

Effect of Ultrasound on Wettability Between Aramid Fibers and Epoxy Resin

L. Liu, Y. D. Huang, Z. Q. Zhang, X. B. Yang

Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, People's Republic of China

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ABSTRACT: Good wetting of reinforced fiber by resin was a main factor in the improvement of the interface adhesion of their composites. Ultrasound with a frequency of 20 kHz was used to improve the wettability between aramid fibers and epoxy resin during the winding process of the composites. The effects of ultrasound on the viscosity and surface tension of epoxy resin and on the surface characteristics of aramid fibers were investigated. The wettability of aramid fibers and treated epoxy resin under different conditions and of aramid fibers and epoxy resin under ultrasonic online treatment were compared. The results indicated that the main action of ultrasound was to force

epoxy resin to impregnate aramid fibers, in addition to the influence of ultrasound on the properties of epoxy resin and aramid fibers. The results of microbond testing showed that the interfacial shear strength (IFSS) of aramid/epoxy composites could be 26% higher than that of untreated composites because of the improved wettability between aramid fibers and epoxy resin subjected to ultrasonic online treatment. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3172–3177, 2006

Key words: fibers; surface; modification; viscosity

INTRODUCTION

Aramid fibers are high-performance organic fibers with excellent specific strength and modulus that are widely used as a reinforcement of composites. But aramid fibers are highly crystalline with a molecular chain oriented along the fiber axis, and the surface of the fibers are smooth and not chemically reactive. Above all, low interfacial strength of its composite can be deduced. So a lot of research has focused on surface modification of aramid fibers to change their surficial characteristics, increase the number of polar functional groups, and improve the interfacial property through chemical^{1–4} and plasma^{5–8} treatments. Both methods are effective to some extent at improving the surficial properties of aramid fibers or the interfacial strength of its composites. However, it has been difficult to treat aramid fibers while its composites are being produced. In our previous research, we used ultrasound online to treat the interface of aramid fibers or carbon-fiber-reinforced composites based on ultrasonic high-frequency vibration.^{9–10} In the present study, we mainly concentrated on ultrasound forcing epoxy resin to impregnate aramid fibers and on cre-

ating an online treatment for the interface of the composites. The wettability between aramid fibers and treated epoxy resin was compared with that between aramid fibers and epoxy resin under ultrasonic online treatment. The effects of ultrasound on the surface characteristics of the aramid fibers and the viscosity and surface tension of the epoxy resin also were investigated. Meanwhile, the interfacial property of aramid fiber/epoxy composites under ultrasonic online treatment also was evaluated.

EXPERIMENTAL

Materials

Uncoated Armos, a kind of aramid fiber fabricated in Russia, was used as the reinforcement. The resin system was a mixture of the epoxy Epo618, 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.

Ultrasonic online treatment of aramid fiber/epoxy resin system

A transducer of ultrasound was applied to the aramid fibers impregnated with a layer of resin when it had just been pulled out of the resin bath, (shown as Fig. 1). The frequency was adjusted lightly around 20 kHz for resonance, and the amplitude was changed in order to investigate the effect of ultrasound. One specimen was directly wound into an NOL ring with a

Correspondence to: L. Li (liuli@hit.edu.cn).

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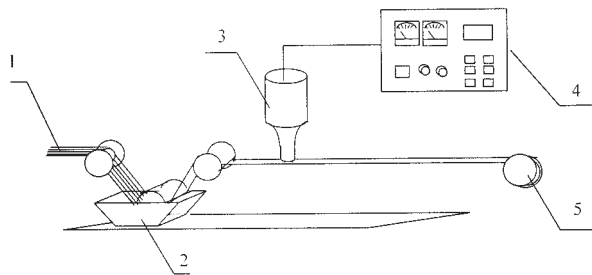


Figure 1 Schematic graph of winding process of NOL ring under ultrasonic treatment: (1) fiber bundles, (2) resin bath, (3) ultrasonic vibrator, (4) ultrasonic generator, and (5) NOL ring.

diameter of 150 mm and then cured into composites for IFSS analysis; another was cut into a specific length for analysis of surface characteristics of the treated aramid fibers.

Ultrasonic-treated epoxy resin

An ultrasonic transducer was directly inserted into the epoxy resin system to treat it at different amplitudes for 5 min. And then the viscosity and the surface tension of the ultrasonic-treated epoxy resin were tested. After the resin system had been treated for a certain time, the viscosity and surface tension were tested again.

Viscosity testing

The ball-falling testing was used to measure the viscosity of the resin system, which could be calculated according to the following equation:

$$\eta = \frac{2gr^2(D - d)t}{9h}$$

where η is the viscosity of resin system, D and d are the densities of the ball and the resin systems, respectively, r is the diameter of the ball, and t is the time it takes the ball to go h , the distance.

Each viscosity value reported was the average of more than 20 successful measurements.

Testing surface tension of the resin system

The Wilhelmy plate technique was used to measure the surface tension of the resin system. The specimens of the untreated resin and the resin treated by ultrasound were put into a SB312-type wetting-testing instrument (China) to test the surface tension.

Wettability analysis of aramid fibers and epoxy resin

Specific-sized bundles of fiber were aligned into a polyethylene pipe that was 3 mm in diameter and 40 mm in length. The bundles were left 2.0 mm outside the end of the pipe and were impregnated into epoxy resin. The amount adsorbed as a result of capillary action and the adsorption time were recorded. The wettability of the treated epoxy resin to the aramid fibers was analyzed using this method.

The simulated wetting test between aramid fibers and epoxy resin under ultrasonic online treatment was performed as shown in Figure 2.

XPS analysis of aramid fiber surface

Both the untreated aramid fibers and those subjected to ultrasonic treatment were successfully extracted from the acetone solvent after 48 h and dried. Some specimens were cut into a certain length for testing.

ESCA-750-type multifunction X-ray photoelectron spectroscopy was used to analyze changes in the proportions of elements such as C, N, and O and their chemical valence on the surface of aramid fibers under ultrasonic action. For the X-ray source, Mg K α was used.

Surface morphology of aramid fibers

The properties of aramid fibers were determined by nitrogen adsorption at -196°C with an accelerated surface area and porosimetry system (ASAP-2405, Micro-mentics). The Brunauer–Emmett–Teller (BET) surface area was calculated from the adsorption isotherms using the BET equation.¹¹ The Dubinin–Radushkevich equation was used to calculated the micropore volume and

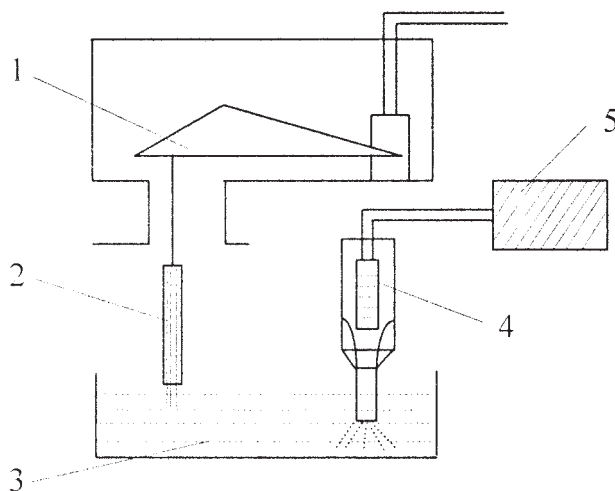


Figure 2 Schematic drawing of simulated wetting experiment of aramid fibers by epoxy resin under ultrasonic online treatment: (1) electrical balance, (2) fiber bundle, (3) vessel, (4) ultrasonic transducer, and (5) ultrasonic generator.

the micropore surface area.¹² The pore size distribution was determined using the BJH model.¹³

Testing for interfacial shear strength

At the different ultrasonic amplitudes, NOL rings with a diameter of 150 mm were fabricated using a filament-winding technique. The testing specimen was chopped 3 mm from the NOL ring and was polished. A microdebonding instrument was used to select and tip a single fiber until the interface of the composite specimen was broken. The breaking force was recorded. More than 50 specimens were tested to ensure precise testing.

RESULTS AND DISCUSSION

Ultrasonic cavitation

Ultrasonic cavitation as a nonlinear acoustic phenomenon was the production of cavities inside a liquid irradiated by ultrasound as a result of the presence of microbubbles in the liquid filled with the liquid vapor. These microbubbles left the liquid field and were in some way able to concentrate the acoustic energy into a small volume and give rise to visible effects.^{14–16}

Two regimes were present in a cavity bubble field: a stable bubble oscillated many times around its radius of equilibrium with small excursions and a short-lived bubble under dramatic volume changes in a few acoustic cycles and terminated in a violent collapse. Both cavitations may occur simultaneously. In a transient cavity, the values of collapsing surface velocity can be fast.

Though the epoxy resin was a viscous liquid, the effect of ultrasonic cavitation also was observed in our experiment. When ultrasonic cavitation occurred, local temperature and pressure would reach very high values in order to induce changes in the epoxy resin, the aramid fibers, and their interface.

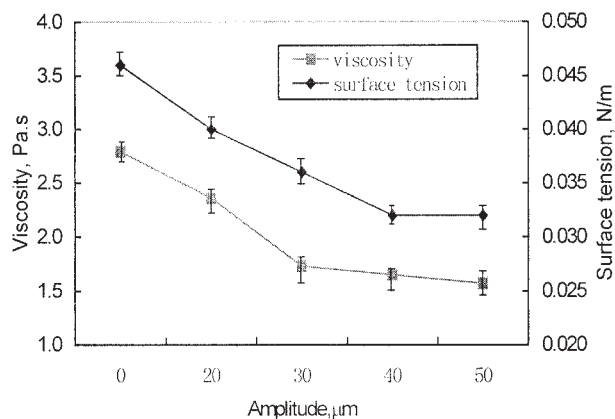


Figure 3 Viscosity and surface tension of epoxy resin under ultrasonic treatment with different amplitudes.

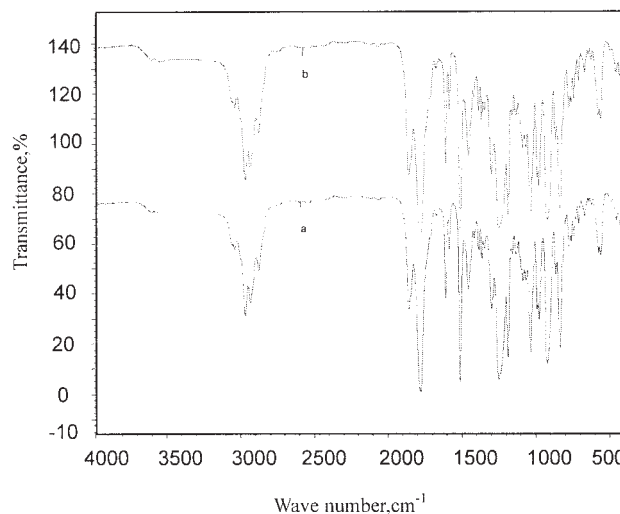


Figure 4 FTIR spectra before and after ultrasonic treatment: (a) untreated, (b) treated for 5 min.

Effect of ultrasound on epoxy resin

When ultrasound was applied to the epoxy resin system, the changes in viscosity and surface tension that occurred are shown in Figure 3.

The viscosity of epoxy resin under ultrasonic treatment with an amplitude of 30 μm was at its minimum, decreasing from 2.75 Pa s for untreated epoxy resin to 1.73 Pa s, a 37% reduction. But the minimum surface tension of epoxy resin was 0.036 N/m, appearing at an amplitude of 40 μm , 27.1% lower than that in the untreated specimen.

The FTIR spectra of the epoxy resin system untreated and treated with ultrasound are shown in Figure 4. A comparison of the two spectra before and after ultrasonic treatment showed that two spectra were wholly the same, indicating that ultrasound with an amplitude of 30 μm would not result in a chemical reaction in the epoxy resin system. Though ultrasonic cavitation can produce enormous power and increase the local temperature, the power was applied to the epoxy resin system instantaneously and was weakened by the ultrasonic effluxion that followed. So ultrasound only played a physical action to break down the intermolecular force and accelerate the molecular movement of epoxy resin system. The rise of local temperature and the acceleration of molecular movement in the epoxy resin system were the main reasons for the decrease in viscosity and surface tension of the epoxy resin system.

The effect of ultrasound on decreasing the viscosity and surface tension of epoxy resin were further analyzed by placing the epoxy resin system after ultrasonic treatment for some hours. The result is shown in Figure 5. The viscosity and surface tension of the epoxy resin system gradually elevated. The viscosity of the resin system was 20 Pa s when it was placed for 3 h, which

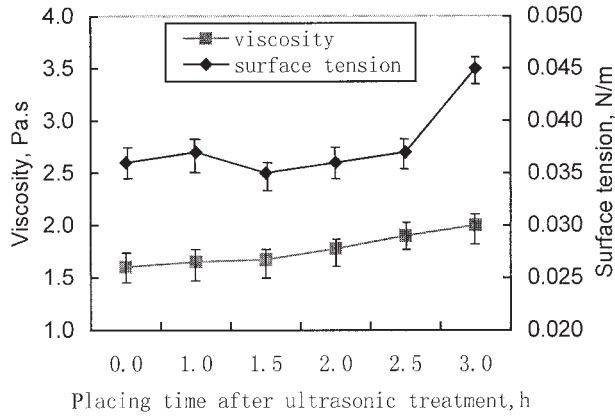


Figure 5 Viscosity and surface tension of epoxy resin versus placing time after ultrasonic treatment.

was lower than that of the untreated specimen. And the surface tension of the resin system reached 0.041 N/m, similar to that of the untreated specimen. This showed further that the decrease in viscosity and surface tension of the epoxy resin by ultrasound resulted from the increase in temperature and speed of molecular movement induced by the ultrasound, which would decrease gradually with the prolongation of the placing time. It should be noted that the viscosity and surface tension of epoxy resin can be maintained almost unchanged within a placing time of 1.5 h, which was enough for us to test the wettability of the treated epoxy resin and aramid fibers.

The wettability between the epoxy resin system with and without ultrasonic treatment and aramid fibers is shown in Figure 6. It was found that the initial speed of the adsorption of the aramid fibers into epoxy resin system and the amount of adsorption amount were enhanced, compared with those for the untreated resin system. At an amplitude of 30 μm , the resin system appeared to have the maximum adsorption speed and

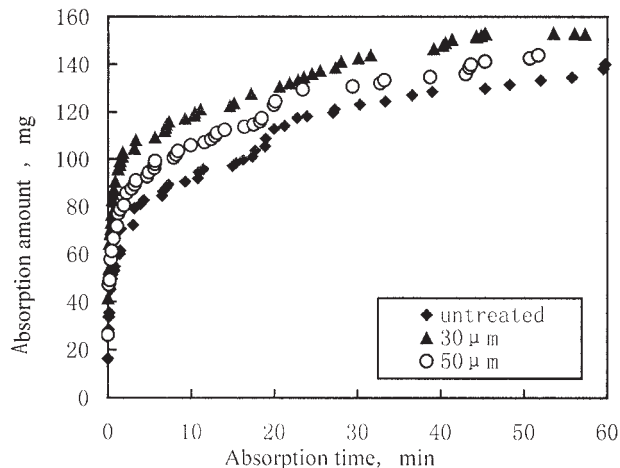
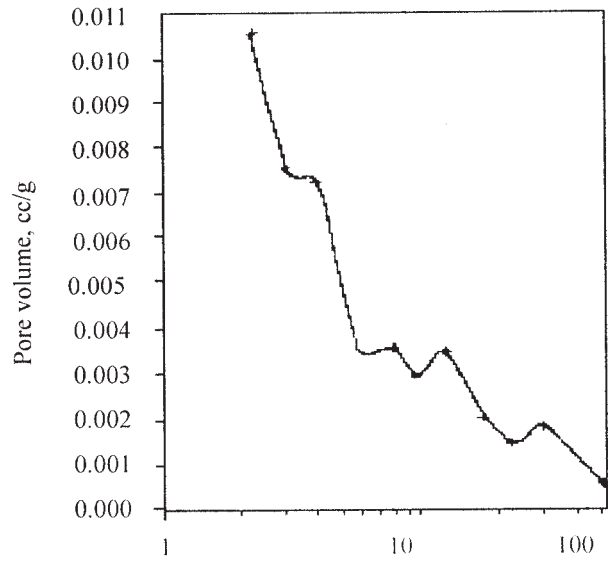
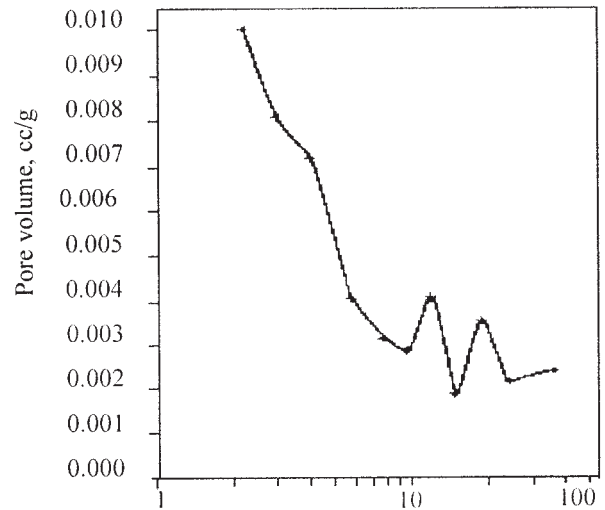


Figure 6 Wetting curves between aramid fibers and epoxy resin treated with different ultrasonic treatments.



(a)



(b)

Figure 7 Diameters of pores on surface of aramid fibers and their distribution: (a) untreated, (b) treated with 30 μm .

amount adsorbed. The results indicated that the wettability between aramid fibers and resin could be improved through the application of ultrasound to the resin system and decreasing the viscosity and surface tension of the epoxy resin system.

Effect of ultrasound on aramid fibers

The characteristics of pore structure on the surface of aramid fibers after ultrasonic treatment are shown in Figure 7 and Table I. From Table I, it can be seen that

TABLE I
Changes in Elements on the Surface of Aramid Fiber Before and After Treatment

	C (%)	O (%)	O/C	N (%)	N/C
Untreated	78.06	13.40	17.17	8.54	10.94
Treated with amplitude of 30 μm	76.58	16.73	21.84	6.69	8.74
Treated with amplitude of 50 μm	79.21	16.74	21.13	4.05	5.11

the diameter of micropores on the surface of fiber increased from 2.79 nm for untreated aramid fibers to 3.51 nm for treated fibers, so that the specific surface area of aramid fibers increased from 12.9 m^2/g for the untreated fibers to 17.5 m^2/g after treatment. When ultrasound was applied to the aramid fibers covered with a layer of the epoxy resin system since having been pulled from the epoxy resin bath, the transient cavity that had occurred in the epoxy resin system collapsed and produced effluxion to etch the surface of the aramid fibers. So the volume of micropores on the surface of the aramid fibers increased. It is known that an increase in the specific surface area and micropore volume would benefit the interpregnation of epoxy resin on the surface of the fibers, thus enhancing the physical interlocking.

The chemical components on the surface of the fibers determined by the XPS test is shown in Table II. Compared with the result for the untreated fiber, the oxygen percentage increased by 24.8% at an ultrasonic amplitude of 30 μm . The reason for the increase in oxygen content on the fiber surface was mainly that ultrasound etched the fiber surface to increase its toughness so that more epoxy resin impregnated inside the micropore of aramid fibers. On the other hand, the ultrasonic effluxion could force molecules of the epoxy resin system further into the micropores of the fibers. And the epoxy resin system molecules inside the microhole could not be removed by acetone extraction after 48 h, so the oxygen content increased after ultrasonic treatment, where the ultrasonic effluxion made a greater contribution to the change in oxygen content.

TABLE II
Characteristics of Pore Structure on Surface of Aramid Fiber Before and After Ultrasonic Treatment

	Specific surface area (m^2/g)	Content of volume (cc/g)	Diameter (nm)
Untreated	12.9	0.009	2.79
Ultrasonic treated with amplitude of 30 μm	17.5	0.015	3.51

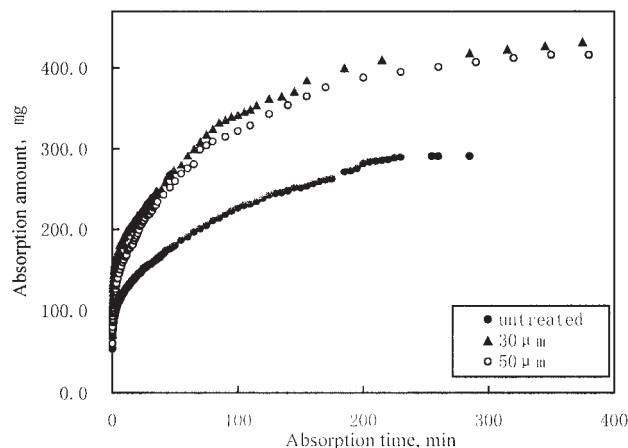


Figure 8 Wetting curves between aramid fibers and epoxy resin treated under ultrasonic online treatment.

It should be noted that it is possible that aramid fibers reacted with epoxy resin under ultrasonic online treatment so as to increase the oxygen content on the surface of the aramid fibers, which will be investigated further as this work is ongoing.

Effect of ultrasound online treatment on wettability

The results from the simulated wettability test of ultrasonic online treatment are shown in Figure 8. Compared with the results shown in Figure 6, the initial adsorption speed and the amount adsorbed under ultrasonic online treatment obviously were enhanced. When the ultrasonic online treatment occurred at an amplitude of 30 μm , the initial adsorption speed and the amount adsorbed at the balance of adsorption between aramid fibers and epoxy resin system were 95% and 33.6% higher, respectively, than those of the untreated specimens. The improvement of wettability between aramid fibers and epoxy resin under ultrasonic online treatment indicated that in addition to the decrease in viscosity and surface tension of epoxy resin system contributing to the improvement of wettability between aramid fibers and epoxy resin, the most important reason for improvement in wettability was that the enormous power from that ultrasonic cavitation could promote the epoxy resin to impregnate the aramid fibers. Good wetting of aramid fibers by epoxy could decrease interfacial defects on the interface and improve the work of adhesion so as to increase the IFSS.

Figure 9 shows the relationship between the IFSS of the aramid fiber/epoxy composites and ultrasonic amplitude. It was found that the IFSS of the aramid fiber/epoxy composites was at the maximum when the ultrasonic amplitude was 30 μm , which was consistent with the wettability result. The results indi-

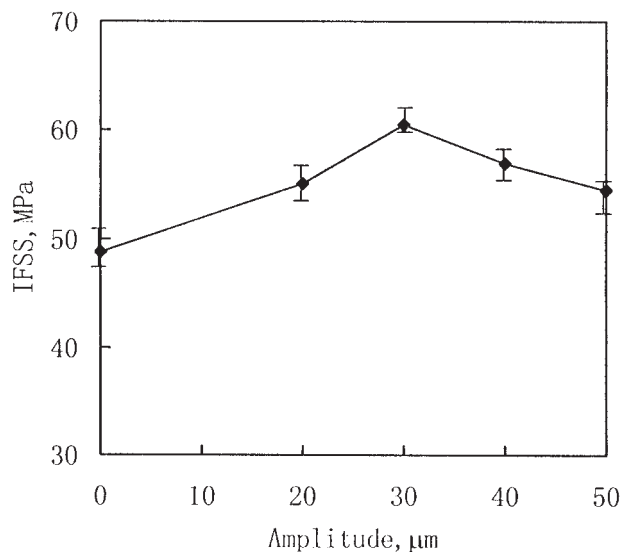


Figure 9 Relationship between IFSS of aramid fiber/epoxy composites and ultrasonic amplitudes.

cated that the better wetting between aramid fibers and epoxy resin induced by ultrasound was the main reason for the improvement in the interfacial performance of their composites.

CONCLUSIONS

An ultrasonic amplitude of 30 μm was an optimal parameter for treating the aramid-fiber-reinforced composites. Under this amplitude, the viscosity and surface tension of the epoxy resin system decreased by 37.0% and 21.7%, respectively, because of the ultrasonic cavitation. Moreover, ultrasonic treatment en-

hanced the surface oxygen content of the aramid fibers. Both effects of ultrasound on epoxy resin and aramid fibers improved the wettability between them and the interface adhesion of their composites. However, the most key factor for increasing the wettability was that ultrasound could force epoxy resin to impregnate the aramid fibers so that the IFSS of their composites increased by 23.6% under ultrasonic on-line treatment with an amplitude of 30 μm .

Reference

1. Wu, S. R.; Sheu, G. S.; Shyu, S. S. *J Appl Polym Sci* 1996, 62, 1347.
2. Yue, C. Y.; Padmanabhan, K. *Compo: Part B* 1999, 30 205.
3. Ramazan, B.; Giuliana, C. T. *Text Res J* 1990, 7, 334.
4. Chou, C. T.; Penn, L. S. *J Adhes* 1991, 36, 125.
5. Fabienne, P. E.; Bruno, C.; Jean, C. B. *J Appl Polym Sci* 1994, 52.
6. Plawky, U.; Londschien, M.; Michaeli, W. *J Mater Sci* 1996, 22, 31.
7. Lin, T. K.; Wu, S. J.; Lai, S. S.; Shyu, S. S. *Comp Sci Tech* 2000, 60, 1873.
8. Zhang, C. X.; Jin, S. J.; Yu, Y. Z. *J Mater Sci Technol* 1993, 6, 423.
9. Liu, L.; Huang, Y. D.; Zhang, Z. Q. *J Appl Polym Sci* 2002, 80, 2764.
10. Huang, Y. D.; Liu, L.; Qiu, J. H.; Shao, L. *Comp Sci Technol* 2002, 62, 2153.
11. Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: New York, 1982.
12. Oubinin, M. M. *Progress in Surface and Membrane*; Academic Press: New York, 1975.
13. Barrett, E. P.; Joyner, L. C.; Halenda, P. H. *J Am Chem Soc* 1951, 73, 373.
14. Mettin, R.; Luther, S.; Ohl, C. D.; Lauterborn, W. *Ultras Sonochem* 1999, 6, 25.
15. Piero, C.; Nikolai, V. D.; Alberto, F.; Anatoly, I. K.; Glauco, I. *Ultras Sonochem* 2000, 7, 213.
16. Ciuti, P.; Dezhkunov, N. V.; Iernetti, G.; Kulak, A. I. *Ultrasound* 1998, 36, 569.