Ultrasonic Modification of Aramid Fiber–Epoxy Interface

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Received 1 March 2000; accepted 2 December 2000

ABSTRACT: An ultrasonic irradiation technique is used during the process of fabricating aramid fiber–epoxy resin reinforced composites to improve the interfacial adhesion performance. Under the ultrasonic treatment, the change of the resin viscosity is studied. The results of a microbond test show obvious improvement in the interfacial shear strength after ultrasonic treatment. The mechanical properties of the composites, such as the interlaminar shear strength and tensile strength, are measured. Combined with the SEM results, these show it is the mechanical properties that are improved and the fracture modes are varied from the interface between the fibers and resin to the fibrillation of fibers and resin. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2764–2768, 2001

Key words: ultrasonic treatment; aramid fiber–epoxy composites; interfacial adhesion; microbond method; mechanical property

INTRODUCTION

It is well known that the mechanical properties of aramid fiber reinforced composites are highly dependent on the interfacial performance between the fiber and the matrix.[1,2] To take full advantage of the mechanical properties of the composites, it is necessary that the interface carry the stress between the fiber and matrix. However, adhesion between the aramid fiber and most matrices is weak due to high crystallization, which leads to a chemically inactive surface, as well as the relatively smooth surface of the fiber, which also leads to minimal resin–matrix entanglement.

Wet chemical[3–6] and gas-plasma[7–9] techniques were previously widely investigated. Both methods primarily improve the interfacial performance by increasing the content of polar groups and the roughness on the surface of the fiber. The effect of the treatment is dependent on the control of the treating parameters such as the treating time and so forth. Other modification methods that were explored include γ-ray irradiation[10] and ultrasound treatments.[11]

The object of this study was to establish an ultrasonic treatment system and determine the optimum ultrasonic parameters to improve the interfacial performance and the mechanical properties of aramid fiber–epoxy composites on-line.

EXPERIMENTAL

Materials

Armos-II fibers, a type of Russian high-performance aramid fiber, were used as the reinforcement composition. The matrix materials were made from Epoxy618 (which corresponds to EPO1441-30 of Shell Chemical Corporation), acid anhydride as the curing agent, and *N*,*N*-dimethyl benzyl amine as the accelerating agent in a ratio of 100:70:1 by weight.

Resin Viscosity Test

The falling ball test was used to measure the viscosity of the resin system. The viscosity of the resin system can be worked out according to the equation developed from the Stokes law:

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Journal of Applied Polymer Science, Vol. 81, 2764–2768 (2001)

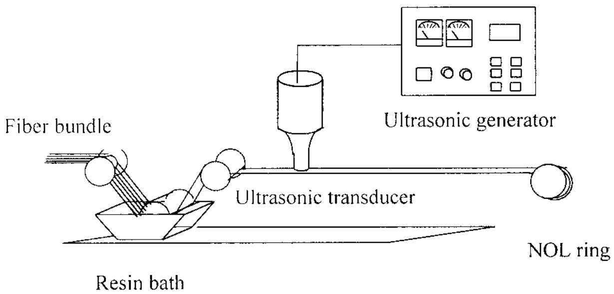


Figure 1 A schematic of the fabricating technology of the NOL ring by the ultrasonic treatment.

$$\eta = \frac{(\rho - \rho_0)gtd^2}{18L\left(1 + 2.4\,\dfrac{d}{D}\right)} \quad (1)$$

where ρ and ρ_0 are the densities of the ball and the resin system; d and D are the diameters of the ball and the cylinder, respectively; t is the time for the ball to pass the two lines drawn on the cylinder; and L is the distance between two lines. Each reported value of the viscosity is the average of more than 20 successful measurements.

When the ultrasound was used, the transducer was inserted into the resin system. After being treated at different ultrasonic amplitudes, the resin system was put into the cylinder to measure the viscosity.

Interfacial Bonding Test

The epoxy resin system droplets were applied to the Armos monofilament (14-μm diameter) using a fine-point applicator. The specimen for ultrasonic treatment was fabricated in such a way that the resin droplet was applied to the monofilament and then treated by the ultrasound at different amplitudes; the resin congregated into an ellipse after being laid down. The diameter of the resin droplet chosen for the experiment was in the range of 20–30 μm. The interfacial bonding test was carried out on the equipment for evaluation of the interface properties of the fiber–resin composite, which was made by Tohei Sangyo of Japan at a crosshead speed of 4 μm/s.

The interfacial shear stress was calculated using the equation

$$\tau = \frac{P}{\pi d l} \quad (2)$$

where P is the maximum load, d is the diameter of the monofilament, and l is the length of the filament embedded in the resin. The report value of τ was calculated from the normal distribution for more than 100 successful measurements.

Mechanical Properties Test

At the different ultrasonic amplitudes, 150-mm diameter NOL rings were fabricated in the manner shown in Figure 1. The interlaminar shear strength (ILSS) of the NOL ring was determined using the short-beam method on a universal test machine. The specimen was tested at a crosshead speed of 0.5 mm/min. The tensile strength of the NOL ring was tested on an Instron testing machine at a rate of 5 mm/min. The fracture topography of the specimen after the mechanical property tests was observed by SEM.

RESULTS AND DISCUSSION

Effect of Ultrasound on Viscosity of Resin System

The values of the viscosity from the ultrasonic treatment at different amplitudes are shown in Figure 2. The figure shows that the viscosity of the resin system decreased with the increase of the ultrasonic amplitude. The tendency toward a decrease of viscosity slowed when the amplitude was beyond 40 μm. At the amplitude of 40 μm the viscosity of the resin system was 1.73 Pa s, 37% lower than that of the untreated specimen.

Under the ultrasonic irradiation, the microbubbles inside the resin system undergo cavitation. These bubbles are compressed and enlarged alternately with the alternation of the ultrasonic pressure and concentrate the acoustic energy in a small volume and give rise to enormous energy when they collapse. At the same time another action of the ultrasound, sound streaming action,

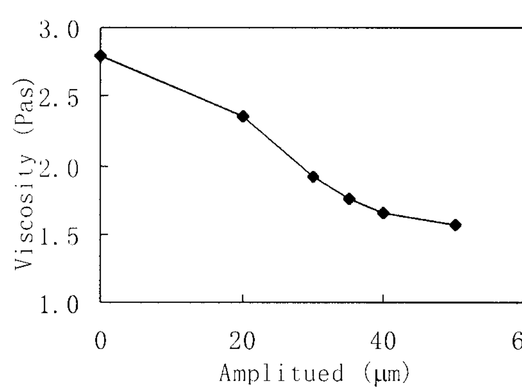


Figure 2 A plot of the viscosity of the resin system versus the ultrasonic amplitude.

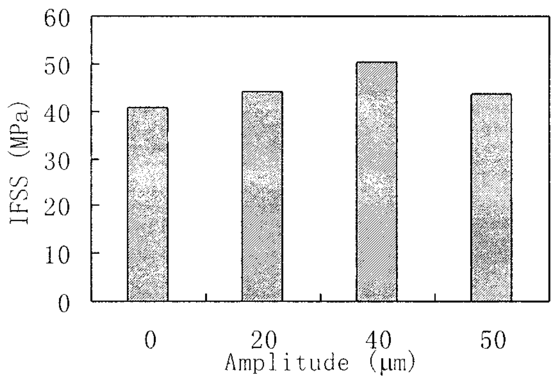


Figure 3 The interfacial shear strength for the different ultrasonic amplitudes.

is also produced. When ultrasound is applied to the liquid, the limited attenuation of acoustic pressure produces a certain grade of pressure in the liquid, which leads to the flow of the liquid. When the amplitude of the acoustic pressure is above a certain value, a circumfluence is formed in the whole liquid, which is a type of nonperiodical liquid streaming called acoustic streaming. The maximum speed of the sound streaming in the liquid can be written as

$$U_{\max} = \sqrt{2}\pi f A$$

where f is the frequency of the ultrasound and A is the amplitude of the ultrasound.

The speed of sound streaming reaches 4.44 m/s when the frequency and the amplitude of the ultrasound are 20 kHz and 50 μm, respectively. So the enormous energy from the cavitation and high-speed agitation of the sound streaming accelerate the movement of the resin molecule, which results in the decrease of the viscosity of the resin system.

It is well known that a decrease of viscosity improves the wetting. Good wetting of the fiber by a liquid resin can increase the interaction at the interface, which in turn enhances the load transfer to the fiber. Thus, it could be forecasted that the interfacial property of the Armos reinforced epoxy matrix composites would increase after ultrasonic treatment because of the improvement of wettability caused by the decrease of the viscosity of the resin.

Interfacial Shear Strength Analysis by Ultrasonic Treatment

The normal distributions of more than 100 measurements were used to calculate the interfacial shear strength from the microbond test (Fig. 3).

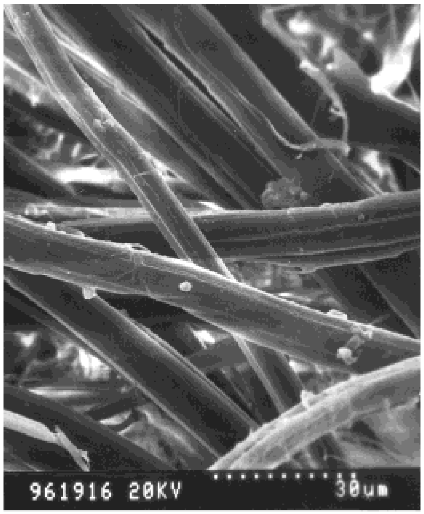
After ultrasonic treatment, the interfacial shear strength values for all the amplitudes in the range of experiments increased. This result indicated that ultrasonic treatment improved the interfacial property of Armos reinforced composites by decreasing the viscosity of the resin system and making the resin impregnate the fibrillium of the Armos fiber. However, when the amplitude was more than 40 μm, the interfacial shear strength value of the specimen was lower than that for 40 μm. This was because the application of ultrasound to the Armos and resin system resulted in two contrary actions in the system. On one hand, the sound streaming action can accelerate the movement of the resin molecule to decrease the viscosity and improve the wettability of the resin. On the other hand, it can agitate the resin system to produce more bubbles on the interface between the Armos and the resin droplet and increase the contact angle of the Armos and resin. Thus, under the relatively low amplitude the main action of the ultrasound was to decrease the viscosity of the resin system because of the agitation action of the sound streaming was weak. At the higher amplitude the viscosity of the resin system was further lowered and the agitation action was increased so that more bubbles were produced easier, and the interfacial performance declined. Therefore, the optimum amplitude to improve the interface of the Armos reinforced composites was 40 μm.

Effect of Ultrasound on ILSS

The values of the ILSS of the Armos/epoxy composites before and after ultrasonic treatment are shown in Table I. The ILSS values of the NOL ring increased with the increase of the ultrasonic amplitude and reached a maximum of 64.5 MPa

Table I Change of ILSS at Different Ultrasonic Amplitudes

Amplitude (μm)	ILSS (MPa)	Standard Deviation	Extent of Improvement (%)
0	57.1	2.55	—
30	60.0	1.98	5.1
45	64.5	1.61	12.9
50	63.6	1.02	11.4
55	62.6	1.30	9.6
60	59.1	1.35	3.5
70	57.7	1.71	—
80	56.3	2.34	−1.4



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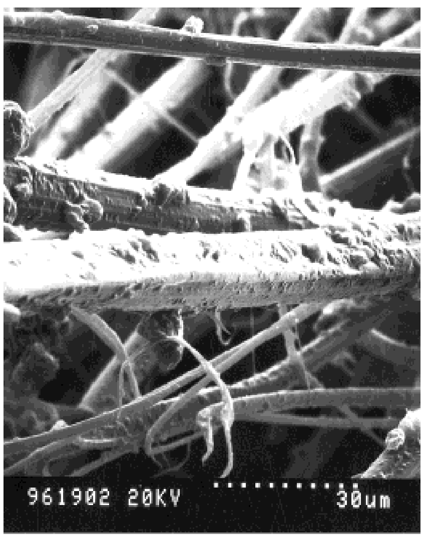

b

Figure 4 SEM fracture topography before and after ultrasonic treatment through the short-beam test. (a) SEM topography of untreated Armos reinforced composites; (b) SEM topography of Armos reinforced composites after ultrasonic treatment.

(12.9% more than that for the untreated) when the amplitude was 40 μm. Subsequently, the ILSS values decreased. When the amplitude was beyond 70 μm the ILSS was lower than that for the untreated. In addition, the change of the standard deviation of the ILSS had the same tendency. Compared with Figure 4, we also find the change of ILSS was consistent with that of IFSS. Thus, the improvement of the interfacial performance under ultrasonic treatment was a main reason to increase the ILSS of Armos/epoxy composites. Moreover, under the ultrasonic action the system of the epoxy resin, curing agent, and accelerating agent was mixed more uniformly so that the properties of the matrix and the ability to transfer the load uniformly were enhanced. Therefore, the uniformity of the resin system also contributed to the improvement of the ILSS.

Figure 4 also shows that after ultrasonic treatment the fracture mode of the composites had changed. For the untreated specimen the SEM showed that the interface between the Armos and the matrix was destroyed, accompanied by the fabrillation destruction of a few Armos fibers, while the fracture mode destroyed most of the Armos and the matrix resin for the specimen by ultrasonic treatment, which further demonstrated that the interface of composites was improved by ultrasound.

Effect of Ultrasonic Treatment on Tensile Strength of Composites

The changes in the tensile strength of the NOL ring by ultrasonic treatment are listed in Table II. The results showed that when the amplitude was under 70 μm, all values of the tensile strength of the composites were higher than those for the untreated samples. The tensile strength data had the same tendency to change as the value of the ILSS, reaching a maximum at the amplitude of 40 μm. The results indicated that the tensile strength of the Armos did not decrease after ultrasonic treatment. The improvement of the tensile strength of the NOL ring was the result of increasing the interfacial performance of the composites by the ultrasonic treatment. Figure 5 shows the fracture for the untreated is the delamination of the NOL ring, and the fracture after ultrasonic treatment shows that all the Armos carried the load synchronously and ruptured to-

Table II Tensile Strength at Different Ultrasonic Amplitudes

Amplitude (μm)	Tensile Strength (GPa)	Standard Deviation	Extent of Improvement (%)
0	1.60	0.076	—
30	1.65	0.066	5.1
45	1.72	0.034	12.9
50	1.71	0.039	11.4
55	1.68	0.047	9.6
60	1.65	0.052	3.5
70	1.62	0.063	—
80	1.53	0.070	−1.4

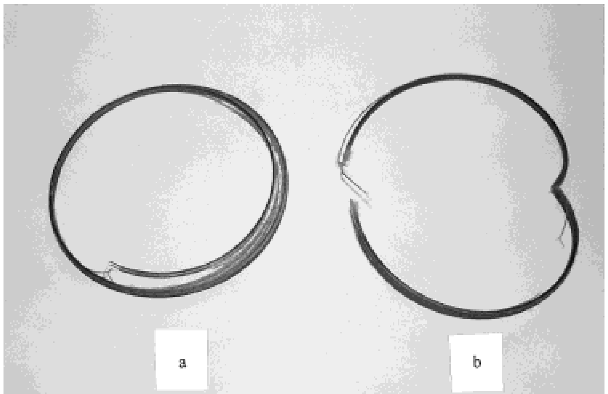

Figure 5 The fracture topography before and after ultrasonic treatment through the tension test. (a) Topography of untreated Armos reinforced composites; (b) topography of Armos reinforced composites after ultrasonic treatment.

gether. The results further proved ultrasound treatment improved the interfaces of the composites.

CONCLUSION

Ultrasonic treatment results in a change of the mechanical properties of Armos reinforced composites. The ILSS and the tensile strength of the composites are markedly improved by ultrasound. The decrease of the viscosity of the resin system after ultrasonic action and the improvement of the interfacial shear strength of the composites demonstrate that the improvement of the wettability by ultrasound is the important factor in increasing the interfacial performance of composites and the subsequent mechanical properties of Armos reinforced epoxy composites. The SEM analysis also demonstrates that the interfacial performance is improved by ultrasound. Thus, we can conclude that ultrasound is a highly effective method to improve the mechanical properties without harmful action.

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