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Using molecular simulation to explore unusually low moisture uptake in amine-cured epoxy carbon fibre reinforced nanocomposites

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ABSTRACT: Reinforced nanocomposites based on a diamine-cured diglycidylether of bisphenol A are reported containing a mono-amino POSS reagent and polyacrylonitrile fibres. Covalent incorporation of mono-amino POSS at 2 wt % leads to especially attractive properties, including an increase (20 K) in glass transition temperature (T_g) and thermal stability (increase in char yield of up to 5 %). The addition of POSS (2 wt %) in DGEBA leads to a reduction in moisture uptake of less than 0.30-0.91 wt %, depending on relative humidity (after 6000 hours), with little effect on T_g (reduction of 9-11 K compared with 11-22 K in the unmodified DGEBA). Molecular dynamics simulation is used to visualise the cured network structure of these nanocomposites, relating free volume to water uptake. Translation of the properties from neat resin to CFRP is very encouraging with a reduction in the equilibrium moisture absorption of up to 29 % in the latter.

1. Introduction

Epoxy resins are one of the most important families of cross-linked, thermosetting polymers [1], which offer a good balance of desirable properties in the neat resin:

flexural strength (125 MPa), tensile strength (55 MPa), compressive strength (130 MPa) and impact strength ($G_{IC} = 100\text{-}125 \text{ J/m}^2$) coupled with a reasonably high glass transition temperature (T_g) of 130-160 ° C, depending on postcure [2]. This has led their widespread use in a variety of applications, including advanced composites, adhesives and as high performance dielectrics for microelectronic applications. Polymerization may occur either in the absence or in the presence of curing agents, and in this particular instance a methylated cycloaliphatic diamine is employed, because of its relatively low cure temperature.

However, the propensity of epoxy resins to absorb moisture is an acknowledged drawback associated with their use in applications in which retention of mechanical properties in hot/wet conditions is key. The epoxy system studied here is space qualified for use in structural composites in satellite applications and thus already displays a comparatively low moisture uptake in the unmodified state. However, as the construction of a larger satellite may take a number of months (even years) to complete, then even thicker structures may reach equilibrium moisture content during this timescale. Once sorbed, this moisture will tend to remain within the matrix until the satellite is deployed in an extra-terrestrial environment, when the dramatic reduction in atmospheric pressure serves to cause the molecular water to be removed (violently in some instances) from the composite, potentially leading to delamination or small vibrations in rigid boom structures, which can disturb the operation of optical benches.

Polyhedral oligomeric silsesquioxanes (or POSS reagents) are well known [3] for the benefits in thermal and mechanical properties that they can confer when incorporated into both thermoplastic [4] and thermoset [5] polymers. The dimensions of the silica polyhedral are such that the materials may be covalently bound and compatible at the molecular scale. We have previously reported [2,6] the attractive balance of physical properties for a series of neat resin blends incorporating POSS, but

this would be of little immediate use if the translation from neat resin to composite fails to succeed. Thus, the aim of the present paper is to examine whether the very favourable influence of POSS is maintained when reinforced with carbon fibres and to relate this to structural changes taking place within the resin on cure through molecular simulation.

2. Experimental

2.1 Materials

The epoxy oligomer, based on DGEBA ($M_w = 175.5 \pm 3.5$ g/mol.) and dimethyl-methylene-*bis*(cyclohexylamine) were characterised using FTIR, Raman and ^1H NMR spectroscopies to confirm identity, and used as received. Aminopropylisobutyl POSS, hereafter referred to as POSS, was obtained from Hybrid Plastics, Inc. (Hattiesburg, USA) characterised using Raman spectroscopy and used as received. The structures are shown in Scheme S1 (supplementary material).

2.2 Blending and cure of polymer samples for thermo-mechanical analyses

The mono-amino POSS (various quantities were studied at 0.5, 1, 2, and 4 wt-% (or 7.7×10^{-5} - 6.1×10^{-4} mol.) was dissolved in minimal amounts of THF followed by the addition of DGEBA (5 g, 28 mmol.). The mixture is heated and stirred at 80°C on a heating plate for 2 hours or until the THF has dissolved. The mixture is then placed into a vacuum oven for 1 hour at 50°C to ensure that all the solvent has been removed. The cyclohexylamine curing agent is then added and stirred for another 20 minutes until a homogenous mixture is formed. The resulting mixture is then poured into aluminium pans and placed in the oven to be cured at 4 hours at 60°C and 3 hours at 130°C. The final compositions along with sample designations are shown in Table S1. The following nomenclature is used: the pure diamine-cured epoxy is designated as

DGEBA; an epoxy blend containing 2 wt % POSS is DEGBA-POSS_{2%}. The same convention is used for the composite, but this is prefixed with a C, thus a composite containing an epoxy blend containing 2 wt % POSS is C(DEGBA-POSS_{2%}). Samples for DMTA measurements were cured in aluminium dishes (55 mm diameter, depth 10 mm) in a fan-assisted oven: heating from room temperature to 60°C (4 hours isothermal) + heating to 130°C (3 hours) followed by a gradual cool to room temperature. Cured samples (Fig. S1) were cut to the correct token size for analysis using a diamond saw.

2.3 Preparation of carbon fibre reinforced composites

The next stage in the investigation was to manufacture composite samples containing a blend of DGEBA/amine and POSS, based on the measurements made on the neat resins. The manufacturing of composite panels (700 mm x 800 mm) comprising polyacrylonitrile fibres was performed by Astrium GmbH Germany using an automated fibre tow placement manufacturing process and a proprietary cure cycle incorporating a maximum curing temperature of 100 °C.

2.4 Characterisation

Vibrational spectra were obtained using a Perkin-Elmer system 2000 FT-NIR-Raman spectrometer operating at 250 mW (Nd-YAG laser) and a Perkin-Elmer FTIR system 2000 spectrometer. For each measurement, 16 spectra were obtained at a resolution of 4 cm⁻¹ and co-added to produce the final spectrum. DSC was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples (6.0 ± 0.5 mg) in hermetically sealed aluminium pans. Dynamic experiments were conducted at a heating rate of 10 K/min. from room temperature to 250°C (heat/cool/heat) under flowing nitrogen (50 cm³/min.). For isothermal analyses samples were heated at 50 K/min. to 60, 70, 80, 90, 100, 110 and 120 °C and held at the final temperature for 1- 3

hours, then cooled to room temperature at 10 K/min. The T_g was determined from the midpoint of the inflexion in the heat flow curve during both the cooling step and the re-scan (heating) experiment. DMTA was carried out in single cantilever mode at a frequency of 1 Hz on cured neat resin samples and composites ($2 \times 15 \times 35 \text{ mm}^3$) using a TA Instruments Q800 operating in static air. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 on cured particulate resin samples and small sections of composite ($7.5 \pm 0.5 \text{ mg}$) in a platinum crucible from 20-800 °C at 10 K/min in nitrogen ($40 \text{ cm}^3/\text{min}$). For the determination of moisture content, samples of cured epoxy nanocomposites ($2 \times 12 \times 30 \text{ mm}^3 \pm 0.5 \text{ mm}$) were conditioned in three chambers each of controlled relative humidity: 33 % RH (containing magnesium chloride), 53 % RH (containing magnesium nitrate) and 75 % RH (containing sodium chloride); each salt solution contained distilled water. Samples were allowed to equilibrate over approximately 12 months and the moisture content of the cured epoxy resins was determined periodically by wiping excess moisture from the surface with a tissue and measuring the increase in mass.

2.5 Molecular Modelling

The molecular modelling program Accelrys Materials Studio [7] (initially version 5.5, which was subsequently upgraded to version 6.0, which is functionally similar) was utilised within this work and all the modelling work was carried out using an in house PC. The potential energy for all models throughout this work was calculated using the Condensed-phase Optimised Molecular Potential for Atomistic Simulation Studies (COMPASS) [8], a force field specifically designed for polymer calculations. Molecular models were all created using a combination of the Materials Studio [7] modules and in-house programs to simulate cure.

2.5.1 Construction of the monomer using molecular mechanics

Initially, the structure of the epoxy-amine adduct/oligomer was simulated at zero Kelvin using molecular mechanics (MM) [9]. The steepest-descent, conjugate gradients and Newtonian [10] methods were performed to minimise the energy of the molecule. This yielded bond lengths that agreed well with published crystallographic data (Table 1) for similar monomers or compounds [11]. The Materials Studio Visualiser was used to create 3D models of the monomers and impurities, which were then packed into a periodic cell, which was repeated in 3D space with voidless packing.

Table 1 Selected Bond lengths in the epoxy resin obtained using molecular mechanics
(zero Kelvin) within Materials Studio (for the given configuration)

Bond lengths (Å) in a single chain model		
	Modelling data	Empirical data [11]
C6-O	1.39	1.39
O-C7	1.41	1.42
C7-C8	1.56	1.55
C8-O	1.41	1.43
C8-C9	1.57	1.55
C9-N	1.50	1.49
N-C10	1.49	1.50

2.5.2 Construction of the cured polymer using the automated cure program

With the virtual space filled with the monomer mixture, control of the model was passed over to an in-house program to proceed with cure [12]. The target density for the cell was set (within the automated program) at 1.15 g cm^{-3} [**Error! Bookmark not defined.**] and the polymer chains were packed to this value. To form the cross-linked epoxy network to different selected degrees of conversion, the automated curing programme was employed with the polymer-consistent force field (PCFF) and cut-off distance of 5.5-7.5 Å; the dynamics duration was set at between 1,000 and 10,000 fs and the simulated cure temperatures were 333 and 403 K.

2.5.3 Simulation of the cured polymer properties using molecular dynamics

The temperature ramped MD simulations were performed using the Temperature Cycle option in the Amorphous Cell Protocols. An NPT ensemble (0.0001 GPa) was used at the selected experimental temperature, with a time step of 1 fs. The Anderson thermostat was used in combination with the Barendsen barostat [13]. COMPASS was used with the atomic van der Waals summation, a cut-off at 9.50 Å, a spline width of 1.00 Å and a buffer width of 0.50 Å. Thus, a collection of MD simulations was run over different temperatures, with decrements of 10 K from the starting temperature. The starting temperature was set at between 573 and 773 K, and a typical total of 31-51 MD simulations were performed, ranging between 773 K and 273 K. At each temperature stage the structure was minimised prior to performing the MD simulation to enable the system to reach equilibration. The T_g of the cured epoxy network was determined by using the methodology and a Visual Basic script developed by Hall *et al.* [12] to find the best fit for a gradient change as a function of temperature (Fig. S2). This output was used to determine the position of the thermal events, but for clarity, the plots have been omitted from the simulated data sets presented later.

3. Results and Discussion

The mechanism of the cure reaction is comparatively well known (Scheme S1) [2].

Kinetic data for the reaction, derived from DSC, yielded activation energies of 57.6 kJ mol⁻¹ (using the Kissinger method [14]) and 61.1 kJ mol⁻¹ (non-isothermal isoconversional kinetic Ozawa method) [15], which correlated well with literature values (50-70 kJ/mol.) [16] using the same treatment. A subtle modification is required when POSS is used as pre-reaction facilitates a well-dispersed blend, which is essential to achieving the optimum properties [17].

3.1 Examination of the thermal stability of the cured epoxy resin and nanocomposites

TGA was initially applied to evaluate the thermal stability of the cured neat resins (Fig. 1). The TGA curves display similar degradation profiles (particularly evident in the derivative data) indicating that the presence of POSS does not significantly alter the degradation mechanism of the epoxy matrix (at this level of incorporation). As expected, the measured char yields increase progressively with the mass of POSS incorporated (Table 2).

Fig. 1. TGA data for cured neat DGEBA and DGEBA-POSS samples (10 K min^{-1} , N_2).

The degradation proceeds in several coincident steps over a range of 300-450 °C. with the initial decomposition (T_{dec}) approximating to 350-450 °C. The first step may be attributed to the breakdown of inter-ring bridges and the cycloaliphatic rings, but comparatively little char formation takes place, in contrast with other more aromatic epoxy resin systems [6]. Aside from the composition containing 0.5 wt %, the addition of POSS has little effect on the T_{dec} ; the char yields increase with the POSS content, due to the formation of an inert silica layer on the surface of materials when decomposition takes place [18,19,20]. The TGA profiles of the CFRP samples (Fig. 2) reinforced composites are inherently more thermally stable than the neat resins with a higher char yield, due to the mass of fibre remaining. The degradation profiles of

C(DGEBA-POSS_{2%}) suggests that these behave in the same manner as C(DGEBA), where at least two coincident processes are apparent.

Table 2 Thermal degradation characteristics of the cured neat epoxy resin samples, containing different quantities of POSS

Sample	Mass loss as a function of temperature (° C)				T _{dec} (° C)	Y _c (%)
	5 %	10 %	25 %	50 %		
DGEBA	343	353	358	378	372	2.4
DGEBA-POSS _{0.5%}	332	344	350	374	363	7.6
DGEBA-POSS _{1%}	340	350	355	377	362	5.1
DGEBA-POSS _{2%}	341	350	355	375	368	5.1
DGEBA-POSS _{4%}	341	350	356	376	368	4.7

Key: T_{dec} at maximum rate of decomposition, char yield (Y_c) recorded at 800 °C.

Fig. 2. TGA thermograms of C(DGEBA) and C(DGEBA-POSS_{2%}).

The onset of degradation denoted by 5% weight loss shows that both C(DGEBA) and C(DGEBA-POSS_{2%}) begin to decompose in the same temperature range at the neat resin blends. The final char yields are also practically the same, indicating that the addition of POSS does not greatly affect the degradation mechanism of C(DGEBA).

Table 3 Thermal degradation characteristics of C(DGEBA) and C(DGEBA-POSS_{2%}).

Sample	Mass loss as a function of temperature (° C)			T _{dec} (° C)	Y _c (%)
	5%	10%	20%		
C(DGEBA)	337	351	369	365	63
C(DGEBA- POSS _{2%})	337	352	373	365	65

Key: T_{dec} at maximum rate of decomposition, char yield (Y_c) recorded at 800 °C.

3.2 Thermo-mechanical characterisation of the cured DGEBA and POSS nanocomposites and reinforced resins

DMTA data for neat resin samples of DGEBA and DGEBA-POSS blends are presented (Fig. 3). The glass transition (α -transition) is clearly visible for DGEBA in the $\tan \delta$ data at 120 °C ($T_{\max}$ at 10 K/min) with a drop in the storage modulus of around 2400 MPa in this region; a subtle lower temperature transition (T_g') is visible between 50-100 °C. The addition of POSS into the DGEBA-amine system effects an increase in T_g , albeit at the expense of modulus. The loadings of both 0.5 wt % and 1 wt % raise the T_g by *ca.* 25 K; both 2 wt % and 4 wt % raise it by 50 K and the coincidence of the T values suggests similarities in the network morphologies.

Fig. 3. Storage modulus (top) and $\tan \delta$ (bottom) data for various DGEBA-POSS samples (designated by the POSS content) as a function of temperature.

The introduction of bulky POSS cages in this case hinder polymer chain motion and therefore increase T_g . The breadth of the $\tan \delta$ peaks can also indicate similarities in the damping behaviour of cured epoxy resins (and other thermosets) and the peak width represents the temperature range over which the glass transition temperature occurs. Thus, a broad $\tan \delta$ peak can be attributed to more heterogeneous networks containing both highly- and less-densely crosslinked regions [21]. In this case, the data show a comparatively narrow distribution indicating a more homogeneous network. The unmodified epoxy blend contains two difunctional reactants yielding a highly crosslinked network. Being a mono-amine, the addition of POSS forms a linear chain in the reaction with the DGEBA with the diamine serving as a crosslinking agent. Consequently, the increasing addition of POSS should lead to a reduction in the crosslink density of the epoxy-anhydride network due to its low functionality. The

crosslink density (ν) for each of the cured epoxy networks was calculated from the DMTA data using (Eq. 1) [22]:

$$\nu = G_e / \phi RT_e \quad (\text{Eq. 1})$$

Where ϕ is taken as unity, G_e is the storage modulus strictly from a sample at equilibrium, but is taken at T_e , where $T_e = (T_g + 50 \text{ K})$. This equation is technically most appropriate for lightly cross-linked materials so it should only be used as a comparison between similar materials (*i.e.* in a homologous series), rather than giving a definitive value for crosslink density. This leads to a value of $\nu = 2.32 \text{ mol m}^{-3}$ for DGEBA, which is somewhat higher than the $\nu = 1.7 \text{ mol m}^{-3}$ for a cured epoxy produced from difunctional monomers [23]. The incorporation of POSS has been shown to lead to both increases and decreases in T_g , where the POSS units can act as either reinforcing fillers or as plasticising agents, depending on several competing factors such as restricting polymer chain movement and increasing free volume.

The calculated values of the cross-link density (Table 4) confirm that in this system only a small amount of POSS is required to increase significantly the cross-link density of the matrix. At temperatures above T_g there are very little changes in the storage modulus. A significant increase in the height of the $\tan \delta$ curve for DGEBA-POSS_{1%} suggests a more cross-linked system due to a better polymer-filler interaction, decreasing the polymer chain motion and ultimately shifting the T_g to a higher temperature. In all cases, an improvement of the cross-link density was also observed. The DMTA data for the for C(DGEBA) and C(DGEBA-POSS_{2%}) are shown in Fig. 4. The addition of POSS into the composite sample led to decreases in both the storage modulus (by 1300 MPa) and the T_g (albeit a modest reduction of 5 K, Table 5).

Table 4 Average cross link density (ν , $\times 10^{-3}$ mol cm $^{-3}$) of DGEBA-POSS systems

Sample	T_e (K)	G_e (MPa)	ν ($\times 10^{-3}$ mol cm $^{-3}$)
DGEBA	446	8.6	2.3
DGEBA-POSS _{0.5%}	469	14.9	3.8
DGEBA-POSS _{1%}	455	17.5	4.6
DGEBA-POSS _{2%}	483	20.5	5.2
DGEBA-POSS _{4%}	485	29.2	7.2

The storage modulus in the rubbery region was also significantly increased. An increase in damping loss ($\tan \delta$ peak height) correlates to a loss in interfacial adhesion [24], but in this case, when POSS is incorporated into the matrix system, the peak height decreases, thus suggesting an increase in the interfacial adhesion between the fibre and matrix. This may be attributed to the restriction in chain mobility of the polymer in the immediate vicinity of the fibre reinforcement.

Fig. 4. Storage modulus and loss modulus (top) and $\tan \delta$ (bottom) data as a function of temperature for C(DGEBA) and C(DGEBA-POSS_{2%})

The enhancement of rubbery modulus seen in similar nanocomposites, but less evident here, has been attributed to the POSS filler effect [25], which includes (i) the

Table 5 Glass transition temperatures for composite samples

POSS (wt %)	T _g (°C) from Loss modulus (E'')	T _g (°C) from Tan δ
DGEBA	124	129
DGEBA-POSS _{2%}	119	124

hydrodynamic effect leading to strain amplification due to the presence of a hard filler in rubbery matrix, (ii) the formation of physical crosslinks – *i.e.* crystalline POSS domains (as the butyl-substituted POSS would be partly crystalline in the matrix) that are covalently attached to a network, (iii) the immobilization of network chains by interaction and formation of a hard interphase layer thus increasing both T_g and rubbery modulus, (iv) the percolation of the filler within a matrix. However, it is important to note that the levels of monoamino-POSS incorporation are quite modest (< 4 wt %) making (i) less significant; that the POSS is well dispersed making (ii) of less significance; that being covalently bonded, the percolation of POSS through the matrix (iv) is severely limited.

3.3 Determination of moisture absorption in the neat resins and nanocomposites

The behaviour of the cured DGEBA and DGEBA-POSS neat resin samples following exposure to atmospheres of different controlled humidities were previously reported [2,6] and similar conditions were maintained here for direct comparisons to be made. All samples displayed Fickian behaviour: the absorption curve (the relationship between the moisture uptake and the square root of time at the beginning of the absorption process) was initially linear and the moisture content reach saturation level (Fig. 5). When POSS was incorporated into the DGEBA formulation, generally an increase in diffusion coefficient is observed (Table 6), which is attributed to an increase in free volume, along with a marked reduction in equilibrium moisture content.

Fig. 5. Water absorption graphs for DGEBA-POSS samples containing different concentrations of POSS at **(a)** 33% RH **(b)** 52% RH and **(c)** 75% RH

For the samples containing 2 wt-% addition of POSS, the maximum moisture absorption is evidently significantly lower than the unmodified DGEBA. Epoxy resins are well known for their ability to sorb moisture and Wright established a semi-empirical guide to demonstrate that an average reduction in T_g of up to 20 K was observed for every 1 % of moisture sorbed [26]. The unmodified epoxy structure featured in this study is routinely employed in advanced composites due to its reduced moisture uptake. As the manufacture of a large component might take months or even several years to complete (and total elimination of moisture from the production environment would be impractical), there is much time available for the sorption of

moisture to reach equilibrium. The epoxy featured in this study is routinely employed in advanced composites for space vehicles. The manufacturing of a large

Table 6 Moisture conditioning of DGEBA-POSS resins at various humidities

RH	Sample	Thickness (mm)	M_m (%)	Diffusivity (x 10⁻⁶ mm²/sec)
33 %	DGEBA	2.02	0.66	7.24
	DGEBA- POSS _{0.5%}	1.77	0.54	8.74
	DGEBA-POSS _{1%}	1.68	0.55	8.55
	DGEBA-POSS _{2%}	1.73	0.39	6.26
	DGEBA-POSS _{4%}	2.10	0.51	8.35
52 %	DGEBA	2.00	1.52	7.77
	DGEBA- POSS _{0.5%}	1.86	1.20	7.82
	DGEBA-POSS _{1%}	1.69	1.22	5.96
	DGEBA-POSS _{2%}	1.86	0.90	9.84
	DGEBA-POSS _{4%}	1.95	1.26	9.87
75 %	DGEBA	1.84	1.57	6.10
	DGEBA- POSS _{0.5%}	1.65	1.25	10.55
	DGEBA-POSS _{1%}	1.51	1.27	5.52
	DGEBA-POSS _{2%}	1.75	0.91	7.95
	DGEBA-POSS _{4%}	1.70	1.27	7.01

satellite might take several months or even several years to complete, and along with long storage time, would provide ample opportunity and time for the sorption of moisture to reach equilibrium. Consequently, the prediction of the effects of moisture uptake has particular importance in this instance. The first stage in this study was to investigate the free volume in a unit cell when POSS was added following cure steps of 60°C and 130°C to mimic the empirical cure schedule.

The data obtained for a relative humidity of 75 % RH were selected for the simulation study. The maximum moisture content for each system was inserted into the models and the thermo-mechanical results were obtained. The electrostatic interaction calculations were passed over to the COMPASS force field through the Forcite module, which includes terms for electrostatic interactions (based on partial charges, calculated from the local environment). The maximum solvent radius used to calculate the free volume was set at 1.4 Å as this is typical with water. Fig. 6a shows an example of the highlighted free volume within a cured network. Once the free volume is mapped. The modelling of moisture ingress is possible through the insertion of water molecules into the available free volume within the cured network of the epoxy system. From the empirical data, 75% out in the cured network, water molecules can be inserted into the model. Fig. 6b shows the same model but the cured network is removed for clarity, to show the position of the water molecules. Table 8 summarises the occupied and free volume of models cured at both temperatures and the extent of cure conversion. In both cases, the same trend can be seen for the occupied and total volume: the total volume increases with POSS content (a bulky pendant group). However, there does not appear to be a definite trend in the percentage free volume; some compositions yield significant reductions in free volume for similar degrees of network conversion. As expected, the higher cure temperature generates a more cross-linked network and lower

free volume. Normally, the insertion of polar molecule in the matrix does not generate satisfactory results for chemical potentials (to find the position of equilibrium) and one should take note that using this method the correct equilibrium water concentration can not be predicted. More accurate approaches such as simulations in the open system [27,28] are needed to correctly predict the solubility accurately.

Table 7 Summary of the volume, surface area and degree of cure of the neat and DGEBA-POSS models cured *in silico* at different temperatures

POSS (wt %)	Occupied vol (Å³)	Free vol . (Å³)	Total vol. (Å³)	Free vol. (%)	Conv. (%)
Model cured <i>in silico</i> at 60 °C					
0	75957.2	850.7	76807.9	1.10	78.7
0.5	76591.9	737.8	77329.8	0.95	73.7
1	80117.4	832.6	80950.0	1.03	72.7
2	81281.2	927.8	82209.0	1.13	74.3
4	85275.9	730.6	86006.5	0.85	74.8
Model cured <i>in silico</i> at 130 °C					
0	76257.8	701.7	76959.5	0.91	80.8
0.5	77535.4	596.7	78132.1	0.76	79.2
1	78530.7	786.2	79316.9	0.99	76.7
2	81337.4	805.9	82143.4	0.98	76.7
4	86124.0	790.9	86914.9	0.91	73.3

Fig. 6 (a) Molecular simulation of DGEBA-POSS_{2%}, (b) highlighted free volume within a cured network water molecules incorporated into the accessible free volume (cured network removed for clarity).

3.4 Thermo-mechanical characterisation of the cured DGEBA and POSS nanocomposites and reinforced resins

The effects on the $\tan \delta$ response of the samples after exposure to moisture are shown in Fig. 7 (storage moduli data are given in Fig. S3). The overall reduction in the $\tan \delta$ values and the shift of T_g to lower temperatures (Table 8) indicates that the sorbed water acts as a plasticiser, increasing chain mobility. Some of the hydrated samples also show a splitting of the $\tan \delta$ peaks which may be attributed to the presence of two types of bound water: singly- and doubly-hydrogen bonded. Single hydrogen bonded water can disturb the inter-chain van der Waals forces in the polymer network resulting in an increase in chain mobility which is known as plasticisation; double hydrogen bonds form with the polymer network due to prolonged exposure and can act as cross-links in between polymer chains. Therefore, the desorption of water during DMTA testing can lead to two peaks, since type 1 bound water can dissipate from the matrix first due to lower activation energy, leaving type 2 bound water which requires higher temperatures for desorption. It has been observed [29] that in some instances POSS bearing aliphatic substituents have migrated to the sample surface of polymer blends

Table 8 A comparison of the T_g and crosslink density of DGEBA and DGEBA-POSS resins before and after moisture testing

RH	POSS (wt %)	Loss modulus (° C)		Decrease in T_g (° K)	M_m (%)	v ($\times 10^{-3}$ mol cm ⁻³)	
		Before	After			Before	After
33 %	0	156	145	11	0.66	6.07	3.63
	0.5	146	137	9	0.54	3.86	3.43
	1	144	135	9	0.55	6.14	3.12
	2	96	89	7	0.39	6.98	0.90
	4	132	123	9	0.51	6.90	4.20
52 %	0	156	137	18	1.52	6.07	3.57
	0.5	146	132	14	1.20	3.86	4.09
	1	144	133	11	1.22	6.14	3.00
	2	96	87	9	0.90	6.98	0.92
	4	132	116	16	1.26	6.90	4.24
75 %	0	156	133	22	1.57	6.07	2.70
	0.5	146	133	13	1.25	3.86	1.90
	1	144	133	11	1.27	6.14	1.99
	2	96	87	9	0.91	6.98	1.07
	4	132	122	10	1.27	6.90	1.87

and dramatically increase the hydrophobicity of the nanocomposites. However, the pre-reaction of the POSS with one component of the blend prior to incorporation makes it less likely that the POSS is drawn to the surface of the resin, since its mobility will be severely restricted. Rather, the POSS becomes well dispersed within the three-dimensional network. This situation is not dissimilar from recent research published by

Fig. 7 Changes in $\tan \delta$ as a function of temperature at varying humidities of (a) 0.5% (b) 1% (c) 2% and (d) 4% DGEBA-POSS samples.

us in the area of POSS nano-reinforced polypropylene matrices [4] in which the dispersion of the POSS (at similar levels of loading, *ca.* 5 wt-%) was confirmed using SEM-EDX. The authors believe that the flexibility of the alkylene tether, by which the POSS is bonded covalently, allows sufficient movement to enable molecular cavities to be hindered by the hydrophobic POSS cage, thus shielding potential sites for hydrogen bonding. Table 9 also summarises the T_g and cross-link density before and after moisture testing. There is always a reduction in the T_g following long-term exposure to moisture, but the addition of POSS has a significant effect in reducing the impact on cure T_g . In the best case, (2 wt %) in DGEBA leads to a reduction in moisture uptake of less than 0.30-0.91 wt %, depending on relative humidity (after 6000 hours immersion), while leaving T_g (reduction of 9-11 K compared with 11-22 K in the unmodified DGEBA).

3.5 Determination of moisture absorption in the reinforced resins and nanocomposites

Humidity testing was applied to C(DGEBA) and C(DGEBA-POSS_{2%}) at 52 % and 75 % RH and the summary of the data are given in Table 9.

Table 9 Comparison of the T_g of composites before and after moisture testing

RH	POSS (wt %)	Loss modulus (° C)		Decrease in T_g (° K)	M_m (%)
		Before	After		
52 %	0	125	120	5	0.52
	2	120	115	5	0.45
75 %	0	125	117	8	0.82
	2	120	114	6	0.58

The moisture absorption profiles of the composite samples are shown in Fig. 8 and follow a Fickian diffusion process. The addition of 2 wt % POSS into the DGEBA-diamine composite system, C(DGEBA-POSS_{2%}), demonstrated a reduction in equilibrium moisture uptake of 29 % at 75 % RH (compared with a reduction of 28 % in the neat resin) and a reduction of 13 % at 52 % RH (compared with a reduction of 9 % in the neat resin).

Figure 8 Water absorption graphs of composite samples at 52 % and 75 % RH as a function of POSS content

The corresponding DMTA results (Fig. S4) show the loss and storage modulus before and after moisture conditioning, demonstrating that although there is some effect on modulus.

4. Conclusions

Preliminary analysis of amine-cured DGEBA neat resin samples suggested that incorporating comparatively low levels (0.5-4 wt %) of POSS had the potential to enhance significantly a variety of key performance parameters (resulting in increased modulus, T_g and, most importantly, reduced moisture absorption). In the current work, we have confirmed the translation of these desirable characteristics from neat resin to the more complex architecture of a carbon fibre reinforced composite structure, avoiding many of the deleterious impacts on the observed physical properties. Detailed MD simulations using COMPASS force field have been performed on a polymer network model comprising the equivalent of 2 wt % POSS to emulate the empirical measurements, underlining the utility of this method when used carefully using empirical data.

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References

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- [1] I. Hamerton. Epoxy resins, in *Encyclopaedia of Chemical Processing*, S. Lee (Ed.) DOI:10.1081/E-ECHP-12000775 (2006) Taylor & Francis.
 - [2] I. Hamerton, W. Tang, J.V. Anguita, S.R.P. Silva. *React. Func. Polym.* 74 (2013) 1-15.
 - [3] G. Li, L. Wang, H. Ni, C. U. Pittman, Jr. *J. Inorg. Org. Polym.* 11 (2001) 123-154.
 - [4] E.R. Smith, B.J. Howlin, I. Hamerton. *J. Mater. Chem. A* 1 (2013) 12971-12980.
 - [5] S. Nagendiran, M. K. Alagar, I. Hamerton. *Acta Mater.* 58 (2010) 3345-3356.

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- [6] I. Hamerton, W. Tang, J.V. Anguita, S.R.P. Silva. *Mater. Today Commun.* 4 (2015), 186-198.
- [7] Accelrys Materials Studio Version v 6.0.0.0 (2012). Accelrys Inc., San Diego, USA.
- [8] H. Sun, S.J. Mumby, J.R. Maple, A.T. Hagler. *J. Amer. Chem. Soc.* 116 (1994) 2978-2987.
- [9] U. Burkert, N.L. Allinger. *Molecular Mechanics*, ACS Monograph (1982) p. 177
- [10] J.M. Goodman. *Chemical Applications of Molecular Modelling*, RSC: Cambridge (1998) pp. 31-60.
- [11] F.H. Allen, D.G. Watson L. Brammer A.G. Oprea, R. Taylor. Typical interatomic distances: organic compounds, in *International Tables for Crystallography* (2006) pp. 790-811
- [12] S.A. Hall, B.J. Howlin, I. Hamerton, A. Baidak, C. Billaud, S. Ward. *PLOS One* 7(8): e42928 (2012).
- [13] H. Berendsen, J. Postma, W. van Gunsteren, A. Dinolaand, J. Haak. *J. Chem. Phys.* 81 (1984) 3684-3690.
- [14] J.H. Flynn. *J. Thermal Anal. Chem.* 27 (1983) 95-102.
- [15] T. Ozawa. *Anal. Chem.* 2 (1970) 301-324.
- [16] S. Vyazovkin, A. Mititelu, N. Sbirrazzuoli. *Macromol. Rapid Commun.* 2 (2003) 1060-1065.
- [17] O. Supova, G.S. Martynkova, K. Barabaszova. *Sci. Adv. Mater.* 3 (2010) 1-25.
- [18] Z. Zhang, A. Gu, G. Liang, P. Ren, J. Xie, X. Wang. *Polym. Degrad. Stab.* 92 (2007) 1986.
- [19] Z. Zhang, G. Liang, X. Wang. *Polym. Bull.* 58 (2007) 1013.
- [20] H. Dodiuk, S. Kenig, I. Blinsky, A. Dotan, A. Buchman. *Internat. J. Adhesion Adhesives* 25 (2005) 211.
- [21] A.R. Kannurpatti, J.W. Anseth, C.N. Bowman. *Polymer* 39 (1998) 2507-2513.
- [22] D.J. Allen, H. Ishida. *J. Appl. Polym. Sci.* 101 (2006) 2798-2809.
- [23] F. Cardona, C. Moscou. Synthesis and characterisation of modified phenolic resins for composites with enhanced mechanical properties, In: *ACMSM 20: Futures in Mechanics of Structures and Materials*, 2-5 Dec 2008, Toowoomba, Australia (2009).
- [24] J.M. Kennedy, D.D. Edie, A. Banerjee, R.J. Cano. *J. Compos. Mater.* 26 (1992) 869.
- [25] N.T. Dintcheva, E. Morici, R. Arrigo, F.P. La Mantia. *Polym. J.* 46 (2014) 160-166.

-
- [26] W.W. Wright, Composites 37 (1981) 201-205.
- [27] H. Eslami, N. Mehdipour, Phys. Chem. Chem. Phys., 2011,13, 669-673
- [28] J. J. de Pablo, M. Laso, U. W. Suter, Macromolecules, 2007, 40 (17), pp 6413-6421
- [29] Y. Tang, M. Lewin, Polym. Adv. Technol. 20 (2009) 1-15.

Molecular dynamics simulation of a DGEBA unit cell containing 2 wt % POSS following cure *in silico* at 60 °C and 130 °C respectively. The model shows the water molecules incorporated into the accessible free volume (red surface).