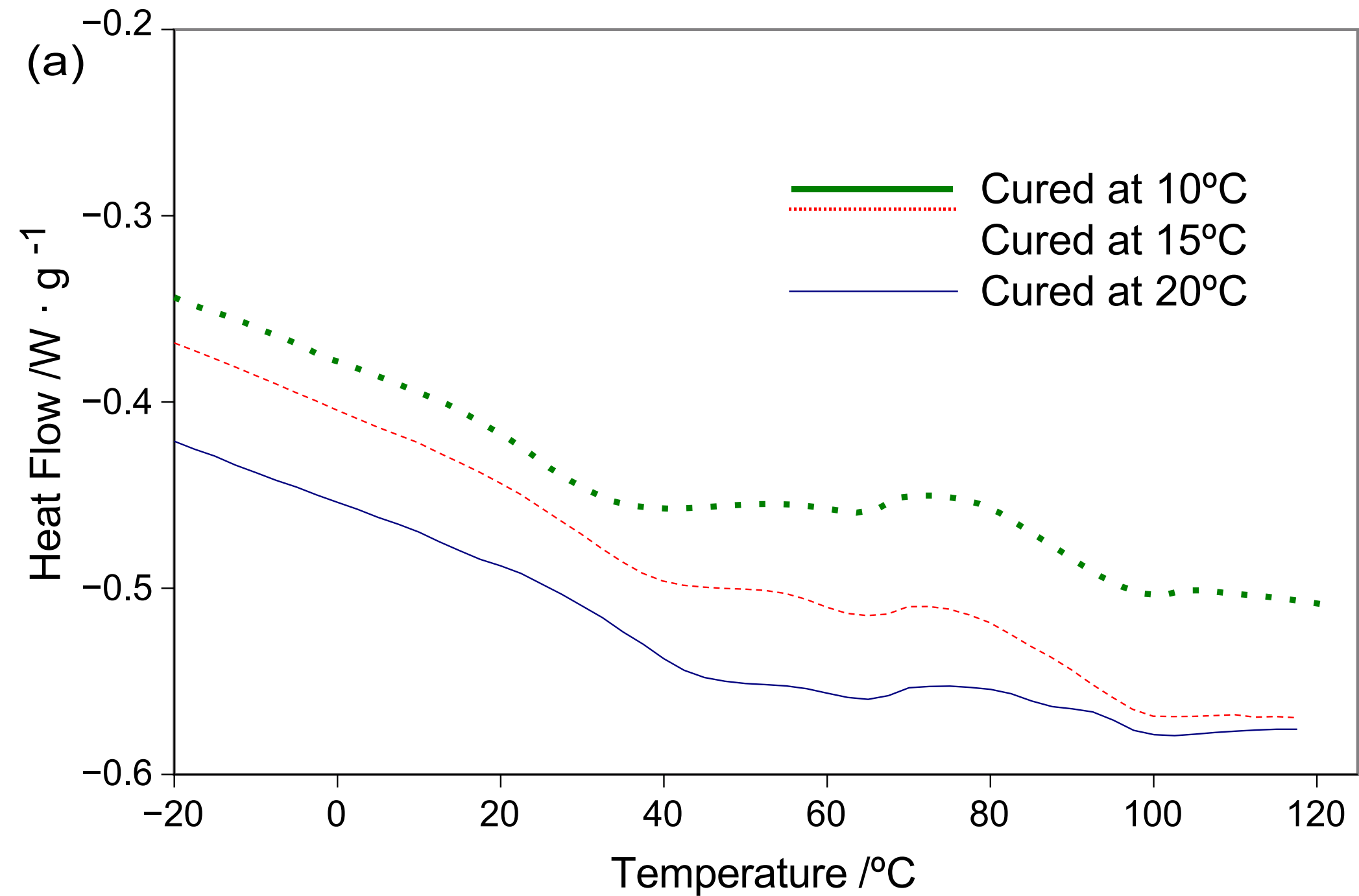


Figure 2b

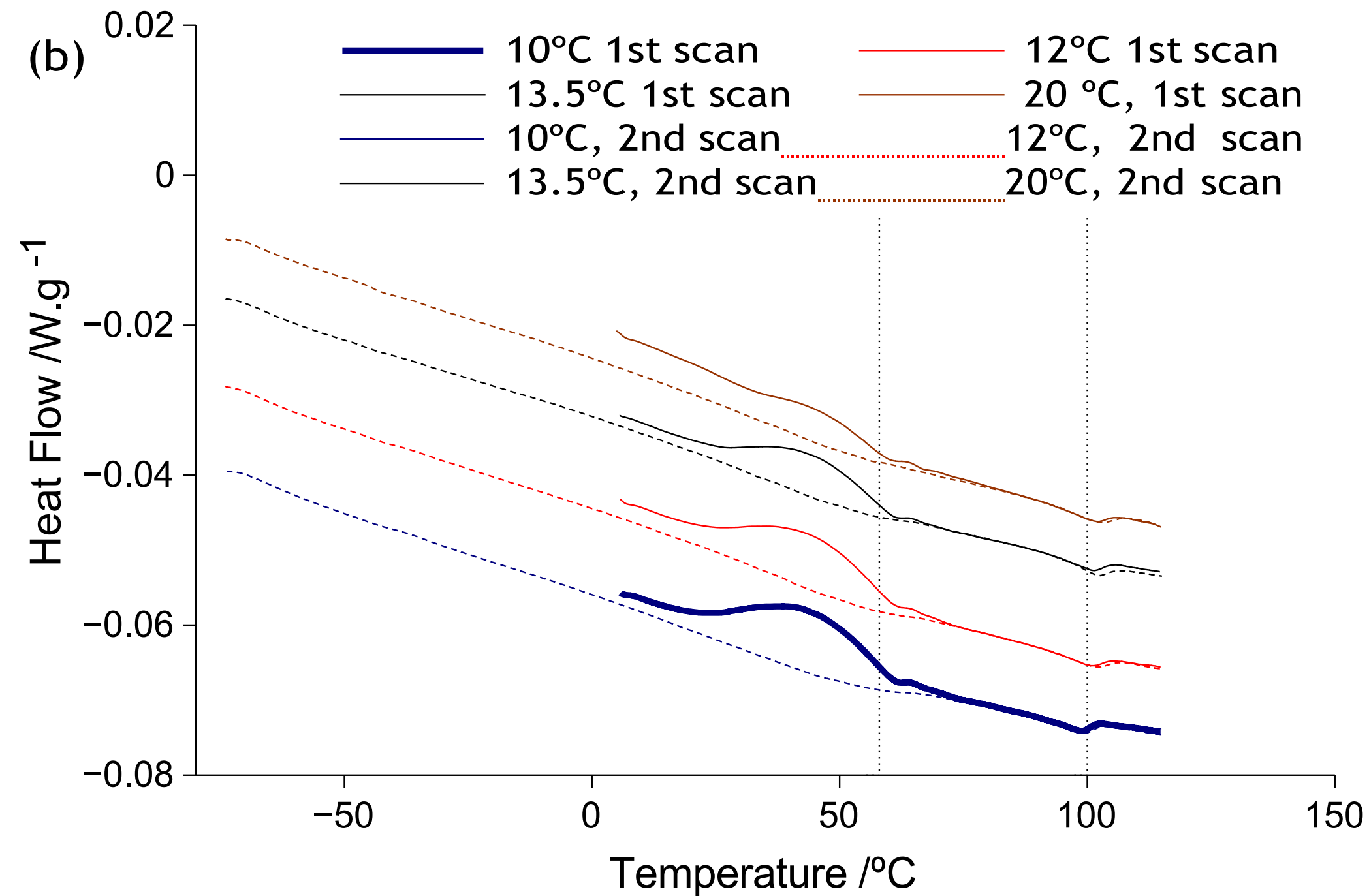


Figure 3a

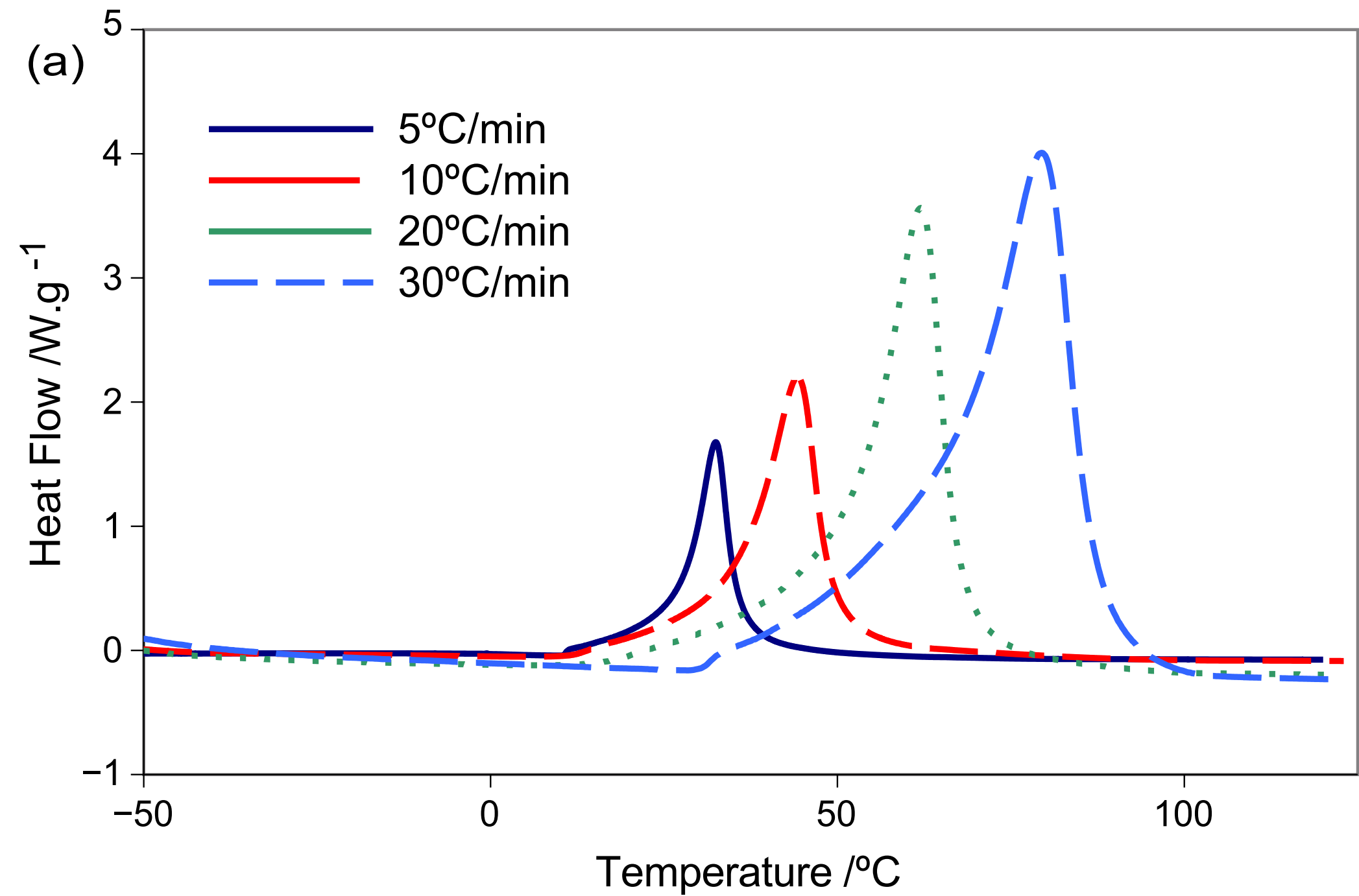


Figure 3b

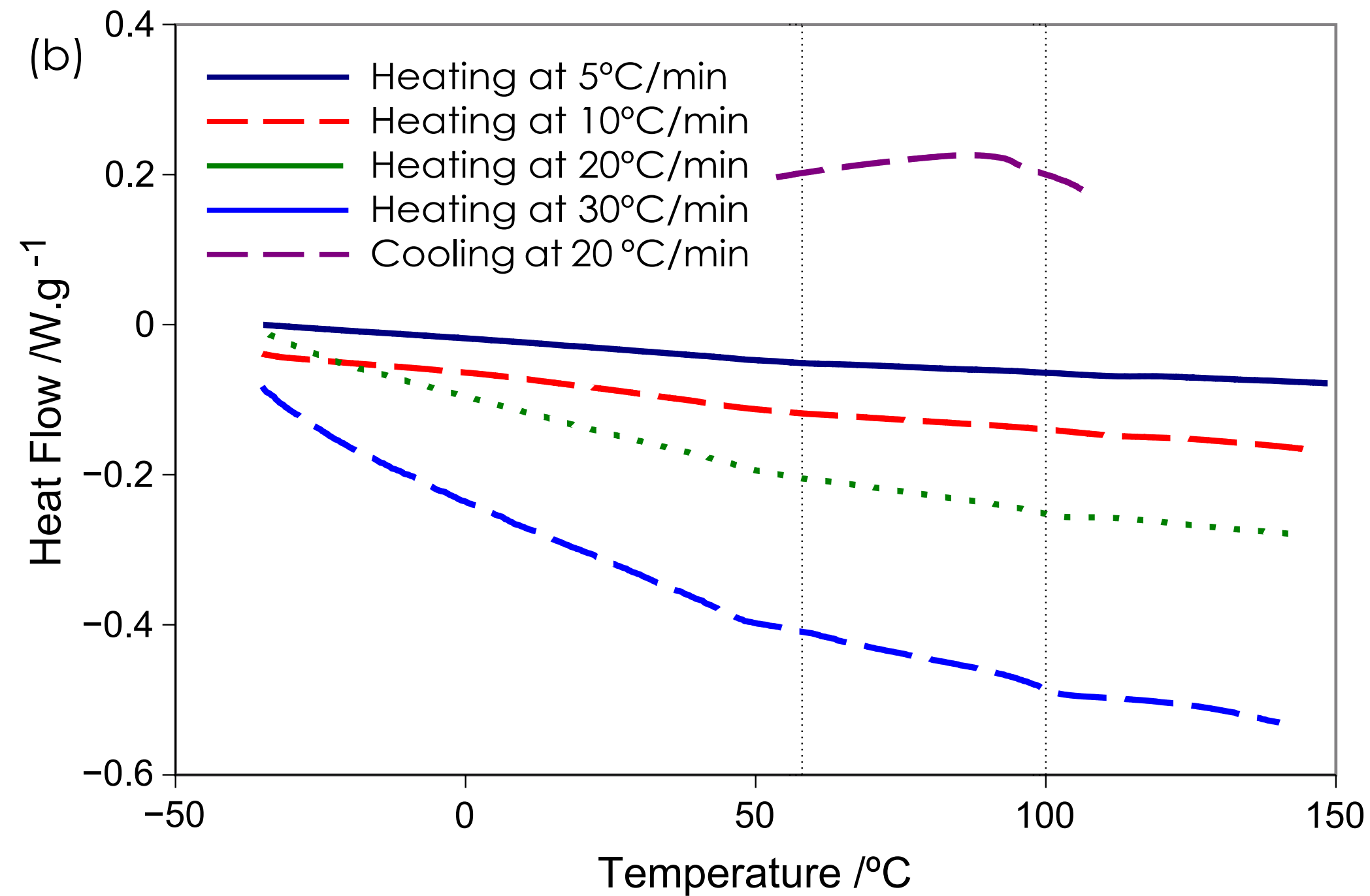


Figure 3c

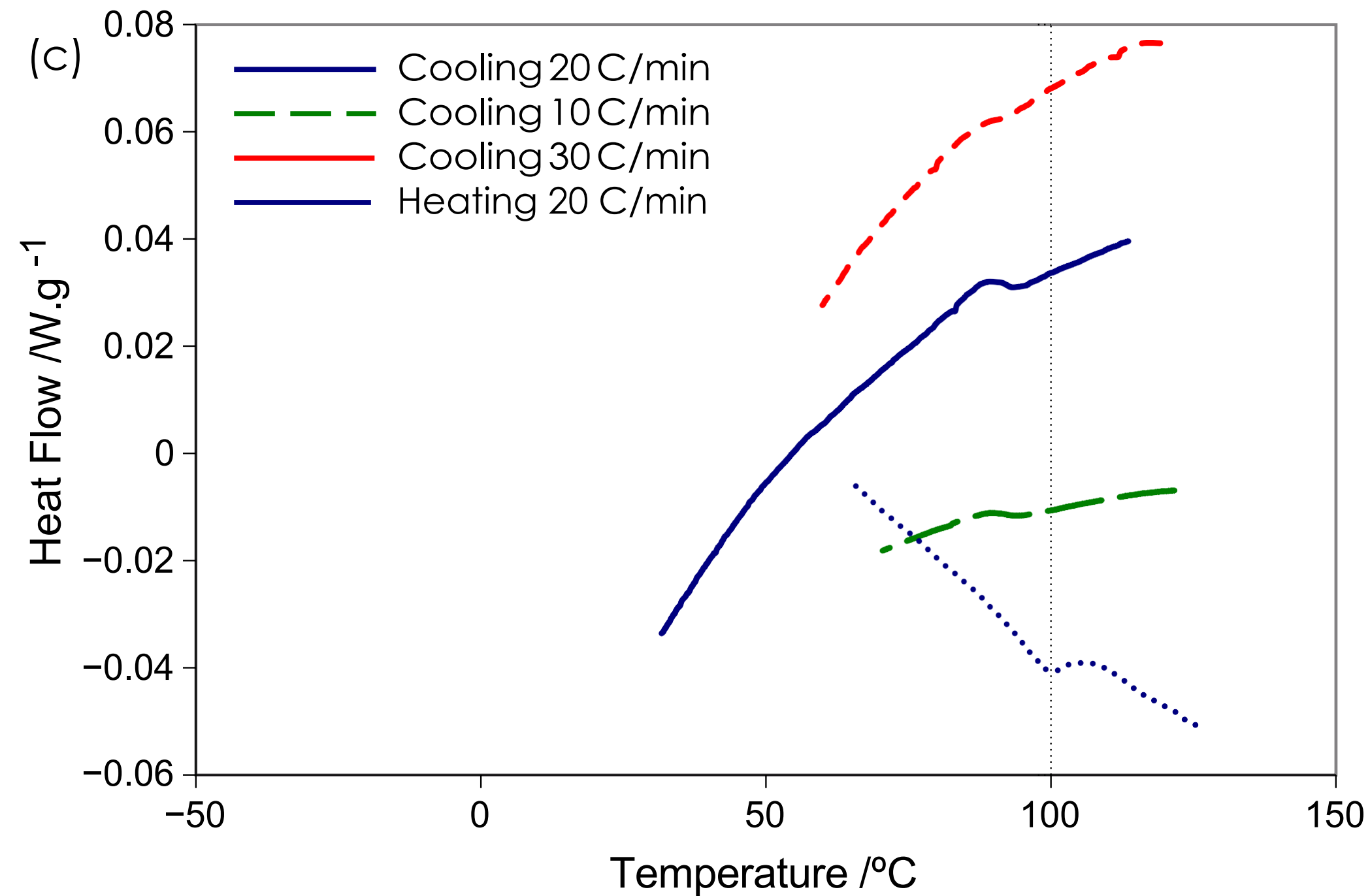


Figure 4

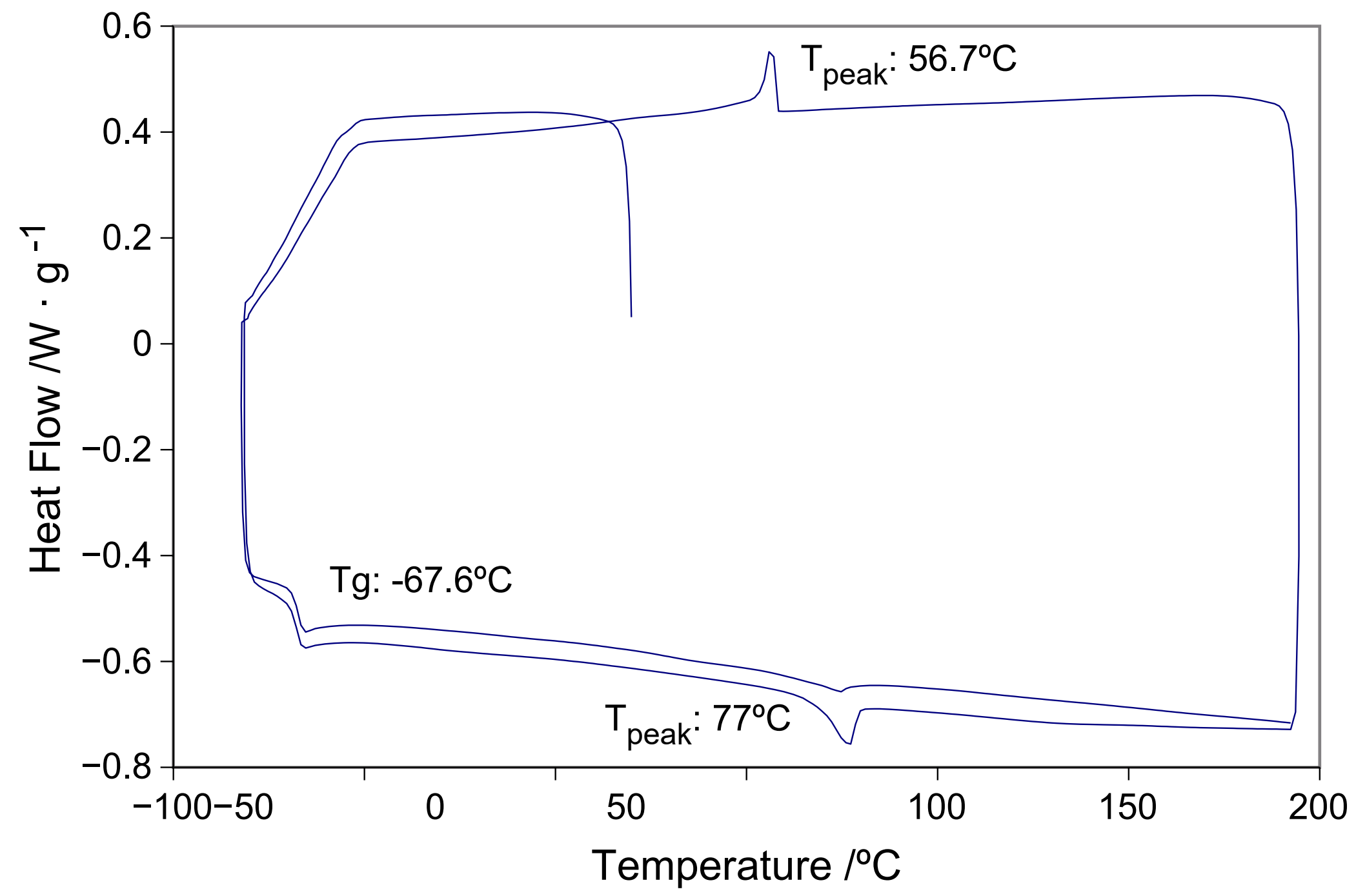


Figure 6

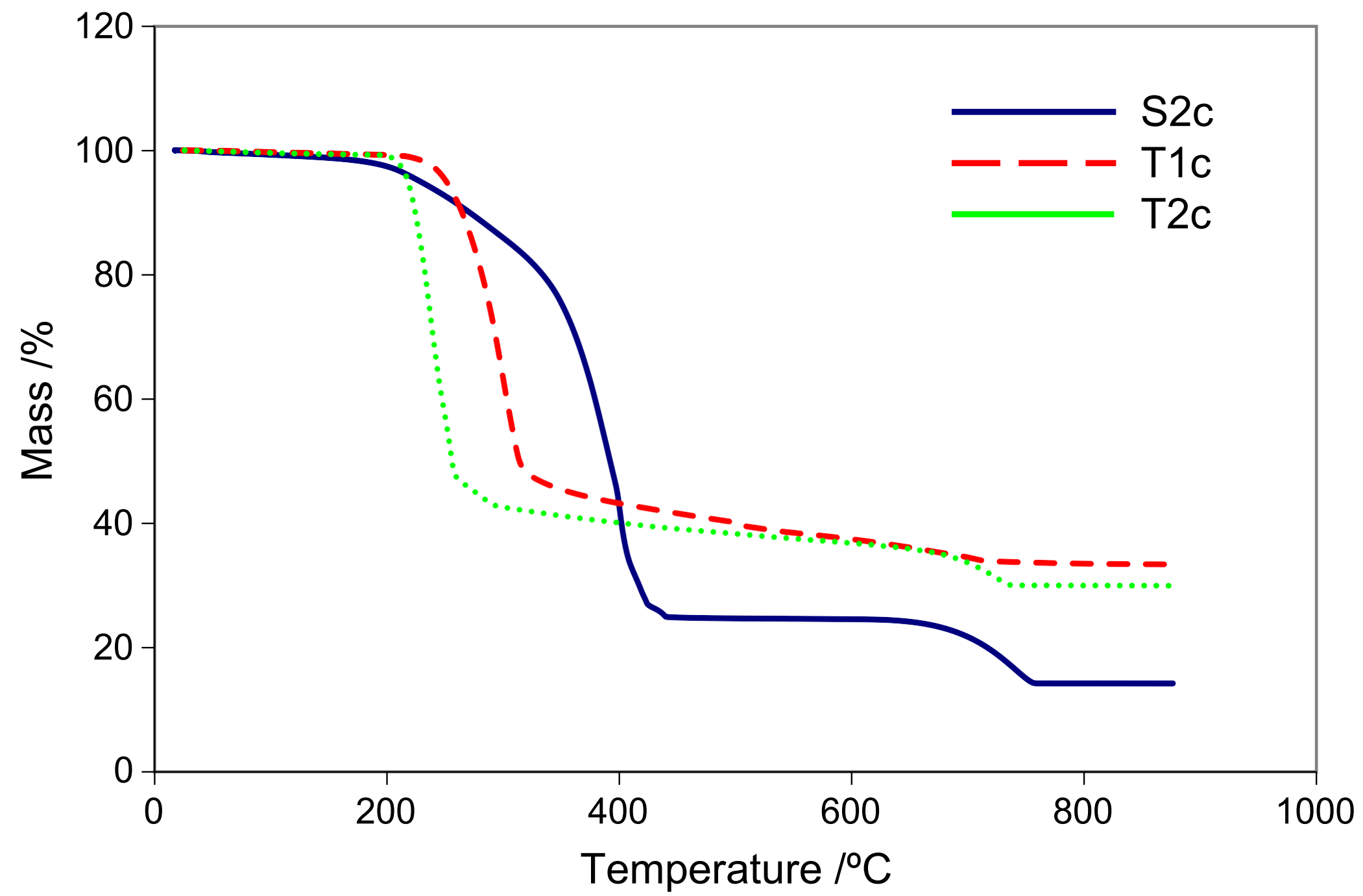


Figure 7

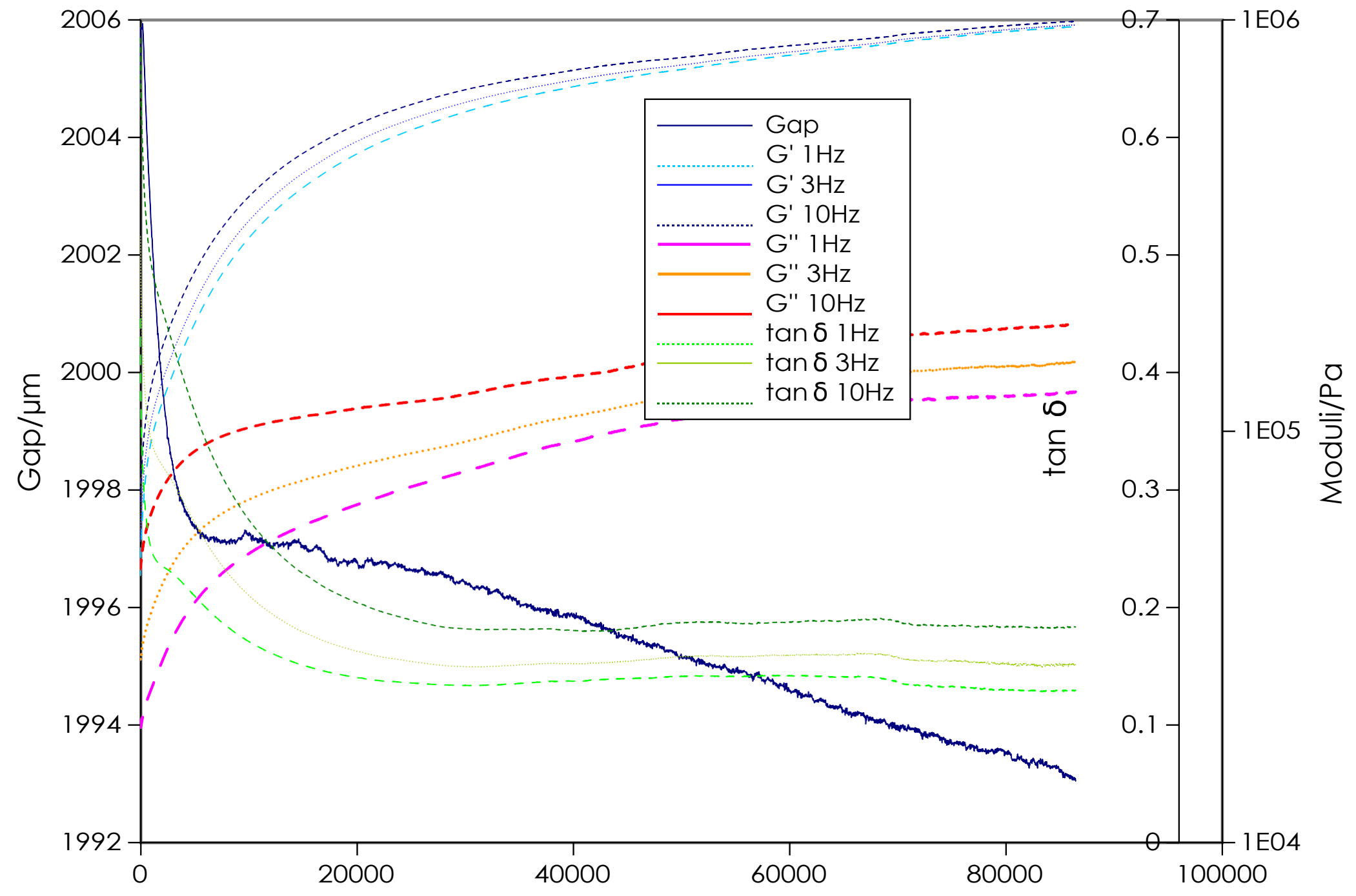


Figure 8

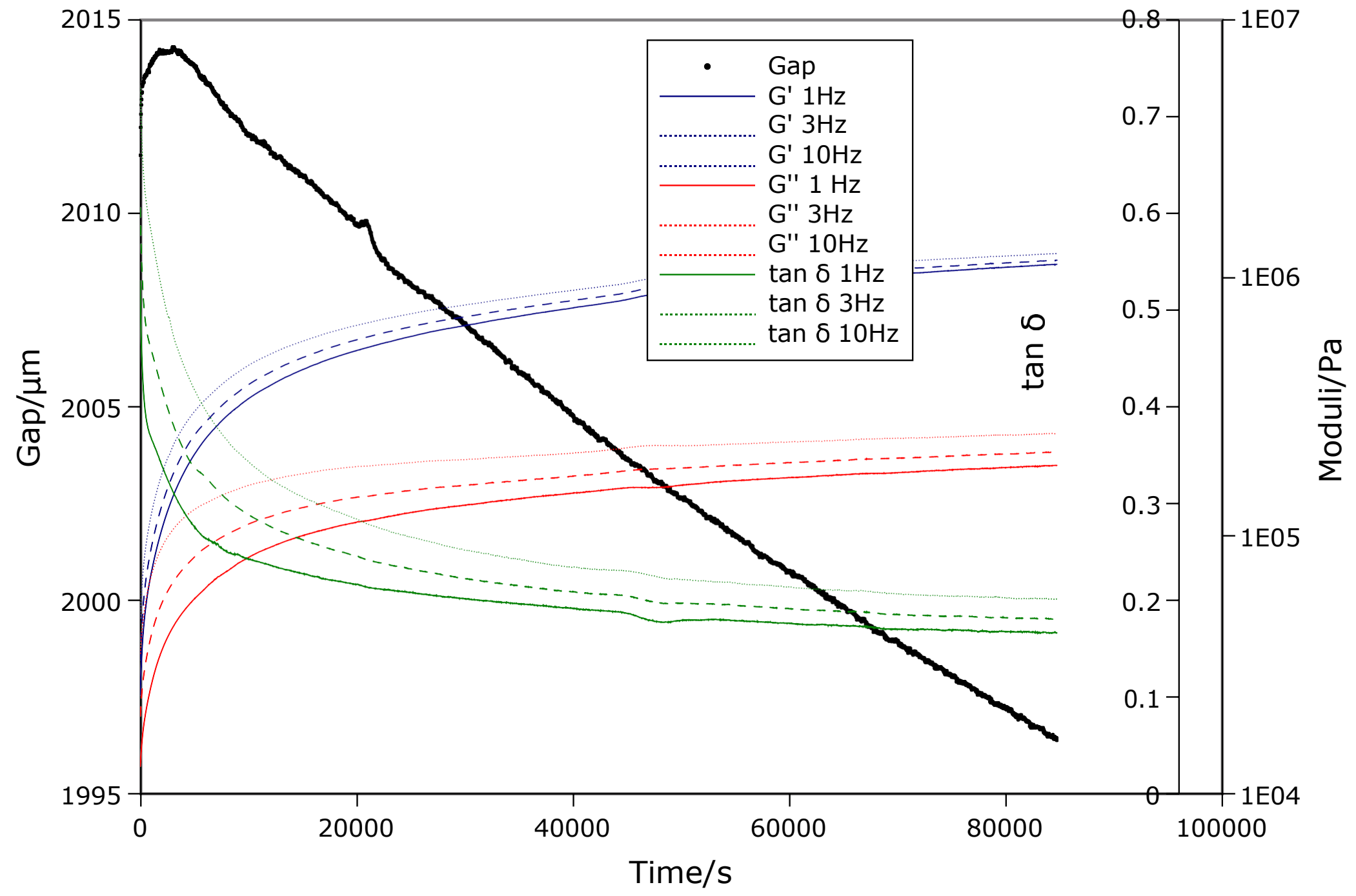


Figure 9

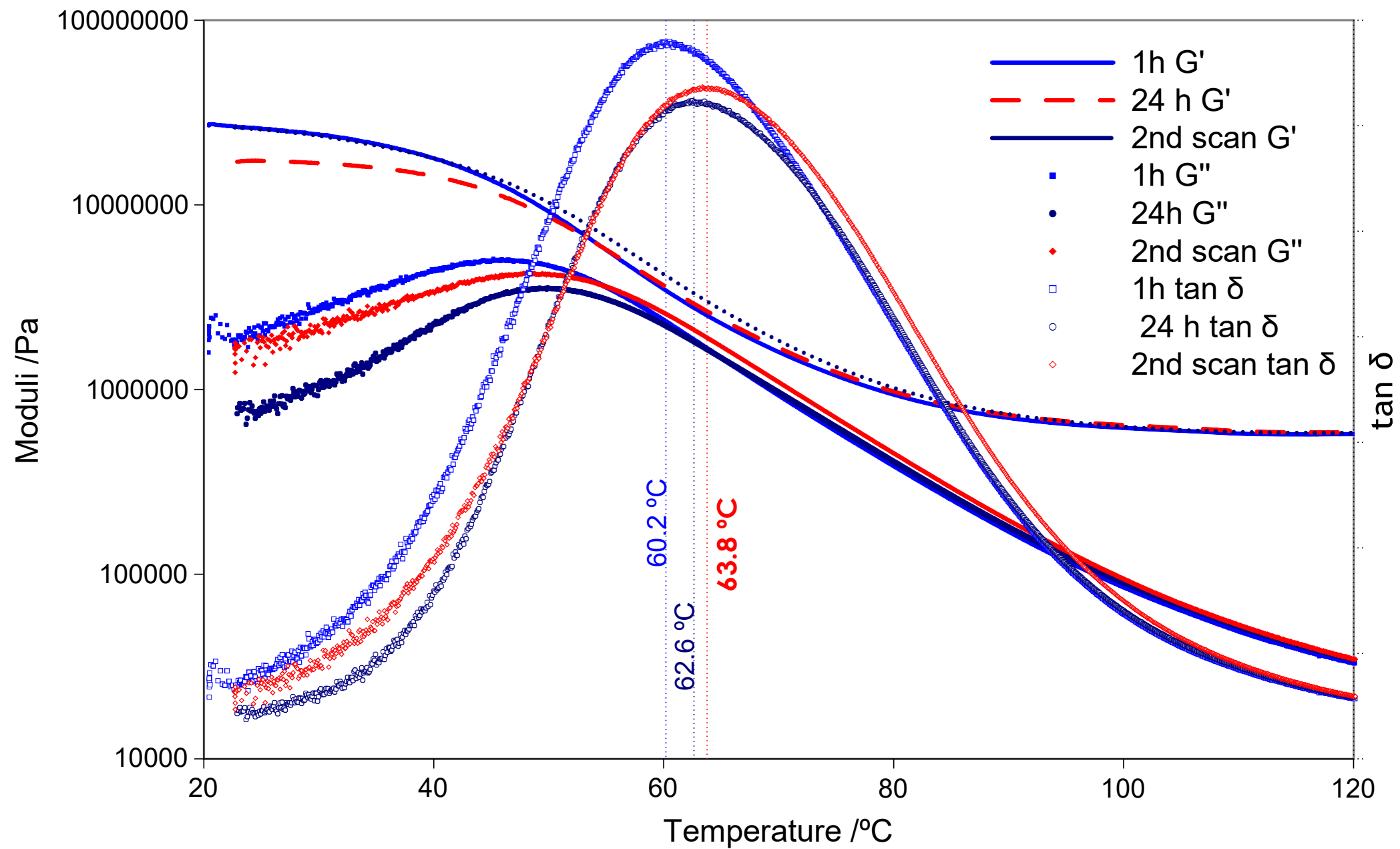


Figure 10

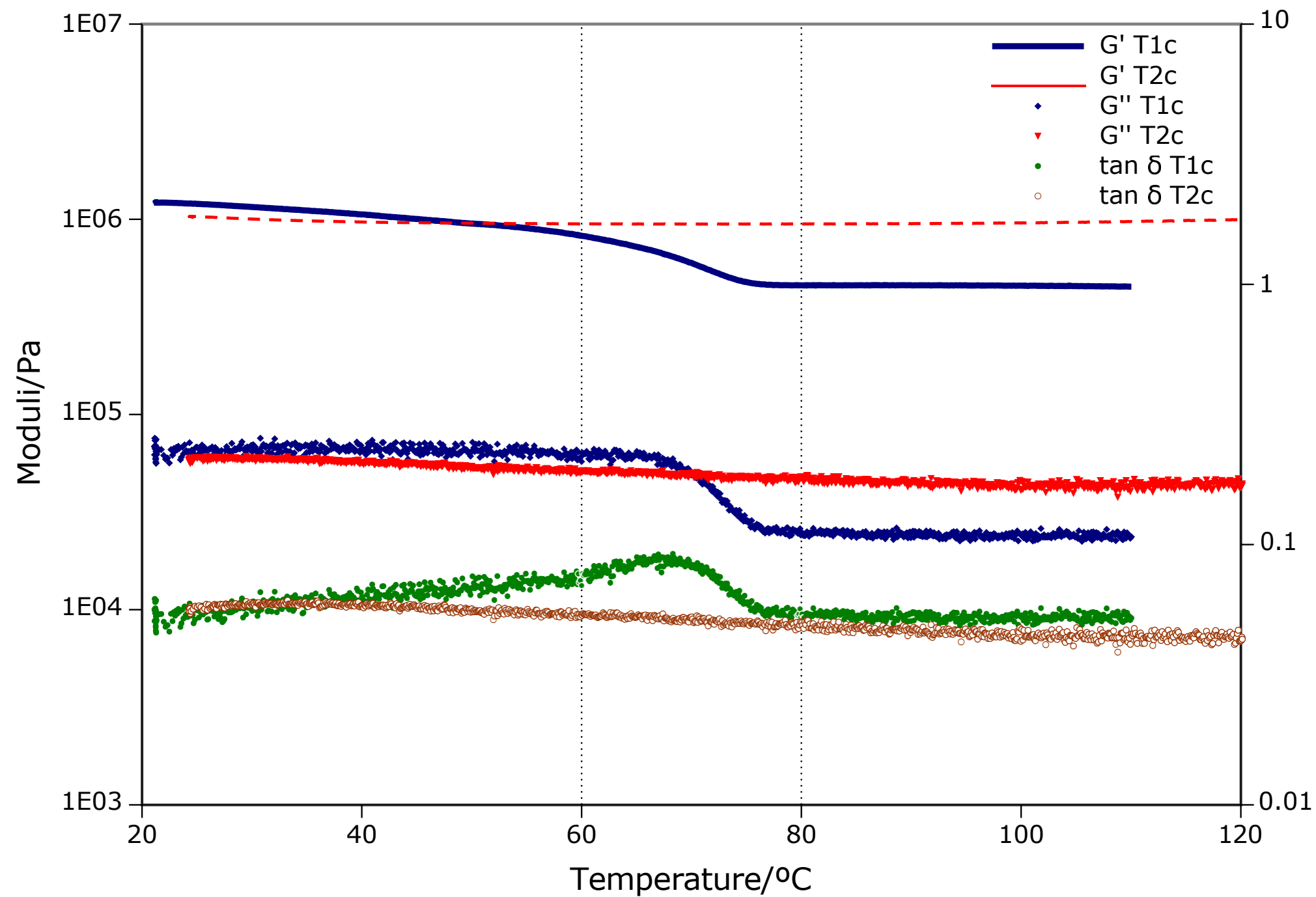


Figure 11

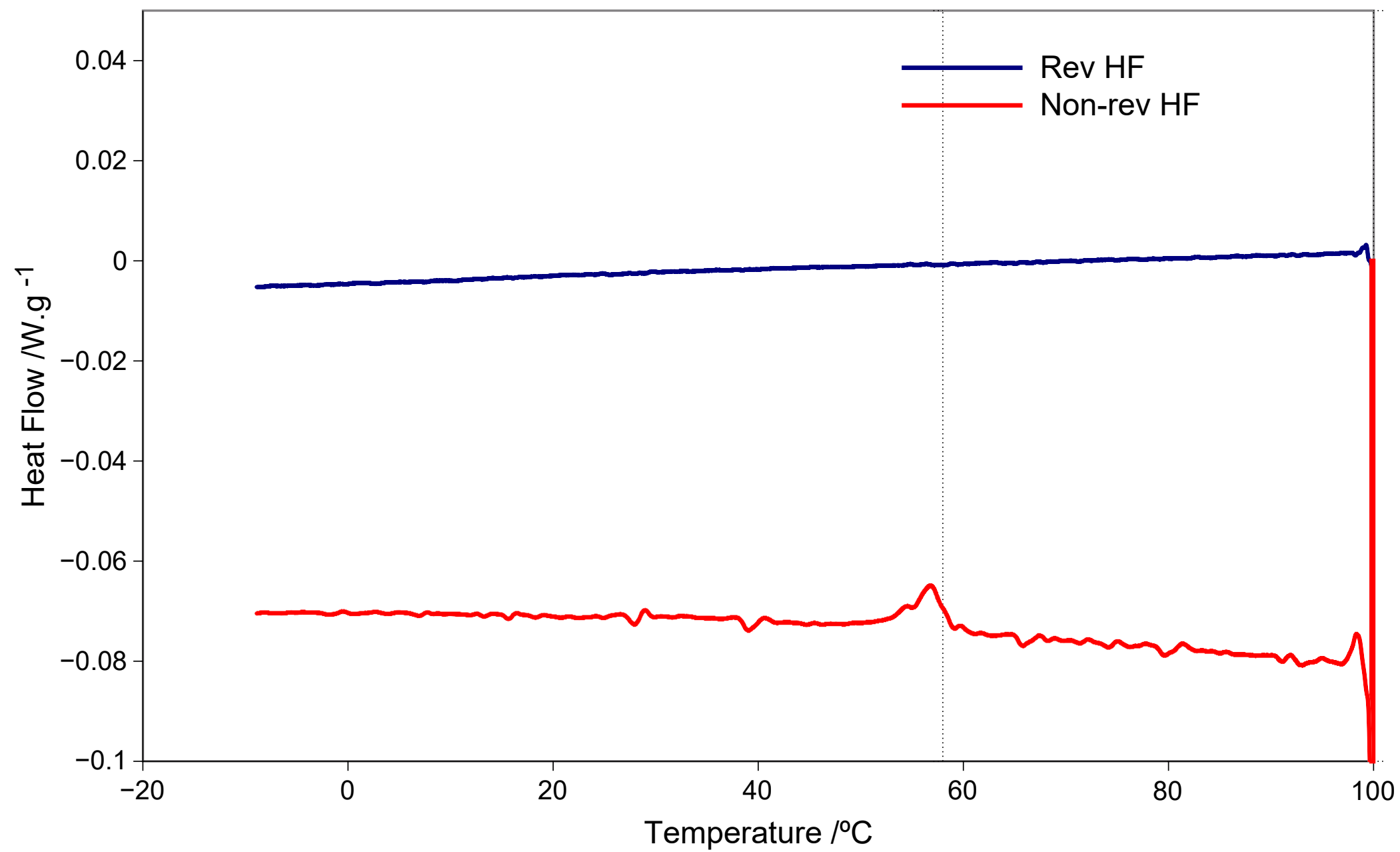


Figure 12

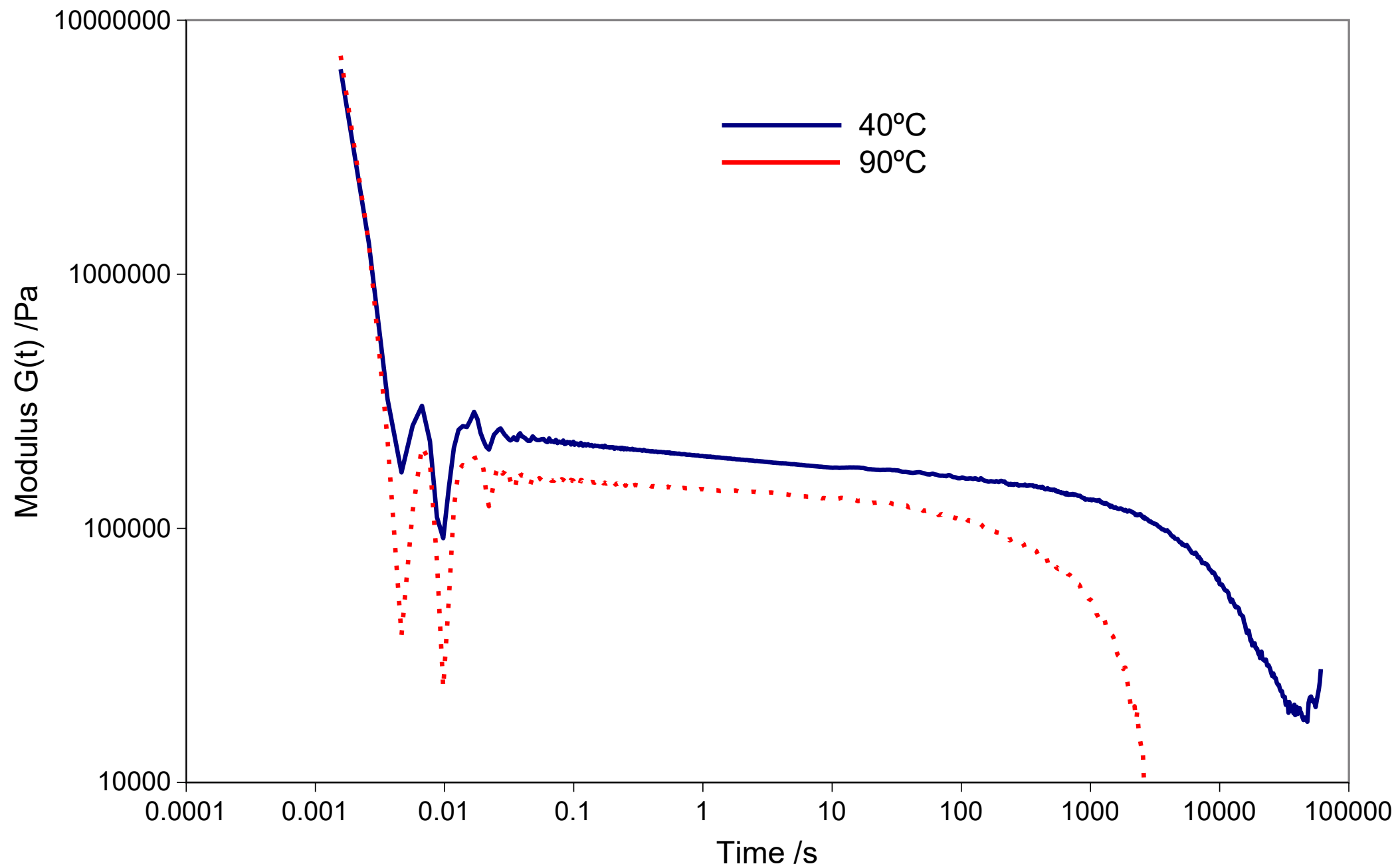


Table 1

| | Curing area /J·g ⁻¹ | Conversion /% | Tg at inflection /°C |
|--------------|-----------------------------------|------------------|-------------------------|
| Iso at 10 °C | 162.1 | 85.3 | 24.69 |
| Iso at 15 °C | 166.0 | 87.4 | 30.58 |
| Iso at 20 °C | 169.5 | 89.2 | 35.09 |