

## The effect of ultraviolet (UV) light postcuring on resin hardness and interlaminar shear strength of a glass-fibre/vinylester composite

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Received: 16 April 2008 / Accepted: 5 May 2008 / Published online: 18 May 2008  
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Thermoset resins formulated with a photoinitiator can be rapidly cured through exposure to ultraviolet (UV) light. The UV light excites the photoinitiator, which breaks down to produce radicals that begin catalytic polymerisation of the resin [1]. Cure can be achieved in minutes or seconds, depending on the light intensity, exposure time and resin thickness. For this reason, the use of UV curing resins is established in the coating and ink industries where it has increased productivity and reduced solvent emissions [2, 3].

In contrast, manufacturing processes for fibre-reinforced polymer-matrix composites are characterised by numerous processing stages, long cycle times and hazardous chemical emissions. Thermoset matrix resins are often catalysed with peroxide catalysts. These resins typically require a thermal postcure, after an initial room temperature cure, to increase properties to an acceptable level. This process takes several hours. Composites are attractive for increased use in engineering structures due to their low density and high specific strength and stiffness. However, cleaner, quicker manufacturing processes are needed to increase their use [4]. Recent work has, therefore, investigated the use of UV curing technology for composite materials. It can be applied to the pultrusion process to manufacture curved structures, with the composite exposed to UV light as it exits the die [5]. UV curing is also effective in composite repair applications, with unlimited pot life and increased productivity cited as major benefits [6, 7]. UV curing composites can be laminated onto previously cured laminates without loss of shear strength at the secondary

bondline [8]. This would allow thick structures to be manufactured by layering and overcome the problem of limited depth of cure. Solvent emissions during composite manufacture with UV curing resins may also be less than for conventionally catalysed resins due to the rapid cure of the resin [8].

To date, the research has focused on composites formulated for UV cure only. Furthermore, UV curing via a free radical mechanism with photoinitiators requires direct exposure to UV light. In practice, component geometry may be too complex to achieve complete and even UV exposure, and much manufacturing is done using closed moulds. An alternative approach is to formulate the resin to enable UV postcuring of a demoulded composite, following an initial room temperature cure.

This letter presents preliminary results on the potential of UV postcuring to increase the properties of bulk vinylester resin and a glass-fibre/vinylester composite. Experimental work on resin hardness and composite interlaminar shear strength was conducted with samples formulated for room temperature cure and UV postcure. The hardness testing will provide a qualitative assessment of the degree of cure in the resin. The composite shear test was chosen as it induces failure through a shear crack at the mid-plane and is therefore sensitive to the resin performance.

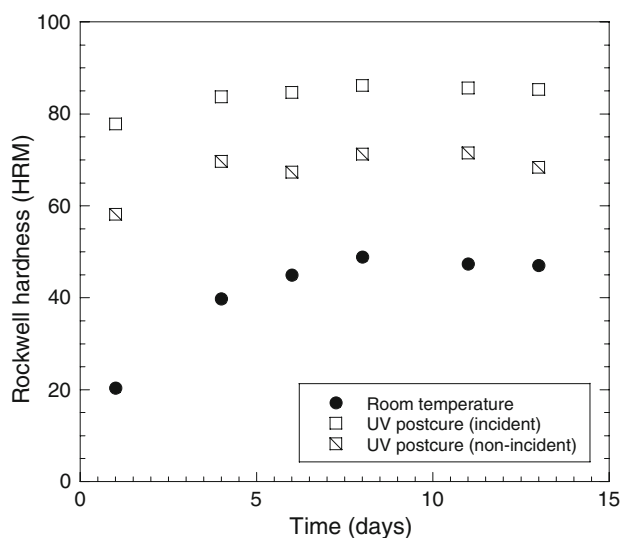
Derakane 411–350 bisphenol A epoxy vinylester resin (Ashland Inc.) was formulated for room temperature cure with a gel time of 20–40 min. The formulation was 0.2 parts per hundred (pph) ratio by weight of cobalt naphthenate (CoNap) promoter and 1 pph of methyl ethyl ketone peroxide (MEKP) catalyst. To enable UV cure, a phosphine oxide-based photoinitiator (Irgacure 819, Ciba Specialty Chemicals) was also added to the resin at 0.5 pph as recommended by the manufacturer. After formulation, the bulk resin was cast to a thickness of 6 mm in two

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80 × 80 mm moulds and allowed to cure for 24 h at a room temperature of approximately 25 °C. One resin cast was then postcured through exposure to UV light for 10 min under a 400 watt mercury vapour lamp. The sample was placed approximately 190 mm from the UV source and only one side (termed the incident side) was exposed. The UV intensity, measured with a Q401 UV light meter, was 0.7, 1.5, 2.7 and 1.9 mW/cm<sup>2</sup> for wavelengths of 300, 365, 400 and 436 nm, respectively.

Rockwell hardness testing for polymers (scale M) was conducted according to ASTM D 785–89. A minimum of five readings were taken for each sample at regular intervals for 14 days after formulation. The UV postcured sample was tested on both the incident and non-incident surfaces. The results are shown in Fig. 1. Immediately after the UV postcure (day 1) the resin hardness increased 3–4 times, suggesting significantly increased degree of cure. There is a difference in hardness between the incident and non-incident sides. This may be due to a thickness effect, whereby the UV intensity diminishes through the sample thickness. Furthermore, the resin hardness on the incident and non-incident sides is lower than for the same resin formulated only for UV cure (that is, only with 0.5 pph of Irgacure 819 photoinitiator) and cured under identical conditions [8]. It is possible that the effectiveness of a UV postcure is reduced by the Trommsdorf effect. In this case, the considerable increase in viscosity due to the room temperature curing stage may have inhibited the rate of further crosslinking. However, this point requires further work.

It is also clear from Fig. 1 that the resin hardness for the room temperature sample increases over time before reaching a plateau after approximately 7 days. This is expected as curing continues slowly over time in resins



**Fig. 1** Rockwell hardness (scale M) for room temperature cure and UV postcure of vinyl ester resin

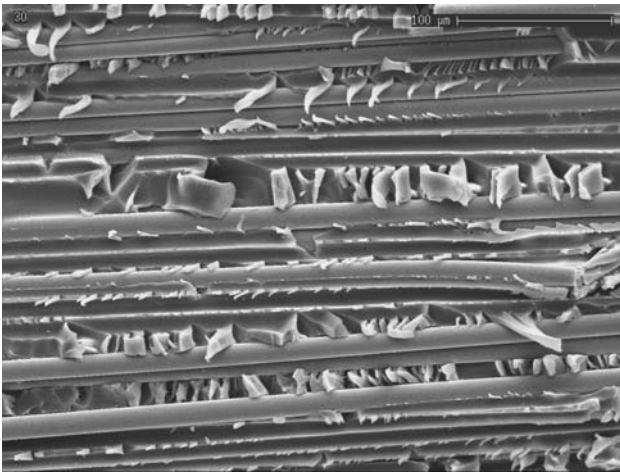
catalysed for room temperature cure. A similar trend is evident, albeit to a lesser extent, in the UV postcured sample with resin hardness approaching 85 on the incident side. This suggests that the room temperature formulation can still cause the cure to evolve even after a step increase in cure attained by the UV postcure. A higher resin hardness value of 90 was measured for thermally postcured vinyl ester resin [9], but the treatment in that case was 4 h at 90 °C as recommended by the manufacturer to attain maximum properties. It has been noted that resin cure can be increased by heat generated during UV exposure [10], but this effect is unlikely to be significant here given the relatively low UV intensity used for postcuring.

A composite laminate for interlaminar shear testing was made by hand lay-up using 24 plies of unidirectional E-glass fibres (Owens Corning R25, 300 g/m<sup>2</sup>) as the reinforcement and the vinyl ester resin as the matrix. Resin formulation and laminate curing, including a 10-minute UV postcure, proceeded as for the bulk resin. Fibre volume fraction of the laminate was approximately 35%. Test samples were cut from the laminate using a water-cooled diamond saw. Centre-loaded interlaminar shear tests were conducted in accordance with ASTM D2344. The average sample length was 50 mm, width 7 mm and thickness 7 mm. Samples were tested on a 3-point bend fixture at 1.3 mm/min in an Instron universal testing machine (model 4505). The span length to thickness ratio was 5 to 1 and the loading pin diameter was 6.35 mm as recommended by ASTM. A minimum of three samples were tested. The interlaminar short beam shear strength ( $\tau_{sbs}$ ), MPa, was evaluated using:

$$\tau_{sbs} = 3P/4wt$$

where  $P$  is the maximum load,  $w$  sample width and  $t$  sample thickness.

The average shear strength for the UV postcured composite was 32 MPa (the standard deviation was 3.5). This result is 28% higher than the shear strength for the room temperature cured counterpart [8]. However, it is 35% lower than thermally postcured and fully UV cured counterparts, which produced comparable interlaminar shear strength of approximately 50 MPa [8]. In addition to the possible Trommsdorf effect, the scattering of UV light by the glass fibres may be reducing UV intensity and inhibiting the rate and degree of cure. Therefore, another three composite samples were manufactured and tested after being given a 30-min UV postcure. The interlaminar shear strength increased to 41 MPa (standard deviation 1.3), indicating that the effectiveness of the postcure can be improved through increased exposure time. An electron micrograph from the interlaminar fracture surface of a 30-min UV postcured sample is shown in Fig. 2. Hackle marks are present in the resin between the fibres. These marks are



**Fig. 2** Fracture surface micrograph from an interlaminar short beam shear sample with a 30-min UV postcure

similar to those observed for thermally postcured and fully UV cured counterparts [8] and indicate a comparable degree of cure.

In summary, the resin hardness and the composite interlaminar shear results indicate that UV postcuring can increase resin cure and improve composite properties. It is also significant that the improvement is achieved in a relatively short time compared to conventional curing methods. Therefore, if satisfactory properties can be achieved, UV

postcuring could be a viable alternative to thermal postcuring in composite manufacturing processes. Further work is required to optimise postcure processing parameters, such as UV intensity and exposure time, to maximise thermal and mechanical properties and achieve maximum depth of cure.

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