

Effects of Compaction and UV Exposure on Performance of Acrylate/Glass-Fiber Composites Cured Layer by Layer

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Received 27 December 2010; accepted 15 May 2011

DOI 10.1002/app.34909

Published online 28 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: With an aim to reducing manufacturing costs, in general and specifically to provide a solution to the thick laminate curing depth issue for composite materials, UV curing technology was combined with a fiber placement process to fabricate acrylate/glass-fiber composites. A novel layer-by-layer UV *in situ* curing method was employed in this article and interlaminar shear strength (ILSS) tests and SEM were used to evaluate the effect of processing parameters, including compaction force and UV exposure dose, on ILSS. The SEM images from short-beam strength test samples and the results of ILSS showed that the fibers' distribution was uniform in the cured matrix resin resulting from the compaction forces and that beneficially

influenced the ILSS of the composite greatly. However, the matrix resin produced large shrinkage stresses when it reached a high degree of conversion (DC) in one-step, which resulted in poor interlaminar adhesion. In addition, the fast curing speed of UV on the composite resulted in poor wetting between fiber and resin, and accordingly resulted in lower ILSS. To overcome these problems and obtain high ILSS value composites, an optimized compaction force and UV exposure dose were determined experimentally. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3799–3805, 2012

Key words: UV curing; composites; acrylate; fibers; mechanical properties

INTRODUCTION

Due to the excellent fatigue resistance, corrosion resistance, and low-density, polymer matrix composites have many broad applications in industrial products. However, the dominant manufacturing process today for polymer composites is still the autoclave facility. There appears to be two primary problems for this traditional autoclave manufacturing method that arise when researchers and engi-

neers try to enlarge the application field of composites. First is the high cost of an autoclave, in particular for large parts,¹ and including the non-lean manufacturing aspects of this antiquated method. The second is related to nonuniform and very lengthy curing of thick laminates.^{2,3} Researchers have long desired to explore and develop low cost out-of-autoclave composite fabrication methods, especially in recent years as larger composite applications are becoming reality (airplane wings and bodies, wind turbine blades more than 70 m, rail cars and truck bodies, etc.). Such methods as microwave cure,^{4–6} electron beam cure,^{7–9} X-ray cure^{10,11} etc., have been favorites, but study results suggest that it will take many years and with high accompanying risk, to apply these technologies successfully for industry.

UV curing is an efficient, energy-saving, and environment-friendly solidification technology.¹² The UV-curing technology to date has been mainly used in thin coating, photoresist in microelectronics engineering. In recent years, some research on UV curing composites has been conducted to develop low cost manufacturing process. Shi and Ranby¹³ cured 2 mm thick laminates of epoxy acrylate-modified unsaturated polyester composite using UV irradiation at room temperature in air. The research from Li

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Contract grant sponsor: NSFC, China; contract grant number: 50875202.

Contract grant sponsor: Important National Science and Technology Specific Projects in Machine Tool; contract grant number: 2009ZX04004.

Contract grant sponsor: Shaanxi Province "13115" Scientific and Technological Key Innovation Project; contract grant number: 2008ZDKG-19.

Contract grant sponsor: Program for Changjiang Scholars Innovative Research Team in University; contract grant number: IRT0646.

Contract grant sponsor: Research Fund of the State Key Lab of Manufacturing Systems Engineering of China.

Journal of Applied Polymer Science, Vol. 123, 3799–3805 (2012)
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et al.¹⁴ showed that fiber reinforced UV curing resin is a fast, strong, durable, and cost effective method to repair low velocity impact damaged composite laminates comparing with ambient environment curing epoxy and heat activated curing prepreg. Pang et al.¹⁵ joined filament wound composite pipe by wet lay-up technique using ultraviolet (UV) curing fiber reinforced plastics (FRPs) and ambient environment curing FRPs as controls, the results showed that the UV curing FRP wrapped composite pipe joints achieved nearly the same bending strength as the control samples. Compston et al.¹⁶ compared the mechanical performance of glass-fiber/vinylester composites cured by UV, room temperature and post-cured, respectively; the results showed that tensile and flexural properties were comparable for each composite, meanwhile the UV-cured composite emitted approximately four times less styrene during lamination and cure in an open mould than the conventional room temperature cured composite. All the conducted research showed that UV curing was a cost-effective curing technology for polymer matrix composites.

However, because of the absorption behavior of UV radiation passing through matter, the thickness of laminates for efficient application of UV curing is limited.¹⁷ Also the lengthy irradiation is needed to cure a thick composite (it normally takes 10–20 min to cure a composite laminate with a thickness of 2 mm). UV lamp would thus produce a mass of heat because of long time irradiation, resulting in thermal stresses in the composites during fabrication processes.

To overcome this cure penetration problem and reduce the exothermic effect during the manufacture of thick UV curing composite, a new automated manufacturing method has been presented in this article. UV curing technology was combined with a fiber placement process to explore a potential industrial manufacturing method for polymer matrix composite through layer-by-layer deposition. The effect of processing parameters, including compaction force and UV exposure dose, on interlaminar shear strength (ILSS) was investigated experimentally. Composites with high ILSS were found to be possible using the method proposed in this article. The results show it is feasible to fabricate composite laminates layer by layer with UV light.

EXPERIMENTAL

Materials

The mixture of epoxy acrylate CN104A75 (Sartomer, Shanghai, China) and cycloaliphatic epoxy resin UVR6105 (Dow, Shanghai, China) was used as the polymer matrix. The corresponding mixture ratio by weight was CN104A75/UVR6105 = 7 : 3. The formu-

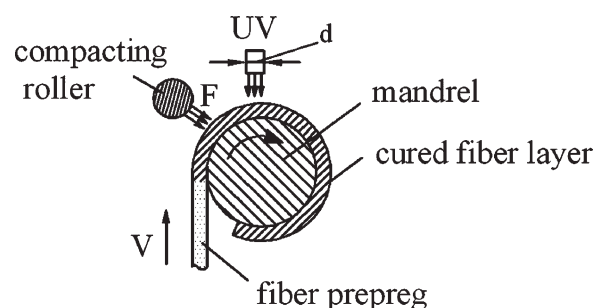


Figure 1 Illustration of UV curable composite fabrication.

lation was 2 parts per 100 (pph) ratio by weight of benzil dimethyl ketal radical initiator, 2 parts per 100 (pph) ratio by weight of hexafluorophosphate Sulfo-nium salt UVI-6990 (Dow) cationic initiator. The resulting matrix resin has a mass density of 1.21 g cm⁻³, tensile strength of 22.64 MPa, and flexural strength of 70.3 MPa. High strength glass fiber SC8-240, was purchased from Institute of Nanjing Glass Fiber (China), with monofilament diameter of 8.0 μm, tensile strength of 4.1 GPa, and elastic modulus of 80 GPa.

Fabrication process of composites

The wet prepreg with 35% resin content was prepared by pulling out a single fiber beam, which had passed through the resin at 30°C from a round hole with 0.5 mm diameter. Then the UV curable composite was fabricated by the setup illustrated in Figure 1. The diameter of the mandrel is 140 mm, the distance between the LED light and the surface of prepreg is 10 mm, the power on the surface of the prepreg is 200 mw; the average width and thickness of the prepreg are 3 and 0.3 mm, respectively; the speed of the rotation is from 0.6 to 3.4 r/mm to get different level exposing power. While being placed on the model surface by fiber placement machine, the wet fiber prepreg was exposed to LED array (365 nm, LED) at the same time. Then a cured composite layer was obtained after UV exposure. The procedure was repeated layer by layer until the needed composite structure was finished.

Characterization of composites

Morphology

The morphology of cross sections of the composites and fracture surfaces from the short-beam strength test samples was observed using a scanning electron microscope (SEM, S-3000N, HITACHI).

Transmission coefficient of composite layer

Transmission coefficient (T) of single layer composite was calculated using eq. (1):

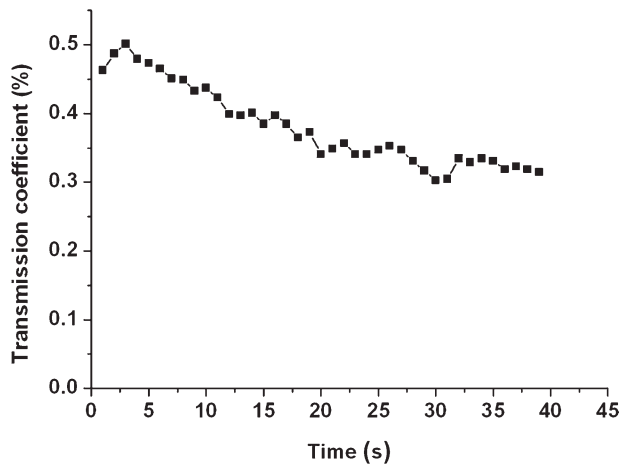


Figure 2 Transmission coefficient of single composite layer versus curing time.

$$T = P_t/P_0 \quad (1)$$

where P_0 is power of incident UV light and P_t is power of UV light at bottom of single composite layer. The UV light power was tested with power meter (Fieldmate, Coherent).

Exposure dose

The exposure dose of composites E (mW mm^{-2}) was calculated according to the eq. (2). Where P (mW) is power of UV light on surface of composite layer, S (mm^2), exposed area of composite in 1 second.

$$E = P/S \quad (2)$$

Degree of conversion (DC)

DC was tested according to China standard GB/T2576-2005.¹⁸ UV-curable acrylate/epoxy resin could be dissolved in acetone before exposing to UV light, but not after exposing to UV light. The Soxhlet extractor was used to determine DC of composite. The uncrosslinked ingredients in the cured composites were extracted by acetone at 80°C for 3 hours, and the samples were then dried at $105 \pm 2^\circ\text{C}$ for 2 hours and weighed. The DC C_r was obtained according to eq. (3).

$$C_r = \left[1 - \frac{m_1 - m_2}{m_1 \times W_r} \right] \times 100 \quad (3)$$

where m_1 is the sample mass before being extracted, m_2 , the sample mass after being extracted, and W_r , resin content of the composite.

Mechanical properties

The mechanical properties of the composites were analyzed in terms of the ILSS. Center-loaded short (curved) beam shear tests were conducted according

TABLE I
Change of DP of a Certain Cured Layer With Layer Numbers Upon

Layer numbers upper the tested layer (n)	0	1	2	3	4	5
DP of tested layer (%)	67.7	87.6	95.4	98.2	98.3	98.3

to ASTM D2344.¹⁹ Samples were tested on a 3-point bend fixture at 1.0 mm/min in the INSTRON 1195. The average of five test samples was taken. The interlaminar short beam shear strength (τ_{sbs}), MPa, was calculated using eq. (4).

$$\tau_{\text{sbs}} = 3P/4wt \quad (4)$$

Where P is the maximum load, w , specimen width, and t , the thickness of the specimen.

RESULTS AND DISCUSSION

Transmission character of composite layer

Because the composite laminate was cured layer by layer, the character of UV transmission through each composite layer would affect the cure and adhesion between adjacent layers. Figure 2 is the correlation between transmission coefficient of single composite layer and curing time. The transmission coefficient of each composite layer was variable during the curing process. The photoinitiator in the matrix resin was almost spent at the first 3 seconds. The resin at the directly irradiated surface of the composite layer cured first and thus became more UV-transparent, allowing deeper penetration of the UV light into the composite layer. This result is in accordance with the result of Ref.²⁰. The increase of the transmission with time could be observed in the first 3 seconds of the UV irradiation in Figure 2. However, after that, the continuous decrease of transmission reflected the change of DC of each composite layer. After 30 seconds, the change of transmission coefficient decreased, which indicated the polymerization of the matrix resin had almost finished. Because of the UV transmission of composite layer, part of the UV light could penetrate the curing composite layer to

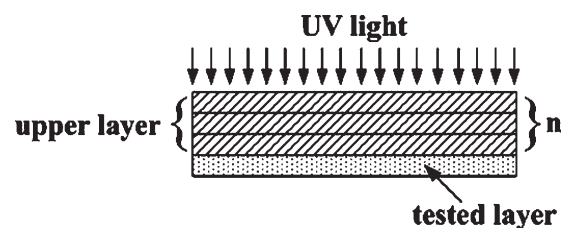


Figure 3 Relative position of tested layer and upper layer.

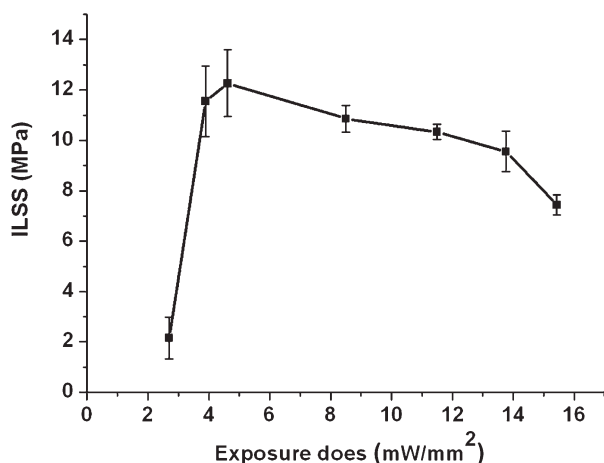


Figure 4 Correlation between ILSS and exposure dose.

reach the earlier cured layer, which would cause further curing of the previously cured composite layer and improved adhesion of the interlayer while the upper layers were being exposed to the UV. This could be verified by the increase of DC with increasing number of composite layers in Table I (Figure 3 is the relative position of tested layer and upper layers). The DC of composite layer increased step by step after every new layer was placed upon it. The DC reached 98% after three layers was added, and then kept a certain value. This suggested that the exposure dose should be controlled during curing process for every layer to pretend composite from over-curing which would result in decrease of mechanics.²¹

The effect of exposure dose on ILSS

Like the effect of temperature on performance of composites in a thermal cure, UV exposure dose has a significant effect on the performance of UV curable composites. Figures 4 and 5 show the correlation between ILSS and UV exposure dose, ILSS and DC,

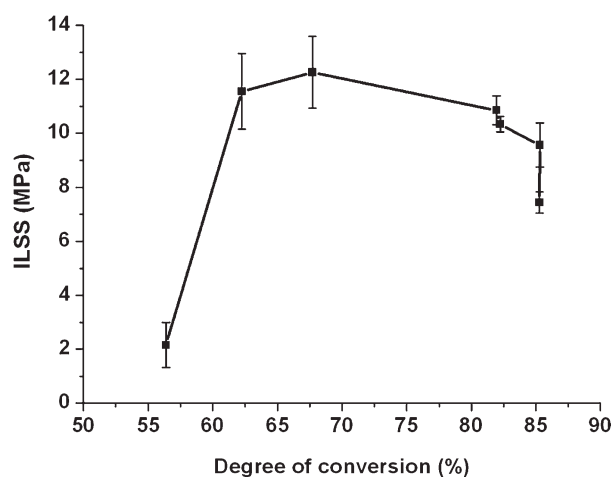


Figure 5 Correlation between ILSS and DC.

respectively. The ILSS increased first and then decreased with exposure dose, and reached the maximum value at 4.62 mW mm^{-2} . There are three reasons leading to the maximum ILSS value for different exposure doses. The first reason is the effect of the shrinkage stress of matrix resin. The cured matrix resin would show certain strengths during exposure to UV light, nevertheless the shrinkage stress resulting from polymerization of resin would

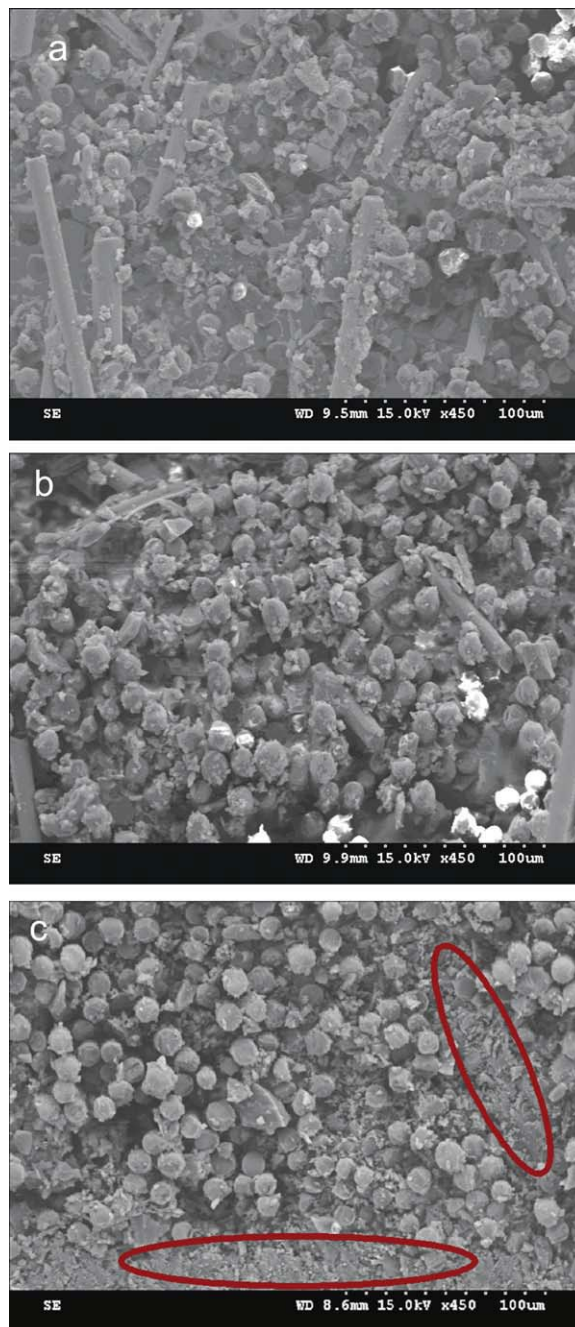


Figure 6 SEM images of section from composite laminate fabricated at different exposure dose (a) 2.69 mW mm^{-2} , (b) 4.62 mW mm^{-2} , and (c) 15.43 mW mm^{-2} . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

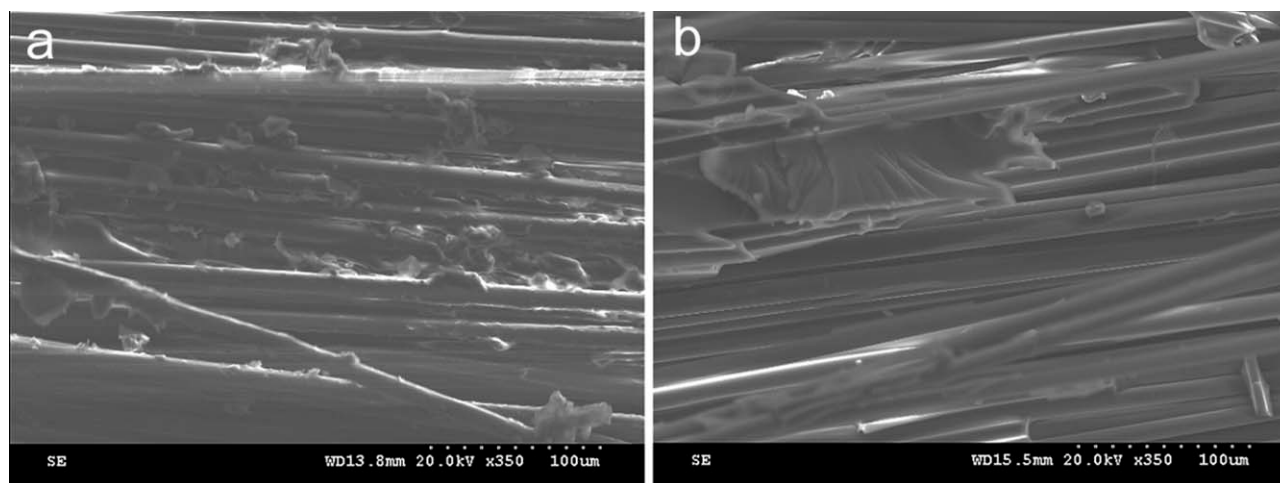


Figure 7 Fracture surface micrographs from interlaminar short beam shear samples fabricated at different exposure doses (a) 4.62 mW mm^{-2} and (b) 15.43 mW mm^{-2} .

reduce the strength of the composite. There would be a balance between the two functions. At low DC, the increase of strength was larger than that of the shrinkage stress, so the ILSS increased with DC; At high DC, the rapid increase of shrinkage stress would cancel out part of the strength from the cured resin, the increase of ILSS would slow down, as shown in Figure 4. However, it is noteworthy that the ILSS reached a maximum DC value of 67.7% whereas higher DC caused the quick reduction of ILSS. The reason is that poor wetting between resin and fibers caused by the fast polymerization speed at high exposure²² counteracted part of the ILSS in addition to the negative effects of the shrinkage stress. The combined effects resulted in the rapid decrease of ILSS. From the UV transmission character of the composite layers (Fig. 2), the DC increased stepwise for a certain composite layer, while the upper composite layers were placed and exposed to UV. The DC would reach a high degree after three additional layers were added (Fig. 2). The stepwise increase of DC of the matrix resin could also reduce the shrinkage stress and strain^{23,24} compared with that rapid increase to an equal DC in one step. This is the exact reason that there is a maximum ILSS value at DC of 67.7%, not 100%.

The second reason is the effect of infiltration of matrix resin between adjacent layers. With the increase of DC, the infiltration of matrix resin driven by compaction between curing and cured layers grew worse above a certain DC. It became very difficult for matrix resin in the bottom of the placing layer to infiltrate into cured composite surfaces because of higher DC. There appeared areas of resin concentration in the composite, as shown in Figure 6(c), and the distribution of fibers in the resin is not uniform. The poor infiltration of matrix resin caused by high DC resulted in the incomplete wet-

ting on the fiber surface, that is, incomplete surface coverage, accordingly the low interfacial function between matrix resin and fiber. It can be observed that the small matrix chipping on the surface of fibers got fewer with the increase of DC; in fact, the fiber surface was very clean compared to the small exposure dose (Figure 7). This indicated that the primary interlaminar fracture form changed from break involving interface and matrix to one of pure interface with increasing of exposure dose.

The third reason is the effect of the mutual restriction between adjacent composite layers. Because the composite was cured layer by layer, the cured composite layer would restrict contraction of the curing layer while liquid matrix resin in the upper layer transformed to solid polymer. Matrix resin would produce large shrinkage stress at high DC because more unsaturated double bonds created covalent bonds. So the higher the DC, the stronger the

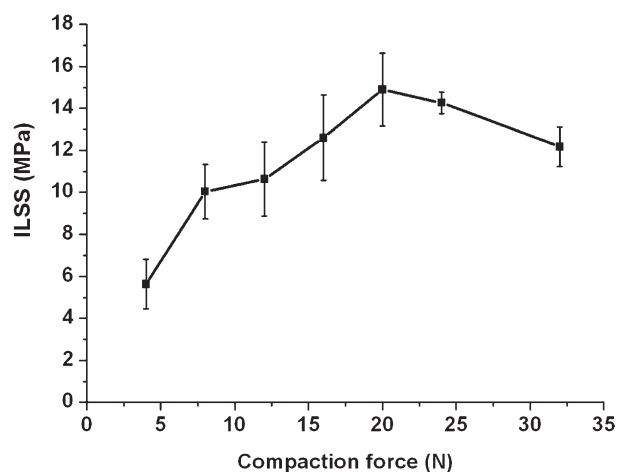


Figure 8 Correlation between ILSS and compaction force.

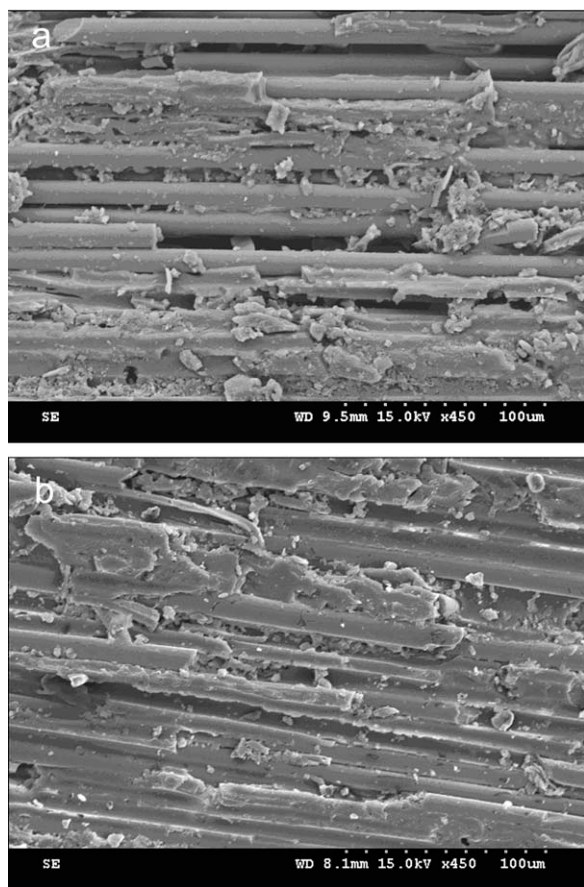


Figure 9 SEM images of distribution of fibers and resin at different compaction force (a) 4 N and (b) 20 N.

restriction force of the cured layer acting on the curing layer—the shrinkage stress could not be released effectively. There would be more shrinkage stress left in the composite laminate, which would result in poor ILSS, even distortion and delamination of the composite laminate.

The effect of compaction force on ILSS of composite

The compaction force played a more important role for the quality of stepwise UV curing composites

compared to that of thermally cured composites. Figure 8 is the correlation between ILSS and compaction force. The ILSS increased by 164.4% when the compaction force increased from 4 to 20 N. The reason is that the compaction force increased the infiltration of liquid matrices resin between adjacent layers, and forced more resin under the bottom of the curing composite layer to infiltrate into the surface of cured composite layer. This could increase interlaminar adhesion and improve the distribution uniformity of matrix resin around glass-fibers, which could be seen in Figure 9(a,b), the distribution uniformity of matrix resin at 20 N compaction force is much better than that at 4 N compaction force. The uniform composite laminate structure would exhibit mechanical coherence, and the glass-fibers would carry the external load more effectively. As a result, the composite laminate exhibited large load bearing capacity and good ILSS. However, the smaller compaction force was not big enough to compact the glass-fiber prepreg and to redistribute liquid matrix resin interlaminarly to form a uniform microstructure. There existed some voids and weak areas in the composite, as shown in Figure 10(a). It also can be observed that larger compaction forces squeezed part of the matrix resin out of glass fibers. This resulted in loss of matrix resin among the glass-fibers and even the absence of matrix resin around the surface of fibers, as shown in Figure 10(c). The density test result in Figure 11 is very consistent with Figure 10. According to Figure 11, the density of composite laminate under low compaction force is small because of existing of some hole in the laminate. The hole became small and small with the increase of compaction force, and even disappeared, so the density of the composite increased. Under large compaction force, the resin was squeezed into the space among the glass fibers to form uniform distribution of fiber and resin, which made the density of the composite laminate decrease because of the smaller density of the resin comparing to the glass fiber. However, for too large compaction force

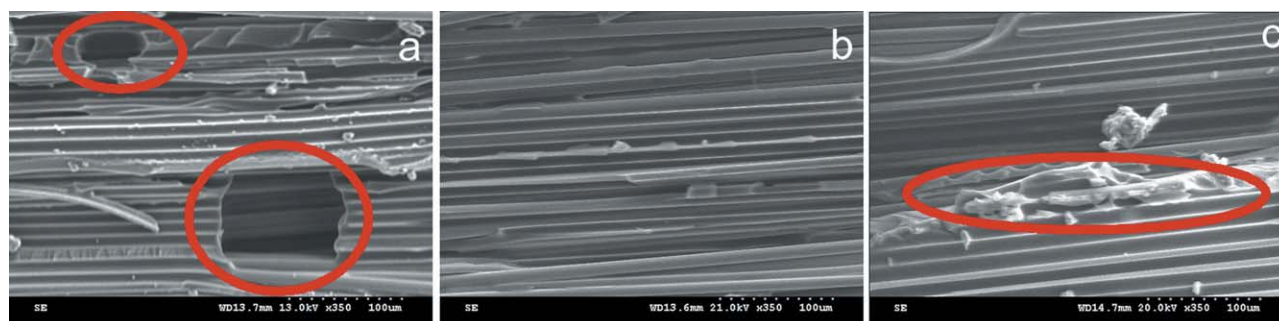


Figure 10 SEM images of Fracture surface from interlaminar short beam shear samples fabricated at different compaction force (a) 4 N, (b) 20 N, and (c) 32 N. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

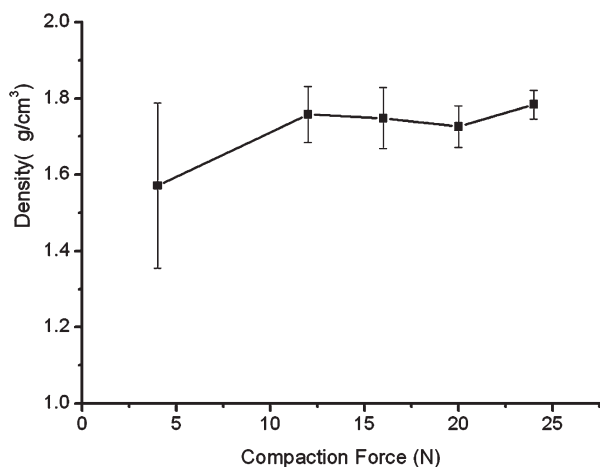


Figure 11 Correlation between density and compaction force.

above 20 N, part of the resin was squeezed out, which resulted in the increase of the fiber content in certain area, and accordingly the increase of the density. From the discussion above, both the smaller and the larger compaction force all resulted in non-uniformity of the composite microstructure. Hence, mechanical performance of the composite would not be coherent, and there would appear some weak areas, which would lead to the low ILSS of composite. The results indicated that the compaction force should be held at a certain level to get good performance of the composite.

CONCLUSIONS

UV curing technology was successfully combined with an advanced fiber placement process to develop a cost-effective polymer composite industrial manufacturing method. The wet glass-fiber prepreg was cured layer by layer with 365 nm LED light while being auto-placed, rather than the old paradigm of curing a thick bulk composites laminate after total layup was completed in a pressurized oven (autoclave). The DC of composite layer increased stepwise when additional layers were placed because of the UV transmission through each composite layer. Based on three kinds of mutual effects, the shrinkage stress and strength from cured matrix resin, the infiltration ability of matrix resin and DC, and restriction force from cured layer and shrinkage stress from curing layer, ILSS of composite reached a maximum value at UV exposure of 4.62 mW

mm^{-2} (at DC of 67.7%) for exposure dose from 2.69 to 15.43 mW mm^{-2} . The compaction force could increase the infiltration of liquid matrix resin and improve distribution uniformity of matrix resin around glass-fibers, which made glass-fibers and cured matrix resin harmonize to undergo loads. As a result, the composite laminate exhibited large load bearing capacity and good ILSS. The research results showed that the polymer matrix composite cured by UV layer by layer using the fiber placement manufacture process is feasible and holds great promise in moving forward on out-of-autoclave cure processing.

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