Mechanism of Mass-Transfer Enhancement in Textiles by Ultrasound

Vijayanand S. Moholkar and Marijn M. C. G. Warmoeskerken
Textile Technology Group, Dept. of Chemical Engineering, University of Twente, P.O. Box 217,
7500 AE Enschede, The Netherlands

Claus Dieter Ohl and Andrea Prosperetti
Physics of Fluids Group, Dept. of Applied Physics, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

The intensification of wet textile processes, such as cleaning and dyeing, by application of ultrasound is well known. In these processes, mass transfer in the interyarn and intrayarn pores of the textile is the basic physical phenomenon. The results of experiments on textile cleaning, based on basic principles of acoustics and cavitation, coupled with analysis of the surface and cross section of the ultrasound-treated textile and high-speed imaging of the cleaning process, are reported. It is revealed that transient cavitation in the vicinity of the textile surface, and not the ultrasound wave itself, is the physical mechanism responsible for the enhanced cleaning effect. Intense microconvection due to the transient bubble motion driven by ultrasound enhances fluid flow and, thus, mass transfer through the textile. © 2004 American Institute of Chemical Engineers AIChE J, 50: 58–64, 2004
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Introduction

Wet finishing, that is, the treatment of textile materials in order to manipulate their properties, forms an important stage in the textile processing chain. It basically involves mass transfer across the textile materials. Intensification of this mass transfer is the basis for the improvement of the processes. Most textiles have a dual porosity, an interyarn and intrayarn porosity. For a fluid flowing through the fabric, the interyarn and intrayarn regions form parallel paths. An analysis of the flow through textile materials (Gooijer, 1998) shows that, during conventional wet-textile treatments, most of the flow occurs in the interyarn region, thus making the intrayarn diffusion process the rate-limiting step in the overall mass-transfer operation.

The intensification effect of ultrasound on various wet textile processes, such as dyeing, washing, rinsing, and scouring, has been known for more than six decades (for example, Würmann et al., 1946; Rath and Merk, 1952; Chuz and Domoroslov, 1962; Thakore et al., 1988; Yachmenev et al., 1998). The physical mechanism underlying this effect, however, is still unclear, although several hypotheses have been proposed, such as reduction of the boundary-layer thickness between the textile surface and bulk liquid, reduction in the size of the dye or dirt particles, and increased swelling of the fibers (Thakore, 1988a, 1988b; Klutz, 1997). Most of the results reported in the literature are system-specific, and very few of them try to establish a link between the observed process enhancement and physical mechanisms. Thus, this literature is of a *black-box type,* where the principal focus is on the results and not on their causation.

In this article, we try to elucidate the physical mechanisms of the ultrasonic enhancement of wet textile processing by focusing on the washing process. We show that cavitation activity, that is, the response of bubbles to the ultrasound wave, taking place in the liquid in the close vicinity of the textile surface, and not the ultrasound wave by itself, is responsible for the intensification of the textile treatment.

Approach

We use general principles of acoustics and cavitation to devise different experiments that help identify the separate contributions of (single-phase) acoustic phenomena (such as acoustic streaming and oscillatory ultrasound velocity) and cavitation to the enhancement of wet textile processing. Our experiments are based on the following well-known properties of cavitation.

Standing Waves. Placing the textile sample at a pressure node or antinode in a standing-wave field can help distinguish between the effects of acoustic and cavitation phenomena. At the pressure antinode, the latter will be dominant due to the large local acoustic pressure amplitude, while the ultrasound-induced oscillatory velocity will be a minimum. At pressure nodes, the reverse will be true. Circulatory acoustic streaming currents will be present in the region between the pressure antinode and the pressure node, but since their velocity is quite small, that is, of the order of a few cm/s, these are unlikely to contribute toward the intensification of the textile process.

Degassing of the Liquid. Cavitation intensity passes through a maximum as the gas content of the medium, in both free and dissolved form, is increased (Leighton, 1994; Moholkar, 2002). At high-gas content, many bubbles form near the acoustic source, which prevents an effective coupling between the source and the liquid, while at very low gas content, the appearance of bubbles is impeded by the paucity of available nuclei.

Denucleation of the Textile. Air pockets trapped in the interyarn and intrayarn pores can act as nuclei for bubble formation in the textile. By comparing results with denucleated and untreated fabric, one can therefore reveal the importance of cavitation due to nuclei within the textile itself.

Variation in the Static Pressure of the System. For a fixed acoustic pressure amplitude, cavitation intensity decreases with rising static pressure, while purely single-phase acoustic phenomena are relatively unaffected by static pressure variations.

In addition to experiments based on these principles, we also used both scanning electron microscopy to study the surface and the body of the textile after exposure to ultrasound, and high-speed photography for the cavitation events.

Model Fabric and Monitors. In order to deduce the physical mechanism of the intensification of mass transfer in textiles with ultrasound, a model wet textile process with a model fabric and a model diffusing substance that acts as a monitor for mass transfer (or, in other words, "a soil simulant") needs to be selected. A proper study of the physical mechanism of the ultrasonic mass-transfer enhancement will require that the model fabric and mass-transfer monitor possess the following properties and characteristics.

- The monitor for the transport (in the form of a particle or a molecule) should not undergo any chemical change during the transport.
- The monitor should not form any strong chemical or physical bond with the fibers of the textile that can hinder its transport across the fabric.
- Monitor concentration in the textile should be uniform.
- The nature of the monitor should be such that it permits a complete removal of the substance upon successful cleaning, which normally would not be possible if chemical reactions between the fabric and the monitor took place.

- The original diffusion rate of the monitor should be slow enough to be "accelerated" by ultrasound.
- The size of the monitor particles should be smaller than the intrayarn pores of the textile, which will ensure the presence of the monitor in these pores. An added advantage of this feature is the separation of the secondary effect of ultrasound, which is hypothesized to be responsible for the intensification of the textile processes, viz., particle-size reduction. Due to very small initial size, any further reduction in the size of the monitor will not occur, and hence this secondary effect can be isolated.
- Preferably, the model fabric should be a plain weave with dual porosity that offers a simple geometry for the transport of the monitor.

In view of these requirements we have selected two model fabrics in this study:

(1) EMPA 101 fabric (ETH, Zurich), which is a plain-weave cotton fabric, 100 g/m^2, soiled with carbon soot and olive oil.

(2) Vlisco cotton fabric, again a plain-weave cotton fabric, 120 g/m^2, dyed with palanil pink disperse dye (Royal Ten Cate, Nijverdal, Netherlands).

Both of these model fabrics satisfy all of the requirements described previously. The carbon particles and disperse dye molecules can be considered to be chemically neutral, in view of the treatment applied before the ultrasonic tests (see below). Their sizes are very small with diffusion coefficients of $\sim 10^{-12}$ m^2/s (as calculated from the Stokes-Einstein equation). In addition they do not form any strong physical or chemical bond with the cotton fibers. The concentration of the monitor in the model fabric is uniform within a single and different samples.

Experimental

The experimental setup is shown in Figure 1. For most of the experiments, we used EMPA 101 as the model textile. The acoustic cell consisted of three detachable glass rings and a Teflon lid. The height of two rings was 15 mm, which corresponds to one-quarter of the wavelength of 25-kHz ultrasound in water (60 mm), while the height of the third ring was 60 mm. The inner diameter of these rings was 50 mm. The cell was
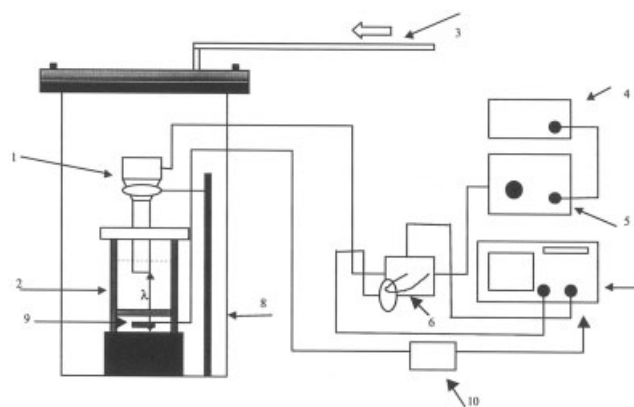
**Figure 1. Experimental setup in the ultrasound unit.**

Legends: (1) Ultrasound horn; (2) experimental cell with textile sample; (3) compressed air (7 bar); (4) signal generator; (5) RF amplifier; (6) voltage and current monitoring unit; (7) digital oscilloscope; (8) high-pressure vessel; (9) hydrophone; (10) charge amplifier.

mounted on a thick stainless steel bottom, acting as a rigid reflector for the ultrasonic waves, with four vertical bars supporting the glass rings placed above each other. The textile sample could be placed in between the glass rings at different distances from the bottom, and the glass rings could be pressed together with the lid on top of the third ring. Rubber gaskets were placed between the textile and the glass rings in order to avoid leakage. Pressure amplitude at the pressure node and antinode was measured by a hydrophone (Brüel & Kaejer Ltd., Type 8103). The ultrasound unit was an specially made horn with a central resonance frequency of 25 kHz driven by a signal generator (Hewlett-Packard Inc., Model 3324A) and a radio frequency amplifier (ENI Inc., Model 2100L). It was mounted onto the shaft of a laboratory jack and the experimental cell was placed on its base, which could be raised or lowered to adjust the distance between the bottom of the cell and the tip of the horn. The horn had a small circular groove in its tip, the significance of which will become apparent later. In order to conduct the experiments under raised static pressure, a high-pressure vessel (volume: 40 L; max. working pressure: 10 bar) was constructed, which could accommodate the entire experimental setup. A standing-wave field was generated in the experimental cell by adjusting the distance between the stainless steel bottom and the tip of the ultrasound horn equal to one wavelength (λ) of ultrasound.

According to the well-known properties of standing waves for plane-wave reflection (Pierce, 1989), pressure nodes occur at a distance of $\lambda/4$ and $3\lambda/4$, while the pressure antinode occurs at a distance of $\lambda/2$ from the rigid reflector. The ultrasound horn was driven at 25 kHz, with a power input of 20 W. For this power input, it produced an acoustic wave with pressure amplitude of $\sim$ 1.3 bar, which is above the transient cavitation threshold in normal water. The experiments were divided into four categories:

(1) Nondegassed fabric and nondegassed washing medium (NDF-NDW);

(2) Degassed fabric and nondegassed washing medium (DF-NDW);

(3) Nondegassed fabric and degassed washing medium (NDF-DW);

(4) Degassed fabric and degassed washing medium (DF-DW).

Experiments in each one of these categories were carried out at the pressure node and at the pressure antinode in the standing-wave field. Thus, there were eight sets of experiments in total. In addition, the static pressure of the experimental system was varied and the eight sets of experiments previously mentioned were conducted at static pressures of 1 (atmospheric), 2, 3, and 5 bar. Since denucleating gassy water is not entirely straightforward, experiments with denucleation of the washing medium could be carried out only for categories NDF-DW and DF-DW, at the pressure antinode and the pressure node. In each set of experiments, three runs were conducted with different pieces of the model fabric in order to assess the reproducibility of the results. The carbon particles on the EMPA 101 fabric are not free to be transported by convection, but adhere to the fiber along with the olive oil. These particles therefore need to be loosened from the surface of the fibers before being transported in the medium. Therefore, the fabric was soaked in a detergent solution (1.75 g/L of sodium dodecyl benzene
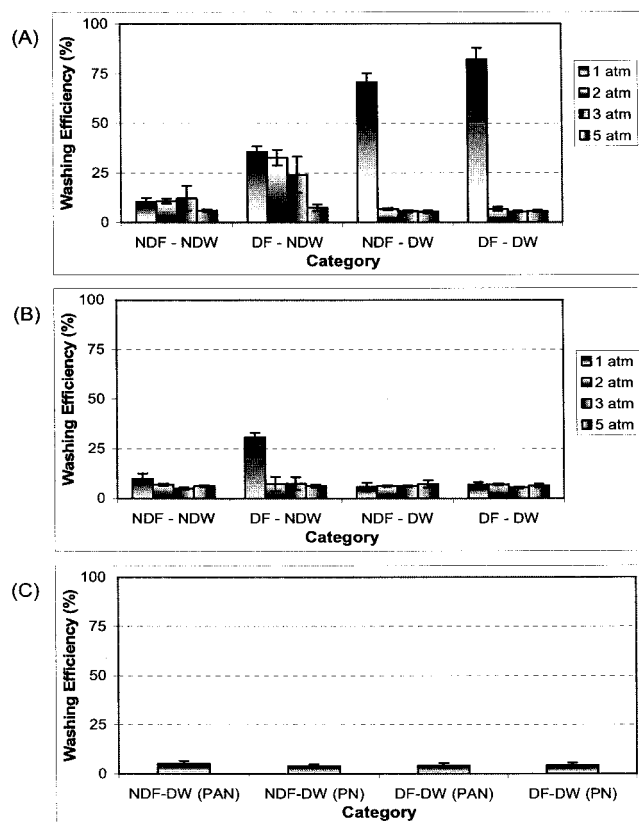
Figure 2. Trends in washing efficiencies in different categories of experiments.

(A) Trends in washing efficiency at pressure antinode with varying static pressure; (B) trends in washing efficiency at pressure node with varying static pressure; (C) results of the washing experiments done with denucleation of the medium.

sulfonate) for 5 min before ultrasonic treatment so as to loosen the carbon particles from the surface of the fibers. Thus, the EMPA 101 fabric meets the criteria for the model fabric and monitor (that the monitor should not form a strong bond with the textile fibers) after soaking in a detergent solution. During soaking, the detergent solution was kept still in order to avoid the transportation of loosened soil away from the fabric. Thus, soaking of the fabric is not likely to cause any major change to the initial lightness of the fabric. In addition, all the textile samples were treated in exactly the same way, and hence, even if few carbon particles were removed during soaking, this feature does not affect the conclusions. In each experiment, 250 mL of water was used as the washing medium. The dissolved oxygen content of the washing medium was $\sim$ 10 ppm for categories NDF-NDW and DF-NDW, while it was lowered to 2 ppm for categories NDF-DW and DF-DW using a chemical method (van der Vlist et al., (1994)). The fabrics were degassed by pressurizing them at 7 bar in degassed water for 12 h, so as to dissolve most of the air pockets trapped in the interyarn and intrayarn pores. The time of ultrasound treatment was 3 min. The small groove in the tip of the ultrasound horn was filled with silicon rubber to avoid random nucleation due to air entrapment. A 10-μL solution of polystyrene latex particles suspended in water (particle size: 0.5
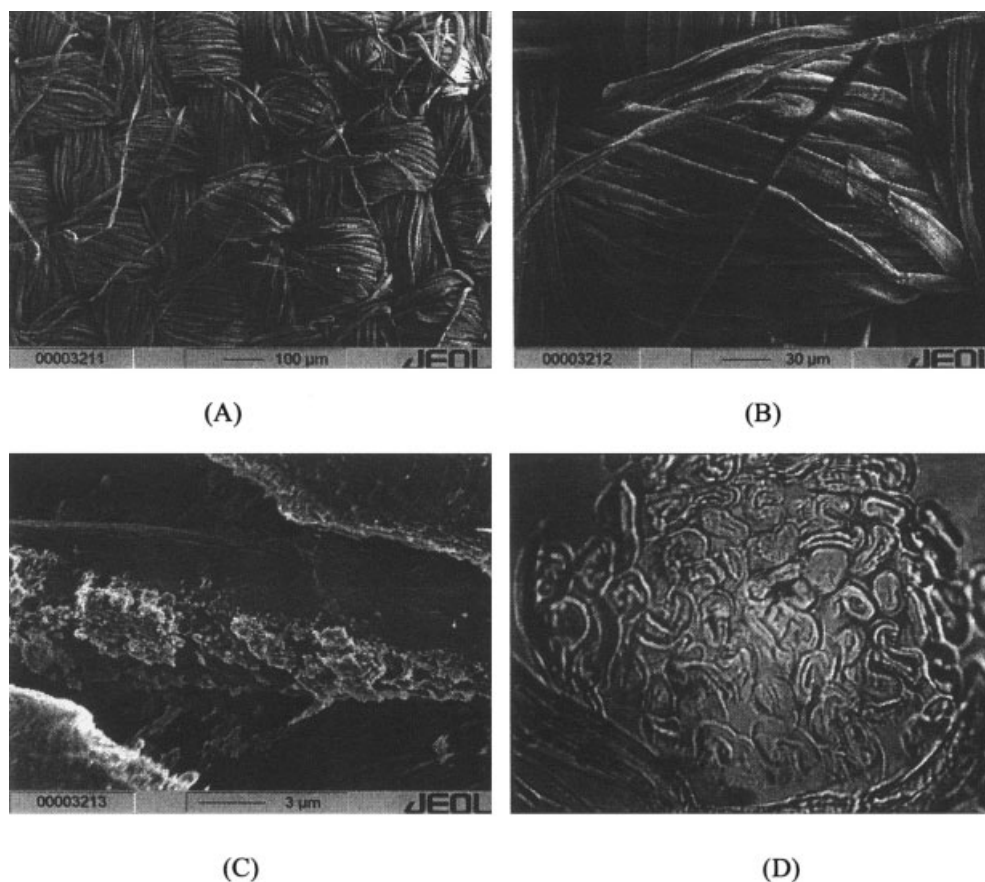
Figure 3. Surface (SEM images) and cross section of the original (untreated) EMPA 101 fabric.

(A) Surface of the fabric (magnification: 100); (B) a single yarn in the fabric (magnification: 400); (C) fiber of the fabric (magnification: 5,500): carbon soot on the surface of the fabric is clearly visible; (D) cross-section of the fabric (magnification: 500). It could be seen that some carbon particles are present inside the yarn. (SEM images were obtained using Jeol Inc. machine, Model GSM 5800. Accelerating voltage: 5 kV; working distance: 10 mm. The cross section was obtained by first soaking the textile in a monomer solution of epoxy resin, while taking care to avoid entrapment of air bubbles. It was then put in an oven where the monomer was converted into a cross-linked polymer with the textile entrapped in-between. Thus, this procedure basically freezes the textile in the resin matrix. Next, slices of the resin matrix (thickness: 7 microns) were obtained with a supercut machine).

μm, conc.: 2 wt. %) was added to the washing medium to facilitate cavitation nucleation. The tiny air pockets trapped on the polystyrene particle suspension can provide nuclei for cavitation (Holland and Apfel, 1990). This procedure ensures consistent nucleation in the washing medium. For the experiments with denucleation of the washing medium, the water was left standing for about 20 min after degassing, to ensure dissolution of the microbubbles left in the system that could possibly form nuclei for cavitation. For these experiments, the polystyrene suspension was not added to the washing medium. After ultrasound treatment, the model fabric was removed from the cell and dried in air.

Quantification of Washing Effect

The washing effect was quantified using the reflectance measurement, which gives an estimate of the soil concentration in the fabric. The reflectometer (X-Rite Inc., Model 968) had a facility for converting the reflectance measurement into L (lightness), a (color shift between green-red) and b (color shift between blue-yellow) values according to the CIELAB scales. The washing efficiency was defined as:

$$\eta = \left[\frac{L_{\text{treated}} - L_{\text{untreated}}}{L_{\text{untreated}}} \right] \times 100.$$

It should be pointed out that the lightness value of white cotton is ~ 87 rather than 100 [TNO-Textiel (Enschede, The Netherlands), personal communication]. Thus, according to the preceding definition, a washing efficiency of 85% would essentially indicate complete removal of the soil from the fabric. The overall washing efficiency in one set was calculated by averaging the L values of all samples in that set.

Results and Discussion

The trends in the washing efficiency with different process parameters are shown in Figure 2. The smallest washing efficiency is seen for categories NDF-NDW (pressure node) and NDF-NDW (pressure antinode). As noted previously, in a gassy washing medium, ultrasound waves undergo strong attenuation as a result of a large bubble population and significant growth of the bubbles by rectified diffusion due to high dissolved gas concentration. As a result, the intensity
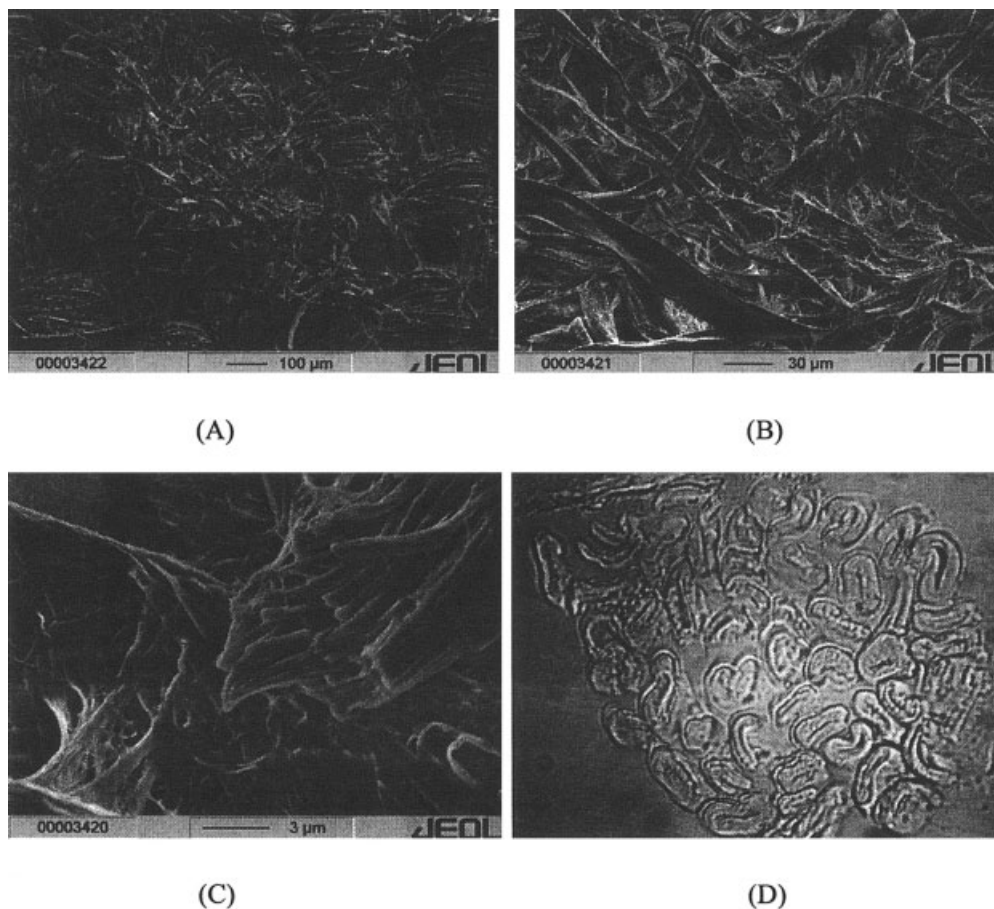
Figure 4. Surface (SEM images) and cross section of the ultrasound-treated EMPA 101 fabric.

(A) Surface of the fabric (magnification: 100); (B) a single yarn in the fabric (magnification: 400); (C) fiber of the fabric (magnification: 500): damage caused to the fabric is clearly visible; (D) cross section of the fabric (magnification: 500): the carbon particles inside the yarn have been removed. (Procedure for obtaining SEM images and crosssection of the fabric is exactly the same as described in Figure 2).

of both cavitation and acoustics-related phenomena are small. Degassing of the fabric alone does not cause a major change in the washing efficiency because, due to the large liquor ratio, only a small fraction of the total cavitation nuclei is contributed by the textile. Thus, phenomena of attenuation of ultrasound waves and rectified diffusion do not change by degassing of the fabric. The slightly higher washing efficiency for the category DF-NDW (pressure node and pressure antinode) could be due to the fact that, since the fabrics were degassed by pressurization in water for 12 h, some soil particles could have diffused away in the medium. The washing efficiency shows a marked rise for the NDF-DW category (pressure antinode). Degassing of the medium, which causes reduction in the bubble population, raises the cavitation intensity due to the smaller attenuation of the ultrasound waves (Moholkar, 2002). Degassing of the fabric along with the medium causes no appreciable change in the washing effect, as indicated by the washing efficiencies for categories NDF-DW (pressure antinode) and DF-DW (pressure antinode). An explanation for this result can be given along similar lines as for the difference between the washing efficiencies for the categories NDF-NDW (pressure antinode) and DF-NDW (pressure antinode) mentioned earlier. On the contrary, the washing efficiency is far

smaller for categories NDF-DW (pressure node), and DF-DW (pressure node) indicating that single-phase acoustic phenomena play a negligible role in the washing process. These results clearly point toward cavitation phenomena as the principal physical mechanism responsible for the enhanced washing process.

The results of the experiments at static pressure of 2 bar reveal a sharp reduction in the washing efficiency for the categories NDF-DW (pressure antinode) and DF-DW (pressure antinode). At the pressure antinode, the washing efficiencies for all four categories, which are already quite low at atmospheric static pressure, do not change much by a rise in the static pressure except for the category DF-NDW, for which the washing efficiency decreases. With the static pressure raised to 3 bar, the washing efficiency for all categories at both the pressure node and antinode drops further. The washing efficiency for all categories at pressure node and antinode is reduced practically to zero when the static pressure is raised to 5 bar. These results further confirm the principal role of transient cavitation phenomena in the washing process. Very low washing efficiencies at the pressure node locations support the conclusion that can be drawn from the experiments at atmospheric pressure that single-phase acoustic phenomena do not contribute to the
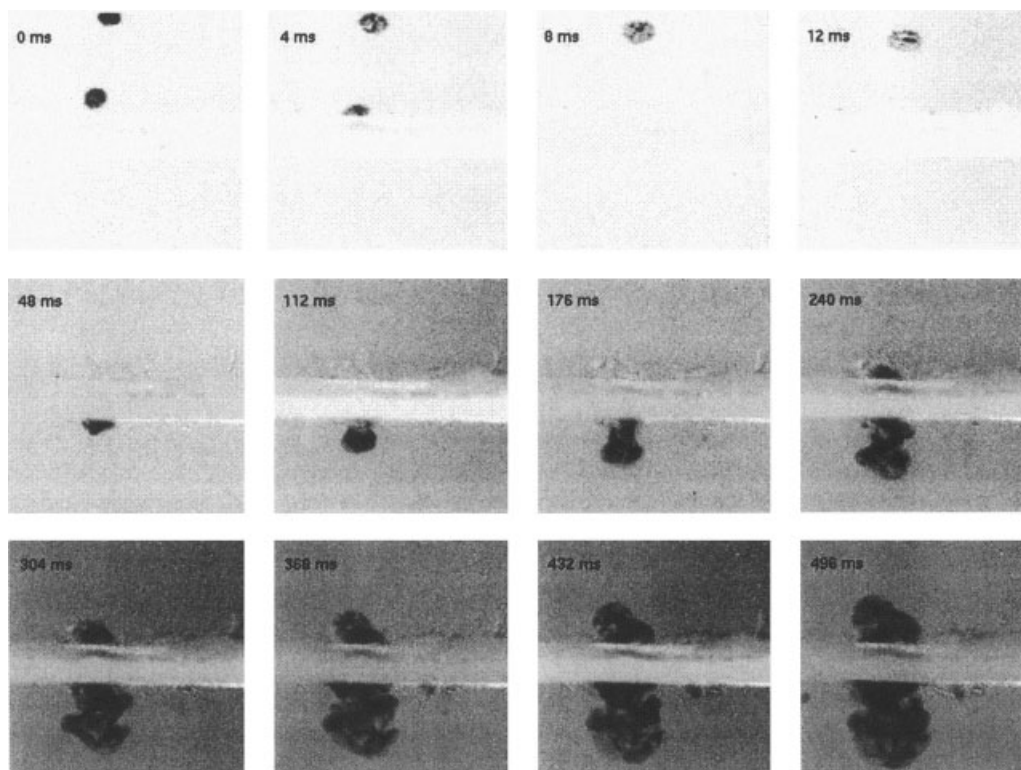
Figure 5. Twelve frames (arranged sequentially in each row from left to right in consecutive rows) from a high-speed movie of the ultrasonic textile washing process.

The ultrasound horn is located at the upper border of each frame with the textile positioned at the center of the frame at the location of pressure antinode. (Frame rate: 250 f/s; frame size: 25 × 25 mm; numbers given on the lefthand upper corner indicate the time of the frame).

washing effect. An interesting observation is the moderate washing efficiency observed for category DF-NDW at 2- and 3-bar static pressures. This could be an effect of the technique for the degassing of the fabric, as pointed out earlier. The results of the experiments done with denucleation of the washing medium (Figure 2C) indicate that this operation decreases the washing efficiency at both the pressure node and antinode further and reduces practically to zero. Lack of change in the washing efficiency at the pressure node after denucleation of the washing medium, as compared to the nucleated washing medium, again suggests that single-phase acoustic phenomena do not contribute to the washing process. Thus, these results further confirm the principal role of cavitation in the washing process. In addition, experiments with denucleation also provide a clear answer for the location of the occurrence of the cavitation events responsible for the washing effect: these events occur in the medium close to the textile surface.

A scanning electron microscope analysis was conducted on the ultrasound-treated textile samples in the category NDF-DW (pressure antinode), because maximum washing efficiency was observed for this combination. In addition, to assess the extent of the depth of the washing effect in the fabric, cross sections of the treated samples were made and analyzed under an optical microscope. Pictures of the surface and cross section of the original and treated EMPA 101 fabric are shown in Figures 3 and 4, respectively. A comparison of Figures 3A–3C and 4A–4C clearly reveals erosion of the surface of the textile sample after ultrasonic

treatment, which gives further evidence of cavitation phenomena. A comparison of the cross sections of untreated and treated fabric (Figures 3D and 4D) reveals the interesting result that the internal fibers of the yarn are not damaged, although the carbon soot particles initially present in the intrayarn pores have been removed after ultrasonic treatment. An analysis of 15 samples of cross sections of treated and untreated model fabric, similar to those shown in Figures 3 and 4, supports this conclusion. This suggests that the intense flow generated in the vicinity of the textile due to cavitation activity is capable of creating an intrayarn convection that enhances removal of the soil from the intrayarn pores. It is likely that this intense microflow due to cavitation would be beneficial in other wet textile processes, such as dyeing. In addition, no erosion or damage is visible inside the yarn, indicating that the cavitation phenomena responsible for the washing occur outside the fabric, in the medium in the nearby vicinity, which causes erosion of only the surface of the sample.

High-Speed Photography Experiments

While the results reported to this point give an indirect indication of the role of cavitation in the enhancement of the washing process, high-speed photography can supply a direct proof of this mechanism. The model fabric used in this part of the study was Vlisco cotton fabric dyed with BASF palanil pink disperse dye. A high-speed camera (Kodak Imager CR 1000) was used for the imaging using a dark-field illumination technique. For these experiments, the cir-

cular groove in the tip of the horn was left unfilled and the polystyrene latex solution was not added to the medium. Figure 5 shows a high-speed photographic record of the ultrasonic washing process taken at 250 f/s. The model fabric is located at the pressure antinode, seen in the center of each frame. In the second frame, two bubble clouds are clearly visible. It can be seen that the first cloud reaches the textile surface, while the second one collapses in bulk medium itself. Dye release is observed to begin in frame 5 from the same location on the textile surface reached by the first bubble cloud. The groove in the ultrasound horn tip entraps air when it is immersed in the liquid, which sheds microbubbles, probably due to a surface instability. These bubble clouds arrive at the first pressure node, which is located at a distance of $\lambda/4$ from the tip of the horn and, as a result of Bjerknes forces and ultrasonic streaming, travel toward the pressure antinode, at which the fabric is located. In this process, they experience larger and larger acoustic pressure amplitudes that drive their volume pulsations. The individual bubbles in the cloud collapse under the influence of the large-amplitude acoustic waves creating intense microconvection that initiates dye release from the textile. It should be noted that, in this experiment, filming started at the same time as the ultrasound irradiation. Hence, during the first four frames of the sequence shown in Figure 5, acoustics-related phenomena are present, although no dye is released from the textile during this period. It is apparent from the picture series that the dye release commences with the approach and collapse of the bubbles near the textile surface, which establishes a firm correlation in space and time between dye removal and bubble activity.

Conclusion

By means of several different experiments, this article has established that the physical mechanism responsible for the beneficial action of ultrasound on textile washing is due to cavitation activity taking place in the immediate vicinity of the fabric. One consequence of this finding with an immediate, if obvious, practical value is that the process will be most efficient if the fabric is placed in the vicinity of the acoustic pressure antinodes. Our high-speed photographic study has demonstrated that cavitation causes intense small-scale flows near the fabric that are sufficiently powerful to dislodge the dirt

particles entrapped in the yarn pores. It can be expected that these microflows will prove beneficial in other wet textile processes such as dyeing. These results may be useful in promoting further research and applications of ultrasound-aided textile processing.

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