Composite Interfaces
Investigation of the interfacial interactions in epoxy nano-composites filled with functionalized graphene based fillers.
--Manuscript Draft--

<table>
<thead>
<tr>
<th>Full Title:</th>
<th>Investigation of the interfacial interactions in epoxy nano-composites filled with functionalized graphene based fillers.</th>
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<tr>
<td>Manuscript Number:</td>
<td>TCOI-2018-0048R1</td>
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<tr>
<td>Article Type:</td>
<td>Original Article</td>
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<tr>
<td>Abstract:</td>
<td>This work discusses the investigation of filler-matrix interfacial interactions in epoxy matrices filled with different loadings of graphene based fillers - graphene oxide (GO) and n-butylamine functionalized graphene oxide (GO-ButA). To probe whether the matrix cure reactivity has any influence on these interactions, two different curing agents have been used - a polyetheramine based and an aliphatic amine based to process the nano-composites. Interfacial interactions have been extensively investigated using rheology, DMA and fractographic analysis. As a complementary technique for a better understanding of these interactions, the use of dielectric spectroscopy has been explored. Rheology and dielectric spectroscopy confirm the fillers' participation in the cure reaction. DMA and fractography show strong interfacial interaction signatures in the slow curing polyetheramine epoxies. The fast curing aliphatic amine epoxies are found to be less amenable in promoting these interactions. However, the filler dispersion quality is observed to be fairly impervious to the curing agent used. Besides surface functionalities of the fillers, the interfacial interactions are seen to be influenced by factors like cure reactivity of epoxy matrices too. Interestingly the thermal stability of the nano-composites is found to be influenced cumulatively by the interfacial interactions and the thermal stability of the fillers.</td>
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<tr>
<td>Order of Authors:</td>
<td>Souvik Chakraborty, M.Tech.</td>
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<td>Michel Barbezat, Ph.D.</td>
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<td>Giovanni Pietro Terrasi, Ph.D.</td>
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<td>Response: The reference list has been modified to accommodate suggested references.</td>
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<td>2.In page 13, line 290: The authors claimed reagglomeration in GO-ButA 0.50wt% leads to earlier development of elastic properties (i.e. faster curing). The logic is not so straight forward. What interaction does agglomeration affect to increasing curing speed?</td>
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<td>Response: From published literature it can be unequivocally said that graphene based materials are much stiffer than epoxy matrices reported here. Based on the fractographic analysis and the evolution of G' (from rheology) as well as dielectric data during isothermal cure, it is clear that the fillers (GO-ButA at 0.50 wt%) reagglomerate with time during cure. As this statement was made in the section about fractography, we reformulated and moved it at the end of section 3.5.1 lines 407-413 for more clarity. Text is highlighted in blue.</td>
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<td>In this particular case we don't mean an increase of curing rate that would be induced by changes in chemical reaction or acceleration due to temperature. In fact we</td>
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anticipate the formation of a percolation network due to this reagglomeration tendency during cure that would lead to localized concentration of stiffer material in an otherwise softer matrix. This is what we have now tried to better formulate at the new location. We have also modified the conclusion section line 533-534 (highlighted in blue) in consistent with our explanation. For the convenience of readers, we have modified Figure 6 (SEM fractography) to include the filler details as well as the curing agent used in each case. This image is being uploaded along with the revised version.

3. It would be much better to including some investigation of how GO and GO-ButA interact with epoxy as well as the curing agent at the molecular level. Specify what the interfacial interaction really is, chemical or physical, what n-Butylamine functionalization contribute to this interaction, and why poor interfacial interaction between GO and Sial-DETA cured epoxy.

Response: We appreciate the reviewer’s suggestion in this regard. The Pre-gel regions from rheology and the dielectric measurements confirm the presence of interfacial interactions leading to earlier cure in filled epoxies with Sial T-403 as the curing agent. These in-situ reactions are expected to be chemical in nature (Zhu et.al. Polymer, 2010, 51, 2643-2651). This is because during isothermal cure (at 80°C), the abundant epoxy groups present in both the resin and GO can react with the amine based curing agent. On the other hand, the amine and amide bonds present in GO-ButA (Chakraborty et.al. RSC Advances, 2016, 6, 67916) can also interact with the epoxy groups in the resin during isothermal cure forming ternary amine and amides. Given the improved dispersion stability observed at RT with GO-ButA (Chakraborty et.al. RSC Advances, 2016, 6, 67916) this is the most likely scenario at elevated temperatures. However, with increased filler loading, the n-butylamine chains present on GO-ButA would sterically hinder the interaction with the long epoxy molecules present in the resin. This would lead to a percolation tendency causing local dispersion heterogeneity (variable ε'' profile in dielectric spectroscopy) responsible for the anomalous evolution of G’ (in rheology) resulting in agglomerated fillers in the cured composites (SEM micrograph, Figure 6e). On the other hand, the faster cure reaction in the Sial DETA cured epoxies (Section 3.1 and 3.5.2 of the manuscript) limits the interaction time and thus the interfacial interaction.

The above explanation has been included in the manuscript in lines 460-475 (highlighted in blue). However, investigation into such studies were beyond the scope of this current project and hence was not pursued further.

4. There is no data provided for GO-ButA as the filler and Sial-DETA as the curing agent. I would appreciate if the author can include it in the SI even if the result may not be reasonable or hard to explain.

Response: From our previous work (Chakraborty et.al. RSC Advances, 2016, 6, 67916) it is clear that the GO-ButA has a more complex structure than GO. Given the curing speed of Sial-DETA where GO doesn’t have sufficient time to interact with the matrix components, it is highly unlikely that GO-ButA would be anything different. Further, we did not find any observable difference in the nano-composite performance with GO as fillers in this reactive epoxy system. Hence we stopped our planned tests with GO-ButA as fillers in Sial-DETA cured epoxies.
Figure 1: Graphical representation of Tg onset (°C), shown here for a neat Sial T-403 (45.5 phr) cured epoxy system.
Figure 2: First run of the non-isothermal DSC thermographs for neat epoxy systems cured with Sial T-403 (45.5 phr) and Sial DETA (11.1 phr). The enthalpy change ($\Delta H$, $\Delta H = -378 \text{ J/g}$, $T_p = 144.3 \degree C$) and ($\Delta H$, $\Delta H = -496 \text{ J/g}$, $T_p = 109.2 \degree C$) are shown.
Figure 3: Graph showing the behavior of different samples over time at temperatures ranging from 25 °C to 80 °C. The graph plots log G' and log G'' (Pa) against time (min). The curves represent different samples:
- Sial T-403, G'
- Sial T-403, G''
- Sial DETA, G'
- Sial DETA, G''

Key observations:
- G' and G'' values are shown on a logarithmic scale.
- The graphs indicate changes in material properties with temperature and time.
Figure 4: Evolution of a) G
Figure 4: Evolution of a) $G$
Figure 5: Evolution of G
Figure 6: Fracture surface SEM micrographs showing the dispersion quality of the fillers in nano-composites. Sial T-403 cured systems: a) GO 0.25wt%, b) Magnified
Figure 7: Variation in Er

The graph illustrates the variation in electrical modulus (δE') as a function of filler loading (wt%) for different samples. The x-axis represents the filler loading in weight percent (wt%), while the y-axis shows the δE' rubbery (%). Different lines represent different samples:

- GO, Sial T-403
- GO-ButA, Sial T-403
- GO, Sial DETA
- Neat Epoxy

The graph shows how the δE' rubbery value changes with varying filler loadings for each sample.
Figure 8: Variation of the dielectric losses ($\varepsilon''$, imaginary part of the complex permittivity) over the measurement frequency range for the a) neat Sial T-403 cured epoxy and
Figure 9: Variation of the dielectric loss spectra ($\varepsilon''$, imaginary part of the complex permittivity) over the measurement frequency range in the a) neat Sial T-403 cured
Figure 10: Variation of the dielectric loss spectra ($\varepsilon''$, imaginary part of the complex permittivity) over the measurement frequency range for the a) neat Sial DETA cured.
Figure 11: TGA spectra of Sial T-403 (45.5 phr) cured epoxy nano-composites with a) GO and b) GO-ButA as fillers.
Figure 11: TGA spectra of Sial T-403 (45.5 phr) cured epoxy nano-composites with a) GO and b) GO-ButA as fillers.
Figure 12: TGA spectra of Sial DETA (11.1 phr) cured epoxy nano-composites.
Interfacial interaction indicator $\rightarrow \delta E'$ in rubbery region

Graphical Abstract

Sial T-403 cured epoxies

Sial DETA cured epoxies

- GO, Sial T-403
- GO-ButA, Sial T-403
- GO, Sial DETA
- Neat Epoxy

Filler Loading (wt%)
Supplementary Information

Investigation of the interfacial interactions in epoxy nano-composites filled with functionalized graphene based fillers.

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S1. Repeatability of the Dielectric Measurements

To discuss the repeatability of the dielectric measurements a few spectra of the nano-composites are presented in Fig. S1. With Sial T-403 the spectra after the 80°C cure cycle is displayed because the postcure is seen to not influence the dipolar spectra. With Sial DETA cured samples the spectra at the end of the measurement (after postcure) is chosen for comparison as a down-shift of the loss spectra is observed after completion of first cure cycle. The full measurement spectra (Freq range: 0.5 – 10⁶Hz) are shown irrespective of the observed noise below 10 Hz. The sample temperature is 25°C in all the cases. Except for the highest loading at 0.50wt% (with GO-ButA, Fig. S1c) the measurements show good repeatability independent of the epoxy matrix considered. This can be a combination of local dispersion heterogeneity as well as the filler reagglomeration tendency as has discussed in the article.
Fig. S1: Test of repeatability of the current method. a) – c) Samples cured with Sial T-403 (45.5 phr) and d) sample cured with Sial DETA. Filler types and loading is mentioned in the legends. Temperature: 25°C.

S2. Differential thermogravimetric (DTG) plots
Fig. S2: The differential thermogravimetric plots (DTG) of Sial T-403 cured epoxies filled with a) GO and b) GO-ButA at different filler loadings and c) Sial DETA cured epoxies are shown. The insets show magnified DTG peaks.
Investigation of the interfacial interactions in epoxy nano-composites filled with functionalized graphene based fillers.

Souvik Chakraborty\textsuperscript{1} \textsuperscript{S}, Michel Barbezat\textsuperscript{2} \textsuperscript{*}, Eduardo Cuervo Reyes\textsuperscript{3} \textsuperscript{SS}, Amit K. Chakraborty\textsuperscript{1} and Giovanni P. Terrasi\textsuperscript{2}

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Abstract

This work discusses the investigation of filler-matrix interfacial interactions in epoxy matrices filled with different loadings of graphene based fillers - graphene oxide (GO) and n-butylamine functionalized graphene oxide (GO-ButA). To probe whether the matrix cure reactivity has any influence on these interactions, two different curing agents have been used - a polyetheramine based and an aliphatic amine based to process the nano-composites. Interfacial interactions have been extensively investigated using rheology, DMA and fractographic analysis. As a complementary technique for a better understanding of these interactions, the use of dielectric spectroscopy has been explored. Rheology and dielectric spectroscopy confirm the fillers' participation in the cure reaction. DMA and fractography show strong interfacial interaction signatures in the slow curing polyetheramine epoxies. The fast curing aliphatic amine epoxies are found to be less amenable in promoting these interactions. However, the filler dispersion quality is observed to be fairly impervious to the curing agent used. Besides surface functionalities of the fillers, the interfacial interactions are seen to be influenced by factors like cure reactivity of epoxy matrices too. Interestingly the thermal stability of the nano-composites is found to be influenced cumulatively by the interfacial interactions and the thermal stability of the fillers.

Keywords: Epoxy nano-composites, Interfacial interaction, Rheology, Dielectric spectroscopy, Thermogravimetric analysis.

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1. Introduction

Epoxy resin is one of the most common thermosetting resins used in industry, which is expected to reach a global market size of USD 8.77 billion by 2021 [1]. However, epoxy matrices are inherently brittle with poor crack resistance. To overcome this shortcoming, researchers over the past few decades have tried to toughen epoxy matrices with pristine as well as with functionalized derivatives (in some cases) of fillers like silica, clay, carbon nanotubes (CNTs) and more recently with graphene [2]. Researchers have also tried to exploit the excellent mechanical, thermal and electrical properties of these carbon nano-materials (CNTs and graphene) to tailor the properties of polymer matrices, which can have potential use in a number of applications [3-11]. In case of epoxy toughening with carbon nano-particles, it has often been observed that the functionalized derivatives of CNT and graphene are more effective than their pristine counterpart when used as fillers [2]. One of the main reasons for this has been argued to be the improved filler-matrix interfacial interaction. This paper is primarily dedicated to investigating the interfacial interactions in epoxy nano-composites with an insight into the filler dispersion quality as well. Conventionally, researchers have used several techniques to study these interactions like with dynamic mechanical analysis (DMA) [12] and fractographic analysis [13] on the final cured composite as well as rheological studies for in-situ measurements [14]. However, a consensus on a particular experimental technique to understand and/or detect the interfacial interaction in epoxy nano-composites is still absent. Herein, these interfacial interactions are discussed using the conventional experimental techniques as mentioned above are used. As a complementary technique we have used dielectric spectroscopy during cure with the same objective. Rheology [15,16] and dielectric [17,18]
studies have been used earlier to monitor the cure of epoxy systems. However, the conjugation of these two to monitor the development of dipolar interactions in neat and filled epoxy matrices, while replicating a cure regime similar to that used to cast bulk epoxy nanocomposites targeted at improved toughening effects, may help detect the interfacial interaction during cure. Towards this end, we search for variations in the dipolar- and conductivity-losses as a function of the matrix composition, at several stages during the curing process.

For this work, epoxy nano-composites have been processed containing two different functionalized derivatives of graphene based fillers - graphene oxide (GO) and n-butylamine functionalized graphene oxide (GO-ButA) at different filler loadings. Both the fillers contain surface functionalities that are likely to interact with the matrix components (resin and/or curing agent). These interactions are expected to affect the dielectric losses in the measurand too, that are likely to be observed from the spectra representing the imaginary part of the complex permittivity ($\varepsilon''$ spectra). Literature generally discusses interfacial interactions with respect to (w.r.t) epoxy resin cured with a single curing agent [5,12,13] or by varying the fillers [2,19-21] without changing the matrix components. The influence of the neat matrices’ cure reactivity upon varying the curing agent is seldom considered. Even with different curing agents, existing literature is mainly directed towards understanding the influence on the neat matrix properties [22,23]. This work however is directed towards understanding the filler-matrix interfacial interactions while considering the influence of the matrix cure reactivity on it. In principal with filled epoxies, for an optimum interfacial interaction the fillers would need sufficient time to interact effectively with the matrix components. Apart from surface functionalities and the particle size of the fillers, the cure reactivity of the neat matrix becomes an important parameter as well in this regard. A fast curing epoxy system is likely to limit the time available for the fillers to interact with the matrix components while a slow curing one will provide an extended interaction time. For this purpose two different curing agents have been
used – a polyetheramine based and an aliphatic amine based. The cure reactivity of the neat epoxies using these two curing agents is discussed first. Then the filler-matrix interfacial interactions are investigated in detail using the conventionally used experimental techniques followed by interpretation from dielectric spectroscopy. In conclusion we use thermogravimetric analysis (TGA) to look at how the interfacial interactions affect the thermal stability of the nano-composites. It has been observed that besides the interfacial interactions, the thermal stability of the fillers also affects the thermal stability of the nano-composites.

2. Experimental

2.1 Material

A commercially available diglycidyl ether of bisphenol A (DGEBA) based epoxy resin (Epikote 828LVEL from Momentive, Switzerland) was used to process the samples. The Epoxy Equivalent Weight (EEW) of the resin was found to be 187.6 (±0.8) g/mol by titration in accordance to ISO 3001 (EEW of Epikote 828LVEL according to product data sheet: 182 – 187 g/mol). Trimethylolpropane tris [poly(propylene glycol), amine terminated] ether purchased from Sigma Aldrich, Germany (denoted henceforth as Sial T-403 since it’s the chemical equivalent of Huntsman’s Jeffamine T-403) was used as one of the curing agents. The Amine Hydrogen Equivalent Weight (AHEW) of Sial T-403 as determined by titrating it against 0.1 mmol/l of HCl was found to be 80.2 (±0.4) g/mol. The stoichiometric formulation for the curing agent as calculated from these values was 42.8 (±0.4) phr (parts per hundred of the resin) [24].

The stoichiometric formulation has generally been defined as the resin to curing agent ratio that typically has the highest glass transition temperature ($T_g$) and the lowest molecular weight between crosslinks ($M_c$) amongst a range of resin-curing agent formulations [25,26]. However, it has also been observed that the max. $T_g$ was achieved at a formulation higher...
than the theoretically calculated values from EEW and AHEW [24]. An explanation for such observations can be found in the work of Haba et.al. [26]. In accordance to the explanation provided, the max. $T_g$ and hence the stoichiometric formulation for the present Sial T-403 cured epoxy system was found to be at 45.5 phr (higher than the theoretically calculated value of ~ 43.0 phr). Unless mentioned otherwise, all the nano-composites cured with Sial T-403 have been cured with 45.5 phr of the curing agent. Fillers used for this epoxy system were as-synthesized GO and GO-ButA at loadings of 0.10wt%, 0.25wt% and 0.50wt% w.r.t. the matrix weight. Hummer’s method [27] was used to synthesize GO and GO-ButA was synthesized by the method reported in an earlier work [28].

The other curing agent used in this work was diethyl triamine, also purchased from Sigma Aldrich, Germany (denoted as Sial DETA, Molecular weight: 103.2 g/mol). Since the exact same chemical was used as in [29], the stoichiometric content for the Sial DETA systems was considered at 11.1 phr. Only neat reference and nano-composites containing as-synthesized GO at 0.25wt% loading were processed. All fillers used here were stored at room temperature and used as-synthesized without further modification.

### 2.2 Processing and sampling for in-situ measurements

Epoxy systems (neat reference and filled resins) were processed in a scale to cast plates of size 120 x 160 x 4 mm$^3$ for further testing of their bulk mechanical properties (please refer to [30] for these details). A measured weight of the filler was first mixed manually with a spatula into a specified amount of epoxy resin and then passed 3 times through a 3 Roll Mill (3RM, SDY 200, Bühler Switzerland). Each roll of the 3RM was 200mm in length with a diameter of 150 mm operating at 20°C during processing. A zero gap was nominally set between the rolls, but the material being processed was expected to open the rolls by an unknown amount that was beyond our control. Since it has been our intention to use the 3RM
to mix the curing agent with the resin before casting, a simple rheology test was carried out to check the feasibility in both the epoxy systems used. Tests were carried out under oscillation mode in a rheometer ($\omega = 10 \text{ rad/sec}$) at 20°C (operating temperature of the 3RM) using neat resins at their respective stoichiometric formulations to check how long it took for the material to show a sudden and rapid rise in viscosity. With Sial T-403 (45.5 phr, deformation: 0.1%) as the curing agent, this time was observed to be 2.5 – 3 hrs giving enough time to clean the rolls before the material started to cure on them. With Sial DETA (11.1 phr, deformation: 0.01%) this time was only 35 – 40 min. Since this was not long enough to ensure cleaning of the rolls, the 3RM was not used to mix Sial DETA.

For processing samples with Sial T-403 as the curing agent, both neat and filled resins (with fillers dispersed in it) were mixed with a stoichiometric amount of 45.5 phr of the curing agent. To ensure a through mixing, the curing agent was first mixed manually with a spatula, followed by a pre-mix in the Over Head Stirrer (OHS, IKA, Germany) at 2000 rpm for 0.5 min and finally by passing it one last time through the 3RM. Both GO and GO-ButA filled nano-composites were processed at filler loadings of 0.10wt%, 0.25wt% and 0.50wt%.

For comparative analysis, neat and filled resins (with GO at 0.25wt%) were mixed with stoichiometric content of Sial DETA (11.1 phr) [29]. Here the curing agent was first manually mixed in the resin (for neat and filled resins) with a spatula and then mixed in the OHS at 2000 rpm for 10 min prior to degassing and casting.

This final mixture was then degassed under vacuum at 80°C (3-10 min) to remove any entrapped air bubbles and then poured into a silicone based release agent coated (QZ13, Huntsman, Switzerland) stainless steel mould to be cast into plates. The excess mixture left after filling up the mould was taken for the in-situ rheology + dielectric measurements. The sampling for the in-situ measurements took anywhere between 20 – 29 min from mixing of the curing agents depending on the processing steps implemented.
2.3 Characterization

Differential Scanning Calorimetry (DSC) measurements of the neat epoxy matrices were carried out with a *Perkin Elmer DSC7*, in a nitrogen atmosphere. Samples were taken for measurements immediately after mixing the curing agent to minimize any possibility of cure prior to the tests. Each measurement consisted of 2 runs within the temperature range of 20 – 300°C at a heating rate of 20°C/min. In between the 2 heating ramps the sample was cooled down at 500°C/min (*max rate offered by the equipment*).

An Eplexor 500 (*Gabo Qualimeter Testanlagen GmbH, Germany*) was used for dynamic mechanical analysis (DMA) in tension mode on samples machined to approximately 60 x 10 x 4 mm³. Tests were carried out by statically deforming the samples by 0.2% and dynamically at 10Hz by 0.015%. Samples were heated at a ramp rate of 2°C/min to 125°C for Sial T-403 cured epoxies and to 200°C for Sial DETA cured samples while keeping the other parameters unchanged. Measurements recorded the storage modulus ($E'$), loss moudulus ($E''$) and the loss factor ($\tan \delta$) in function of temperature. DMA typically provides three different glass transition temperatures depending on their definition as has been explained in [31]. Here we shall focus mainly on the one that defines the start of the transition from glassy to the rubbery state – $T_{g \text{onset}}$. $T_{g \text{onset}}$ is marked as the temperature corresponding to the point of intersection of the tangents of the glassy region and the region of the rapid drop in modulus (*Sial T-403 cured neat epoxy, Figure 1*) of the E' curve.

[Figure 1 near here]

SEM micrographs were taken using a *Nova NanoSEM 230 from FEI* on fracture surfaces of bulk nano-composites after sputter coating (*EM ACE600 High Vacuum Sputter Coat-
er from Leica) 3nm of Pt. Micrographs were captured in the secondy electron mode by applying an accelerating voltage of 5kV under high vacuum.

Rheology measurements were carried out with a Physica MCR301 (Anton Paar GmbH, Germany) with disposable Al stubs (Ø 25mm) meant for parallel plate geometry (PP25, Standard DIN 53018-1) screwed to the rheometer shaft. The gap between the disposable stubs and the cup holder was set initially to 200 µm while maintaining the normal force from the rheometer shaft at 0 N for the entire test duration. The rheometer measurements were carried out to simulate a cure cycle as mentioned below. They were performed at a constant angular frequency of 10 rad/s, but the deformation was varied depending upon whether Sial T-403 (0.10%) or Sial DETA (0.01%) was the curing agent in order to have a minimum torque on the shaft. The rheometer was coupled to an impedance spectrometer from Novocontrol Technologies for real time recording of the dielectric spectra during cure. The spectra were recorded using WinDETA software within the frequency range of 0.5 – 10⁶ Hz.

The cure cycle followed in the rheometer for the in-situ measurements was programmed to simulate a cure regime employed to cast plates for bulk mechanical testing. It was: 5 min at 25°C to temper the sample to a uniform temperature followed by heating to 80°C for isothermal cure. Ramp up to 80°C was carried out as quickly as possible in the rheometer to reduce the possibility of any cure during the ramp up. The sample was then kept for 30 min to simulate the condition of casting in a pre-heated oven and to avoid any measurement errors due to temperature fluctuations. Subsequently, it was kept at 80°C for further 4hrs that constituted the first cure step. The sample was slowly cooled down thereafter and maintained at 25°C for 30 min. (simulating the demoulding step). This was followed by postcuring the sample at 125°C for 3hrs for Sial T-403 cured systems and at 160°C for 1hr for the Sial DETA cured systems. The rate for heating and cooling during postcuring was maintained at 1°C/min.
The change in the dielectric behaviour of the samples (*neat and filled epoxy systems*) with cure progression was analyzed by comparing the dielectric spectra recorded at several stages during the measurement (*shown in Figures 8 - 10*) - at 25°C right before cure started (*red spectra*), at 80°C right at the start of the first cure cycle (*orange spectra*), after 1 hr of cure at 80°C (*green spectra*), after 2 hrs of cure at 80°C (*blue spectra*), after completion of cure and the sample had cooled to 25°C (*violet spectra*) and finally after completion of the post-cure process and the sample cooled down to 25°C (*black spectra*). Therefore in total we have six stages, which should provide the information about the changes taking place at different moments during cure. It will also allow to examine the effect of different fillers, if any, in more detail.

For investigation of the thermal stability of the nano-composites and the neat epoxies thermo gravimetric analysis (*TGA, Netzsch TG 209F1*) were carried out within the temperature range of 30°C – 900°C under nitrogen atmosphere at a heating rate of 20°C/min.

### 3. Results and Discussion

This section starts with a look into the cure reaction of the neat epoxy matrices to understand the matrix reactivity. The filler-matrix interfacial interactions in the nano-composites using conventional experimental techniques are discussed next. This is followed by our proposed dielectric spectroscopic analysis. Investigation on the thermal stability of the nano-composites using TGA concludes this section.

#### 3.1 Cure reactivity of the neat epoxy systems

The cure reactivity of the individual neat (*can also be called as unfilled or reference*) epoxy systems is investigated using DSC and rheology measurements. Later on these meas-
urements may help understand whether the cure reactivity influence the filler-matrix interfa-
cial interaction in the nano-composites.

The negative enthalpy change ($\Delta H$, J/g) confirms the exothermic cure reaction. The higher $\Delta H$ (Figure 2) for neat Sial DETA system ($\Delta H = -496$ J/g) indicates its more exother-
mic cure reactivity than Sial T-403 ($\Delta H = -378$ J/g) cured epoxies. Another interesting aspect is the difference in peak temperature ($T_p$, °C) observed. The shift in $T_p$ to lower values is indica-
tive of a faster cure [32] in the Sial DETA ($T_p = 109.2$ °C) system in comparison to Sial T-403 system ($T_p = 144.3$ °C). For measurement values please refer to Table 1.

Rheology is used to complement the above understanding of the reference epoxy sys-
tems. The evolution of storage modulus ($G'$, Pa) and loss modulus ($G''$, Pa) of the reference epoxy systems during cure is shown in Figure 3. $G'$ is indicative of the elastic/solid state properties of the analyzed sample while $G''$ is indicative of its viscous properties and corre-
sponds to the real part of dynamic viscosity ($\eta' = G''\omega$) [33]. At room temperature (R.T., 25°C region marked in Figure 3) both $G'$ and $G''$ is seen to increase for Sial DETA while they re-
main fairly constant in the Sial T-403 system. This indicates that the Sial DETA system cures even at R.T. - resulting in increased viscosity and the consequent development of elastic properties. Absence of such observations in the Sial T-403 systems confirms that the Sial DETA systems are more reactive. Raising the temperature to 80°C for isothermal cure reduces the viscosity of both epoxies ($G''$, hollow symbols, Figure 3). In Sial T-403 system $G''$ is ob-
served to increase with cure while $G'$ remains fairly constant. This region is defined as the pre-gel region wherein the sample shows a viscous/liquid like behaviour [33]. The end of pre-
gel region of the reference epoxies cured with Sial T-403 (~24 min) and Sial DETA (~12
min) is marked (*dashed vertical line*) by the sudden increase in \( G' \) (*elastic properties*) which
with the progression of cure is seen to crossover \( G'' \) (*Figure 3*). However, this transition is ob-
served to occur twice as quickly in Sial DETA system. These observations confirm that
amongst the two epoxy systems in use here, the Sial DETA cured ones are more reactive and
show a quicker cure.

[Figure 3 near here]

[Table 1 near here]

### 3.2 Rheology Measurements

Rheology can also be used to assess the filler dispersion quality in nano-composites
[14] and to understand the influence of fillers on cure reaction [34]. The storage modulus \( (G') \)
provides information of the elastic properties of the analyzed samples and can act as indica-
tors of filler disperion quality [14]. Agglomerated fillers are likely to form a percolation net-
work within the epoxy thus increasing the material stiffness resulting in an increase in \( G' \). The
loss modulus \( (G'') \) is indicative of the viscous properties of the samples. Figure 4 and Figure 5
show the evolution of \( G' \) and \( G'' \) in the epoxy nano-composites from the start of measurement.

In Sial T-403 (*Figure 4*) cured systems an ever increasing trend of \( G' \) and \( G'' \) is observed even
1 hr after the start of measurements. This indicates that the material has not completely solidi-
fied. While in Sial DETA cured systems (*Figure 5*) both the storage and loss moduli becomes
fairly constant after ~20 min measurement time – indicative of complete material solidifica-
tion. This difference in the moduli evolution is primarily related to the reactivity of the two
epoxy systems.
G' at room temperature (R.T., 25°C region in Figure 4a and Figure 5) has been observed to be sensitive to filler dispersion in the epoxy matrix [14]. When compared to the reference epoxy, agglomerate free filler dispersion in the matrix leads to reduced G' at R.T. Functionalization of fillers is seen to aid in this process as the attached functional groups on the filler surface help to promote interfacial interaction and discourage the formation of percolation networks which will otherwise lead to increased stiffness (increase in G' w.r.t. reference epoxy) [14,34]. Of all the Sial T-403 cured nano-composites (Figure 4a), higher G' value for GO at 0.50wt% w.r.t. the neat reference is possibly indicative of its filler re-agglomeration tendency at R.T. Interestingly in Sial DETA system, GO at 0.25wt% indicates a re-agglomeration tendency (Figure 5) while no such indications are observed in the Sial T-403 cured resins (Figure 4a). Addition of nano-fillers also lead to increased viscosity irrespective of the epoxy matrix i.e. increase in G'' w.r.t. epoxy reference (Figure 4b, Figure 5) [35]. Unlike with Sial T-403, in epoxy matrices cured with Sial DETA the loss modulus (G'', viscous properties, Figure 5) at R.T. is not observed to remain constant but shows an increasing tendency which is mainly due to its reactive nature.

Raising the measurement temperature to 80°C for isothermal cure is seen to lower the viscosities in Sial T-403 systems (Figure 4b) more significantly than in Sial DETA cured systems (Figure 5). As discussed in the previous section, the end of pre-gel region for the neat epoxy matrices is marked with a dashed vertical line (Figure 4 and Figure 5). It is interesting to note that except for GO at 0.50wt% all other Sial T-403 cured filled epoxy systems show an earlier end of their pre-gel region. This is indicative of the participation of the fillers in the
curing process – inducing an earlier cure, thus resulting in quicker development of elastic behaviour. It is also a clear indication of filler-matrix interfacial interaction during cure arising from the in-situ reaction between the matrix components and the functional groups present on the filler surface [14]. GO-ButA at 0.50wt% (Figure 4a) show an anomalous G' evolution which is not observed in any of the other epoxy systems. With Sial DETA, both the neat and the filled (GO at 0.25wt%, Figure 5) epoxies show a similar end to their pre-gel regions. It is suspected to be due to the limited time available to the fillers to interact efficiently with the matrix components in this reactive epoxy system. This shows the influence of the curing agent in the development of filler-matrix interfacial interaction.

3.3 Fractography

Filler dispersion quality in the final nano-composites is assessed from the SEM micrographs of a few chosen fracture surfaces. These interpretations from the bulk composites may help complement the understanding from the rheology measurements. Except for GO-ButA at 0.50wt% (Figure 6e) a uniform and fairly agglomerate free filler dispersion is observed in the bulk nano-composites (Figure 6) irrespective of the epoxy system (cured with Sial T-403 or Sial DETA). The few agglomerations are encircled in black with the filler clusters (red arrows) marked in the magnified inset.

Researchers have also tried to use failure mechanism related features as indicators of the filler-matrix interfacial interaction [13]. At the filler loadings being investigated here, the main failure mechanism in graphene based systems are expected to be crack pinning and/or crack deflection [21]. Crack pinning mainly involves inhibiting the growth of a crack front by pinning it against a rigid obstacle – here the fillers. This pinned crack then has to move
around the filler in order to advance down the fracture surface often leaving behind a tail like feature [36]. Crack pinning creates two crack surfaces around the fillers that later on may join together at same or different heights [21]. In these nano-composites (Figure 6) crack pinning seems to be the common failure mechanism irrespective of filler content and type as well as the epoxy system used (Figure 6f is Sial DETA cured epoxy, rest are all Sial T-403 cured). A strong evidence of pinning is observed in the GO filled Sial T-403 cured systems (Figure 6a-c, encircled white). The magnified image in Figure 6b reveals significant matrix material behind the filler showing strong crack pinning signature which will likely lead to joining of the crack faces at different heights.

During crack deflection, the crack face runs along the filler-matrix interface [21] which leads to creation of new surfaces due to off-plane loading [37] that results in increased fracture surface roughness that is more prominently evident in Sial T-403 cured epoxies (Figure 6a – 6e). These observations and the evidence of typical crack pinning signatures of bow-line feature (black arrows, especially in the Sial T-403 cured resin) at the highest filler loadings (0.50wt%) are indicative of good filler-matrix interaction in the Sial T-403 cured epoxies even in the reagglomerated matrix (Figure 6e, GO-ButA at 0.50wt%). These signatures are apparently not so evident in the Sial DETA cured epoxy (Figure 6f) which can lead to the conclusion of relatively inferior interfacial interactions.

### 3.4 Dynamic Mechanical Analysis (DMA)

The storage modulus in the rubbery region \( (E', \text{ Figure 1}) \) [38] and the glass transition temperature [31] from DMA can also be used as parameters to investigate the filler-matrix in-
terfacial interaction [12,13] in the bulk nano-composites. Both of these are affected by the polymer chain dynamics which in turn is influenced by filler-matrix interfacial interaction.

Addition of both GO and GO-ButA results in an increment of $E'_r$ in comparison to the neat epoxy reference (Figure 7, Table 1) which is indicative of the degree of filler-matrix interaction [13,38]. In Sial T-403 cured systems a maximum increment of 9.4% in $E'_r$ is observed in GO filled systems and 11.5% in GO-ButA filled systems. These increments are mainly influenced by the presence of nano-fillers which restrict the mobility of epoxy molecules [39] in the rubbery region due to improved filler-matrix interfacial interaction often resulting in higher degree of crosslinking [38]. In Sial T-403 cured systems, $E'_r$ is observed to monotonically increase in GO-ButA filled systems with filler content whereas it is seen to drop off slightly at higher GO content (absolute values in Table 1). Based on our discussions in the previous sections, an explanation for the observed increment in $E'_r$ with GO-ButA at 0.50wt% is maybe due to the reagglomeration of the fillers with cure leading to the increase in the material stiffness at higher temperatures. The minor increase of 1.7% in $E'_r$ in Sial DETA systems with 0.25wt% of GO is another evidence of the restricted interfacial interaction in this reactive epoxy system.

[Figure 7 near here]

However, these interactions do not seem to impact the glass transition temperature ($T_{g\text{ onsets}}$) as severely as the $E'_r$ which is not an exception as has been reported in literature [13]. Presently in Sial T-403 systems, the increment is < 2°C of the reference epoxy while in Sial DETA cured epoxies the $T_{g\text{ onsets}}$ is seen to marginally reduce. For absolute values please refer to the Table 1. In view of the discussion so far coupled with the limited interaction time likely
to be available in the reactive Sial DETA system to develop a good filler-matrix interfacial interaction it is possible that the surface functionalities on the fillers essentially remain inert/unreacted in the matrix.

### 3.5 Dielectric Spectroscopy

So far we have been discussing some of the commonly implemented conventional techniques (Section 3.2-3.4) to detect and investigate filler-matrix interfacial interaction in epoxy nano-composites. In this section we shall look at whether dielectric spectroscopy can contribute to a better understanding for our system. Each epoxy system is discussed separately here. Although the measurement frequency range has been $0.5 \text{ Hz} - 10^6 \text{ Hz}$, spectral features within $10 \text{ Hz} - 10^6 \text{ Hz}$ are only shown here as the data below 10 Hz was found to be too noisy (Figure S1 of supplementary information).

#### 3.5.1 Samples with Sial T-403 as the curing agent.

Figure 8 shows the frequency dependence of the dielectric losses (imaginary part, $\varepsilon''$, of the complex permittivity, in a log – log scale) for the reference epoxy cured with Sial T-403 and with different content of GO as fillers. Every line corresponds to the dielectric losses at a certain stage during cure and the colour coding is the same for all panels in the figure - at 25°C right before cure started (red spectra), at 80°C right at the start of the first cure cycle (orange spectra), after 1 hr of cure at 80°C (green spectra), after 2 hrs of cure at 80°C (blue spectra), after completion of cure and the sample has cooled down to 25°C (violet spectra) and finally after completion of the post-cure process and the sample cooled down to 25°C (black spectra). In all the above cases, the spectrum before cure (red and orange spectra) is dominated by the conductivity losses at frequencies below 1 kHz (straight line with a slope of -1) and a dipolar loss peak centered somewhere in the MHz region (partially falling out of our
measurement range). The conductivity contribution to the losses is evidenced by the straight line with slope -1 in the log-log plot, seen as increasing $\varepsilon''$ with decreasing frequency in the low-frequency end of the plot. With cure the relaxation peak is expected to shift towards lower frequencies as the polymer chains becomes bulky due to cross-linking and hence it takes much longer for the dipoles to oscillate and relax [40,41]. Also, the ionic conductivity is expected to disappear as well, observed as a downshift of the corresponding straight line until it disappears under the left side tail of the dipolar loss peak.

[Figure 8 near here]

The slight down-shift of the straight line in the earliest stage (red and orange spectra) with the increasing filler content suggest that the filled samples are able to start curing more effectively than the neat resins at room temperature. This also complements our rheology interpretations about the fillers influencing the matrix cure. However besides this, no clear change can be seen with increasing content of GO. No significant difference is observed in the dipolar responses as a result of the fillers, probably due to the small amount of fillers added. For all concentrations, the conductivity contribution disappears during the first hour of cure. Note that already for the green line (spectra at 2h after the start of 80°C cure cycle) the contribution from the conductivity has become negligible. That is, the -1 slope is not observed and the $\varepsilon''$ value of 0.4 at 10 Hz implies that the conductivity is well below $10^{-11}$ S/m, at least three orders of magnitude smaller than the value at the same frequency for the fresh mix. The dipolar loss-peak shifts down in frequency and broadens with the cure, in a similar fashion for all the samples, indicating the increased correlation among the dipolar units in the material and their disappearance with polymerization. It should be also noted that, as the main dipolar loss-peak shifts down in frequency, a second broad peak seems to enter in the explored fre-
frequency range from above (violet spectra). For instance it is observed that a maximum in the losses of cured samples occur at about 100 kHz. This peak is also present in the neat sample and therefore is neither due to, nor affected by, the fillers. In general, within the studied frequency range no clear systematic change in the dipolar loss is observed with the increase of fillers up to 0.50wt%. An important conclusion on the curing with Sial T-403 is that, from the dielectric response, the postcure process seems to play no role. The signals before and after postcure (violet and black lines respectively, temperature: 25°C) are practically identical.

In Figure 9 the data from the samples with GO-ButA as fillers are shown. The spectral organization and colour code follow the same pattern as in Figure 8. The dependence of the spectrum on curing and concentration of fillers is in this case very similar to what is observed for the GO filled samples, with one exception. The samples with highest amount of fillers (0.50wt%) show a significant down-slope from 10Hz to 1kHz in the losses of the cured samples that is not observed in any of the other cases.

We anticipate this relates to the reagglomeration tendency of the fillers as observed in the SEM micrographs (Figure 6e). At higher concentration of 0.50wt% of GO-ButA, more agglomerates are observed and it is hypothesised that the fillers start to reagglomerate with time during isothermal cure (at 80°C). This promotes the formation of a percolation network which eventually leads to the observed early increase of G’ in the sample of same composition compared to other systems as shown in Figure 4a. In summary, all available data consistently indicate a different behaviour at this composition (GO-ButA 0.5w%).

[Figure 9 near here]

3.5.2 Samples with Sial DETA as the curing agent.
At the start of the measurement Sial DETA cured (Figure 10) samples show features similar to those observed in the Sial T-403 cured samples i.e., there are two main features - the ionic conductivity and the up-rise at high frequencies presumably from a dipolar loss-peak (not fully visible due to the limited frequency range). However, the conductivity contribution for Sial-DETA cured samples is one order of magnitude higher than that for the Sial T-403 cured ones. This higher conductivity is a truly starting value (i.e., the conductivity of the starting materials) and it is not a consequence of a slower chemical reaction. We can be certain of it because, as a matter of fact, the conductivity disappears with the cure in these Sial-DETA cured samples much faster than in the Sial T-403 cured ones. Note that the straight line contribution with slope -1 is already absent for the Sial-DETA cured samples at the start of the 80°C cure cycle (orange spectra). The quick transition is due to the highly reactive cure reaction of this epoxy system. This is also probably the reason behind the small variations observed among the spectra of compositionally identical samples. However, this reactivity does not seem to significantly influence the filler dispersion in the bulk nano-composites as has been observed in Figure 6f.

Dipolar losses in the Sial-DETA samples appear at higher frequencies than in the Sial T-403 samples. Note that from the curvature of the red lines in Figure 10 one can clearly infer that the peaks are centered at frequencies about one order of magnitude higher than those in Figure 8 and Figure 9. Both spectra in Figure 10 show the typical down-shift in frequency of the dipolar losses, and the broadening of the peak, associated with the increase in the effective mass of the dipolar unit and the increase in the correlation among the dipoles. Yet, there is another difference with respect to the Sial T-403 cured samples. In the present case the spectra after 80°C cure and after post cure are not identical (the difference between violet and black lines). There is a clear broadening and a slight down-shifting of the dipolar loss-peak which indicate that chemical reactions involving polar groups are still taking place during
post cure. However, it should be considered that the higher postcure temperature for Sial DETA cured epoxies ($160^\circ C$) in comparison to the Sial T-403 cured ones ($125^\circ C$) may have been influential for such an observation. With these current processing conditions it appears that adding 0.25wt% of GO does not show a significant effect on the time evolution of the dipolar response.

Comparing the dielectric responses of the three different sets of samples (GO and GO-ButA filled Sial T-403 cured epoxy systems and GO filled Sial DETA cured epoxy system) one can conclude that up to 0.50wt% of filler loading, there is no systematic influence of the fillers on the dipolar response of the samples and that the main difference among the series is due to change in the curing agent.

Raihan et.al. [42] have recently reported that the dielectric measurements are affected by the size, shape and orientation of the dispersed fillers and as has been already reported in [28] these fillers show a range of particle size distributions. This combined with the possibility of local dispersion herogeneity in the measured samples may affect the repeatability of these measurements, details of which can be found in the supplementary section (SI). The pre-gel regions from rheology and the dielectric measurements confirm the presence of interfacial interactions leading to earlier cure in filled epoxies with Sial T-403 as the curing agent. These in-situ reactions are expected to be chemical in nature [14]. This is because during isothermal cure (at $80^\circ C$), the abundant epoxy groups present in both the resin and GO can react with the amine based curing agent. On the other hand, the amine and amide bonds present in GO-ButA [28] can also interact with the epoxy groups in the resin during isothermal cure forming ternary amine and amides. Given the improved dispersion stability observed at RT
with GO-ButA [28] this is the most likely scenario at elevated temperatures. However, with increased filler loading, the n-butylamine chains present on GO-ButA would sterically hinder the interaction with the long epoxy molecules present in the resin. This would lead to a percolation tendency causing local dispersion heterogeneity (variable \(\varepsilon''\) profile in dielectric spectroscopy, Supplementary section S1) responsible for the anomalous evolution of \(G'\) (in rheology) resulting in agglomerated fillers in the cured composites (SEM micrograph, Figure 6e).

On the other hand, the faster cure reaction in the Sial DETA cured epoxies (Section 3.1 and 3.5.2) limits the interaction time and thus the interfacial interaction.

### 3.6 Thermo Gravimetric Analysis (TGA)

In [28] GO-ButA was found to be thermally more stable than GO. And, from the discussion so far the filler-matrix interfacial interactions are seen to be more prominent in the slow curing Sial T-403 cured epoxies than in the fast curing Sial DETA epoxies. The TGA measurements of these nano-composites may help understand whether the thermal stability of these nano-composites is influenced only by the interfacial interactions or in combination with the thermal stability of the fillers as well.

In agreement with known consensus [43] the epoxy nano-composites here are seen to have a two-step degradation – between 350°C - 450°C of the epoxy groups and 450°C – 700°C due to char formation from the thermal degradation of the epoxy and the fillers. In the Sial T-403 cured epoxies, the onset of degradation temperature (\(T_d, °C, at 5%\) weight loss, Figure 11-12) is seen to drop slightly by ~2-4°C at lower GO contents before finally showing an increment of ~4°C at 0.50wt%. The reduction of \(T_d\) in GO filled system have already been observed and is suspected to be due to the easier thermal decomposition of the oxygen containing functionalities (OCFs) of the filler [43]. On the other hand, adding GO-ButA to the epoxy is seen to increase \(T_d\) by ~15-30°C (Figure 11, Table 2). Interestingly in the Sial T-403...
cured epoxies the temperature corresponding to the max. of differential thermogravimetric plot ($T_{DTG\ max}$ °C, Fig. S2 of supplementary section) is seen to increase within ~3°C with GO and by ~10-20°C with GO-ButA as fillers (Table 2, Figure S2). A shift in $T_{DTG\ max}$ to higher temperatures is generally indicative of improved thermal stability of the GO-ButA filled nano-composites [44,45].

[Figure 11a near here]

[Figure 11b near here]

However, addition of GO do not seem to influence the thermal stability of the Sial DETA cured epoxies with only nominal increment in $T_d$ and $T_{DTG\ max}$ (~1°C in both cases, Figure 12, Table 2, Figure S2) and indicates that interfacial interactions do have an influence on the thermal stability of the composites [5,44,46]. Interestingly the explanation in [43] regarding the presence of OCFs reducing thermal stability does not seem to hold in this fast curing epoxy.

[Figure 12 near here]

These observations reveal that in the slow curing Sial T-403 epoxy, the thermal stability of the nano-composites is influenced not only by the interfacial interactions but also the thermal stability of the fillers themselves [44]. This is probably why GO-ButA filled epoxies have a higher $T_{DTG\ max}$ as compared to GO filled ones. However, from the present findings it cannot be conclusively stated whether the limited interfacial interactions is the reason for the almost similar thermal stability of the GO filled nano-composite and the neat reference in the Sial DETA cured epoxy.
4. Conclusion

It has been established that of the two different epoxy matrices in use here, the Sial DETA cured epoxy is more reactive than the Sial T-403 cured one. The rheology measurements confirm that the fillers (GO and GO-ButA) participate in the cure reaction as is observed from the shorter pre-gel regions of the filled systems as compared to the neat reference in the Sial T-403 cured epoxy. This is evidence of interfacial interactions (in-situ reaction) between the filler and the matrix components bringing about an earlier cure. The lower storage modulus ($G'$, Pa) w.r.t. the neat epoxy indicates a good filler dispersion quality in the nano-composites at filler loading up to 0.25wt% (with both GO and GO-ButA). However, at the highest filler loading of 0.50wt%, GO show a pre-gel region comparable to that of the neat epoxy and GO-ButA shows an anomalous evolution of $G'$. The anomalous $G'$ evolution at 0.50wt% of GO-ButA is a probable reflection of the fillers’ reagglomeration tendency which is confirmed from the SEM micrographs. The reagglomeration tendency will lead to the formation of a percolation network and is also suspected to be the reason behind the observed increment of the storage modulus in the rubbery region ($E_r'$) from DMA. The Sial DETA cured epoxy systems show similar pre-gel regions for the neat as well as the filled (GO at 0.25wt%) epoxy matrix. The increment in $E_r'$ is found to be only 1.7% with Sial DETA as the curing agent in comparison to 7.5% with Sial T-403 as the curing agent in epoxies containing 0.25wt% of GO. These are indicative of better interfacial interactions in the Sial T-403 cured epoxy arising from the restricted mobility of epoxy molecules in the rubbery region due to the presence of nano-fillers. These interpretations are further complemented by the strong crack pinning and crack deflection signatures observed from the SEM micrographs for the Sial T-
403 cured epoxy. The likely reason for improved interfacial interaction in the Sial T-403 cured epoxy is the extended time available to the filler to interact with the matrix components in this slow curing system in comparison to the Sial DETA cured epoxy. From the dielectric measurements we observed that the speed of the initial curing can be tracked with the disappearance of the ionic conductivity of the mix. Besides this, the dipolar peaks almost look similar for all the samples. We also found out that despite the faster initial cure of the samples with Sial DETA, dipolar units are seen to be affected during the post-cure treatment. Another interesting observation was with 0.50wt% of GO-ButA, for which an anomalous G’ evolution (from rheology) was observed, also shows an unusual evolution of the dielectric losses, with higher losses in the low frequency end of the spectrum. Non-uniform filler dispersion or reagglomeration might cause the remnants of a frequency dependent conductivity which is one of the phenomenon that can lead to a straight line with slope between -1 and 0 (excluding both ends) in the losses [47]. However, in order to confirm this, better quality data at lower frequencies would have been needed, while our measurements down to 0.5 Hz were unfortunately noisy. It should be considered that low frequency measurements require longer times; which can become comparable with typical curing times, resulting in an undesired change of the system during measurement. Finally it was observed that the thermal stability of the nanocomposites seems to be effected only in the matrix with good interfacial interactions i.e. in Sial T-403 cured epoxy rather than the Sial DETA cured one. Moreover, GO-ButA filled samples are observed to be thermally more stable than the GO filled ones. This is anticipated to be a cumulative effect of good interfacial interactions and better thermal stability of GO-ButA.

Acknowledgement
The authors would like to thank Mr. Yeesong Ko and Dr. Dietmar Haba for their help with setting up the first trials with the dielectric spectrometer. Mr. Iurii Burda is thanked for ar-
ranging the SEM sessions. Mr. Daniel Völki is acknowledged for his help with the sample preparation. The authors are grateful to Mrs. Beatrice Fisher for carrying out the DSC and TGA measurements reported in this study. Dr. Andreas J. Brunner is acknowledged for his valuable inputs and suggestions in preparing this manuscript. AKC acknowledges the sponsorship of a studentship to SC by Empa.

Reference:


Table 1: Overview of the DMA parameters of the nano-composites and the DSC parameters of the neat epoxy reference reported in this study. <...>: Denotes the average of all the individual measurement values. δEr': Change in the crosslink density w.r.t. neat epoxy reference value.

<table>
<thead>
<tr>
<th>Sample</th>
<th>&lt;Er'&gt; (MPa)</th>
<th>δEr' (%)</th>
<th>&lt;Tg onset&gt; (°C)</th>
<th>&lt;ΔH&gt; (J/g)</th>
<th>&lt;Tp&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy, Sial T-403</td>
<td>22.8 (+0.6)</td>
<td>--</td>
<td>88.9 (+0.8)</td>
<td>388.2 (+14.2)</td>
<td>146.2 (+2.6)</td>
</tr>
<tr>
<td>GO 0.10wt%, Sial T-403</td>
<td>25.0 (+0.5)</td>
<td>9.4</td>
<td>90.2 (+0.8)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>GO 0.25wt%, Sial T-403</td>
<td>24.6 (+0.4)</td>
<td>7.5</td>
<td>90.1 (+0.7)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>GO 0.50wt%, Sial T-403</td>
<td>24.7 (+0.6)</td>
<td>8.1</td>
<td>89.9 (+0.9)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>GO-ButA 0.10wt%, Sial T-403</td>
<td>24.7 (+0.3)</td>
<td>8.2</td>
<td>90.5 (+0.7)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>GO-ButA 0.25wt%, Sial T-403</td>
<td>24.9 (+0.2)</td>
<td>9.0</td>
<td>89.6 (+0.6)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>GO-ButA 0.50wt%, Sial T-403</td>
<td>25.5 (+0.3)</td>
<td>11.5</td>
<td>90.7 (+0.5)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Neat Epoxy, Sial DETA</td>
<td>58.4 (+0.7)</td>
<td>--</td>
<td>138.7 (+0.5)</td>
<td>508.7 (+18.2)</td>
<td>110.2 (+1.4)</td>
</tr>
<tr>
<td>GO 0.25wt%, Sial DETA</td>
<td>59.4 (+1.0)</td>
<td>1.7</td>
<td>138.4 (+0.2)</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 2: Measured parameters from the thermo gravimetric analysis (TGA).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Td (°C)</th>
<th>TDTG max(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
**Figure Captions:**

Figure 1: Graphical representation of $T_{g \text{onset}}$ (°C), shown here for a neat Sial T-403 (45.5 phr) cured epoxy system.

Figure 2: First run of the non-isothermal DSC thermographs for neat epoxy systems cured with Sial T-403 (45.5 phr) and Sial DETA (11.1 phr). The enthalpy change ($\Delta H$, J/g) and the peak temperature ($T_p$, °C) of the individual systems are mentioned.

Figure 3: $G'$ (filled legends, Pa) and $G''$ (hollow legends, Pa) in log scale from rheology measurements of the neat epoxy matrices cured with Sial T-403 (45.5 phr) and Sial DETA (11.1 phr). The end of pre-gel region in each system is marked with a dashed vertical line.

Figure 4: Evolution of a) $G'$ and b) $G''$ in the epoxy nano-composites cured with Sial T-403 (45.5 phr). The temperatures of measurement are mentioned in each of the figures. The red dotted vertical line shows the demarcation for the pre-gel region for the neat epoxy reference.

Figure 5: Evolution of $G'$ and $G''$ in the epoxy nano-composites cured with Sial DETA (11.1 phr). The temperatures of measurement are mentioned in the figure. The red dotted vertical line shows the demarcation for the pre-gel region for the neat epoxy reference.

Figure 6: Fracture surface SEM micrographs showing the dispersion quality of the fillers in nano-composites. Sial T-403 cured systems: a) GO 0.25wt%, b) Magnified image of the white encircled region in a), c) GO 0.50wt%, d) GO-ButA 0.25wt% and e) GO-ButA 0.50wt%. Sial DETA cured systems: f) GO 0.25wt%. The crack pinning signatures are encir-
Figure 7: Variation in $E_r'$ with filler content in the two different epoxy systems tested. The change in the $E_r'$ is expressed as % increment w.r.t. neat epoxy reference, hence the neat epoxy reference is expressed as the base line irrespective of the epoxy systems considered.

Figure 8: Variation of the dielectric losses ($\varepsilon''$, imaginary part of the complex permittivity) over the measurement frequency range for the a) neat Sial T-403 cured epoxy and filled with GO at loadings of b) 0.10wt%, c) 0.25wt% and d) 0.50wt%. Spectral legends mentioned in a) has been followed in the other images as well.

Figure 9: Variation of the dielectric loss spectra ($\varepsilon''$, imaginary part of the complex permittivity) over the measurement frequency range in the a) neat Sial T-403 cured epoxy and filled with GO-ButA at loadings of b) 0.10wt%, c) 0.25wt% and d) 0.50wt%. Spectral legends mentioned in a) has been followed in the other images as well.

Figure 10: Variation of the dielectric loss spectra ($\varepsilon''$, imaginary part of the complex permittivity) over the measurement frequency range for the a) neat Sial DETA cured epoxy and filled with GO at b) 0.25wt%. Spectral legends mentioned in a) has been followed in the other images as well.

Figure 11: TGA spectra of Sial T-403 (45.5 phr) cured epoxy nano-composites with a) GO and b) GO-ButA as fillers.

Figure 12: TGA spectra of Sial DETA (11.1 phr) cured epoxy nano-composites.