Simultaneous Improvements in Flammability and Mechanical Toughening of Epoxy Resins through Nano-Silica Addition

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ABSTRACT
Polymers in transport, and many other engineering applications, are required to be mechanically tough as well as resist ignition and flame spread. These demands are often in competition for many polymer types especially when adding flame retardants. With nano-silica additives, we show that improvements in both properties of a polymer can be achieved simultaneously. In this study, an epoxy resin is evaluated for its flammability and mechanical properties with step wise additions of nano-silica. The fracture toughness was significantly improved. In the single edge notch bending test, the addition of 36\% nano-silica particles doubled the toughness and increased the flexure modulus by 50\%. Flammability was studied via time to ignition at constant irradiation, and via a UL94 test coupled with mass loss and surface temperature measurements. Modelling in GPyro was done and yielded good agreement with the temperature measurements taken. Adding up to 36\% nano-silica, the time to ignition increased by 38\% although a sharp decrease was observed at 24 \% SiO\textsubscript{2} addition. We show that the increased time to ignition is mostly due to a higher thermal diffusivity, increased inert content, as well as a strengthening of the residue surface layer, which acts as a mass barrier for pyrolysate. This outer skin was analysed using a scanning electron microscope coupled with an energy dispersive X-ray spectrometer. We found that in the skin the nano-silica particles agglomerate at the surface forming a strong continuous structure together with the char residue from the epoxy. Improvements in the flammability as seen in the UL94 test were measured with mass loss showing a 30\% reduction after 20 s, and surface temperatures at the ignited end being up to 75 K lower compared to the pure epoxy. Modelling in GPyro supported the temperature measurements taken. Despite the improvements seen, all samples ignited, failing the test with dripping and showing that the improvements recorded in time to ignition did not fully translate over to the UL94 test. Overall we show that the flammability and toughness of epoxy could be improved simultaneously with nano-silica. Using up to 36\% nano-silica, the significant modification of thermal properties could be explored in relation to fire properties for epoxy. Increasing the thermal diffusivity as well as skin formation are the main parameters improving the flammability and show a path for potential improvements in other composites as well.

KEYWORDS: epoxy, nano-silica, ignition, flame spread

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INTRODUCTION

Polymers are widely used in everyday life due to their low cost, versatility, light weight, and ease of production. Epoxies are especially popular in aerospace design, but are also used in tooling and electrical applications, as well as flooring, coatings, adhesives, and more [1,2]. With a wide range of applications, good chemical resistance, and tensile strength the global epoxy market was estimated in 2013 at $18.5 billion [3].

Despite the many benefits, polymers including epoxies suffer from an inherent problem of flammability [4,5]. This limits the range of applications unless the material is modified such that it passes the fire safety requirements. This is typically achieved by adding a range of flame retardant additives. The most commonly used flame retardants can be grouped by their primary mechanism. Some retardants, such as bromine containing ones, inhibit the radical process of the fire with the aim of chemically quenching the flame. The formation of a heat and mass transport barrier via continuous char or inorganic surface layers is another common method. Less of the pyrolysis gases are then released into the environment. Endothermically decomposing hydrated nano-particles are also sometimes used to cool the sample, delaying ignition as less pyrolysis gases are produced when the sample is at a lower temperature [6–10]. These methods generally work well to reduce flammability although typically lead to a reduction in mechanical properties, especially affecting toughness [11,12]. Finding an additive that increases toughness while simultaneously reducing the flammability would be a significant improvement.

There has been some research into the toughening of epoxies with nano-particles such as nano-silica [13,14]. The toughening mechanism of nano-silica in epoxy has been reported to be primarily due to two effects. Localised plastic shear-band yielding initiated through the stress concentration forming around the nano-particle is the primary one, and plastic void growth as the particle de-bonds from the epoxy matrix the secondary effect [15–17].

Nanocomposites as a group of materials are known to improve flame retardancy by forming a mass barrier to pyrolysis gases as well as increasing the melt viscosity [18, 19]. The barrier formation manifests itself especially in the heat release rate (HRR) in the cone calorimeter. While the total heat released does not significantly change, the average HRR can be significantly lowered by using nano-composites. This is attributed
to the nano-particles agglomerating at the surface as the sample softens, and the surface recedes as it is consumed by the fire. The layer forming at the surface then hinders the pyrolysis gases from migrating to the environment [18,20,21].

Nano-silica has been investigated in the past for providing improvements in flame retardancy [20–27]. The main flame retardant effects identified are the formation of a mass barrier for pyrolysis gases as well as an increased inert content reducing the amount pyrolysate available. The added inert content can be seen as increased residual mass in the TGA. This has been erroneously described in the literature as improving the thermal stability of the epoxy [25,26,28].

An aspect of the nano-silica which has not been discussed in the literature with respect to fire properties is the change in thermal properties at high nano-silica loadings. Most flammability research involving nanosilica has been performed on systems with low loadings of up to 15%. At higher loadings the changes to the thermal properties are starting to become significant [29, 30] but have to the best of our knowledge not yet been investigated for their effect on flammability. This has been related in the past for other systems to improvements in flammability [31,32].

EXPERIMENTS

The samples used were cast from Bisphenol A diglycidyl ether (DGEBA) (LY556, Huntsman, UK) and hardened using isophorone diamine (Vestamin IDP, Evonik Industries, Germany). 18% reactive diluent of 1,6-hexanediol diglycidylether (HDE) (Polypox R18, Dow Chemical Co., Germany) was added to lower the viscosity and ease processing. Functionalised nano-silica with an average diameter of 20 nm was added at 3 concentrations from 12 to 36% in 12% increments. The nano-silica was obtained pre-dispersed at 40% in DGEBA (Nanopox F400, Evonik Hanse) or HDE (Nanopox F640, Evonik Hanse) to achieve the desired concentrations. Surface functionalisation with amine and the spherical shape of the particles ensure good dispersion as has been shown in samples prepared in the same fashion [33]. Table 1 summarises the compositions of the samples used. The material properties shown were extracted from the literature [30].

Hand mixing using wooden mixing sticks was carried out for 15 mins to ensure consistency. The resin mixture was heated to 40 °C to reduce the viscosity which appeared to not be significantly changed by the addition of the nano-silica. Degassing was carried out for 1 h in a vacuum pot to remove any trapped gases. IPD hardener was added to the resin to cure it according to the necessary stoichiometric ratio. After a further 10 min of degassing, the resin-hardener mixture was poured into a silicone mould of 15 mm depth. Curing was carried out at room temperature (20 °C) for 24 h after which samples were demoulded and placed into an oven at 85 °C for 24 h to complete the curing process.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Units</th>
<th>C0</th>
<th>C12</th>
<th>C24</th>
<th>C36</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>%</td>
<td>82</td>
<td>70</td>
<td>58</td>
<td>46</td>
</tr>
<tr>
<td>Diluent</td>
<td>%</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Nano-silica</td>
<td>%</td>
<td>0</td>
<td>12</td>
<td>24</td>
<td>36</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>1200</td>
<td>1269</td>
<td>1338</td>
<td>1408</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W/m²K</td>
<td>0.241</td>
<td>0.248</td>
<td>0.271</td>
<td>0.312</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>J/kgK</td>
<td>1204</td>
<td>1161</td>
<td>1116</td>
<td>1068</td>
</tr>
</tbody>
</table>

Two types of flammability tests were conducted. The first one used the standard cone heater [34]. Samples machined into 90 × 90 mm² plaques of 10 mm thickness were exposed to 30 kW/m² up to the point of spontaneous ignition. The heat flux was calibrated using a Huskeflux SBG01 heat flux gauge before every set of experiments. The irradiation was chosen to be in the typical range of a developing fire [18]. A 1.5 mm diameter, K-type thermocouple was inserted into the sample centre at 5 mm depth to record the core temperature. After ignition, the sample was immediately extinguished using a jet of inert gas and cooled in cold water bath of 10 mm depth. The water bath was chosen to be shallow as to not disturb the skin formed for further analysis.
Representative samples of each composition are selected following the cone testing for analysis using a scanning electron microscope (SEM) (Hitachi S-3400N) coupled with an energy dispersive X-ray spectrometer (EDX) (Oxford Instruments INCAx-act). The structure of the surface layer is investigated to understand the effect of nano-silica addition to surface layer creation. EDX analysis identifies chemical make up of areas so that structures found can be attributed to the epoxy or nano-silica. Samples selected were cast in epoxy to preserve the degraded surface as well as possible. After curing, a notch was placed on the bottom surface and the sample fractured using a hammer to obtain a clean surface for use in the SEM. The fracture surface was coated with 50 nm of gold to reduce sample charging in the SEM.

The UL94 test conducted is modified from the standard procedure to give an in-depth understanding of the effect of the nano-silica addition. The 50 W methane flame is applied for 10 s as per the standard [35]. Mass data is measured at 2 Hz to 0.01 g accuracy by placing the sample holding rig onto a Mettler Toledo MS4002SDR scale. The mass loss data is then compared after set time intervals to assess if the nano-silica additions change mass loss. A reduction in mass loss would indicate improved flame retardancy. Additionally, a FLIR A655SC IR camera is used to measure the surface temperature of the samples to assess any change in heating rate induced by the additives. A schematic of the set up is shown in Fig. 1. For the UL94 test, 13 x 125 mm\(^2\) strips were milled from the panels to a thickness of 2 mm. The cone and modified UL94 tests were conducted with 3 repeats for each experiment and composition.

Two standard tests were conducted to assess the effect of nano-silica addition to mechanical properties. The fracture toughness was measured using the single edge notch bending (SENB) specimen test following ISO-13586 [36]. Samples machined to 8 x 16 x 70.4 mm\(^3\), pre-notched, and then pre-cracked by tapping the sample with a razor blade cooled in liquid nitrogen, were prepared. The sample was then loaded into the three point bending machine and tested. The fracture toughness, \(K_{IC}\), could then be calculated via Eq. 1:

\[
K_{IC} = \frac{P}{bw^{1/2}} f(\alpha)
\]

The fracture energy, \(G_{IC}\), can then be calculated using the fracture toughness following Eq. 2:

\[
G_{IC} = \frac{K_{IC}^2}{E_t} (1 - \mu^2)
\]

Poisson’s ratio is taken to be 0.35, typical for epoxies [37]. \(E_t\) can be obtained from the initial slope of the force-displacement graph obtained in the experiment. As this method uses linear elastic fracture mechanics it is referred to as the LEFM method. The fracture energy is also calculated via a second method which uses the work done by the machine on the sample. This can be done by calculating the area under the force-extension graph. This second method is referred to as the ‘Energy’ method.
The glass transition temperature was measured using dynamic mechanical thermal analysis (DMTA) [38]. In this method a sample undergoing a controlled temperature ramp is oscillated and its storage and loss modulus recorded. The phase difference between storage and loss modulus can then be calculated, the peak of which then corresponds to the glass transition temperature, $T_g$. The mechanical tests on the SNEB were repeated 6 times and the DMTA was performed once.

MODELLING

Computational modelling in GPYRO was done for both of the flammability experiments conducted. Simulations were used to verify whether the heat transfer mechanisms identified in the experiments are the driving forces of the behaviour. GPYRO is an open source code [39] capable of modelling heat and mass transfer (Eqs. 3, 4, 5) combined with pyrolysis chemistry.

$$\frac{\partial (\bar{\rho} \bar{h})}{\partial t} = \frac{\partial}{\partial z} \left( \bar{k} \frac{\partial T}{\partial z} \right) + \sum_{k=1}^{K} (-\dot{\omega}''_{di}) \Delta H_s - \frac{\partial q''_r}{\partial z}$$ (3)

$$\frac{\partial \bar{\rho}}{\partial t} = -\dot{\omega}''_{g}$$ (4)

$$\frac{\partial (\bar{\rho} Y_i)}{\partial t} = -\dot{\omega}''_{di}$$ (5)

The pyrolysis reactions are modelled via an Arrhenius reaction as shown in Eq. 6.

$$\dot{\omega}_i = \frac{\partial m''_i}{\partial t} = m''_{i0} A_i e^{-E_i/RT} \left( \frac{m''_i}{m''_{i0}} \right)^{n_i}$$ (6)

The boundary condition (BC) at $z = L$ is an adiabatic condition as per Eq. 7. The heated surface ($z = 0$) is treated as a BC with convective and radiative heating, shown by Eq. 8.

$$-\bar{k} \frac{\partial T(L)}{\partial z} = 0$$ (7)

$$-\bar{k} \frac{\partial T(0)}{\partial z} = \bar{e} q''_{e} - h_c (T_{amb} - T(0)) - \bar{e} \sigma (T_{amb}^{4} - T^{4}(0))$$ (8)

Two different domains were modelled corresponding to the cone and the UL94 experiments conducted. Fig. 2a shows the 1D domain used to model the cone experiments. A constant irradiation boundary condition with 30 kW/m$^2$ is heating a slab of 10 mm thickness. The back side is assumed to be perfectly insulated. Fig. 2b shows the 1D domain used to approximate the UL94 experiment. The heating is assumed to be primarily convective with an ambient temperature of 2026 K and a convective heat transfer coefficient of 54 W/m$^2$K [40]. The radiative heating from the flame used in the UL94 test has not been studied well in the literature and so it is varied between 0 and 40 kW/m$^2$. 40 kW/m$^2$ was chosen as a typical upper bound of radiative heat transfer from flames [41]. The range obtained by this varying of boundary condition is indicated by error bars. The domain used is a simplification of the full complexity of the UL94 test however it serves to inform the experimental observations.
The kinetics and reaction scheme were obtained from the literature [42]. The nano-silica is assumed to be inert and added as a separate species, with properties shown in Table 1 (assuming a linear rule of mixing). The kinetic parameters, yields, and heats of pyrolysis are shown in Table 2. The reaction scheme is shown in Eqs. 9 and 10.

$$DGEBA \rightarrow \nu_i DGEBA_{int} + (1 - \nu_i)Gas$$  \hspace{1cm} (9)

$$DGEBA_{int} \rightarrow \nu_c DGEBA_{char} + (1 - \nu_c)Gas$$  \hspace{1cm} (10)

Table 2. Parameters used for the modelling of the reactions [42].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pre-exponential Factor ((s^{-1}))</th>
<th>Activation Energy ((kJmol^{-1}))</th>
<th>Yield ((-))</th>
<th>Heat of Pyrolysis ((Jkg^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1.72 \times 10^7)</td>
<td>111</td>
<td>0.97</td>
<td>5000</td>
</tr>
<tr>
<td>2</td>
<td>(9.86 \times 10^{16})</td>
<td>259</td>
<td>0.12</td>
<td>130 000</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

The mechanical tests were performed on the samples as described in the previous section and an overview of the data recorded is shown in Fig. 3. The plane strain fracture toughness \((K_{IC})\) increases linearly with nano-silica concentration up to about 24%, after which it drops. Similar behaviour can be seen for the fracture energy, where a peak is recorded at the 24% nano-silica samples. The LEFM and Energy approach for fracture energy are in good agreement except at the highest loading where some discrepancy appears. This shows that the nano-silica can increase the toughness to approximately twice the original value.

The flexure modulus increases approximately 1.5 times compared to the unfilled value. The glass transition temperature is a property which is not improved by adding nano-silica. \(T_g\) reduces by approximately 30 °C, a trend which has been noted before for these types of composites [15,16,37].

We conclude that the mechanical properties can be significantly improved, although the toughness reaches a limit around 24% loading where no further improvements can be made.
In the cone the samples were irradiated at 30 kW/m² up to spontaneous ignition. As the samples heated, a thin skin formed which was detached from the polymer matrix by the pressure of the pyrolysis gases. As the nano-silica concentration was increased the skin became more continuous with only one or two exit spots for pyrolysis gases. At 36% nano-silica a strong structure formed above the sample which did not collapse when the sample cooled and the pyrolysis gases ceased to inflate it. As this skin hinders the flow of flammable pyrolysis gases, less pyrolysate is released into the environment, delaying the formation of a flammable mixture above the sample, and hence ignition [18]. Fig. 4 shows an ignited sample. It can be seen that the flames do not originate on the parts covered by the skin which has formed. Where the skin has formed into a continuous skin, it is slightly inflated indicating that pyrolysis gases increase the pressure inside.
Fig. 5. Cross section of a sample embedded into resin to preserve the fragile skin. The discoloured surface of the epoxy can be seen at and the continuous skin formed.

Fig. 5 shows a sample which was encased in resin and the fractured along the middle. The resin was added to preserve the fragile skin so that the void formed between it and the epoxy can be seen.

Fig. 6 shows a top view of samples with varying nano-silica concentration after the cone experiments. All samples show some charring, but with increasing nano-silica concentration a stronger skin was formed.

The average time to ignition (TTI) with standard deviation is shown in Fig. 7. It can be seen that the addition of the nano-silica increases the time to ignition. It should be noted that one sample with 36% nano-silica did not ignite and is not included in the average for that composition. The relatively large error bars highlight the large scatter in these types of experiments. Nonetheless the average time to ignition increased up to 38% with SiO_2 added. Raising the TTI of materials increases the fire safety properties significantly, as it allows people a longer time to react to a fire incident. This is therefore a significant improvement brought by the nano-silica addition.

The samples containing 24% nano-silica performed significantly worse than all other samples and do not follow a monotonous trend. Further confirmation of this measurement was obtained when a freshly prepared new panel of material, carefully cured, with 24% nano-silica yielded the same results. Further samples containing 18 and 30% were tested behaving similarly and are also shown in Fig. 7. It is hence thought that around this concentration another effect of nano-silica addition appears which requires further investigation.

As it can be seen in Fig. 8, the core temperatures are higher as the nano-silica concentration is increased. This experimental observation is further supported by the data from the GPYRO simulations. The simulations predicted a weaker effect than experimentally observed but the close matching of the data supports that the increased thermal diffusivity due to nano-silica is responsible for the higher core temperatures. Simultaneously to the core heating, the surface temperature is reduced, as shown by the simulation and in agreement from basic heat transfer. This can be illustrated in the simulation at 50 and 100 s where the surface temperature was approximately 15 K lower at 36% nano silica loading than in the pure epoxy case. So when a sample has a higher thermal diffusivity, heat diffuses faster in the sample, increasing core temperature, and reduc-
Fig. 7. Time to ignition observed in the cone experiments for increasing nano-silica concentration and estimated change in time to ignition using Eq. 12.

Reducing surface temperature increases the time to ignition. The classical theory of ignition can be used to estimate TTI for thermally thick samples is shown in Eq. 11 [5].

\[
t_{ig} = \frac{\pi k \rho c}{4} \left( T_{ig} - T_o \right)^2 \left( \frac{\dot{q}}{\rho c} \right)^2
\]  

(11)

\[
t_{ig} = k \rho c \cdot \text{Const}
\]  

(12)

Eq. 11 shows that if the external conditions and ignition criteria are kept constant, and only the thermal properties \( k, \rho, \) and \( c \) changed, Eq. 12 can be used. The initial, ignition, and boundary conditions are replaced by a constant, calibrated empirically on the pure epoxy, and the material properties, shown in Table 1, can then be used as scaling parameters to estimate the change in TTI. This estimated change in TTI is plotted in Fig. 7. At the time of ignition the sample has heated significantly so that it behaves no longer semi-infinite, but large thermal gradients exist allowing for Eq. 12 to be used. Good agreement supports the change in thermal diffusivity to be a significant factor in ignition delay.

This equation does not take the skin formed into account which is thought to also affect the TTI. It is hard to dissect the relative importance of skin formation and thermal diffusivity however Eq. 12 indicates that the increase in thermal diffusivity is expected to be significant. Gpyro was not used to predict TTI as suitable ignition criteria could not be found.

Cone samples were fractured for analysis using the SEM. High magnification was chosen to investigate the degradation layers at the surface. Fig. 9 shows a composite image of a surface layer at two magnifications and a reference image of nano-silica. Fig. 9 (a) shows the degraded surface layer at 2,500 \( \times \) magnification. Enhancing further, shown in Fig. 9 (b) to 50,000 \( \times \), nano-silica agglomerations can be seen. Fig. 9 (c) shows a reference image of pure nano-silica. These images support the hypothesis that nano-silica strengthens the degraded surface layer by agglomerating at the surface as the same pyrolyses.

To further test the hypothesis of nano-silica agglomeration in the skin and to analyse the effect of varying the nano-silica concentration, EDX was used to measure the relative presence of carbon and silica at the surface, just below the surface and in the un-degraded bulk of the material. Fig. 10 shows low magnification SEM images and EDX results of the areas investigated of a 12% nano-silica containing sample (a) and a 36% one (b). The EDX signals to the right of the SEM images indicate that the relative amount of nano-silica to carbon increases significantly towards the surface and as the nano-silica concentration is increased to 36%.

![Graph showing time to ignition for increasing nano-silica concentration](image-url)
Fig. 8. Cone temperature data in the sample’s core (5 mm depth) as it undergoes heating. Error bars are shown but many not visible due to the good repeatability of the measurement. The white filled markers indicate temperatures predicted by Gpyro.

Fig. 9. (a) Sample cross section with the irradiated surface being to the right (× 2,500). (b) Enhanced section showing nano-silica agglomerates (× 50,000). (c) Reference image of pure nano-silica.

This supports the findings from the SEM that nano-silica agglomerates at the surface, integrating into the skin and forming a mass barrier to the pyrolysate gases, improving the flame retardancy.

In the enhanced UL94 test, the improvements in flame retardancy existed but were less pronounced. All samples ignited and dripped after the first flame application failing with a V- rating and indicating that nano-silica is not sufficient on its own to pass this flammability test. A discrepancy between cone and UL94 performance for nano-composites has been shown in the literature. For example, significant improvement are seen in the cone which do not translate well over to the UL94 test [19, 26]. It is generally thought that the benefit of nano-additives on UL94 performance relate to an increase in melt viscosity [18].

By analysing the mass loss after ignition as well as the change in surface temperature, a better understanding into the effect of nano-silica on UL94 performance can be gained. Fig. 11 shows the mass loss after 15 and 20 s in the UL94 test. This corresponds to 5 and 10 s after the 50 W flame has been removed, and the sample has ignited with the flame slowly spreading across it. It can be seen that improvements relating to the mass lost are brought by SiO$_2$. The mass loss could be reduced by up to 46% after 15 s and 29% after 20 s with 36% nano-silica added.
Fig. 10. SEM images showing the areas for the EDX analysis was applied for a 12% (a) and 36% (b) nano-silica containing sample after degradation in the cone. To the right of the SEM image the relative signals of carbon, oxygen, and silica can be seen.

Fig. 11. Non-dimensional sample mass after 15 and 20 s into the UL94 test. Higher mass indicates less pyrolysate produced and improved flammability characteristics.

The reduced mass loss can be attributed to two factors. Nano-silica acts as a mostly inert filler [25] reducing the reactive material available and, as noted previously, increases the thermal diffusivity. The increased diffusion of heat into the sample reduces surface temperatures, which in turn reduces the pyrolysis rate which is strongly dependent on temperature. To investigate this, the IR camera data was analysed at the bottom edge of the sample where the flame is applied. Fig. 12 (a) shows the area over which temperature data was averaged. Absolute temperature measurements require accurate measurements of emissivity over the whole degradation process as the char build up might change the emissivity. Because of this, the change in average surface temperature relative to the pure epoxy sample is presented.

In addition the temperature change as predicted by Gpyro at 10 s is shown in Fig. 12. Good agreement is found, giving confidence in the measurements taken despite the large experimental error bars. As the flame is removed after 10 s into the test no simulation data is available for 15 s as the boundary condition would change.

The IR data obtained agrees well with the thermocouple measurements in the cone. As the core temperature of the sample was increased in the cone due to the increase in thermal diffusivity, the surface temperature as measured in the UL94 test decreased accordingly. The change in surface, as well as core temperatures shown
earlier, appears to be linear with nano-silica concentration. The repeatability for IR measurements is not as
good as it was for thermocouple measurements, however this is expected as the UL94 test has a less constant
heating regime as the flame forming on the material can flicker due to buoyancy.

After this analysis, no clear reason could be found for the worse performance of the samples near 24%
nano-silica composition. It is hypothesized that because the skin is partially formed, the pyrolysate gases
are redirected from under the skin, escaping at certain positions resulting in spots of high pyrolysate con-
centrations, thus reaching a locally flammable mixture at shorter times. However further work is needed to
investigate the interaction of the two effects.

CONCLUSION

Mechanical and flammability tests were carried out on epoxy samples with increasing amounts of nano-silica.
At a loading of 36% , the nano-particles were able to double the toughness and increase the flexure modulus
by 50%. The glass transition temperature was decreased by 30 °C.

As well as improving the mechanics significantly, the flammability was reduced simultaneously. Time to
ignition under the cone was increased by close to 40%. The reason for the delay of ignition is thought to
be primarily due to increased thermal diffusivity. Using the standard model of ignition from the literature,
the time to ignition was extrapolated by changing the thermal properties. This yielded good agreement with
observed experimental data supporting the hypothesis.

Using an enhanced UL94 test measuring sample mass and surface temperature, it could be confirmed that in
this experiment, just like in the cone, the changes to the thermal properties, as modified by the nano-silica,
dominate the ignition and early flame spread. Mass loss was decreased through the presence of nano-silica as
the surface is up to 75 °C cooler reducing the pyrolysis rate at the surface.

Using a scanning electron microscope couple with an energy dispersive X-ray spectrometer, the surface layers
formed under the cone were analysed. It was found that the nano-silica agglomerates in the degraded surface
layer, thereby strengthening it. This surface layer then acts as a mass barrier to the pyrolysate gases improving
the flame retardancy.

The two flame retardancy effects observed appear to work in parallel and are therefore difficult to separate
experimentally. Since the changes in temperature observed could be explained via modelling without invoking
the mass barrier effect, the heat transfer effects are thought to be the dominant at least up to ignition.
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