

Thermal stability and water uptake of high performance epoxy layered silicate nanocomposites

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Abstract

Intercalated and ordered exfoliated layered silicate nanocomposites based on three different epoxy resins of different structures and functionalities were synthesized using an octadecyl ammonium modified smectite clay. Water uptake properties of series of each nanocomposite system with different organoclay concentrations were determined by gravimetric measurements over a period of time. The diffusion coefficients were determined and the effect of the absorbed water on the thermal relaxations investigated. The equilibrium water uptake of all nanocomposites was reduced compared to the neat epoxy system but the rate of water diffusion remained unaffected. Further, the thermal stability of the different nanocomposites was determined using thermogravimetric analysis. The nanocomposites showed slightly reduced thermal stability, as indicated by a slight decrease in onset of degradation, whilst the final char concentration increased for greater organoclay concentrations.

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1. Introduction

The use of organically modified layered silicates (OLS) as a reinforcing filler for flexible epoxy resin systems with low glass transitions has shown significant improvement in the mechanical properties (modulus and toughness in some cases) when dispersed on a nanometer scale [1–3]. More recently, it was found that these fillers also show potential for use in more highly cross-linked resin systems with high glass transition temperatures, as commonly used in aerospace and other high performance applications [4–6]. However, in order to qualify for the use in these applications with increased technical demands and economic and legislative requirements, knowledge of the performance of this new class of material under extreme environmental condi-

tions such as moisture and elevated temperatures is required.

The water uptake of neat epoxy resin systems [7–12] or epoxy-based fiber composites [13,14] has been widely discussed and is known to have significant effects on the overall properties of the polymer or composite material. The water molecules are often assumed to occur in two different environments in the polymer matrix: the water is either strongly interacting with specific (polar) groups of the epoxy matrix or clustered together in free volume micro-voids as “free water”. The water sorption behavior is hence considered to depend on free volume properties and type and concentration of polar groups in the epoxy system. Whilst the effect of water sorption is reversible to a certain extent, the combination of elevated temperatures and absorbed water may also lead to irreversible degradation which is a particular concern in high performance applications. The major drawbacks of water sorption that have often been reported are its plasticizing effect, leading to a reduced glass transition temperature, decreased modulus and compressive strengths, chain scission and hardener degradation as

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well as possible detachment of the resin from the fiber in composite materials. De'Néve and Shanahan [11], for example, show that Young's Modulus changes from before and after exposure to water at between 40 and 70 °C, and degradation products can also be seen by infrared analysis.

Major studies by Massam and co-workers [15,16] have investigated the resistance of glassy DGEBA based nanocomposites towards organic solvents and water. It was found that the absorption of methanol, ethanol and propanol was faster in the neat epoxy system, compared to the nanocomposite and that properties of the neat systems were much more affected by the absorbed solvent. In the case of water however, only the rate of absorption was reduced. The equilibrium water uptake was found to be relatively unaffected. It was further observed that the barrier to solvent uptake was more significant in the exfoliated composite compared to the conventional or intercalated layered silicate composite. Shah et al. [17] have recently reported a study on moisture uptake of vinyl ester based organically modified montmorillonite nanocomposites. Although the moisture diffusivity was decreased through the clay addition, the equilibrium moisture uptake was found to increase with the amount of layered silicate added. It was also reported that the diffusion coefficient did not differ significantly between two different clay modifications, which gave different dispersion or separation of the layered silicate. It was theorized that the decreased diffusivity might be ascribed to the restricted motion of polymer chains, which are associated with the clay particles. The increase in total water uptake was ascribed to the attraction the clay particles show to moisture.

Along with water uptake, the thermal stability of the nanocomposite is investigated in this study. As well as the epoxy matrix, the alkylammonium compatibilizer, which is well established as a common surface modifier for the layered silicate to achieve good intercalation or exfoliation, is also sensitive to degradation at elevated temperatures. A widely applied technique to assess the thermal stability of a material is the thermo-gravimetric analysis (TGA), where the sample material is usually exposed to a constantly increasing temperature under a defined inert or oxidizing atmosphere, whilst changes in the sample weight are recorded.

Improved thermal stability has been reported for several thermoplastic layered silicate nanocomposites [18–21]. To date, the thermal stability of epoxy nanocomposites has only been investigated for DGEBA based systems. All studies have reported improvement in thermal stability with addition of layered silicate [3,22,23]. Park et al. [22] reported an increased activation energy of decomposition, increased temperature of maximum rate of weight loss and increased integral procedural decomposition temperature for epoxy nanocom-

posites when compared with the cure epoxy. However, the initial decomposition temperature of the nanocomposite was slightly decreased.

The mechanism of the improvement of thermal stability in polymer nanocomposites however is not fully understood. It is often stated [22–25] that the enhanced thermal stability is due to improved barrier properties and the torturous path for volatile decomposition products, which hinders diffusion out of the material. Recently, Zhu et al. [21] found for polypropylene-clay nanocomposites that the structural iron in the dispersed clay may also act as a trap for radicals and hence improve thermal stability. Gilman et al. [26,27] reported that the layered silicates appear to enhance the performance of the char layer, which acts as an insulator and mass transport barrier and therefore reduces the mass loss rate and improves flammability and thermal stability.

The work presented in this paper investigates if there is a major change in the water uptake properties and thermal stability of a series of high performance nanocomposites that have shown improved toughness and stiffness through the incorporation of OLS [4].

2. Experimental

2.1. Materials

Three different epoxy resins were used as the polymer matrix: diglycidyl ether of bisphenol A (DGEBA), DER 331 Dow epoxy resin, triglycidyl *p*-amino phenol (TGAP), Araldite MY0510 of Ciba Speciality Chemicals and tetrafunctional tetraglycidyl diamino diphenylmethane (TGDDM) Araldite MY720 of Ciba Speciality Chemicals. The hardener, Ethacure 100, of Albemarle Corp. is a mixture of two diethyltoluene diamine (DETDA) isomers, containing 74–80% 2,4 isomer and 18–24% 2,6 isomer. The organoclay used is a commercially-available octadecyl ammonium ion-modified montmorillonite layered silicate of Nanocor Inc., Nanomer I.30E. A range of epoxy nanocomposites containing 0%, 2.5%, 5% and 10% organoclay were prepared. The synthesis of the nanocomposite materials was the same as described previously [4]. Prior to sample preparation, chemicals were dried for 12 h at 50 °C under vacuum to avoid moisture. The layered silicate was dispersed in the resin at 80 °C using a stirrer at 500 rpm for 30 min. The curing agent was added and mixed under vacuum for another 60–90 min at approximately 70 °C. The blends were cured for 2 h at 100 °C, 1 h at 130 °C, 12 h at 160 °C followed by a postcure for 2 h at 200 °C. An epoxide to amine ratio of 1:0.9 was chosen for each nanocomposite to ensure an excess of epoxy groups since residual amine can be deleterious to moisture uptake and ultimate properties.

2.2. Wide angle X-ray scattering (WAXS)

WAXS measurements were taken from each sample using a Rigaku Geigerflex generator. The acceleration voltage was 40 kV. A current of 22.5 mA was applied using Ni filtered CuK α radiation. Measurements were taken in a range of $2\theta = 1\text{--}25^\circ$.

2.3. Transmission electron microscopy (TEM)

TEM microtome specimens were cut with a Porter-Blum MT-2B ultramicrotome using a DiaTech diamond knife. The samples of 70–90 nm thickness were collected on hexagonal 300 mesh copper grids. Micrographs were obtained from a Philips CM20 transmission electron microscope operating at 200 kV in bright field mode.

2.4. Water uptake

Three specimens of each material with the dimensions of $40\times 10\times 2$ mm were stored in a test tube filled with distilled water and the temperature stabilized with a water bath at $80\pm 1^\circ\text{C}$. After certain time intervals, the samples were taken from the test tubes, dried with a paper towel and the weight was determined on analytical scales.

2.5. Dynamic mechanical thermal analysis (DMTA)

The apparent glass transition temperature, T_g , of the dry nanocomposites as reported previously [4] and after water uptake experiments were determined on a Rheometric Scientific dynamic mechanical thermal analyzer, DMTA IV and are labeled the α -relaxation in this work. Relaxations at lower temperatures in the glassy state are known as the β -relaxation. Samples were clamped in a medium frame using a small center clamp in the dual cantilever mode. Temperature scans at frequencies of 1 Hz were performed from -100 to 50 and from 50 to 300°C at $2^\circ\text{C}/\text{min}$. Experiments were conducted in two stages to avoid high internal stresses in the specimen due to thermal expansion.

2.6. Thermogravimetric analysis

TGA analyses were performed on a Mettler Toledo TGA/SDTA851 $^\circ$ thermo gravimetric analyzer. Coarsely ground samples of 10–15 mg were heated from 50 to 800°C at a scanning rate of 5°C under a constant nitrogen flow of 45 mL/min.

3. Results and discussion

3.1. Nanocomposite structure

To verify the morphology of the cured epoxy resin-layered silicate blends, the materials were investigated by means of wide-angle X-ray scattering (WAXS) and transmission electron microscopy (TEM). All epoxy resin systems intercalated the organically modified layered silicate with an increase in the average d -spacing. The initial d -spacing of the organically modified layered silicate was determined to be 23 Å. The average distance between silicate layers in the nanocomposites was found to be approximately 80 Å for the DGEBA, 45–50 Å for the TGDDM and TGAP based composite systems. In general, comparison of XRD and TEM results was in good agreement. Typical TEM images of the DGEBA and TGDDM nanocomposites are shown in Fig. 1. More details of these materials are given in Refs. [4,6].

3.2. Water uptake

An example for the water sorption as a function of time is illustrated in Fig. 2 for the series of TGAP based nanocomposites. Equilibrium water sorption values for all systems are shown in Table 1. Interestingly, it can be seen that the DGEBA based systems generally absorb less water than the two resin systems of higher functionalities, with values for the TGDDM based materials being below those for TGAP.

The water sorption behavior is often related to the free volume of a material. Soles et al. [28,29] found a

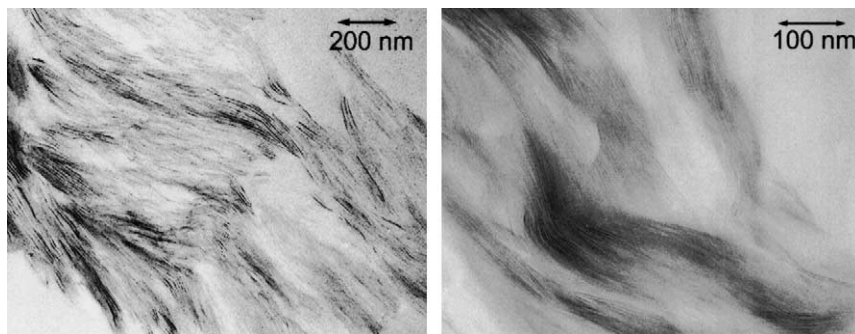


Fig. 1. Typical TEM micrographs of DGEBA (left) and TGDDM (right) nanocomposites containing 7.5% OLS.

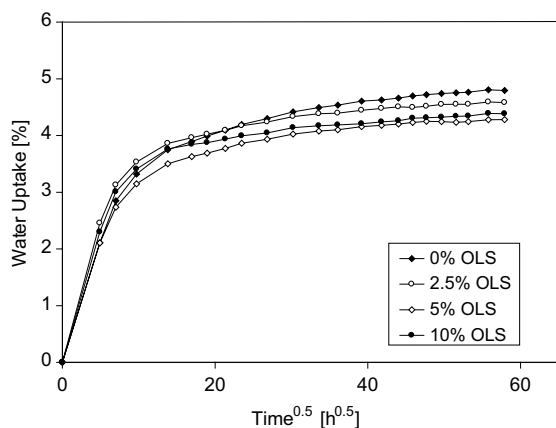


Fig. 2. Water sorption curve of a series of TGAP based nanocomposites containing different concentrations of OLS.

strong correlation between the hole volume fraction extrapolated to absolute zero when polymer motion has ceased and the ultimate water uptake of epoxy resins, whilst the diffusion coefficient was not affected by the free volume fraction. Recent work by Tscharkhtchi et al. [30], in contrast reported that after water sorption tests the water was essentially dissolved in the network of an epoxy system due to the polar groups present in the polymer. The experiments showed very little volume change without any clustering or microvoiding. It was proposed that water is originally dissolved in the network, rather than located in the free volume.

Free volume properties of selected materials of the range of nanocomposites studied in this paper have been investigated by positron annihilation lifetime (PAL) spectroscopy elsewhere [6]. It was found that the

DGEBA-based materials showed the highest overall free volume. However, the differences in free volume properties between the resin systems were not significant. Hence it is assumed that the variation in equilibrium water uptake is mainly related to the polarity of the polymers and hence to the amount of bound water, rather than the free water trapped in micro-voids of free volume in the nanocomposite matrix, in good agreement with Tscharkhtchi et al. [30] for neat epoxy systems. It should be noted that the PAL results were obtained at room temperature [6], as opposed to the work of Soles et al. [29] who did the temperature dependent PAL work, and extrapolated to very low temperatures.

The equilibrium values show that the neat epoxy systems generally absorb more water than the layered silicate composite materials. A monotonic decrease in water sorption with increasing clay concentration, however, could not be found. The diffusion behavior of water into epoxy systems has shown to be in good agreement with Fick's second law of diffusion [8,9]. For the one-dimensional diffusion through an infinite plate Fick's second law of diffusion is commonly expressed as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

with C being the concentration of the diffusing substance (water), t the time, D the diffusion coefficient and x the length. It was further shown by Crank [31] that this correlation can be simplified for the initial stage of water absorption with $\frac{M_t}{M_\infty} \leq 0.6$ as

$$\frac{M_t}{M_\infty} = \frac{4}{L\sqrt{\pi}} \sqrt{Dt} \quad (2)$$

with M_t being the amount of water diffused into the polymeric material and M_∞ the amount of water ab-

Table 1

Equilibrium water uptake, diffusion coefficient and α and β -transition peak temperatures as determined from DMTA measurements before and after water sorption determined at 1 Hz

Sample	Equilibrium water uptake (%)	Diffusion coefficient D ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$)	Relaxation peak temperature ($^{\circ}\text{C}$)/Width at half peak height					
			Dry specimen			Wet specimen		
			α -Peak	α -Width	β -Peak	α -Peak	α -Width	β -Peak
DGEBA 0% OLS	2.810	4.3	187.0	33	-57.9	161.7	48.5	-65.5
DGEBA 2.5% OLS	2.425	4.7	183.1	37	-58.5	166.3	41.2	-64.4
DGEBA 5% OLS	2.405	4.9	182.5	36	-60.0	162.8	40.9	-65.4
DGEBA 10% OLS	2.659	3.8	174.3	39	-62.9	155.3	45.5	-63.8
TGAP 0% OLS	4.797	2.3	280.8	41	-49.1	236.7	45.1	-59.0
TGAP 2.5% OLS	4.597	3.7	278.1	49	-52.8	236.2	63.2	-58.5
TGAP 5% OLS	4.274	3.1	271.0	45	-52.7	244.6	52.1	-58.5
TGAP 10% OLS	4.330	3.6	262.7	53	-55.9	244.5	70.4	-54.0
TGDDM 0% OLS	3.967	2.3	259.6	37	-53.4	248.6	65.3	-62.4
TGDDM 2.5% OLS	3.746	3.0	248.1	37	-54.7	229.8	43.1	-64.5
TGDDM 5% OLS	3.732	4.1	242.0	48	-56.2	236.2	61.7	-64.4
TGDDM 10% OLS	3.778	3.1	240.2	48	-58.8	228.1	60.9	-63.5

sorbed at equilibrium or infinite time. Data from the first few measurements of our experimental series have been fitted to this equation and the diffusion coefficient was determined. Results for the diffusion coefficient, D , are shown in Table 1. The order of magnitude of the diffusion coefficients are in good agreement with values reported for other epoxy resin systems [8,10], but no clear trend existed with varying organoclay concentration. It clearly is quite dependent on the precise nature of constituents and morphology, since Massam and Pinnavaia [16] find that the rate of water uptake varied with clay addition, and not the equilibrium uptake.

3.3. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis measurements were performed on each sample after 3670 h storage in distilled water at 80 °C. Fig. 3a–c shows the $\tan \delta$ traces of dry and wet TGAP resin system, as well as the TGAP nanocomposite containing 10% organoclay as an ex-

ample. Table 1 summarizes the α -relaxation (apparent T_g) and the secondary, β -relaxation peak temperatures for the wet and dry nanocomposites, as well as the width of the α -relaxation peak (width at half peak height).

The effect of the layered silicate on the thermal relaxation of the dry specimens has been the subject of previous discussions [4] and it was found that both, the α - and β -relaxation peak temperature are constantly decreased with increasing organoclay concentration, possibly to a number of reasons, such as changes in reaction chemistry, lower crosslink density or a plasticizing effect of the clay compatibilizer or entrapped resin or hardener monomers. In particular, this is seen in other systems with rigid amines and high functionality epoxy resins [5]. Comparison of the α -relaxation traces between wet and dry samples show that the absorbed water decreases the T_g significantly, along with increased broadening of the peak width. It can be found that the decrease in T_g is not a monotonic decrease as a function of the amount of water absorbed. It was found (see in

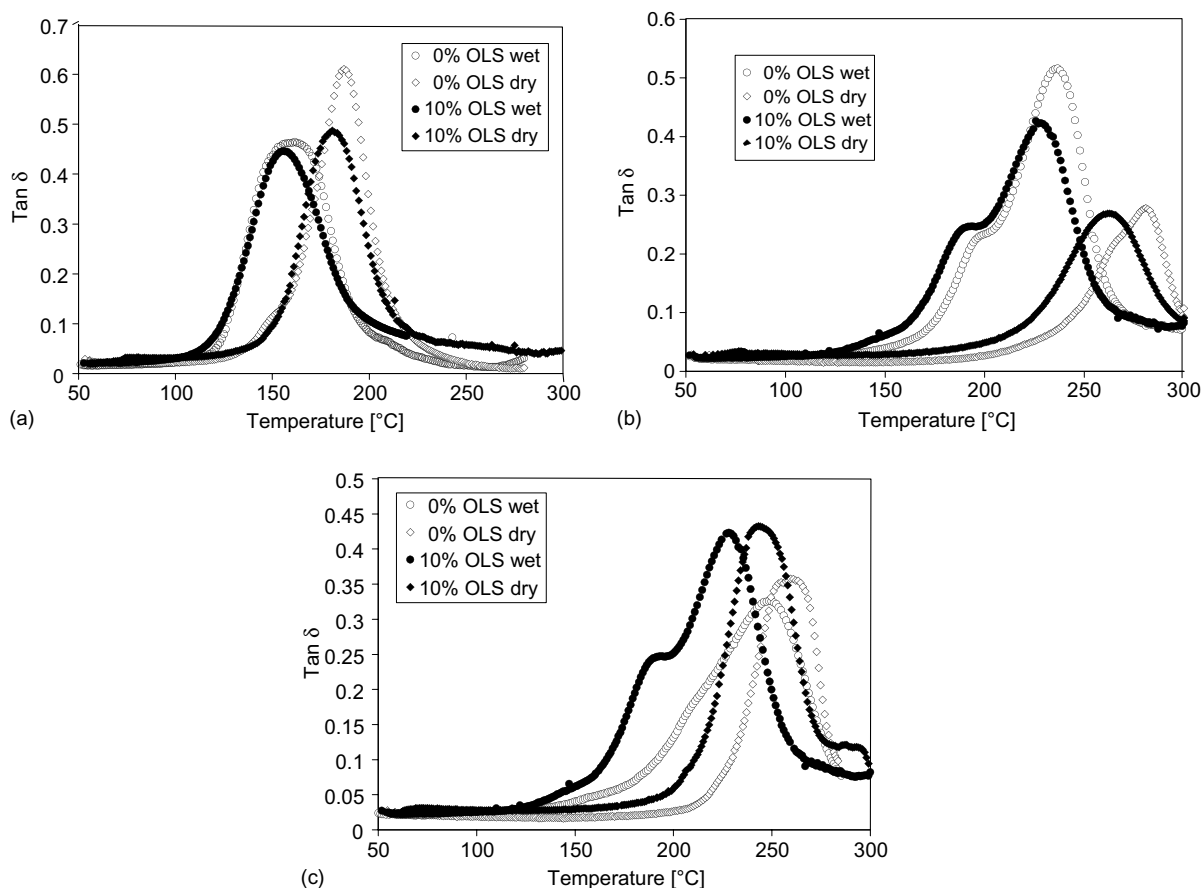


Fig. 3. (a) Dry and wet $\tan \delta$ traces of DGEBA nanocomposites as determined from DMTA at 1 Hz. (b) Dry and wet $\tan \delta$ traces of TGAP nanocomposites as determined from DMTA at 1 Hz. (c) Dry and wet $\tan \delta$ traces of TGDDM nanocomposites as determined from DMTA at 1 Hz.

Fig. 3b and c) that both wet and dry samples of the higher functionality epoxy resins (TGAP and TGDDM) show a shoulder or an indication of a new peak at lower temperatures. The low temperature peak varied randomly in intensity between different organoclay concentrations and did not follow a clear trend with increasing filler concentration. Since most systems only showed a broad shoulder, the temperature location of this is not recorded in Table 1. It is well known that the high glass transition temperature epoxy resins do not always reach their ultimate T_g during post-cure, as the curing process is diffusion-controlled in the glassy state, and hence very slow [5,32,33]. As reported previously [6], for selected samples of the specimen investigated here, FTIR measurements of the residual epoxy groups after cure showed that all systems showed relatively low concentrations. However, the values for high functionality epoxy resins were slightly greater than those of DGEBA. Dynamic temperature DMTA measurements after cure below the ultimate T_g often show more than one peak in the $\tan \delta$ traces (the low peak/shoulder being related to the undercured region and the higher, more prominent peak arising from the glass transition of the more highly crosslinked region, probably also including some of the less crosslinked region that has additionally reacted during thermal measurement). This aspect is made clearer in Fig. 3a, in which the lower functionality DGEBA only shows a single peak—dry and with moisture—indicating that a more fully, even degree of crosslink density was achieved. The additional peak is weak in the dry TGAP and TGDDM samples, but increases in prominence after water sorption, simply moving to lower temperatures on addition. It is possible that the water preferentially locates in areas of lower crosslink density, forming a more plasticised phase and thus a stronger DMTA peak.

Fig. 4 shows the broad β -relaxation peaks of cured TGDDM and the TGDDM nanocomposite containing 10% OLS as an example. Values for all systems can be found in Table 1. Similar to the changes in T_g , a reduced β -relaxation peak temperature can be found for the wet specimens.

3.4. Thermal stability

The thermal stability of epoxy nanocomposite series cured at the 100 °C cycle was determined using thermogravimetric analysis, TGA, under a nitrogen atmosphere. Figure shows an example of a TGA trace obtained from the neat TGDDM system and the TGDDM nanocomposite containing 10% organically modified layered silicate. As illustrated in the figure, the onset and the end set temperature were determined from the intersection of the two tangents. Furthermore, the peak degradation temperature was determined from the first derivative of the TGA curve using the Mettler Toledo STAR^c software.

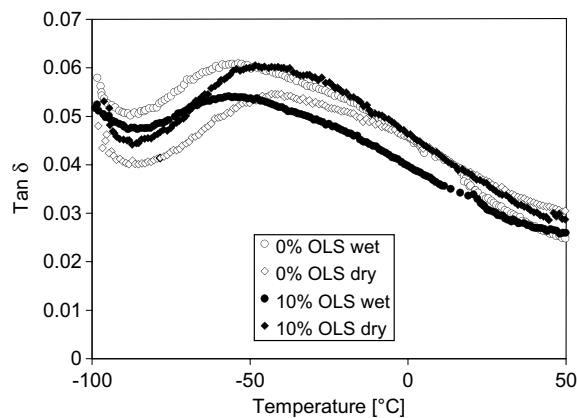


Fig. 4. Dry and wet $\tan \delta$ traces of TGDDM and TGDDM nanocomposites as determined from DMTA in the subambient state at 10 Hz.

Table 2 shows values for the onset, the end set, the temperature interval between onset and end set (ΔT_{emp}) as well as the degradation peak temperature (degradation peak), determined as the peak of the first derivative and the total weight loss at 700 °C (Fig. 5).

In general, a slightly decreased onset temperature can be observed with increasing organoclay concentration for the TGDDM nanocomposites. A similar trend is shown for the peak degradation temperature of the DGEBA and TGAP nanocomposite series. Values for TGDDM, however, show some scatter around a value of about 378 °C rather than a constant trend of decreasing temperatures with clay addition. The interval between degradation onset and end shows a slight trend of broadening for the DGEBA and TGAP series. However, this cannot be observed for the TGDDM series and is not consistent with the reduced onset and peak degradation temperatures.

It is important to note that TGA curves of resin systems with and without organoclay generally show the same behaviour in the lower temperature regime before the onset of degradation. A separate degradation of the interlayer exchanged ions is not observed, however it should be noted that the organo-ion concentrations are very low, some 25–30 wt.% of the treated clay fraction. It is assumed that the interlayer exchanged ions are well embedded or incorporated into the polymer matrix. TGA traces of the neat organoclay are shown in Figure, with the degradation of the compatibilizer starting at about 200 °C. This is in good agreement with the degradation behaviour observed for other exfoliated epoxy organoclay nanocomposites by Wang and Pinnavaia [3] and Gu and Liang [34] who recently found that onset temperatures of degradation also were lowered, especially in the case of the longer alkyl ammonium chains. Likewise, the potential reasons outlined earlier leading

Table 2
Thermal stability parameters of various nanocomposite systems as determined from TGA

System	Onset (°C)	End set (°C)	Δ Temp (°C)	Degradation peak (°C)	Total wt. loss at 700 °C (%)
DGEBA 0% OLS	358.3	405.5	47.2	371.6	88.0
DGEBA 2.5% OLS	357.4	403.9	46.5	369.7	88.6
DGEBA 5% OLS	351.9	402.2	50.3	368.7	85.0
DGEBA 7.5% OLS	351.4	400.7	49.3	367.7	83.4
DGEBA 10% OLS	346.7	401.5	54.8	366.7	80.7
TGAP 0% OLS	342.5	385.5	43.0	360.0	78.5
TGAP 2.5% OLS	344.7	386.9	42.2	357.4	69.0
TGAP 5% OLS	341.0	388.7	47.7	353.3	79.6
TGAP 7.5% OLS	339.0	389.0	50.0	354.3	74.0
TGAP 10% OLS	338.9	389.7	50.8	355.3	72.9
TGDDM 0% OLS	345.4	417.4	72.0	374.9	84.3
TGDDM 2.5% OLS	340.0	423.2	83.2	378.2	81.2
TGDDM 5% OLS	348.5	415.1	66.6	377.6	80.1
TGDDM 7.5% OLS	343.2	420	76.8	379.9	79.1
TGDDM 10% OLS	344.5	419.4	74.9	380.7	77.5

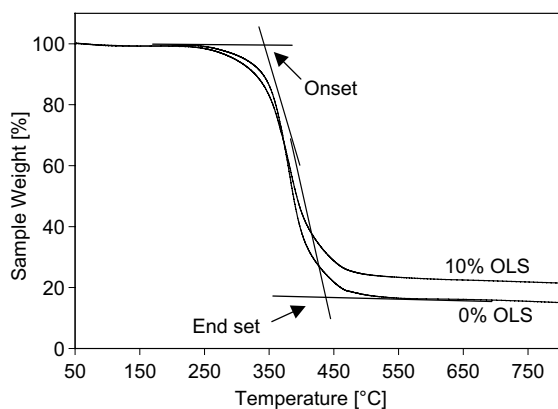


Fig. 5. TGA of TGDDM and TGDDM nanocomposite containing 10% OLS.

to lower glass transition temperatures (such as low crosslink density, plasticisation of the epoxy matrix by the organo-ion and so on) are also likely to lead to greater degrees of degradation (Fig. 6).

Xie et al. [35] recently reported a detailed investigation of the non-oxidative thermal degradation chemistry of quaternary alkylammonium modified montmorillonite. The onset of true organic decomposition (rather than water desorption which could be observed at lower temperatures) was found to be 180 °C and the decomposition process divided into four stages: the desorption of water and other low molecular weight species (below 180 °C), the decomposition of organic substances (200–500 °C) the dehydroxylation of the aluminosilicate (500–700 °C) and the residual organic carbonaceous evolution at 700–1000 °C. Furthermore, the work suggested a Hoffmann's elimination reaction as the mechanism of the initial thermal degradation.

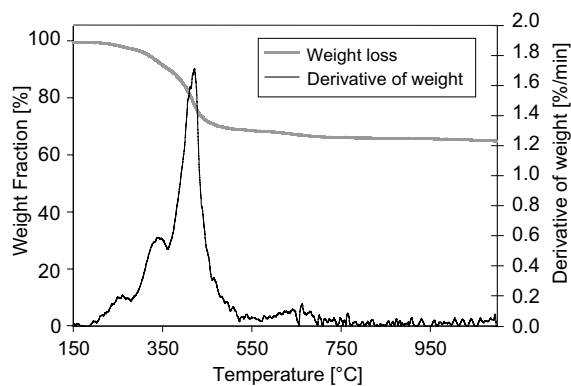


Fig. 6. Thermogram of the organically rendered layered silicate, Nanocor I.30E.

The total weight loss of the different materials after the dynamic temperature scan to 700 °C is also shown in Table 1. Whilst the total weight loss is not generally in direct proportion with the amount of clay added, a trend of reduced weight loss or improved char formation respectively can be observed with organoclay addition. When comparing the 0% and 10% layered silicate containing systems, the additional weight of the remaining char is in good correlation to the inorganic content of the filler given that the organoclay cations are roughly one third of the clay additive.

4. Conclusions

The water uptake behaviour, a major concern in glassy high performance epoxy resin systems, was

investigated. Measurements of the water sorption at a temperature of 80 °C showed that the equilibrium water uptake of all nanocomposites was reduced compared to the neat epoxy system. The concentration of layered silicate did not correlate proportionally with the reduction in equilibrium water uptake. The absolute reduction varied between 0.4% and 0.5% for DGEBA and TGAP and 0.2% for the TGDDM nanocomposites, whilst the rate of water diffusion remained unaffected.

The thermal stability of series of nanocomposites was investigated by means of thermogravimetric analysis in an inert nitrogen atmosphere. Nanocomposites showed slight indications of reduced thermal stability, as indicated by a decreased onset in thermal degradation in the order of 5–10 °C at a clay concentration of 10%. The final char concentration was increased with increasing organoclay concentrations. The changes in thermal stability are of very low significance and it is unlikely that they would be considered as a drawback to any possible industrial application. Other work such as by cone calorimetry indicates that significant decreases in heat release rate occur upon addition of nanoclays [25–27,36], however it is often necessary to combine the clays with other additives in order to obtain the required synergies and flame retardancies desired [37].

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References

- [1] Lan T, Pinnavaia TJ. Clay-reinforced epoxy nanocomposites. *Chem Mater* 1994;6:2216–9.
- [2] Wang Z, Lan T, Pinnavaia JT. Hybrid organic–inorganic nanocomposites formed from an epoxy polymer and a layered silicic acid (magadiite). *Chem Mater* 1996;8:2200–4.
- [3] Wang Z, Pinnavaia JT. Hybrid organic–inorganic nanocomposites: exfoliation of magadiite nanolayers in an elastomeric epoxy polymer. *Chem Mater* 1998;10:1820–6.
- [4] Becker O, Varley RJ, Simon GP. Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high-functionality epoxy resins. *Polymer* 2002;43:4365–73.
- [5] Kormmann X, Thomann R, Mülhaupt R, Finter J, Berglund LA. High performance epoxy-layered silicate nanocomposites. *Polym Eng Sci* 2002;42:1815–26.
- [6] Becker O, Cheng YB, Varley RJ, Simon GP. Layered silicate nanocomposites based on various high-functionality epoxy resins: the influence of cure temperature on morphology, mechanical properties and free volume. *Macromolecules* 2003;36:1616–25.
- [7] Mikols WJ, Seferis JC, Apicella A, Nicolais L. Evaluation of structural changes in epoxy systems by moisture sorption–desorption and dynamic mechanical studies. *Polym Compos* 1982;3:118–24.
- [8] Grave C, McEwan I, Pethrick RA. Influence of stoichiometric ratio on water absorption in epoxy resins. *J Appl Polym Sci* 1998;69:2369–76.
- [9] Nogueira P, Ramirez C, Torres A, Abad M, Cano J, Lopez J, et al. Effect of water sorption on the structure and mechanical properties of an epoxy resin system. *J Appl Polym Sci* 2001;80:71–80.
- [10] Johncock P, Tudgey GF. Some effects of structure, composition and cure on the water absorption and glass transition temperature of amine-cured epoxies. *Br Polym J* 1986;18:292–302.
- [11] De'Néve B, Shanahan MER. Water absorption by an epoxy resin and its effect on the mechanical properties and infra-red spectra. *Polymer* 1993;34:5099–105.
- [12] Pethrick RA, Hollins EA, McEwan I, Pollock EA, Hayward D. Effect of cure temperature on the structure and water absorption of epoxy/amine thermosets. *Polym Int* 1996;39:275–88.
- [13] Choi HS, Ahn KJ, Nam J-D, Chun HJ. Hygroscopic aspects of epoxy/carbon fiber composite laminates in aircraft environments. *Composites: Part A* 2001;32:709–20.
- [14] Andreopoulos AG, Tarantili PA. Water sorption characteristics of epoxy resin–UHMPE fibers composites. *J Appl Polym Sci* 1998;70:747–55.
- [15] Wang Z, Massam J, Pinnavaia TJ. Epoxy-clay nanocomposites. In: Pinnavaia TJ, Beall GW, editors. *Polymer-clay nanocomposites*. Chichester: Wiley; 2000. p. 127–48.
- [16] Massam J, Pinnavaia TJ. Clay nanolayer reinforcement of a glassy epoxy polymer. *Mater Res Soc Symp Proc* 1998;520:223–32.
- [17] Shah AP, Gupta RK, GangaRao HVS, Powell CE. Moisture diffusion through clay/vinyl ester nanocomposites. *Polym Eng Sci* 2002;42:1852–63.
- [18] Okada A, Kawasumi M, Usuki A, Kojima Y, Kurauchi T, Kamigaito K. Nylon 6-clay hybrids. *Mater Res Symp Proc* 1990;171:45–50.
- [19] Hwu JM, Jiang GJ, Gao ZM, Xie W, Pan WP. The characterization of organic modified clay and clay-filled PMMA nanocomposites. *J Appl Polym Sci* 2002;83:1702–10.
- [20] Chang J-H, Seo B-S, Hwang D-H. An exfoliation of organoclay in thermotropic liquid crystalline polyester nanocomposites. *Polymer* 2002;43:2969–74.
- [21] Zhu J, Uhl FM, Morgan AB, Wilkie CA. Studies on the mechanism by which the formation of nanocomposites enhances thermal stability. *Chem Mater* 2001;13:4649–54.
- [22] Park S-J, Seo D-I, Lee J-R. Surface modification of montmorillonite on surface acid–base characteristics of clay and thermal stability of epoxy/clay nanocomposites. *J Colloid Interface Sci* 2002;251:160–5.
- [23] Kotsilkova R, Petkova V, Pelovski Y. Thermal analysis of polymer-silicate nanocomposites. *J Therm Anal Calorim* 2001;64:591–8.

- [24] Burnside SD, Giannelis EP. Synthesis and properties of new poly(dimethylsiloxane) nanocomposites. *Chem Mater* 1995;7:1597–600.
- [25] Gilman JW, Kashiwagi T. Polymer-layered silicate nanocomposites with conventional flame retardants. In: Pinnavaia TJ, Beall GW, editors. *Polymer–clay nanocomposites*. Chichester: Wiley; 2000. p. 193–206.
- [26] Gilman J, Kashiwagi T, Brown J, Lomakin S, Giannelis E. Flammability studies of polymer layered silicate nanocomposites. In: 43rd International SAMPE Symposium, 1998.
- [27] Gilman JW. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. *Appl Clay Sci* 1999;15:31–49.
- [28] Soles CL, Chang FT, Bolan BA, Hristov HA, Gidley DW, Yee AF. Contributions of the nanovoid structure to the moisture absorption of epoxy resins. *J Polym Sci Part B: Polym Phys* 1998;36:3035–48.
- [29] Soles CL, Chang FT, Gidley DW, Yee AF. Contributions of the nanovoid structure to the kinetics of moisture transport in epoxy resins. *J Polym Sci Part B: Polym Phys* 2000;38:776–91.
- [30] Tscharkhtchi A, Bronnec PY, Verdu J. Water absorption characteristics of butane diol-3,5-diethyl-diaminotoluene networks. *Polymer* 2000;41:5777–85.
- [31] Crank J. *The mathematics of diffusion*. Oxford; 1956.
- [32] Varley R, Hodgkin J, Hawthorne D, Simon GP. Toughening of a trifunctional epoxy system. IV. Dynamic mechanical relaxation study of the thermoplastics-modified cure process. *J Polym Sci Part B: Polym Phys* 1997;35:153–63.
- [33] Becker O, Simon GP, Varley RJ, Halley P. Layered silicate nanocomposites based on various high-functionality epoxy resins: the influence of an organoclay on resin cure. *Polym Eng Sci* 2003;43:850–62.
- [34] Gu A, Liang G. Thermal degradation behaviour and kinetic analysis of epoxy/montmorillonite nanocomposites. *Polym Degrad Stab* 2003;80:383–91.
- [35] Xie W, Gao Z, Pan W-P, Hunter D, Singh A, Vaia R. Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. *Chem Mater* 2001;13:2979–90.
- [36] Gilman JW, Jackson CL, Morgan AB, Harris R, Manias E, Giannelis EP, et al. Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites. *Chem Mater* 2000;12:1866–73.
- [37] Zanetti M, Camino G, Canavese D, Morgan AB, Lamelas FJ, Wilkie CA. Fire retardant halogen-antimony-clay synergism in polypropylene layered silicate nanocomposites. *Chem Mater* 2002;14:189–93.