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# 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 resistant to ignition and flame spread. These demands are often for many polymer types in competition, especially when adding flame retardants. With nano-silica addition, 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 for the heat transport and chemical kinetics in Gpyro was done and yielded good agreement with the temperatures measured. Adding up to 36% nano-silica, the time to ignition increased by 38% although a sharp decrease was observed around 24% SiO<sub>2</sub> addition. We show that the increased time to ignition is mostly due to a higher thermal diffusivity, increased inert skin content, as well as a strengthening of the residue outer skin, 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.

## 1. 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 high tensile strength the global epoxy market was estimated at \$ 18.5 billion in 2013 [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 the ones containing bromine 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

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**Nomenclature**

$A$	pre-exponential factor [ $s^{-1}$ ]
$b$	sample thickness [m]
$c$	specific heat capacity [J/kg-K]
$E$	activation energy [kJ/mol]
$E_t$	tensile modulus [MPa]
$\Delta H$	heat of pyrolysis [J/kg]
$G_{IC}$	fracture energy [MPa]
$h$	enthalpy [J/kg]
$h_c$	convective heat transfer coefficient [ $W/m^2-K$ ]
$k$	thermal conductivity [ $W/m-K$ ]
$K_{IC}$	fracture toughness [MPa $m^{1/2}$ ]
$L$	depth of the sample [mm]
$m$	mass [-]
$n$	condensed phase reaction [-]
$N$	number of condensed phase reactions [-]
$P$	load at failure [MPa]
$\dot{q}''$	heat flux [ $kW/m^2$ ]
$R$	universal gas constant [J/mol-K]
$T$	temperature [ $^{\circ}C$ ]
$t$	time [s]
$w$	sample width [m]
$Y$	mass fraction [-]

$z$	depth into the sample [m]
<i>Greek</i>	
$f(\alpha)$	geometry calibration factor [-]
$\varepsilon$	emissivity [-]
$\kappa$	radiative absorption coefficient [ $m^{-1}$ ]
$\mu$	Poisson's ratio [-]
$\nu$	yield [-]
$\rho$	density [ $kg/m^3$ ]
$\sigma$	Stefan-Boltzmann constant [J/K]
$\dot{\omega}'''$	reaction rate per unit volume [ $kg/m^3-s$ ]

*subscripts*

$amb$	ambient
$0$	initial
$e$	external
$d$	destruction
$g$	gas
$i$	condensed-phase species index
$ig$	at ignition
$r$	in-depth radiation
$s$	solid

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 nanoparticles 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 nanocomposites. 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 of pyrolysate available. The added inert content can be seen as increased residual mass in the TGA [26,28]. This has been erroneously described in the literature as improving the thermal stability of the epoxy [25].

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 nano-silica 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].

**2. Experiments**

The samples used were cast from Bisphenol A diglycidyl ether (DGEBA) (LY556, Hunstman, 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, Germany) or HDE (Nanopox F640, Evonik Hanse, Germany) 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  $^{\circ}C$  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  $^{\circ}C$ ) for 24 h after which samples were

**Table 1**  
Overview of composition used in these investigations. Thermophysical properties extracted from the literature [30].

Constituent	Units	C0	C12	C24	C36
Epoxy resin	%	82	70	58	46
Diluent	%	18	18	18	18
Nano-silica	%	0	12	24	36
Density	$kg/m^3$	1200	1269	1338	1408
Thermal conductivity	$W/m^2K$	0.241	0.248	0.271	0.312
Specific heat capacity	$J/kgK$	1204	1161	1116	1068

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