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Article *in* JEC Composites Magazine · August 2016

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Cure kinetics of a fast-cure epoxy with silica nanoparticles

This article describes how the strong exothermic reaction of a fast-cure epoxy can be better controlled with the addition of non-reactive silica nanoparticles, further enhancing the benefits of a fast process, the toughness and the ability to understand the properties of thicker composite parts.

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Fast-cure epoxy systems are used for the mass production of composite parts with cycle times in the minute range. However, the use of fast-cure resins results in new challenges regarding the understanding of their properties and processing behaviour. One of the major difficulties with fast-cure resins is their strong exothermic reaction during cure, which may result in a significant temperature overshoot and large temperature (and therefore T_g, shrinkage and residual stress) gradients over the thickness. Further, the resin viscosity evolution strongly affects the impregnation process.

Cure cycle optimisation through modelling of heat transfer and flow helps to find more suitable process parameters to reduce the exothermic reaction. However, in some cases it is also necessary to reduce the cure temperature with a negative influence on the cycle time. A possible approach is to reduce the exothermic mass of the resin itself, which can be achieved by adding non-reactive particles to the resin. In composite manufacturing, any such particles must be small enough that they are not filtered out during infusion processes, for example silica nanoparticles with a diameter of 20 nm [1]. The addition of silica nanoparticles up to 20 wt.% has been shown to increase stiffness and fracture energy [2] without having a strong influence on the viscosity of the epoxy matrix [3].

This article focuses on a fast-cure resin for automotive applications, XB3585/XB3458, supplied by Huntsman, Switzerland. This epoxy has a cure time of 5 min at 100°C. The results are compared to HexFlow RTM6, a commonly used RTM epoxy. Nanopox F400 from Evonik Hanse, Germany, was supplied as a masterbatch containing 40 wt.% of silica nanoparticles predispersed in a diglycidyl ether of bisphenol A (DGEBA) epoxy resin. These particles were then mixed with the XB3585 resin and the masterbatch resin in order to produce formulations including 10 wt.% and 20 wt.% of silica nanoparticles.

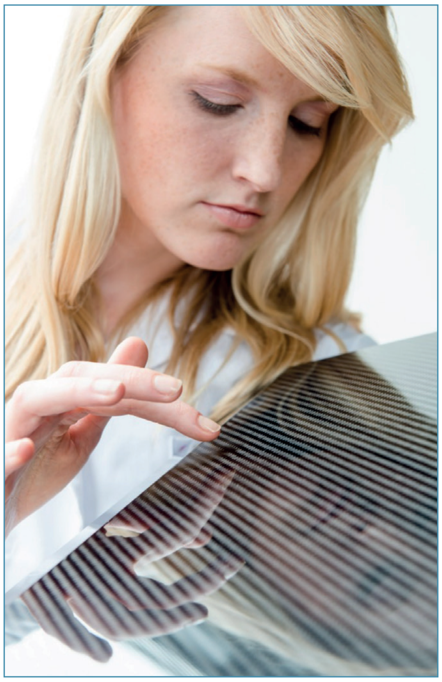

Fig. 1: Part of a convertible roof cover manufactured with a toughened, fast-cure resin

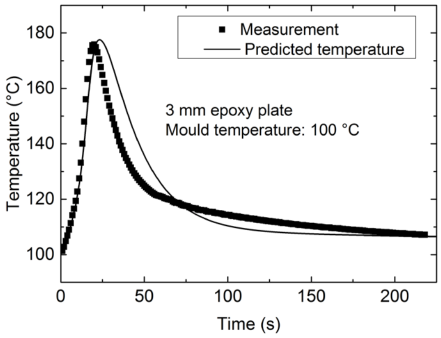

Fig. 3: Temperature progression during cure of the XB3585/XB3458 epoxy resin [3]

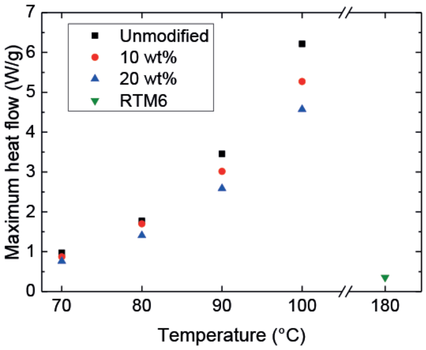

Fig. 4: Comparison of the maximum heat flow of the epoxy systems under isothermal conditions [5]

Cure kinetics of fast-cure epoxy

As the epoxy cure reaction is exothermic, the resin temperature can overshoot the mould temperature. When manufacturing a composite plate in a mould, the magnitude of the overshoot depends on the mass of resin and the plate thickness. The heat flow in the resin is limited by the low thermal conductivity (0.2 W/(m °C)) of the epoxy, meaning that heat will not readily dissipate once produced.

The exothermic reaction during cure can be characterised by measuring the heat flow using differential scanning calorimetry (DSC). The severity of the exothermic reaction depends on the total heat of reaction (integral of the heat flow curve) and the time span in which the heat is released. Isothermal DSC measurements of the XB3585/XB3458 and RTM6 systems are shown in Fig. 2. Two important differences between these two epoxies explain why the XB3585/XB3458 system has a much higher tendency to overshoot the mould temperature than RTM6:

i) The total heat of reaction derived from dynamic DSC measurements is in the same order of magnitude for both materials with a slightly higher value of 494 ±4 J/g for the fast-cure resin and 457 J/g for RTM6 [4]. However, the release of a similar amount of energy within a much shorter time span results in a higher heat flow. The heat flow of the XB3585/XB3458 system at 100°C is a factor of 20 higher than RTM6 at 180°C, their respective recommended processing temperatures.

ii) The heat flow of the XB3585/XB3458 system peaks very early in the cure process, indicating that a large amount of heat is released at cure reaction initiation. In contrast, a slow, steady increase of the heat flow can be measured with RTM6.

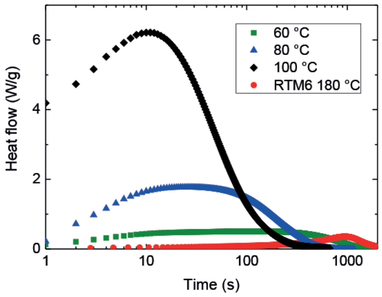

Fig. 2: Isothermal DSC measurements of the XB3585/XB3458 system compared to RTM6 epoxy resin

A temperature progression measured during cure is shown in Fig. 3 for a 3-mm-thick bulk epoxy plate manufactured using an aluminium mould at 100°C. The temperature increased from 100°C to 176°C within 20 seconds. Typically, the temperature distribution during such a strong overshoot is not homogeneous but rather shows a significant variation with the maximum temperature in the centre of the mould, and only a small overshoot close to the mould surface. These phenomena affect the part during processing and can result in defects of the final part such as material decomposition or internal stress.

Influence of silica nanoparticles

Dynamic and isothermal DSC measurements were conducted and the maximum heat flow was extracted, as shown in Fig. 4. The heat flow was found to be inversely proportional to the wt.% of silica nanoparticles. The glass transition temperature, T_g, remained unaffected with a constant value of 121 ±1°C. These results indicate that the particles do not influence the cure reaction adversely, but do reduce the exothermic mass.

The temperature overshoot was reduced from 176°C for the unmodified epoxy to 166°C and 157°C with the addition of 10 wt.% and 20 wt.% of silica nanoparticles respectively. The importance of this temperature reduction for the modelled case can be shown by comparing

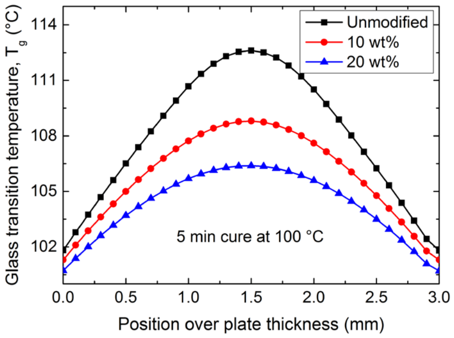

Fig. 5: Modelled glass transition temperature gradient over the plate thickness during cure [5]

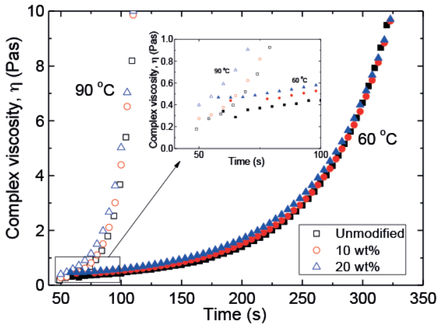

Fig. 6: Initial viscosity of the XB3585/XB3458 epoxy resins [3]

the glass transition temperature (T_g) distributions over the thickness, as shown in Fig. 5. In the case of the unmodified epoxy, the difference between the T_g at the edge and in the middle is 11°C. The addition of 20 wt.% of silica nanoparticles results in a difference of only 5.5°C. The temperature distribution over the thickness was not completely dismissed with the addition of silica nanoparticles but significantly reduced, leading to more uniform properties over the thickness.

As, typically, the addition of particles can increase the viscosity, the effect of particle concentration on the initial viscosity and cure cycle evolution was also studied. The effect of silica nanoparticles was found to be relatively small for silica contents up to 20 wt.% (Fig. 6), whereas a higher wt.% results in an exponential viscosity increase. The influence of silica nanoparticles on the viscosity of the fast-cure resin becomes negligible at about 10 Pas as the cure reaction kinetics dominate the evolution of the viscosity, explaining why no effect on the gelation time was noticed.

Modelling

The temperature distribution during cure can be modelled by incorporating the cure kinetics into the heat transfer equation [3]. The prediction is shown in Fig. 3. Modelling the temperature makes it possible to calculate the viscosity, the degree of cure and the glass transition temperature (more details are available in a previous study [3]). The T_g gradient over the thickness of a 3 mm bulk epoxy plate without and with 10 and 20 wt.% silica nanoparticles is shown in Fig. 5. These models may be implemented into flow simulations to predict the flow front during fibre impregnation in liquid composite moulding (LCM) processes.

Conclusions

The addition of silica nanoparticles is a suitable method to reduce exothermic heat generation during cure without influencing the curing reaction itself. This allows the use of fast cure cycles, makes the process more controllable and leads to more uniform properties over the thickness of the part. Since the viscosity is only slightly increased with contents up to 20 wt.%, the silica nanoparticles are well suited for liquid composite moulding (LCM) processes. Modelling of the cure kinetics, heat transfer and viscosity combined with flow simulations may help to find the optimum process parameters during preform impregnation. ☐

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