**Stoichiometry and Molecular Dynamics of Anhydride-cured Epoxy Resin Incorporating Octa-Glycidyl POSS Co-Monomer**

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**ABSTRACT**

The influence of octa-glycidyl (OG) cubic silsesquioxane and reaction stoichiometry (stoichiometry factor, *SF*) on the cure chemistry and molecular dynamics of an anhydride-cured epoxy resin is reported. Fourier transform infrared spectroscopy revealed that an excess of epoxide groups suppresses esterification, as does the substitution of the epoxy pre-polymer with OG. Suppressed glass transition temperature (*Tg*) is reported for any given *SF* on addition of OG; these results are supported by the dielectric α relaxation behaviour. System-to-system network variations arising from changes in the degree of esterification and etherification are not sufficient to form discrete dielectric β processes. Finally, we propose an interpretation for the γ dielectric relaxation involving both competing origins reported in the literature, namely *γ1* (local motions of main-chain segments) and *γ2* (unreacted moieties). These attributions explain the observed dielectric features and relate these to the chemical composition of each system.

**KEYWORDS:** OG POSS; Epoxy Stoichiometry; Anhydride; Molecular Dynamics

**INTRODUCTION**

The silsesquioxanes are organosiliceous three-dimensional moieties discovered during the 1940’s [1]. The nomenclature indicates that each silicon atom bonds, on average, to 1.5 oxygen atoms (sesqui-) and 1 hydrocarbon (-ane) with a generic formula of (RSiO1.5)n, where R could be hydrogen, hydrocarbon or organofunctional groups [2]. POSS compounds conform to random (non-caged), partially-caged or caged geometry, with the latter consisting of an inorganic silica-based core surrounded by organic groups attached to the vertices [3]. The cubic POSS structure (R8Si8O12), consists of an octameric core with an edge length of ~0.5 nm [4] and is the most widely used silsesquioxane. In 1998, Laine *et al.* [5] suggested that cubic POSS, functionalised with epoxide terminated vertex groups, could be used as an epoxy pre-polymer and cured with regular amine hardeners, which would facilitate the design of novel materials with considerable potential for a number of applications. In fact, cubic POSS was first considered as an epoxy monomer one year earlier, when Crivello and Malik homopolymerised octa-functional POSS via a photoinitiated process [6]. Since then, various studies have attempted to establish structure/property relations in such systems by developing POSS/amine systems based upon different tethering end-groups, comparing them with commercial epoxy resins [7] and exploring the curing reactions by varying the epoxide/amine compositional ratio [8–10]. The effects imposed by the hardener’s structure have also been demonstrated by comparing POSS/amine systems based upon different hardeners [11], while similar POSS/amine systems have been used as matrices filled with rubber particles displaying enhanced elastic modulus values and thermal stability [12]. Furthermore, amino-functionalised POSS has been used as a hardener to cure commercially available epoxy resins [13], leading to improved thermomechanical properties compared with the POSS/amine systems described above.

Despite such advances, systems based solely upon POSS pre-polymers exhibit relatively poor mechanical properties [7,8] and increased cost compared to commercial epoxy resins. Thus, such moieties have alternatively been used as nanofillers [14]. As expected, the molecular topology of epoxy/POSS systems is dependent on the POSS vertex functionality and, therefore, POSS can be considered as: (1) physically dispersed (no covalent bonding) [15]; (2) pendant (one covalent bond) [16]; (3) linearly attached within the macromolecular backbone (two covalent bonds) [17]; (4) a network node (multiple covalent bonds) [18]. As a general trend, high functionality makes POSS more compatible with the matrix and inhibits aggregation phenomena, which are often reported in POSS with less than eight reactive vertex groups [18]. Octa-functional POSS has been reported to improve mechanical performance (e.g. impact strength [19], elastic modulus and yield stress [20]), electrical performance (e.g. resistance to corona discharge and AC breakdown strength [21]) and thermal performance (e.g. thermal stability [22,23] and coefficient of thermal expansion [24]) of the modified epoxy resin. Despite its reactivity, octa-functional POSS has, however, often been considered as a non-reactive nanofiller instead of a co-monomer, which may negatively impact the epoxy system’s stoichiometry, as a result of vertex group tethering. Our group has demonstrated various negative effects of unbalanced epoxy stoichiometry in a series of epoxy systems either directly, by altering the epoxide/hardener composition [25,26], or, indirectly, by adding particles displaying a reactive surface chemistry [27,28]. Accordingly, where high POSS loadings are required, the direct incorporation of POSS within epoxy, without modifying the stoichiometry, can be problematical.

The majority of studies of POSS-filled epoxies concerns amine-cured systems. However, anhydride-cured resins are also of major importance in some industrial sectors, especially in the electrical industry, due to their low-exotherm curing reaction, low curing shrinkage, excellent insulation performance and thermal stability [29]. Furthermore, their curing process is fully temperature-controlled, without premature crosslinking being involved.

Figure 1 outlines typical crosslinking reactions that occur during anhydride-curing of epoxy resins. The primary mechanism is the anhydride ring opening that occurs via an alcoholysis reaction involving the anhydride ring and a hydroxyl group, commonly attached to the backbone of the epoxy pre-polymer molecule. The outcome of this reaction is the formation of a half-ester: an ester bond on the backbone of the epoxy pre-polymer molecule and a pendant carboxylic acid group (see Figure 1a). Crosslinking continues with epoxide ring opening and the formation of a di-ester alcohol via two predominant routes: (a) esterification; (b) etherification. The former involves the reaction of the pendant carboxylic group with an epoxide ring, resulting in one ester and one hydroxyl group (see Figure 1b). Etherification occurs through the reaction of a hydroxyl group with an epoxide ring, resulting in the formation of one ether and one hydroxyl group (see Figure 1c). It is accepted that in the absence of catalysts, accelerators, or initiators, etherification is the dominant process, with one mole of anhydride reacting with one mole of epoxide [30]. However, in practice, catalysts are often used, promoting either anionic (usually bases) or cationic (usually acids) polymerisation, with the dominant processes then being esterification or etherification, respectively, effectively altering the epoxide:anhydride molar ratio [31].

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**FIG. 1.** Uncatalysed epoxy - anhydride crosslinking process: after anhydride ring opening (a), either esterification (b) or etherification (c) reactions may occur. The groups indicated in red are reactive, while those in blue are not.

In the case of the catalyst being a Lewis acid (e.g. boron trichloride - amine complex), this acts as a cationic initiator and accelerates the crosslinking in a comparable manner to the widely used boron trifluoride-amine complexes [32]. The cationic polymerisation of epoxy resins has been firmly established [33–35] and is based on the disassociation of the acid molecules at elevated temperatures followed by activation of epoxide groups, with the formation of oxonium ions, (Figures 2a and 2b). These protonated groups may react with other epoxy molecules via two routes, as portrayed in Figures 2c and 2d. In the case of anhydride-based curing, the abovementioned process accelerates curing by feeding the system with hydroxyls.



**FIG. 2.** Cationic catalysis of epoxy resin using boron trichloride - amine complex as a catalyst. (a) Catalyst disassociation, (b) initiation with the formation of oxonium ion and propagation through: (c) activated chain end or (d) activated monomer mechanisms.

The brief account given above demonstrates the relative complexity of anhydride curing, which possibly explains the limited number of studies of anhydride-cured systems incorporating POSS. Nevertheless, Herman Teo *et al.* [36] studied the cure kinetics of an epoxy/POSS/anhydride system in the presence of a catalyst and showed that the epoxide groups of the POSS react slower than the epoxide functionality of the resin pre-polymer, such that a pre-reaction of the POSS with the anhydride had to be used. However, this effect cannot be generalised, since the epoxy pre-polymer used in that study was N,N,N’,N’-tetraglycidyl-4,4’-diaminodiphenyl methane (TGDDM), which displays increased catalytic activity of its epoxide groups due to their attachment to tertiary amines, resulting in accelerated TGDDM reactivity compared to the POSS. As such, the general effect of POSS co-monomers on epoxy/anhydride network formation has not yet been clearly defined.

In the work reported here, a set of anhydride-cured epoxy resin hybrid systems containing various contents of octa-functional POSS were prepared using three methodologies: (a) direct POSS incorporation, resulting in increased epoxide content; (b) balancing the reaction stoichiometry; (c) deliberately increasing the anhydride content above optimum. The constituent materials used in this study were chosen so that the POSS and pre-polymer epoxides were both attached to typical glycidyl molecules, so as to display similar reactivities. Furthermore, for reasons such as those described above, our primary focus here concerns systems where the majority of epoxide groups are provided by the epoxy monomer. Comparison between the abovementioned hybrid systems, in terms of chemical composition (as revealed by vibrational spectroscopy), glass transition temperature (*Tg*) and dielectric molecular dynamics will give insight into the effects of POSS on the cure reaction and chemistry, as well as its impact on the molecular network after stoichiometric compensation, depending on the constituents’ chemistry, has been achieved.

**EXPERIMENTAL**

**Materials**

The resin components used in this study were supplied by Huntsman and are ARALDITE CY 225, a bisphenol A diglycidyl type (BADGE, CAS-No: 25068-38-6, molar mass: 384.6 g/mol) epoxy pre-polymer and ARADUR HY 925, a methyltetrahydrophthalic anhydride compound (MTHPA, CAS-No: 11070-44-3 – molar mass: 153.8 g/mol) premixed with a trichloro(N,N-dimethyloctylamine)boron amine complex initiator (BCl3:DMOA, CAS-No: 34762-90-8). The POSS was supplied by Merck (PSS-octa[(3-glycidyloxypropyl)dimethylsiloxy] substituted, CAS-No: 136864-48-7 – molar mass 1931.11 g/mol) and is commonly known as octakis(glycidyldimethylsiloxy)octa-silsesquioxane, or simply OG [8]. The epoxy equivalent molar mass of the BADGE prepolymer and the OG are: 192.3 g/mol (5.2 equiv/kg) and 241.4 g/mol (4.1 equiv/kg), respectively. The chemical structures of the constituents detailed above are presented in Figure 3.



**FIG. 3.** Chemical structures of: (a) BADGE; (b) MTHPA; (c) BCl3:DMOA; (d) OG.

**Preparation of OG/BADGE/MTHPA samples**

The sample preparation processes are described below; every formulation prepared and examined in this study is detailed in Tables 1 and 2. To provide a convenient and consistent notation in the text that follows, the manufacturer’s claimed optimum stoichiometry (80 phr of hardener) is represented as a stoichiometry factor (*SF*) of 1; thus, *SF*< 1 corresponds to systems containing a relative excess of epoxide groups, while *SF*> 1 represents a relative excess of hardener. The sample formulations used in this study are shown in Table 1.

***Simple addition of OG***

The required quantity of BADGE was pre-heated at 50 oC to reduce its viscosity and a stoichiometric amount of MTHPA was added and mixed under mild magnetic stirring. The OG was then added to the mixture and stirring continued for a further 5 min. The process continued with vacuum degassing for 20 min at 50 oC. Subsequently, the liquid-phase mixture was vacuum-transferred into metallic-plate moulds, with Melinex films 200 μm in thickness being used as spacers. The curing process included a first step at 90 oC for 2 h, followed by a second step at 140 oC for 8 h; these parameters were derived from an optimisation study and are in line with the manufacturer’s suggestions. After that, the samples were left inside the oven gradually to reach room temperature and, then, were demoulded and stored within a vacuum desiccator. The simple addition of OG into the epoxy/anhydride mixture inevitably displaces the stoichiometry towards *SF*< 1.

***Stoichiometric addition of OG (samples with balanced stoichiometry)***

In this case, the BADGE/MTHPA amounts were readjusted by taking into account the epoxide contribution of the OG. Effectively, the total epoxide content of the system (OG epoxides plus BADGE epoxides) was calculated and the amount of MTHPA added such that *SF*= 1. Such systems, where a molar percentage of the epoxide groups is supplied by the OG, are defined with respect to this parameter: *mol%OG‑epoxides*. Apart from the stoichiometric calculations, the rest of the sample preparation steps remained as described above.

***Samples with excess hardener***

In order to demonstrate the effects of excess MTHPA hardener, a number of systems was also produced such that *SF*> 1.

**TABLE 1.** List of samples based on the stoichiometric factors and the OG content.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Excess epoxides | | | | Balanced Stoichiometry | Excess anhydrides | | |
| *SF* | 0.81 | 0.9 | 0.95 | 0.98 | 1 | 1.05 | 1.1 | 1.19 |
| mol%OG-epoxides  (wt%OG) | 0  (0) | 0  (0) | 0  (0) | 0  (0) | 0  (0) | 0  (0) | 0  (0) | 0  (0) |
|  |  |  | 2  (1.4) | 2  (1.4) |  |  |  |
|  |  | 5  (3.5) |  | 5  (3.5) |  |  |  |
|  | 10  (6.9) |  |  | 10  (6.9) |  |  |  |
| 20  (13.6) |  |  |  | 20  (13.6) |  |  | 20  (13.6) |

From the above account, it is evident that the formulation of each system is defined with respect to two parameters: *SF* and the mol%OG-epoxides. Henceforth, for convenience, samples will be referred to using the designation X/YOG, where X indicates *SF* and Y indicates the mol%OG‑epoxides values, respectively. For example, a sample represented by 0.81/20OG is characterised by *SF* = 0.81 and mol%OG-epoxides = 20%, while the reference epoxy system will be referred to as 1/0OG.

The indicated compositional parameter space was chosen for the following reasons. First, mol/%OG-epoxides values of 0%, 2%, 5%, 10% and 20% were selected to provide a good coverage of formulations that were likely to be of most practical relevance whilst, simultaneously, spanning a sufficiently wide composition range to reveal underlying trends of behaviour. Second, *SF* values of 0.81, 0.9, 0.95, 0.98, 1, 1.05, 1.1 and 1.19 were chosen (a) to evaluate the veracity of the supplier’s assertion that *SF*= 1 corresponds to the optimal epoxide:anhydride ratio (through consideration of *SF* values close to 1) and (b) to span a sufficient range around the ideal to reveal underlying trends of behaviour (through consideration of *SF* values of 0.81, 0.9, 1.1 and 1.19). Data were obtained from relevant subsets of samples from within this compositional range using the techniques described below, the precise choice of specimen being determined in each case by the utility of the technique and the issue of interest.

**TABLE 2.** Mass of the constituents used for each sample; BADGE (E), hardener (H) and OG

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *SF* | 0.81 | 0.9 | 0.95 | 0.98 | 1 | 1.05 | 1.1 | 1.19 |
| Mass (g) | E: 4.12  H:2.69  OG: 0.00 | E: 4.00  H: 2.9  OG: 0.00 | E: 3.95  H: 3.00  OG: 0.00 | E:3.91  H:3.07  OG: 0.00 | E: 3.89  H: 3.11  OG: 0.00 | E: 3.80  H: 3.20  OG: 0.00 | E: 3.72  H: 3.28  OG: 0.00 | E: 3.59  H: 3.41  OG: 0.00 |
|  |  |  | E: 3.83  H: 3.07  OG: 0.1 | E: 3.80  H: 3.10  OG: 0.1 |  |  |  |
|  |  | E: 3.75  H: 3.00  OG: 0.24 |  | E: 3.67  H: 3.09  OG: 0.24 |  |  |  |
|  | E: 3.62  H: 2.90  OG: 0.48 |  |  | E: 3.45  H: 3.07  OG: 0.48 |  |  |  |
| E: 3.36  H: 2.69  OG: 0.95 |  |  |  | E: 3.03  H: 3.03  OG: 0.95 |  |  | E: 2.73  H: 3.32  OG: 0.95 |

**Characterisation methods**

Fourier transform Infrared spectra were obtained from each system in attenuated total internal reflection mode (ATR – FTIR) utilising a Thermo Scientific Nicolet iS5 FTIR spectrometer equipped with iD7 AR diamond crystal plates. The apparatus was calibrated with a background check before each sample was characterised. Each spectrum is an average of 16 measurements in total and, to aid comparison, the respective data were routinely standardised using a standard normal variate correction approach. The effect of variations in *SF* and mol%OG-epoxides on the *Tg* of the matrix polymer was investigated via differential scanning calorimetry (DSC – Perkin-Elmer DSC7). This was calibrated with reference to the melting temperature of high purity indium prior to any data acquisition. Each measurement involved two heating scans and one cooling scan between 25 oC and 140 oC at a heating/cooling rate of 10 oC/min, to eliminate the sample’s thermal history. Each *Tg* was then determined from the point of inflection of the second heating programme, with the *Tg* value quoted for each system being the average of three repeat measurements (with standard deviation). Dielectric spectra were obtained with a Solartron 1296 dielectric interface combined with a Schlumberger SI 1260 impedance/phase gain analyser. The test cell was located within a Janis Research STVP‑200‑XG cryostat and the temperature was controlled with a Lake Shore 332 cryogenic temperature controller. All samples were gold coated (K550X Sputter Coater) for 3 min on each side, to give 20 mm diameter electrodes and, after mounting in the test chamber, were kept under a helium atmosphere throughout the whole series of tests, to avoid condensation and ice blockages (at low temperatures) and oxidation phenomena (at high temperatures). The cooling fluid was liquid nitrogen and data were collected over a temperature range from -160 oC to 160 oC (10 oC steps). At each measurement temperature, the frequency sweep was from 10-1 to 105Hz; an AC voltage of 7 V was used.

**RESULTS AND DISCUSSION**

As described above, the composition of the epoxy systems considered in this study varied systematically with respect to the mol%OG-epoxides and *SF*. The effect of such parameters on both the network architecture and the functional groups retained within each system is described below.

**FTIR spectra of OG/BADGE/MTHPA systems**

FTIR spectra obtained as described above from the three liquid precursors are shown in Figure 4. The spectrum of the BADGE pre-polymer contains a peak related to epoxide rings (~915 cm-1), several peaks attributable to ethers (1250-1010 cm-1), as well as a rather weak peak related to hydroxyl groups (~3500 cm-1) [37–39]. The FTIR spectrum of the OG also contains an oxirane peak, a strong contribution from Si–O–Si bonds (disilyl ether, ~1070 cm‑1), which stems from the silica cage [40] and the vertex disilyl ether segments (see Figure 3d); these overlap with, and largely swamp, the organic ether-related absorbance (~1050-1010 cm‑1). Finally, the MTHPA spectrum contains prominent peaks related to the entire anhydride group (~1860 cm-1 and ~1770 cm-1) [41], together with functional group segments, such as ester (~1730 cm-1) [30], carboxyl (~1705 cm-1) [42] and C–O–C (890-970 cm-1 and 1070-1080 cm-1) [41,43]. The data presented in Figure 4 are, therefore, consistent with the molecular structures shown in Figure 3.



**FIG. 4.** FTIR spectra obtained from the liquid reactants: BADGE; OG; MTHPA.

Figure 5 shows equivalent FTIR spectra acquired from two sets of cured samples; results from X/0OG systems are presented in Figure 5a; results from X/20OG systems are presented in Figure 5b. In discussing these, consider three spectral regions, namely, around 1730 cm-1 (ester groups), around 3500 cm-1 (hydroxyl groups) and around 1150 cm-1 (organic ether groups).

Consider, first, the spectra obtained from the X/0OG sample set. In the 1/0OG reference epoxy system, it can be seen that the region between 1860 cm-1 and 1705 cm-1, which was characterised by four distinct peaks for the unreacted anhydride hardener (Figure 4), is now dominated by a sharp peak centred at 1730 cm-1, which is related to ester moieties formed during crosslinking (see Figure 1b). From the inset in Figure 5a, the difference between 0.81/0OG and 1/0OG appears marginal but, displacing the reaction stoichiometry to *SF* > 1 results in the appearance of shoulders at both higher and lower wavenumbers. These shoulders are assigned to carboxyls (~1705 cm-1) and entire anhydride groups (~1770 cm-1), as indicated above. The carboxyl shoulder is more pronounced, showing that the excess anhydride molecules present in 1.19/0OG are more likely to have opened and remained as branches in the half-ester state, with pendant carboxyls (see Figure 1b), with a smaller fraction remaining completely unreacted. This interpretation is consistent with the significant change in the form of the hydroxyl group peak (~3500 cm-1) in the data obtained from 1.19/0OG, where the broadening to lower wavenumbers is an indication that the ‑OH groups present in this system are part of carboxyl groups or carboxyl dimers [44]. Varying *SF* has similar effects in the OG-filled epoxy resin systems, as evinced by Figure 5b. Considering the inset in Figure 5b, the width of this peak varies in a comparable manner to that discussed above for the X/0OG sample set, as does the hydroxyl band.



**FIG. 5.** FT-IR spectra of: (a) X/0OG and (b) X/20OG sample sets.

From the above discussion it appears that varying the anhydride content affects the ester region of the spectrum and, in the case of systems with *SF* > 1, results in the retention of unreacted anhydrides and related residues within the system. However, interpretation of the ether regions is complicated by the presence of ether groups within the reactants as well as ether link formation during crosslinking. Of particular interest, here, is the effect of material formulation on the curing reaction, the relative importance of esterification and etherification reactions (see Figure 1) and the resultant network structure that forms. As indicated previously, the data discussed above were processed using a standard normal variate approach and, while this is sufficient for many purposes, the detailed interpretation of small spectral variations is questionable. Nevertheless, the peak at 1509 cm-1 is generally ascribed to phenyl carbons and, as such, has been used elsewhere as an internal calibrant [38,45,46]. Since the BADGE content of each of the systems used here is known (see Table 2), absorption at this wavenumber provides a means of scaling each spectrum to reflect the known composition, thereby permitting more quantitative comparisons of specific spectral features.

Figure 6 presents two composite plots of scaled data, which focus on the spectral regions associated with ester groups (see Figure 6a) and ether groups (see Figure 6b). Although clarity is compromised by including, in each, the scaled data from all six of the formulations considered here, we feel that this compromise is necessary given the aims of the analysis. From Figure 6a, the ester absorption varies in the X/0OG systems as follows: 1.19/0OG > 1/0OG > 0.81/OG. The X/20OG systems also evince comparable relative behaviour. Thus, in both system sets (with and without OG), an abundance of anhydride groups promotes crosslinking through esterification. This is consistent with Figure 1b and the above discussion of Figure 5. Furthermore, Figure 6a also indicates that for any given *SF*, the substitution of BADGE epoxide groups with OG epoxide groups acts to suppress crosslinking through esterification, such that the strength of the 1730 cm-1peak is the weakest of all in 0.81/20OG, where both the excess epoxide concentration and the inclusion of OG act additively.

Figure 6b presents the ether region of the spectrum, which we will consider with respect to three wavenumber ranges: 1250-1230 cm-1; 1180-1140 cm-1; 1100-1000 cm-1. Absorption around 1240 cm-1 has previously been ascribed to antisymmetric stretching of phenyl ethers [37,47] and should therefore be determined by the BADGE content. However, from Figure 6b, it is evident that this absorption band contains two component peaks, located at ~1250 cm-1 and at ~1230 cm-1, which vary from system-to-system in terms of their relative intensity. Comparison of the strength of the absorption at 1230 cm-1 and that at 1509 cm-1 indicates that both of these features are related to the same basic structural units and, in view of previous attributions, *in toto*, we feel that both of these can be associated with the BADGE. In contrast, the absorption at 1250 cm-1 does not vary with composition in the same way, suggesting that its source is rather different, possibly affected by the presence of the OG [48]. As such, we conclude (a) that the above further validates the data scaling procedure used and (b) suggest that it is an oversimplification simply to associate absorption around 1230 cm‑1 with phenyl ethers.

Absorption in the range 1180-1140 cm-1 is generally associated with organic ether bonds and, as such, should reflect the phenyl ethers from the BADGE, aliphatic ethers from the OG and ether groups formed during curing. Consider first the X/0OG system set, where 1.19/0OG and 1/0OG exhibit a comparable absorption across this region, which is significantly in excess of that seen in 0.81/0OG. From Table 2, the reactants used in 0.81/0OG provide the highest intrinsic aromatic ether content of these three systems, which implies that this region of the spectrum is strongly influenced by aliphatic ether groups formed during curing. However, for each *SF*, the X/20OG systems are characterised by *reduced* absorption in this spectral region compared with the X/0OG systems, despite the OG containing aliphatic ether groups within its structure. Such variations make detailed interpretation of this spectral region, in isolation, difficult, due to the various contributory factors that could be involved. Consequently, consider now the ether region from 1100 cm-1 to 1000 cm-1, which provides a complementary perspective, albeit that the strong disilyl ether absorption precludes comparison of absolute absorption values obtained from X/20OG samples with those obtained from X/0OG samples. As for the range 1100-1000 cm-1, absorbance at ~1040 cm-1 has also been associated both with the symmetric stretching of aromatic ethers [47] and, elsewhere, with the stretching of aliphatic ethers [37]. Within the X/0OG sample set, the highest absorption at 1040 cm-1 occurs in 1/0OG, with both 1.19/0OG and 0.81/0OG exhibiting significantly lower, but comparable, levels of absorption at this wavenumber. Within the X/20OG sample set, the absorption is globally increased due to overlap with the strong disilyl ether peak around 1070 cm-1 plus, potentially, as a consequence of the aliphatic ethers present in the OG. Of the three X/20OG samples, the highest absorption at 1040 cm-1 is seen in 0.81/20OG with lower levels of absorption at this wavenumber evident, in order, in 1/20OG and 1.19/20OG. This difference in the relative behaviour of the X/0OG and X/20OG systems requires comment.

The precise interpretation of the 1040 cm-1 absorption peak, in isolation, is complicated by the fact that its attribution is uncertain, as highlighted above. Nevertheless, consider first, systems containing no OG, where absorption at this wavenumber is likely to be reflective of the ether groups present in the reactants plus any ether groups formed during crosslinking. From Table 2, it is clear that the ether content from the reactants (aromatic ethers) increases with decreasing *SF* and, therefore, were this absorption to be related *only* to aromatic ether groups from the reactants, then the strength of the absorption would similarly increase with decreasing *SF*, which is not the case. As such, the fact that the highest intensity is observed in 1/0OG implies that etherification reactions during curing are important in defining the strength of this absorption band and, as such, we infer that the increased absorption seen in 1/0OG is indicative of significant levels of crosslinking through etherification in this system. Consider, now, the X/20OG systems, which differ from X/0OG in the influence that the OG has on absorption at 1040 cm-1, which may involve four factors: aromatic ethers from the BADGE component; disilyl ether groups in the OG; aliphatic ethers present within the structure of OG; ether groups formed during curing. As such, the X/0OG and X/20OG systems are very different in terms of the moieties that can contribute to the observed absorption at 1040 cm-1. In view of this, it is not possible fully to interpret this facet of the FTIR data in isolation, albeit that, the relatively high level of absorption seen at this wavenumber in 0.81/20OG may be indictive of significant crosslinking through etherification in this system: that is, in the system containing both excess epoxides *and* OG. We return to this point in the sections that follow.



**FIG. 6.** Scaled FTIR plots focusing on the spectral regions associated with ester groups (a) and ether groups (b).

Nevertheless, to aid comparison of the key ester- and ether-related absorbance bands, the relative strengths are ranked in Table 3, ascending in strength from bottom to top.

Although precise interpretation of the above FTIR data is complex, a number of broad conclusions can nevertheless be drawn:

* For both X/0OG and X/20OG sample sets, *SF*< 1 suppresses crosslinking through esterification.
* Within X/0OG and X/20OG sample sets, the highest level of esterification was seen in the 1.19/YOG specimens. Spectra acquired from 1.19/YOG also evince the presence of unreacted anhydride residues.
* For any given *SF*, the substitution of BADGE epoxide groups with OG epoxide groups serves to suppress esterification further, such that the lowest overall level of esterification was seen in 0.81/20OG.
* Evaluation of the extent of etherification during curing is complicated by the related functional groups present in the reactants.
* When both related spectral regions are considered in concert, it seems probable that within the X/0OG sample set, the highest degree of etherification occurs within 1/0OG.
* No firm conclusions can be drawn concerning etherification reactions in the X/20OG systems based on FTIR data alone, since the 1180-1140 cm-1 and 1100-1000 cm-1 spectral regions appear inconsistent. We attribute this to the relative importance in each spectral region of contributions from aromatic, aliphatic and disilyl ethers.
* Inclusion of OG influences the cure reaction and the network topology that results, even when appropriate stoichiometric compensation is made to account for the associated additional epoxide groups that are introduced.

**TABLE 3.** Summary of the relative strength of the absorption peaks related to ester and ether groups ranked in terms of increasing strength, bottom to top.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | X/0OG Systems | | | X/20OG Systems | | |
|  | Ester  (~1730 cm-1) | Ether  (~1150 cm-1) | Ether  (~1040 cm-1) | Ester  (~1730 cm-1) | Ether  (~1150 cm-1) | Ether  (~1040 cm-1) |
|  | 1.19/0OG | 1.19/0OG & 1/0OG |  |  |  | 0.81/20OG |
| 1/0OG |  |  |  |  | 1/20OG |
|  | 0.81/0OG |  | 1.19/20OG |  | 1.19/20OG |
|  |  | 1/0OG | 1/20OG | 1.19/20OG & 1/20OG |  |
| 0.81/0OG |  | 0.81/0OG & 1.19/0OG |  |  |  |
|  |  |  | 0.81/20OG | 0.81/20OG |  |

**Glass transition of OG/BADGE/MTHPA systems**

Figure 7 shows the impact of *SF* and mol%OG-epoxides on the *Tg*, of the systems considered here. In the case of X/0OG, *Tg* decreases for *SF* ≠ 1 in an asymmetric manner, as previously reported (excess anhydrides suppress *Tg* less than excess epoxides) [25]. The measured *Tg* value of the 0.98/0OG system slightly exceeds that of 1/0OG, which implies that the optimum stoichiometry corresponds to a system containing a slight excess of epoxide groups. While the magnitude of this difference is sufficiently small (~1 oC) to be attributable to sample-to-sample variations or uncertainties in the data, comparable behaviour is also seen in the 0.98/2OG system, suggesting that it is real. Nevertheless, the optimum stoichiometry appears very close to *SF* = 1, broadly validating the manufacturer’s suggested formulation. Inclusion of OG progressively suppresses *Tg*, even when stoichiometric compensation is made (OG-filled systems with *SF* = 1 in Figure 7). Overall, the X/0OG and X/20/OG systems display comparable asymmetric variations in *Tg* for *SF* ≠ 1, indicating that displaced stoichiometry and addition of OG affect *Tg* in an additive manner.

Comparison of the FTIR data with the results presented in Figure 7 reveals broad consistency: (i) the FTIR data indicate suppressed crosslinking by esterification when OG is present in the system and/or when *SF* < 1; (ii) at least within the X/0OG sample set, the highest degree of etherification occurs in 1/0OG system; (iii) when *SF* > 1, unreacted anhydride residues were detected. It is reasonable that these factors, which are directly associated with compositionally driven variations in the crosslinking reactions, in isolation or in concert, result in reductions in *Tg*, as seen in Figure 7. Furthermore, it is evident from Figure 7 that 1.19/20OG and 0.81/20OG are characterised by comparable values of *Tg*, despite the reduced level of crosslinking through esterification in 0.81/20OG revealed by FTIR. This, therefore, implies that this is compensated by an increased level of crosslinking through etherification in the latter system, which aligns with the increased absorbance seen in this system around 1040 cm-1 (see Table 3).



**FIG. 7.** DSC data showing the effect of material formulation on *Tg*.

Previously, the effect of reactive POSS on the *Tg* of epoxy resins has been attributed to a number of factors, including perturbed reaction stoichiometry, reactant molecular topology, tethering groups, etc. The silica cage has been proposed to restrict macromolecular motion and/or introduce free volume into the host polymer; these factors would be expected, respectively, to increase and decrease *Tg* [49]. For example, Fu *et al.* [19] introduced a mercapto-functionalised POSS into an anhydride-cured BADGE system and reported a slight decrease in *Tg*, which they explained through the above competing processes. Specifically, the silica cage was suggested both to modify molecular dynamics and to introduce additional free volume – with the latter dominating – such that an overall reduction in *Tg* was observed. Despite mercapto groups reacting slowly with epoxides [50], it was claimed that bonding between the POSS and BADGE occurred; nevertheless, the effect of the reactive mercapto groups was not related to the *Tg* reduction [19]. Elsewhere, Takala *et al.* [51] used OG POSS as a filler (without stoichiometric compensation) for an anhydride-cured BADGE resin and reported a gradual reduction in *Tg*, which they attributed to the flexible vertex-bonded side chains acting to promote molecular mobility. However, the lack of any consideration of stoichiometry effects adversely impacts the general veracity of such a conclusion. A similar *Tg* decrease was observed by Heid *et al.* [21], where glycidyl POSS was introduced into an amine-cured BADGE system; although these workers claimed stoichiometric compensation, the method used to evaluate this was not disclosed for “confidentiality reasons”, precluding any objective assessment of the methodology. In that study, the observed reduction in *Tg* was attributed to interactions between the POSS molecules and the formation of aggregated “crystalline zones” which, these workers suggested, served to increase the molecular chain mobility. Elsewhere, Williams *et al.* [20] functionalised POSS with hydroxyl-terminated moieties and incorporated it into a BADGE resin, homopolymerised in the presence of a tertiary amine catalyst. A reduction in *Tg* consistent with the POSS content of the system was observed and attributed either to decreased crosslinking density or to the flexibility of the POSS vertex groups. Xiao *et al.* [52] prepared anhydride-cured systems with either OG or BADGE monomers and reported rather higher *Tg* values for the latter system, referring to the flexible glycidyl groups of the POSS compared with the rigid ones from the BADGE. The post-curing duration was shown by Herman Teo [36] to increase *Tg*; although this was attributed to the low reactivity of their POSS compared with their epoxy monomer, the absence of any equivalent study of post-curing effects in a reference, unfilled, epoxy system must question the extent to which the data can solely be attributed to the POSS. Indeed, a prolonged curing process was shown by Villanueva *et al.* [53] to affect both a POSS-filled epoxy and an unfilled reference in the same manner. Several other studies utilising POSS as the only monomer [7,9,11,40] have reported steric hindrance effects that depend on the tether group structure. Such effects are, however, not applicable in the case of the work reported here, since the tether group structures (glyceryl groups) are the same for OG and BADGE. Since a *Tg* reduction was observed in stoichiometrically balanced OG-filled samples compared with stoichiometric-balanced reference epoxy system, it is evident that the POSS molecule additionally affects the network topology/molecular dynamics apart from any impact on *SF*. Indeed, pendant non-reactive-POSS slightly decreased the *Tg* of a BADGE-based system [54], an effect attributed to increased free volume due to loosened molecular packing. As such, we suggest that the variations in *Tg* shown in Figure 7 result from modifications to the curing reactions (as revealed by FTIR) and changes in network topology (revealed by the reduced *Tg* values in 1/YOG samples). This interpretation is tested below via dielectric spectroscopy.

**Dielectric theory, relaxations & molecular dynamics**

Dielectric spectroscopy is a widely recognised method for monitoring processes such as epoxy curing [55], since polar species, either pre-existing or formed by the crosslinking reactions, are affected by the electric stimulus. The complex relative dielectric permittivity (*ε\**) can be written:

(1)

where *ε’* and *ε’’* represent the real and imaginary parts of the relative permittivity. The reorientation of polar groups under an applied AC electric field results in alterations of the *ε’* and *ε’’* spectra (relaxations). Conventionally, the associated relaxation processes are labelled *α*, *β*, *γ*, etc with ascending frequency (or descending temperature), with the α process being attributed to cooperative segmental chain motions and the other, so-called secondary relaxations, being associated with local motions dependent on the chemical structure of the system (see Figure 8).



**FIG. 8.** Plots of the temperature dependence of (a) real and (b) imaginary parts of the complex relative permittivity for the indicted systems.

A quantitative interpretation of such dielectric data can be made via the Havriliak-Negami (HN) formulism, [56] where the complex permittivity (in the time domain) is described as:

(3)

or (in the frequency domain):

(4)

In the above equations:

* is the angular frequency
* is the HN relaxation time and is related to the maximal loss peak position of a given relaxation mechanism.
* is the baseline permittivity, unaffected by dipole contributions, charge migration, etc.
* is the “dielectric strength” and describes the temperature dependent intensity of a given relaxation mechanism.
* and are asymmetry factors, where and .

Equation (4) can be furtherly analysed to give the *ε’* and *ε’’* constituents as:

(5)

and

(6)

where

(7)

Due to the peak asymmetry, the peak position of a given relaxation is described by:

(8)

The dielectric strength *Δε* is determined by:

(9)

where *ε0* is the vacuum permittivity, *T* the temperature, *μ* the mean dipole moment of the process, *N/V* the number density of dipoles involved and *g* the so-called Kirkwood-Fröhlich factor [57]. In systems where a given relaxation involves contributions from different types of dipoles, the measured cumulative *Δε* value will vary according to the respective numbers of the different dipoles present and should be written:

(10)

Upon peak analysis, the frequency and temperature relation of the obtained loss peak maxima can be fitted to the following equations. The α relaxation is a non-linear process and can be expressed by a Vogel - Fulcher – Tammann [58] (VFT) equation:

(11)

where *fmax* is the peak location, *f0* a pre-exponential factor, *B* a constant and *Tv* the so-called Vogel temperature (or ideal *Tg*), which is usually 30-70 oC lower than the experimental *Tg*. The secondary relaxations are expected to follow a simple Arrhenius-like behaviour expressed by:

(12)

where *EA* is the activation energy of the respective relaxation and *kB* the Boltzmann constant.

**Dielectric spectra of OG/BADGE/MTHPA systems**

The following section presents data obtained from just four systems (1/0OG, 1/20OG, 0.81/20OG, 1.19/20OG) in order to show (a) the effect of introducing OG and (b) the effect of excess epoxide or anhydride groups. A principal objective of the included dielectric analysis is to present complementary data to support interpretation of the DSC and FTIR results presented above and, therefore, data from other formulations have not been included on grounds of brevity, since their inclusion adds little to the key messages.

Figure 9 depicts the variation of *ε’* with frequency at 20 oC, from which, it can be seen that the 0.81/20OG system is characterised by increased *ε’* across the complete frequency range compared with both 1/YOG systems. This behaviour is consistently observed in the glassy state (i.e. at temperatures below the α relaxation), as shown in Figure 8a. The equivalence in the data obtained from the two 1/YOG systems indicates that the presence of OG has little direct effect on the measured *ε’* value. Excess hardener (1.19/20OG) results in the lowest *ε’* values. While it has been shown elsewhere [59,60] that reduced *ε’* values in epoxy systems are an indication of molecular immobilisation, the variations seen in Figure 9, when taken together with the DSC data shown in Figure 7 imply that this is not the sole factor at work here: 1/0OG and 1/20OG are characterised by equivalent values of *ε’*, yet the *Tg* of the former system is higher than that of the latter. As such, it is not just global molecular constraints but also the number of polar groups, their nature and the local molecular topologies that determine the measured permittivity.



**FIG. 9.** Frequency dependence of the real part of the relative permittivity of the indicated systems, measured at 20 oC.

***The α Relaxation***.

Figure 10 shows the measured frequency dependence of *ε’’* at temperatures above the DSC *Tg* (black squares). From this, it appears that these data include a large charge transport component (slope = -1 on logarithmic axes) and, therefore, the following relationship was used to provide an evaluation of the charge transport-free dielectric loss [61].

(13)

The results from this procedure (*ε’’deriv* values) are presented as red lines overlaid in Figure 10, which include α relaxation peaks that shift to higher frequencies with increasing temperature. In epoxy resins, the α process has been observed and characterised since the early 1960s via dynamic mechanical and/or dielectric spectroscopies [62–65] and is typically attributed to segmental chain motions triggered by the glass transition.



**FIG. 10.** Imaginary part of the relative dielectric permittivity data acquired within a high temperature regime, to reveal the dielectric α relaxation of: (a) 1/0OG; (b) 1/20OG; (c) 0.81/20OG; (d) 1.19/20OG. The black squares represent the experimental *ε’’* values; the red lines correspond to the logarithmic derivative *ε’’* values calculated using equation (13); the α relaxation is indicated by the arrows.

At temperatures above 120 oC, an additional low frequency process is evident. This process has been associated with the normal mode [54,66] that is typically seen in the rubbery state of polymers containing polar groups on the backbone and attributed to long-range motions of the end-to-end dipole vector along the polymer chain. Alternatively, this dielectric feature may be a consequence of interfacial phenomena related to local heterogeneities caused by the hardener’s aromatic structure [67] or may simply reflect electrode polarisation [68]. In the OG-filled samples, additional features are observable, presumably related to interfacial phenomena associated with the OG. However, since none of these phenomena is central to the topic being addressed here, further speculation on their origin is not warranted.

Figure 11a shows the VFT behaviour of the *α* relaxation of the examined samples. From this, it is evident that the inclusion of OG, irrespective of *SF*, displaces the α relaxation peaks towards higher frequencies, providing a further indication that the presence of the OG reduces network constraints. Varying *SF* has an additive effect, such that the frequency of the α relaxation at any temperature is further increased in 0.81/20OG and 1.19/20OG, with excess epoxides having a larger effect than excess anhydrides. As such, the behaviour shown in Figure 11a aligns well with the DSC data and the molecular interpretations derived from the FTIR data. Furthermore, the *Δε* values observed for this relaxation process (Figure 11b) also confirm that the addition of OG has a consistent effect, despite the differences in the *SF* of each sample. The 1/0OG reference system displays the highest *Δε* values throughout the investigated temperature range, implying the highest degree of cure [69]. The other systems are all characterised by lower overlapping *Δε* values, suggesting that the α relaxation strength is affected more by the presence of the OG than changes in *SF*. Indeed, the silica cage of non-reactive POSS has been reported to cause similar α relaxation behaviour due to a synergy of increase in free volume (shift to higher frequency) and local immobilisation (reduced *Δε*) [54]. The behaviour described above is consistent with loosened molecular packing acting to increase free volume and molecular mobility. Finally, comparison of the data presented in Figure 11 with published results [70–72] reveals a high degree of consistency with respect to parameter values, the frequency-temperature dependence and the reduction in *Δε* seen with decreasing inverse temperature.



**FIG. 11.** Dielectric data pertaining to the α relaxation of the indicated systems: (a) loss peak position as a function of frequency and temperature (dashed lines correspond to VFT fitting); (b) temperature variation of *Δε*.

***The β Relaxation***.

Figure 12 shows *ε’*’ data obtained at lower temperatures, in which, a clear β relaxation peak can be seen that progressively moves to higher frequencies with increasing temperature (frequency shift indicated by the arrows). Furthermore, these data also evince additional processes at higher frequencies, for example, at ~1000 Hz at -90 oC in 1.19/20OG (arrowed), the origin of which is shown, in the following section, to be the *γ* relaxation.



**FIG. 12.** Imaginary part of the relative dielectric permittivity data acquired within an intermediate temperature regime, to reveal the dielectric β relaxation of: (a) 1/0OG; (b) 1/20OG; (c) 0.81/20OG; (d) 1.19/20OG. All four plots are scaled equivalently to aid comparison.

Figure 13a presents the variation in the frequency of the β relaxation of the four systems considered here, following analysis using the HN formulism. From this, it is evident that, in all cases, the temperature dependence of the β relaxation conforms well to the Arrhenius equation, giving activation energy values that are equivalent in 1/0OG and 1/20OG and slightly reduced in 0.81/20OG and 1.19/20OG. While this may reflect less constrained networks in the off-stoichiometric systems, the uncertainty in each quoted value is at least 0.01 eV, such that the differences are not statistically significant. The activation energies reported here are consistent with values reported in the literature for systems based upon comparable reactants [73]. Figure 13b shows the variation in *Δε* as a function of temperature and material composition; these data are characterised by a slight decrease in *Δε* with increasing temperature, as reported elsewhere for the β relaxation [74]. In addition, these data also indicate a small reduction in *Δε* on introducing OG and a further reduction in the systems characterised by non-optimal stoichiometries.

In epoxy resins, the β relaxation was first reported in 1959 [75] and, since then, has been extensively studied to reveal its origins. Initially, it was proposed to be equivalent to the transition of methylene sequences observed in thermoplastics which, in the case of epoxy networks, are present in the diglycidyl ether segments [76], while later, it was assigned to rearrangement of the cyclohexane ring of the anhydride [64]. In 1967, Dammont *et al.*[65] ascribed it to the flexible hydroxyl-ether segments formed during curing and, since then, this relaxation has commonly been associated with the degree of crosslinking. Typically, it is attributed to hydroxyl-ether containing segments [69,77–82] or, in the case of ester-based curing, to diesters/monoesters [83] or, in systems containing both hydroxyl-ethers and diesters, to both [84]. In some cases [73,85,86], the β region has been characterised by several features assigned to: rotation of phenyl rings [87–90]; diphenyl propane segments [91]; adsorbed moisture (termed ω mode) [92]; phase-transitions of various fillers [93–95]; secondary/tertiary amines or increasing molecular length [55]. The greatest number of β mode features, analysed in a single spectrum was four [96]. However, such features are not universally observed and, consequently, an alternative, recent interpretation related such effects to structural alterations caused by dehydration processes occurring during the post-curing processing [97].



**FIG. 13.** Dielectric data pertaining to the *β* relaxation of the indicated systems: (a) loss peak position as a function of frequency and temperature (dashed lines correspond to Arrhenius fitting); (b) temperature variation of *Δε*.

From the above discussion, it is evident that the β relaxation is commonly associated with dipolar species produced during crosslinking, the concentration of which increases monotonically with the crosslink density [71]. As such, the relatively low *Δε* values displayed by 0.81/20OG and 1.19/20OG compared with 1/20OG and 1/0OG are consistent with such a molecular interpretation: non-optimal stoichiometries result in a reduction in the crosslink density and fewer associated dipoles. Furthermore, at any temperature, the frequency of the β relaxation varies in the following way: 0.81/20OG > 1/20OG > 1/0OG > 1.19/20OG. Comparing 1/20OG and 1/0OG, this suggests that the associated dipoles are less constrained in the system containing OG, which is consistent with our previous proposition of loosened molecular packing, increased free volume and increased molecular mobility. However, the variation in the frequency of the β relaxation in the X/20OG sample set must arise from a different source and, to discuss this, we return to our FTIR data. It was indicated that, in these three systems, the extent of cross-linking through esterification varies as follows, 1.19/20OG > 1/20OG > 0.81/20OG, which is not unreasonable given that this process requires the involvement of an anhydride group. Although it was not possible reliably to ascertain the equivalent composition dependence of the degree of etherification by FTIR, it is evident from above that 1.19/20OG and 0.81/20OG are characterised by comparable values of both *Tg* and *Δε*, which implies comparable levels of crosslinking in both systems. That is, that the reduced level of esterification in 0.81/20OG is compensated by an increased level of etherification; these two crosslinking processes do not, however, generate moieties that are sufficiently distinct to result in two discrete dielectric processes. As such, our data are fully explicable in terms of the moieties formed during crosslinking. In contrast, alternative interpretations of the β relaxation, such as contributing phenyl-rings, do not align well with the body of data presented here.

***The γ*** ***Relaxation***.

Figure 14 shows *ε’’* data acquired at temperatures selected in order to portray the γ relaxation of the examined samples. Before any detailed analysis, consider the overall form of the *ε’’* data shown. Comparison of Figures 14a and 14b reveals a generic increase in *ε’’* on inclusion of OG. At -160 oC, the spectra appear comparable in both systems, with a peak maximum at ~2 Hz; conversely, at -120 oC the peak maximum lies at ~5 Hz in 1/0OG while, in 1/20OG, it is located at ~800 Hz.



**FIG. 14.** Imaginary part of the relative dielectric permittivity of the cured: (a) 1/0OG; (b) 1/20OG; (c) 0.81/20OG; (d) 1.19/20OG. The data were acquired over a low temperature regime to reveal the dielectric γ relaxation. All four plots are scaled equivalently to aid comparison.

Consider, now, the data obtained from 1.19/20OG at -160 oC, where two peaks are clearly visible (at ~10 Hz and ~200 Hz), with the high frequency component becoming increasingly evident, at higher temperatures. Finally, the data obtained from 0.81/20OG reveal increased losses at all frequencies and all temperatures. Increasing the temperature results in increasing losses, particularly at higher frequencies, which could be indicative of the presence of a high frequency process that increases in both magnitude and frequency, such that when sufficiently pronounced, its maximum is located above the accessible frequency range.

To test the above notion more quantitatively, the experimental data were analysed via the HN formulism, using an iterative, multi-step process based on the hypothesis that the experimental data presented in Figure 14 should be represented by two overlapping HN relaxations, termed γ1 and γ2, appearing at lower and higher frequencies, respectively. The detailed steps in our method are described in the Supplementary Material. The reliable outputs to emerge from this procedure are summarised in Figures 15a and 15b which, respectively, present the Arrhenius behaviour of the identified processes and the associated *Δε* values.



**FIG. 15.** Derived parameter values from HN analysis of the *γ* relaxation for the indicated systems: (a) loss peak positions as a function of frequency and temperature (dashed lines correspond to Arrhenius fitting); (b) temperature variation of the *Δε* values of the γ relaxations. Filled symbols: γ1 mode; open symbols: γ2 mode.

Considering first γ1, it is evident that this process is, in all systems, characterised by: behaviour that is consistent with the Arrhenius equation; comparable activation energies, with values mostly falling around 0.07 eV; values of *Δε* that increase progressively with decreasing inverse temperature, in line with previously reported behaviour [74]. Extrapolation to -90 oC leads to γ1 then falling in the frequency range 103 – 3 x 104Hz, which agrees well with the location of the higher frequency process noted earlier in Figure 12. In contrast, the data pertaining to γ2 are more sparce and are characterised by system-to-system variability. In 1.19/20OG, where the data presented in Figure 14d evince a clear γ2 relaxation peak, HN analysis results in an activation energy of about 0.04 eV and a very low value of *Δε*. In contrast, in 0.81/20OG, the derived *EA* for γ2 is increased by about an order of magnitude and this process is then characterised by high *Δε* values that approach those of γ1. For the 1/0OG and 1/20OG systems it was only possible to extract γ2 parameters in the case of three data sets and, therefore, we will not discuss these beyond highlighting the following for γ2 in 1/20OG: *Δε* is low and the *EA* appears to align with the behaviour exhibited by 0.81/20OG.

From this analysis, we suggest that γ1 relates to a process that is consistent across all four systems and is not greatly affected by changes in *SF*. Conversely, γ2 varies greatly with changes in *SF*; the influence of OG on γ2 cannot be considered due to the weakness of this process in the systems characterised by *SF* = 1 and the consequent absence of a sufficiently large body of reliable data.

The γ relaxation has previously been related to dipolar processes involving different structural units. Hirai and Kline proposed that this mode is related to unreacted epoxide chain ends [98], since they observed that post-curing resulted in either the disappearance of the γ relaxation or its merging with the β mode. Johari *et al.* [55] reported that the γ relaxation decreased to half its initial intensity upon completion of curing and, consequently, similarly related it to the presence of unreacted species. However, these workers acknowledged that further, thermally activated motions of the BADGE chains might contribute to this relaxation; an equivalent interpretation was also proposed by Dammont *et al.* [99], who described the γ mode as rising from the vibrations of main-chain sequences of four or more methylene groups, albeit it was still faintly observable in systems with shorter sequences. Pangrle *et al.* [96] proposed a main-chain origin for the γ mode, specifically relating it to polar ether linkages, in that they observed the peak to be largely invariant to network changes, such as crosslinking density/type, reacting groups and moisture content. Chang *et al*. [88], though initially ascribing the γrelaxation to ether segments, reported evidence of another peak in the close vicinity of the γ process, which they suggested may be related to unreacted epoxides when data were acquired from the uncured prepolymer. Mijović *et al.* [100] examined the spectra of various epoxy molecules (including BADGE) and, in addition to the typical α (segmental), β (hydroxyl), γ (epoxide) modes, reported a fourth relaxation, which they termed the δ mode. This they ascribed to the ether unit, which was invariant to the molecular structure/mass of the tested components. In summary, the bulk of published work concerning the origin of the γ relaxation in epoxy resins has attributed the γ relaxation either to the presence of unreacted epoxides (i.e. the motion of chain end moieties) [55,70,82,100–103] or to local motions of the glyceryl backbone (methylene sequences including ethers) [81,88,93,96,104,105].

In the context of the related literature presented above, we suggest that the data in Figures 14 and 15 are best interpreted as follows. Considering first γ1, the variation in the *Δε* value with composition parallels the variation in the β relaxation’s *Δε* value with composition presented in Figure 13b, where 1/0OG is similarly characterised by the highest *Δε* and the off-stoichiometric systems by the lowest. This suggests that γ1 is similarly related to the motion of main-chain dipoles, which, therefore, leads us to assume that the contribution to the γ1 relaxation arises from the motion of main-chain segments such as ether-containing methylene sequences. This interpretation mirrors that of studies concerning balanced stoichiometry systems, where few unreacted end groups should be present and their resulting contribution is rather weak. For example, a study considering pendant non-reactive POSS [54] attributed the γ relaxation to sequences of methylenes (equivalent to our γ1) and the behaviour with POSS addition was similar to the one reported here: a shift to higher frequency due to increased free volume resulting from the presence of the silica cage, an interpretation which we also adopt since it aligns well with our previous discussion of the α and β relaxations. As such, it would be anticipated that OG-containing systems, especially 1/20OG, would be characterised by increased *Δε* values compared with systems not containing OG, due to the relatively long OG vertex glyceryls compared with those of BADGE; however, this is not the case. Two possible explanations for this are given here. First, in the X/20OG systems, the glyceryl dipolar motion is affected by the two attached methyl groups present in the OG vertex linking chain, thereby negating the effect of the longer methylene segment in these systems. Second, longer methylene segments exist in 1/0OG due to a more advanced stage of crosslinking compared with every other sample (aligning with the reported DSC data). This association complies with the notion that the off-stoichiometric samples contain reduced methylene sequence lengths and potentially implies that the 1/0OG contains a relatively higher crosslinking density than the 1/20OG.

In considering γ2, first contrast 1.19/20OG and 0.81/20OG, which differ greatly in terms of the overall frequency dependence of *ε’’* at temperature around -140 oC. Specifically, the factors that define γ2 (shape, *EA*, frequency) differ between these two systems, which we relate to differences in their molecular origin. We suggest that the strong γ2 component seen in 0.81/20OG arises from the excess unreacted epoxides: this interpretation mirrors that of studies concerning either off-stoichiometric systems [102] or studies of the curing process that, consequently, involve high concentrations of unreacted moieties during the initial stages of the reaction [103]. For example, Mijović *et al.* [102] reported a γ relaxation that was characterised by a minimum *Δε* value at the optimum stoichiometry and increased *Δε* values in off-stoichiometric samples (either excess epoxides or hardener), while Beiner *et al.* [103] reported a γ relaxation intensity that was inversely proportional to curing completion. Additionally, this interpretation aligns well with our previously published data [27], where an excess of epoxide groups resulted in increased intensity in the high frequency tail of the reported γ relaxation. Our interpretation would then attribute the weaker γ2 signal in 1.19/20OG to the excess anhydride-based species (identified by FTIR to be predominantly half-esters), leading to its different characteristics compared with that in 0.81/20OG. In stoichiometrically well-balanced systems 1-2% of the epoxide groups are expected to remain unreacted, due to steric hindrance [77]. As such, 1/0OG and 1/20OG should, theoretically, contain comparable numbers of epoxide and anhydride groups in unreacted form. The similarity in the shape and *EA* value of the γ2 in 1/20OG and 0.81/20OG is therefore a reflection of the increased value of Δ*ε* that results from the epoxide-related contribution to *γ2*, which consequently dominates over any contribution from retained anhydride residues. The lack of reliable numerical data concerning *γ2* in 1/0OG precludes a detailed discussion, but the overall reduction in *ε’’* compared with 1/20OG despite *SF* being the same in both systems, suggests that either fewer residual unreacted moieties remain in 1/0OG (aligning with the γ1 analysis) and/or that increased constraints exist in this system, particularly if BADGE epoxides were preferentially consumed during curing, as has been suggested [36]. Decreased relaxation intensity has been reported, elsewhere, to be related to chain immobilisation and molecular constraints [54]. Indeed, comparison of the likely γ2 positions in 1/0OG with 1/20OG suggests that they lie at significantly lower frequencies in the former system, which is consistent with an increased level of constraint. While sufficient reliable data concerning 1/0OG makes further speculation of limited value, we would point out that such an interpretation is, however, consistent with factors such as the decreased *Tg* value in 1/20OG compared with 1/0OG.

Regarding the *EA* of the γ relaxation, various values have been reported in the literature [73,74,100], ranging from 0.1 to 0.4 eV; in this respect the *EA* values presented in Figure 15a and associated with different molecular origins for the γ2 process are in broad agreement, falling in the range 0.06-0.34 eV. However, previous studies of *EA* have assumed a singular γ process including contributions from different species (i.e. amalgamating γ1 and γ2). Those studies that have suggested the existence of different contributing species in the γ region [88,100] did not include a molecular dynamics analysis, such that no *EA* values were reported. Consequently, direct comparison of the *EA* values reported here for the separated γ1 and γ2 processes with the ones reported in the related literature are not directly meaningful.

Finally, we return to Figures 8 and 9 to provide a molecular interpretation for the observed dependence of *ε’* on material composition. The dipolar contributions to *ε’* will reflect the number of dipoles acting in each system and their ability, due to structural constraints, to respond to the applied field. That is, it will reflect the values of *Δε* determined for the processes that are active which, in this case at room temperature are: β; γ1; γ2. As discussed above, our interpretation of the β relaxation is that it arises from moieties generated during crosslinking and, as such, is affected by the number of crosslinks formed and the nature of the crosslinking reactions. From Figure 13, relatively low *Δε* values are therefore displayed by 0.81/20OG and 1.19/20OG compared with 1/20OG and 1/0OG. The γ1 process stems from comparable main-chain moieties and, therefore, exhibits a similar dependence on material composition. Finally, our interpretation of γ2 is that it is related to unreacted dipoles and is therefore greatly dependent on stoichiometry, with residual epoxide groups leading to much higher *Δε* values than anhydride residues: presumably this is related to the former being located at chain ends and the latter as intra-node branches. From this starting point, the contribution to the room temperature *ε’* from unreacted anhydrides and epoxides should largely be determined by the residual epoxide content of each system. In this way, it is possible to explain the data shown in Figures 8 and 9, whereby the highest value of *ε’* is exhibited by 0.81/20OG, the lowest by 1.19/20OG and intermediate and comparable values by 1/20OG and 1/0OG.

**CONCLUSIONS**

Epoxy resins with various *SF* and mol%OG-epoxides were prepared and characterised via FTIR, DSC and dielectric spectroscopy. FTIR evinced that in systems with *SF* < 1, the consequent deficit of anhydrides results in suppression of crosslinking through esterification, which normally proceeds through reactions involving the hardener. While this interpretation is chemically reasonable, the presence of OG at *SF* = 1 appears additionally to result in reduced esterification. DSC revealed the effect of material formulation on *Tg*, which was reduced for *SF* ≠ 1 in a typical asymmetric manner. The observation that off-stoichiometric systems are characterised by comparable *Tg* values suggests that the reduced level of crosslinking through esterification in systems with *SF* < 1 is compensated through etherification, even though this was not clearly demonstrated by FTIR. We associate the additional reduction in *Tg* that results from the introduction of OG for any given *SF* to two possible factors: (i) modified cure chemistry (relative importance of esterification and etherification) and (ii) loosened molecular packing, promoting increased free volume and molecular mobility. Analysis of dielectric spectra via the HN formulism revealed molecular dynamics that are consistent with the above interpretation. As commonly reported for epoxy systems, the dielectric α relaxation conforms to a non-linear VFT behaviour with the associated *Tv* parameter behaviour paralleling the *Tg* values derived by DSC. We, as elsewhere, associate the dielectric β relaxation with polar groups formed during crosslinking; the variation in the extent of esterification and etherification from system-to-system is not, however, evident in the dielectric data, presumably, because the relevant moieties that result from these two curing reactions are not sufficiently different to result in two discrete dielectric processes. The origin of the dielectric γ relaxation in epoxy resins has been a topic of some contention in the literature, with the bulk of published work ascribing this either to local motions of the glyceryl backbone or to the presence of unreacted species. From the results reported here, we were able to rationalise this apparent difference. First, the process we have termed γ1 results from the local motion of glyceryl segments and is, therefore, not markedly affected by *SF*, rather by free-volume variations. This interpretation suggests a somewhat advanced crosslinking stage in 1/0OG compared with 1/20OG, potentially adding this as an additional factor on the reduced *Tg* effect. The process termed γ2 may arise from the motion of unreacted epoxide chain ends and/or unreacted anhydride moieties and, as such, the intensity of this component varies markedly with *SF*. This interpretation results in a clear γ2 analysis in systems with *SF* ≠ 1, while it, additionally, implies that 1/0OG displays somewhat less unreacted epoxides than 1/20OG; nevertheless, the small body of reliable γ2 data in these systems rendered further speculation of limited value.

**Declaration of interest**

None

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