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Degree of cure and tensile properties of vinylester resin cured with ultraviolet light

A. CVETANOVSKA, P. COMPSTON
Department of Engineering, Faculty of Engineering and Information Technology, The Australian National University, Canberra ACT 0200, Australia
E-mail: Paul.Compston@anu.edu.au

Ultraviolet (UV) curing technology is well established in the coating and ink industries [1, 2]. The ink or resin is formulated with a photoinitiator, which initiates the rapid cross-link cure mechanism upon exposure to UV light. This technology has brought significant advantages to these industries, such as control and ease of formulation and operation, reduced costs, rapid production times and reduced emissions of volatile organic compounds (VOCs) [3, 4].

The main challenge facing the fiber-reinforced composites industry is the growing demand for cleaner and more cost effective manufacturing processes [5]. The increased speed of cure available through UV curing technology could address both these issues; costs are reduced through improvements in productivity, and the time over which VOCs such as styrene are emitted is shortened. Recent work by Li *et al.* [6] on repair of impact damage with composite patches showed that an epoxy-based UV curing system is a fast, strong, durable, and cost effective alternative to ambient temperature curing and heat activated curing prepreg systems. Shi and Ranby [7] drew similar conclusions for polyester-based composite cured using UV light. In general though, published work on characterization of UV curing composites is limited. Additional work is required to accelerate the adoption of UV curing technology for composite manufacture, especially in high volume industries such as marine structures and construction.

The first step in the adoption process is to determine if UV cured systems have comparable mechanical properties to those cured by conventional methods. This letter presents preliminary results of and investigation into the mechanical properties of a common vinylester matrix-resin for glass-fiber composites cured with UV light. The properties are compared with samples cured at room temperature and samples given a thermal post-cure. A qualitative assessment of the degree of cure in each system will be made using hardness testing. This is followed by a comparison of tensile properties.

Derakane 411-350 vinyl ester resin (Dow Chemical) was formulated for room temperature with 0.2 parts-per-hundred (pph) Cobalt Naphthenate (CoNap) promoter and 1 pph methyl ethyl ketone peroxide (MEKP) catalyst. For UV curing, the resin was formulated with a commercially available phosphine oxide based photoinitiator (Solcat S2, Soltek Pty. Ltd., Australia) at 0.5 pph as recommended by the manufacturer. After degassing, the resin was poured into 80 × 80 mm square aluminum moulds. Two plates of the room temperature curing resin were allowed to cure at room temperature for a minimum of 24 h before demolding. One of the plates was given a further post cure at 90 °C for 4 h. This is the highest temperature post cure as recommended by the manufacturer [8]. The UV curing resin was placed under a 400 W mercury vapor lamp (MVL) for 10 min. The spectrum of the MVL was measured with a Q401 UV light meter over an 80 × 80 mm area, 194 mm directly under the centre of the bulb. The readings show reasonably high intensities in the UVA range required for activation of the photoinitiator. The 80 × 80 mm area was chosen as readings showed negligible variation in UV intensity, giving a uniform cure profile.

The degree of cure was assessed with Rockwell hardness testing according to ASTM D785-89. The Rockwell hardness scale M, with minor and major load of 10 and 100 kg respectively, and indenter diameter 6.35 mm was used. Nominal sample thickness was 6 mm. A hardness value was determined by taking the average of at least 5 readings. The room temperature system was tested 2 days after casting. The depth of cure in the UV cured samples was assessed by taking hardness values from the top and bottom surfaces. Tensile strength and modulus were determined according to ASTM D 638M-91a and using the M-III specimen geometry of gauge length 7.5 mm, and nominal width and thickness 3.5 mm. Testing was conducted on an Instron 4505 universal testing machine (UTM) at a crosshead displacement rate of 1 mm/min. An extensometer attached to the specimen measured the elongation used to calculate the modulus. A minimum of 5 specimens of the room temperature and UV cured resins were tested. The room temperature system was tested three days after casting. Tensile properties for the post-cured resin were measured in previous work [9].

Hardness values for each resin system are presented in Fig. 2. (The coefficient of variation for each set of results was less than 6%). The room temperature system shows a comparatively low hardness reading, indicating a low degree of cure. The post-cured system gave the highest hardness values and consequently can be regarded as having the highest degree of cure. As post-curing accelerates the cross-linking/cure process, and the process is based on vigorous conditions of 90 °C for 4 h, this system is likely to represent maximum, or at least a very high, degree of cure. Therefore these

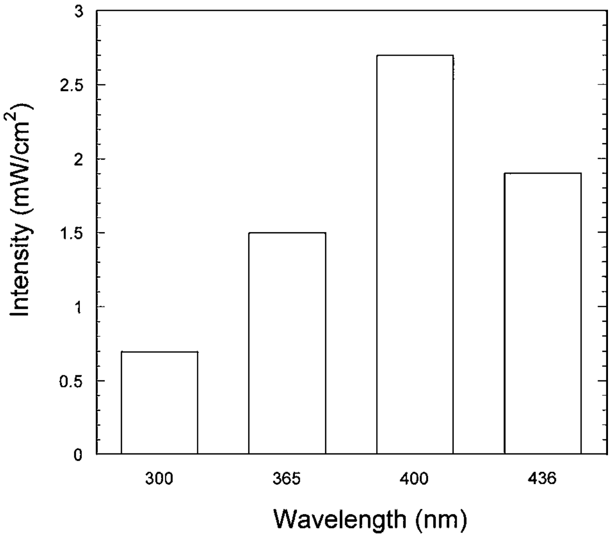


Figure 1 UV spectral output and intensity of the 400 W mercury vapor lamp.

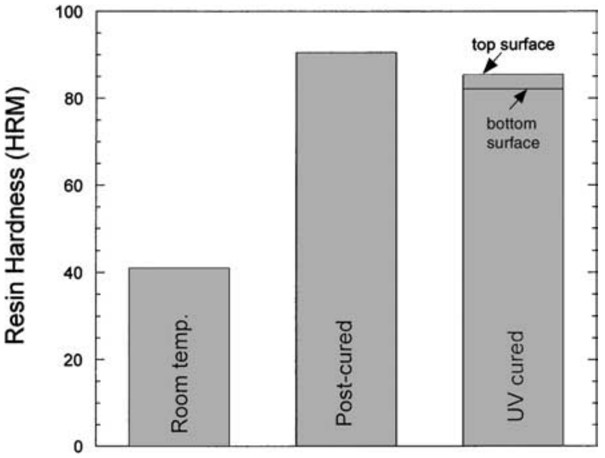
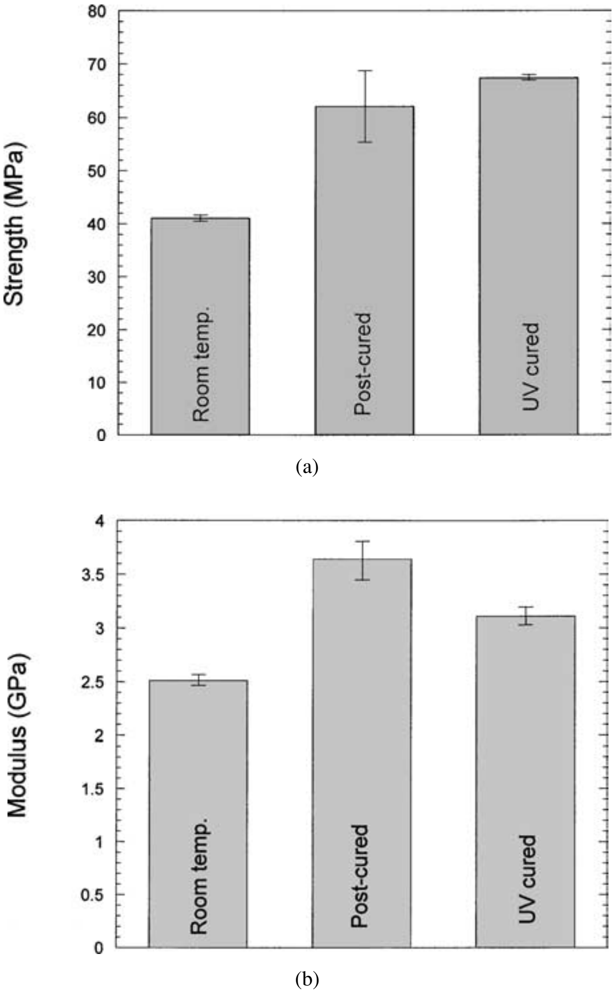


Figure 2 Hardness of room temperature cured, post-cured and UV cured resin. Error bars signify +/−1SD.



(a)

(b)

Figure 3 Tensile properties of room temperature cured, post-cured and UV cured resin: (a) strength and (b) modulus.

results can be used as a benchmark. The UV system gave hardness values that are significantly higher than the room temperature cured samples and only slightly lower than the post-cured samples. The hardness of the bottom surface on UV samples is 3.8% less than the top surface, most likely due to diminishing light intensity through the thickness of the sample. Nevertheless, the bottom surface hardness is still close to that of the post-cured sample and it can be concluded that the 6 mm thick samples have a very high degree of cure after only 10 min of light exposure. Tensile strength and modulus results are shown in Fig. 3a and b respectively. The room temperature system shows significantly lower tensile properties than both post-cured and UV resin. The tensile strength and modulus of the UV cured resin compares well with the post cured resin, though the order of the results is different. The strength of the UV system is higher than the post-cured system, but the modulus is lower. This could be due to a difference in the styrene content. Due to the speed of cure, the UV system is likely to have higher styrene content with more styrene cured in the crosslinks. The post-cured system, which was allowed to cure initially for 24 h at room temperature in an open mold, would have emitted more styrene. An increased styrene content may have a plasticizing effect in the UV system, leading to lower modulus and allowing a higher load and strength to be attained before brittle fracture, which was characteristic of all samples. The effect of increased styrene will, though, require further investigation.

Achieving a high degree of cure and excellent mechanical properties in only a few minutes has several important implications for the manufacture and handling of glass-fiber composites. A reduction in the time to when components can be demolded and handled will increase productivity. Attainment of high mechanical properties also means that components can be used immediately. This may not always be the case for room temperature cured components that have not been post-cured, as there is a time delay of several days until the maximum properties are realized. Further disadvantages of room temperature curing systems such as the need to manufacture a part before the gel time is reached, and the sensitivity of the gel time itself to variations in room temperature and humidity during manufacture, are also eliminated.

Overall, the mechanical properties of the UV system surpass those of initial room temperature cure and are comparable to the post-cured system. Importantly, these properties are realized within minutes of exposure to UV light, providing excellent opportunity for productivity gains. Further work will address mechanical properties of UV cured glass-fiber reinforced composites. Work on suitable manufacturing processes for potential applications is also required.

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