

# EFFECT OF FUMED SILICA ON THE GLASS TRANSITION OF AN EPOXY

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The effect of fumed silica on the glass transition temperature ( $T_g$ ) of a fully cured trimethylolpropane epoxy resin was investigated by modulated temperature differential scanning calorimetry (TMDSC) and dynamic mechanical analysis (DMA). The fumed silica used here is a by-product of the silicon and ferrosilicon industry, consisting of micro and nano particles. The  $T_g$  of the composites was affected by the filler content. Different trends were observed for filler contents above and below the 30 wt%. Up to 30%, the behavior can be explained as a predominating agglomerates effect. For 30% and higher filler contents, single particles seem to play a more important role.

The dispersion of nano-particles in a polymer matrix has a significant impact on the properties of nanocomposites. Methods to improve the dispersion of nano-particles into the matrix include, but are not limited to, mechanical mixing and ultrasonic dispersion, surface modification of nano-particles and sol-gel process. In this work, fumed silica-epoxy composites were prepared and characterized by thermal analysis methods. The properties of the non conventional epoxy resin, based on trimethylolpropane, make it particularly suitable for the manufacture of composites. The fumed silica used here was obtained as a by-product of the silicon production in the top of large electrical melting furnaces, which is a non conventional production. Hence, the particle size and the purity of the fumed silica are variable, reflecting the furnace operation at the time it was collected. In any case, the silica weight proportion is greater than 95%. According to Schadler, three dimensional nanofillers are relatively equally-axed particles, with a length lower than 100 nm in their largest dimension. Hence, the fumed silica used in this work has its specific particle size distribution, including micro and nano-particles. This makes it different from other micro or nano-sized silica powders, and therefore, combined effects of both are expected. The aim of this work is to evaluate the effects of fumed silica on the viscoelastic properties of the resulting composites.

A two component epoxy system was used. It consisted of a diglycidyl ether of trimethylolpropane based resin, Triepox GA, from Gairesa-Spain and 1,3-benzenedimethanamine 99% pure, from Aldrich, as curing agent. The 1,3-benzenedimethanamine is an aromatic amine hardener. Triepox GA is a highly thyrotropic resin with low density and curing capability at room temperature on its own, without either plasticizers or additives. The fumed silica was provided by Ferroatlántica I+D, Spain. It was obtained as a by-product of the silicon production in electrical

melting furnaces. This process involves the reduction of high purity quartz, at temperatures above 1800 °C. The silica fume is formed when the SiO gas, resulting from the reduction of quartz, is mixed with oxygen at the top of the furnace producing silica spherical particles. It is a fine powder with colour ranging from almost black to slightly-off white, depending on its carbon content. Its mean particle size is 0.15  $\mu\text{m}$  and 41.9 % of the particles have a diameter below 0.2  $\mu\text{m}$ . The values obtained through surface area analysis typically fall about 20  $\text{m}^2 \text{g}^{-1}$ . Chemically, the fumed silica consists of amorphous SiO<sub>2</sub> of variable purity.

## Sample preparation

Composite samples for DMA tests were prepared with filler contents of 5, 10, 20, 30, 40, 50 and 60 wt% of fumed silica. Both the epoxy resin and the hardener were mixed in stoichiometric proportions. Resin and silica mixtures were stirred for 15 minutes and then sonicated for 5 minutes at room temperature to disperse the filler agglomerates. The composite pastes were poured into silicone moulds whose cavity dimensions were 0.8 x 4 x 30 mm. This resin was reported to cure at room temperature, having a  $T_g$  about 90 °C. The samples were cured at room temperature for 24 hours and post-cured in an oven at 90 °C for 2 hours. For the TMDSC-glass transition tests, cured samples were cut from DMA samples. The sample mass was adjusted so that each sample contained about 3 mg of resin, independently of the filler content.

## Characterization methods

The composite and neat resin samples were evaluated by DSC and DMA. Differences between  $T_g$  measured by DSC and DMA are due to the frequency effect on  $T_g$  values.  $T_g$  values obtained from 1 Hz DMA data for  $E''$  or  $\tan \delta$  peak are always a few degrees higher than DSC  $T_g$  values obtained at 10 - 20 °C/min heating rates.

The DSC experiments were performed on a TA Instruments MDSC Q-1000 attached to a refrigerating cooling system. This instrument can be operated in both modulated and standard modes. The following calibrations were performed, according to manufacturer recommended procedures: Tzero, enthalpy constant, temperature and modulated heat capacity. A range of temperature from -20 to 300°C was chosen, as per recommendations from the literature. Sapphire standard and crimped aluminum crucibles were used for heat capacity calibration in modulated conditions.

DSC was operated in modulated mode in order to separate the reversing  $C_p$  from non reversing phenomena such as enthalpic recovery, residual cure and possible degradation processes taking place in cured samples. The thermal program consisted of a 5 °C min<sup>-1</sup> average heating ramp from -20 to 200 °C. The modulation amplitude was 1.6 °C and the period 60 s. The viscoelastic properties of the cured composites were evaluated by DMA on a Rheometric DMTA IV instrument. Calibration was performed as per manufacturer recommendations included in the Rheometric Orchestrator software. The tests were conducted in tensile mode. The samples were about 0.8 mm thick and 4 mm width. A fixture gap of 10 mm was used. A strain sweep test was performed at room temperature in order to find experimental conditions in the viscoelastic linear region for subsequent experiments. This was done by varying the strain amplitude while keeping the frequency at 1 Hz. A strain amplitude of 0.005% and 1 Hz frequency were chosen. A constant heating ramp of 2 °C min<sup>-1</sup> was applied in all the experiments.

## Results and discussion

Fig. 1 shows the reversing heat flow plots and their derivatives obtained by MTDSC from the cured samples.

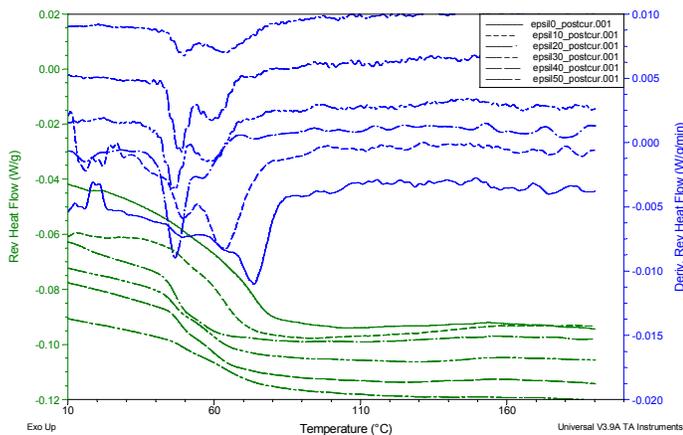


Fig. 1.

The glass transition can be identified on the reversing heat flow traces as an abrupt change around 60 °C. The  $T_g$  can be assigned to the peak value of the derivative. A plasticizing effect of the filler can be observed in Fig. 3, where all the filled samples present a shifting of the peak derivative to lower temperatures with respect to the neat resin sample. A double peak can be observed on the derivative plots at the glass transition temperature region. It indicates a double glass transition, which was not observed in the case of the neat resin sample. The relative heights and locations of the peak values are shifted when increasing the filler content.

Figure 2 plots the storage modulus,  $E'$ , loss modulus,  $E''$ , and damping factor,  $\tan \delta$ , obtained in a DMA temperature ramp from a cured sample. The  $E'$  decrease observed in the 50 to 100 °C range correspond to the glass transition

relaxation of the polymer. The  $T_g$  is also evidenced by a small peak of  $E''$  and by a well defined peak of  $\tan \delta$ . Thus, the maximum peak value of  $\tan \delta$  was the chosen criterion to compare the  $T_g$  values obtained by DMA.

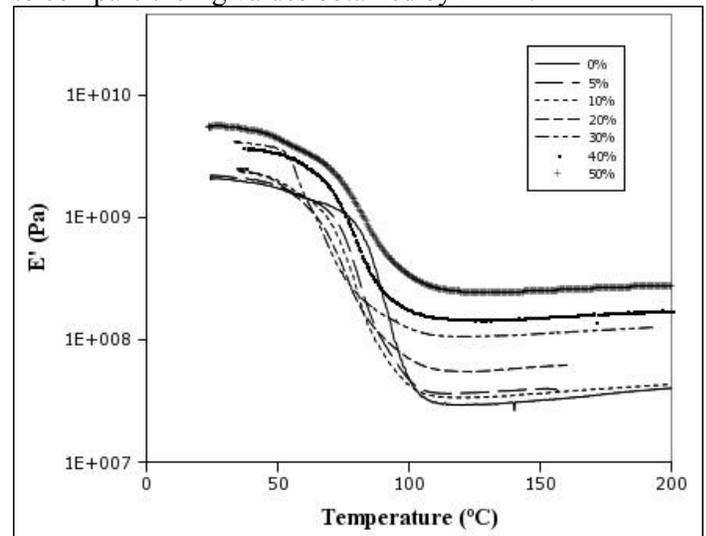
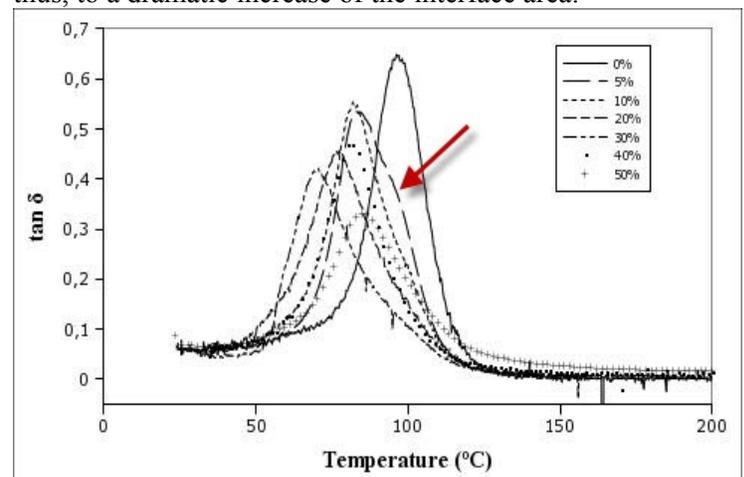


Fig. 2

A plasticizing effect of the filler can be observed in Fig. 3, where all the filled samples present a shifting of the  $\tan \delta$  peaks to lower temperatures with respect to the neat resin sample. Another effect of the filler is a broadening of the  $\tan \delta$  peaks. This indicates higher heterogeneity of the composites crosslinked structure [45]. The normalized  $\tan \delta$  area increases with the filler content up to the 50%. It can be explained as an effect of the effective polymer-filler interfacial area, which increases with the filler content. The maximum difference is observed in the 30 to 40% range, which corresponds to the agglomerates destruction and thus, to a dramatic increase of the interface area.



## Conclusion

Double glass transition was observed by TMDSC and DMA in the fumed silica-epoxy composites, while the cured neat resin presented a single glass transition. One of the glass transitions is due to the neat resin and the other to the polymer-filler interface. A plasticizing effect of the filler was also observed, which is probably due to the nanoparticle effect.