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LETTER

Resin hardness and interlaminar shear strength of a glass-fibre/vinylester composite cured with high intensity ultraviolet (UV) light

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Thermoset resins such as epoxy and vinylester are common matrices for glass-fibre reinforced polymer composites. When formulated with photoinitiator, these resins can be cured in minutes through exposure to ultraviolet (UV) light [1]. The UV radiation excites the photoinitiator in the resin and creates radicals that begin catalytic polymerization [2]. UV curing is a novel technology for composite materials processing but its adoption could offer major productivity gains. Conventional cure methods for thermoset-based composites involve the addition of a hardener or catalyst to the resin for an ambient temperature cure followed by a thermal post-cure treatment to attain full cure. This approach requires several hours, or days, of processing time. The increased speed of cure possible through UV curing can also reduce the emission of volatile organic compounds (VOCs) from the resins, such as styrene from vinylester [3].

Fibre-reinforced composites have excellent specific properties and are attractive for applications where reduced weight can result in increased fuel efficiency. Quicker and cleaner manufacturing processes are needed to increase their use [4] and UV-curing technology could address these needs. Therefore, recent research effort has been directed towards UV-curing composites. They can exhibit similar mechanical properties to their thermally post-cured counterparts [3] and can be used for rapid repair of large composite structures [5]. The technology can be applied to the pultrusion process, with the composite exposed to UV light as it exits the die [6]. A further application is as a relatively quick (up to 30 min) post-cure stage [7] that can produce resin properties similar to those achieved with a thermal post-cure. This approach may be useful for parts that cannot be exposed directly to UV light during an initial processing or moulding stage.

The total UV radiation required to effect cure is characterised by the dosage, measured in J/cm^2. This is a product of the two main processing parameters, the UV intensity (or irradiance) measured in W/cm^2 and the exposure time. A dosage in the range of 7.5–12 J/cm^2 can be sufficient to cure relatively thin ($\sim$0.8 mm) composites [8]. Much of the research on UV-curing composites to date has been conducted at relatively low dosages, due to low intensities in the order of mW/cm^2. Exposure times in the range 10–30 min have therefore been required [3, 8]. The use of high intensity UV light could reduce the cure time further [1].

This letter presents preliminary experimental results on properties achieved for bulk vinylester resin and a glass-fibre/vinylester composite cured through exposure to high intensity (25 W/cm^2) UV light. Resin hardness was characterised for a range of exposure times to provide a qualitative assessment of the degree of cure in the resin. Composite interlaminar shear strength was characterised using samples from a laminate cured using an ideal exposure time determined from the bulk resin testing. The interlaminar shear test was chosen as it induces delamination failure at the mid-plane of the composite, and is therefore sensitive to the resin performance.

Swancor 901-35 bisphenol A epoxy vinylester resin (Swancor Ind. Co. Ltd., Taiwan) was formulated with 0.5 parts per hundred (pph) ratio by weight of phosphine oxide-based photoinitiator (Irgacure 819, Ciba Specialty Chemicals). The bulk resin was poured into a 10 mm diameter cylindrical mould to a depth of 8 mm. The mould

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was placed under a high-intensity UV spotlight (Omnicure 2000) that emitted UV light in the UVA/UVB range through a fibre optic light guide. The diameter of the aperture at the tip of the guide was 1 mm and the distance from the tip to the surface of the resin was 20 mm. Several samples were cured at a constant intensity of 25 W/cm^2 with the exposure time increased from 5 to 30 s in 5 s increments. Only the top surface of the resin (termed the incident surface) was exposed to the UV light.

Rockwell hardness testing for polymers (scale M) was conducted according to ASTM D 785-89. A minimum of three readings were taken from the incident and non-incident surfaces of each sample. The average hardness results are shown in Fig. 1. It is clear that 15 s of exposure is required before the hardness is the same for both the incident and non-incident surfaces of the 8 mm thick sample. This corresponds to a dosage of 375 J/cm^2. The similarity in hardness gives a qualitative indication that the degree of cure is similar on both surfaces. Exposure times of up to 30 s did not, within scatter, increase the hardness further. The maximum hardness values were in the range of 85–90. Previous study reported a hardness value of 90 for vinylester resin that received a thermal post-cure treatment of 90 °C for 4 h [9]. This thermal post-cure was recommended by the resin manufacturer to attain maximum properties. Therefore, the hardness results for the UV-cured resin in the current study indicate that a high degree of cure has been attained.

A composite laminate for interlaminar shear testing was made by hand lay-up using 10 plies of 80 × 80 mm unidirectional E-glass fibres (Owens Corning R25, 300 g/m^2) as the reinforcement and the 901-35 vinylester resin as the matrix. Styrene monomer was added to the resin at 15 pph

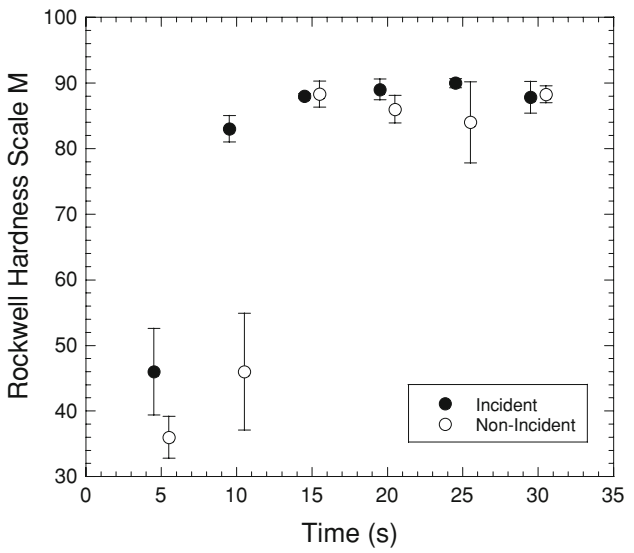

Fig. 1 Rockwell hardness (scale M) for bulk resin as function of exposure time (Error bars signify ± 1 SD)

ratio to reduce viscosity and aid fibre wet-out during the lay-up. The matrix resin was formulated with the photo-initiator as described for the bulk resin. The UV spotlight was fixed to a robot arm 20 mm above the laminate and passed over it at 1.5 mm/s at an intensity of 25 W/cm^2. Under these conditions the light flooded an area of diameter 20 mm; therefore it was passed over the laminate four times to ensure a minimum exposure of 15 s, and dosage of 375 J/cm^2, per unit area of the laminate. The total cure time was less than 4 min. The curing conditions for the laminate match those for the bulk resin where hardness was the same on both surfaces. Since the laminate thickness was expected to be significantly less than the bulk resin sample, it is expected that 15 s exposure is sufficient for through-thickness cure.

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 40 mm, width 9.1 mm and thickness 3.2 mm. The average fibre volume fraction was 37%. Samples were tested on a three-point bend fixture at 1.3 mm/min in an Instron universal testing machine (model 4505). The span length to thickness ratio was 5:1 and the loading pin diameter was 6.35 mm as recommended by ASTM. A minimum of five samples were tested. The interlaminar short beam shear strength (τ_{sbs}), MPa, was evaluated using:

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

where P is the maximum load, w specimen width and t is the thickness of the specimen. Delamination at or close to the mid-plane was the observed failure mode in each sample.

The average interlaminar shear strength was 51 MPa (with standard deviation of 4.7 MPa). This compares well with the interlaminar shear strength of 50 MPa reported previously for a thermally post-cured glass/vinylester composite [3]. An electron micrograph of the delamination fracture surface from one of the interlaminar shear samples is shown in Fig. 2. The deformation features between the fibres are hackle marks, which are caused by the coalescence of micro-cracks initiated by shear loading. These marks are commonly observed for mode II shear failure [10, 11] and are also similar to those observed for thermally post-cured glass-fibre/vinylester counterpart [3].

The shear strength result and the observed fracture behaviour support a conclusion that a high degree of cure and mechanical performance can be attained with high intensity UV curing. This study is also significant in that it shows the potential for high speed UV curing technology in automated composite fabrication processes that could eliminate time consuming ambient cure and post-cure stages. This concept can be termed in situ curing. One

Fig. 2 Fracture surface micrograph from an interlaminar short beam shear sample

example of this concept is robotic composite placement, where the composite would be cured in situ through exposure to high intensity UV light immediately after placement into a mould [12]. This type of process typically involves composite layers less than 1 mm thick, therefore full cure could be achieved with shorter exposure times and lower dosages than those reported here. Further work will be conducted to optimise the processing parameters and dosage to rapidly cure thin layers of composite with high intensity UV light while achieving acceptable mechanical and thermal properties.

References

1. Endruweit A, Johnson MS, Long AC (2006) Polym Compos 27:119
2. Studer K, Decker C, Beck E, Schwalm R (2003) Prog Org Coat 48:92
3. Compston P, Schiemer J, Cvetanovska A (2008) Compos Struct 86:22
4. Bannister M (2001) Compos Part A 32:901
5. Li G, Ghebreyesus A (2006) Compos Struct 72:105
6. Britnell DJ, Tucker N, Smith GF, Wong SSF (2003) J Mater Process Technol 138:311
7. Compston P, Dexter D (2008) J Mater Sci 43:5017. doi: 10.1007/s10853-008-2701-3
8. Crivello JV, Narayan R, Sternstein SS (1997) J App Polym Sci 64:2073
9. Cvetanovska A, Compston P (2004) J Mater Sci 39:1791. doi: 10.1023/B:JMSC.0000016186.59458.a1
10. Compston P, Jar P-YB, Burchill PJ, Takahashi K (2001) Compos Sci Technol 61:321
11. Freidrich K, Walter R, Carlsson LA, Smiley AJ, Gillespie JW (1989) J Mater Sci 24:3387. doi:10.1007/BF01139070
12. Di Pietro A, Compston P, Gresham R, Hovland G (2008) In: Subic A et al (eds) Meeting the challenges to sustainable mobility. RMIT University Publishing (ISBN 9781921426155), Victoria, Australia