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Attaching Different Kinds of Proteinaceous Nanospheres to a Variety of Fabrics Using Ultrasound Radiation

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Abstract: The application of a rapid, non-destructive, cost-effective technique such as ultrasonic emulsification for the coating of different textiles was explored. The technical benefits for this research were the generation of multifunctional materials and their combinations through environmentally friendly processing technologies. We have shown for the first time that ultrasonic waves can be used to coat proteinaceous micro- and nanospheres (PM) of BSA (Bovine Serum Albumin) protein and casein on the surface of cotton and polyester (PE) fabrics. The creation and the anchoring of the microbubbles to the fabrics were performed by a one-step reaction, and the process is usually stopped after 3 min. The PM of bovine serum albumin (BSA) bonded to cotton and polyester fabrics has shown stability for ~9 months. The PMs were shown to be attached more strongly to the polyester than to the cotton, and sustained stronger washing conditions on PE. The diameter of the BSA and the casein spheres on cotton was in the range of 0.8–1.0 μm, while on the PE it varied between 60 and 120 nm.

Keywords: nanosphere · protein · protein adsorption · surface modification · textiles

1. Introduction

The present report relates to the attachment of proteinaceous micro- and nanospheres to a variety of fabrics using ultrasound radiation. The application of a rapid, non-destructive, cost-effective technique such as ultrasonic emulsification for the coating of different textiles was explored. The technical benefits of this research were the generation of multifunctional materials and their combinations through environmentally friendly processing technologies. Protein binding to various kinds of textile fabrics has been previously reported.[1–5] In those studies,[1–5] different techniques of binding proteins to textiles were employed. The methods include: infra-red heating, agglutination, using adhesive compounds which improve the bonding of the threads to rubber and proteins, and bonding proteins or polysaccharides having organosiloxane side chains (which are responsible for binding). Polymeric spheres were also anchored to textiles, with or without cosmetically or pharmaceutically active molecules, by using the agglutination properties of these polymers, or by using self-adhesive or thermo-adhesive polymeric microspheres.[6–11] The microspheres attached to the surface of textiles could be used as a drug carrier agent. The release properties of the micro/nanocapsule could be controlled by using proteins with different durability to proteases. In the present work we have shown, for the first time, that ultrasonic waves can be used to coat proteinaceous spheres (PM) of bovine serum albumin (BSA) and casein on the surface of cotton and polyester (PE) fabrics. The creation and the anchoring of the microbubbles to the fabrics were performed by a one-step reaction, and the process is usually stopped after 3 min. Pristine BSA, f-BSA, and casein spheres were attached to cotton and polyester fabrics by using sonochemical radiation. Protein microspheres have a wide range of biomedical applications, including their use as echo contrast agents for sonography,[12] magnetic resonance imaging contrast enhancement,[13] and oxygen and drug delivery.[14–15]

Ultrasonic emulsification is a well-known process and occurs in biphasic systems. Emulsification is necessary for microcapsule formation. Micrometer-sized gas- or liquid-filled microspheres can be produced from various kinds of proteins such as BSA,[16–18] human serum albumin (HAS),[19] hemoglobin (Hb),[20] and a mixture of two proteins.[21] According to the mechanism proposed for the sonochemical formation of PM, the micro/nanospheres are formed by chemically cross-linking cysteine residues of the protein with the HO_2 radical formed around a micron-sized gas bubble or a non-aqueous droplet. The

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chemical cross-linking is responsible for the formation of the microspheres and is a direct result of the chemical effects of ultrasound radiation on an aqueous medium.

The formation, characterization, and properties of the sonochemically-made PM were recently reviewed.[22] The current research is the first of its kind in which proteinaceous micro/nanospheres were bonded to cotton and polyester fabrics. The size of the cotton and polyester substrates was 5 × 5 cm. The starting materials in the bonding of the PM were an aqueous solution of the protein, dodecane, and the fabrics. One of the three different proteins used in the current experiments, f-BSA, is fluorescent.[23] The f-BSA protein has an excitation peak at a wavelength of 488 nm and its emission peak is at 521 nm, which is in the lower green region of the visible spectrum. The BSA spheres bonded to cotton and polyester fabrics showed stability for a period of ~9 months.

In this work we have attempted to understand the mechanism of binding different kinds of proteinaceous micro/nanospheres to cotton and polyester fabrics by separately analyzing the increase in color intensity (K/S%), compared to a control sample of bare cotton and polyester surfaces. Proteinaceous spheres bound to cotton or polyester increased dye affinity, especially for acid dyes such as Coomassie Brilliant Blue G (C.I. Acid Blue 90), which is known to show an increased affinity for proteins. Proteinaceous micro/nanospheres on the fabrics were measured by the modified Lowry method,[24] demonstrating the bonding strength of the PM to the substrate. K/S values (color staining levels) at 620 nm were measured with an ACS Chroma Color Reflectance Spectrometer. The intensity of the color of the dye is a direct method for estimating the amount of the microsphere coating of those fabrics. The products were analyzed and characterized by light microscopy (Apo-Tome AxioImager.z1 microscope), AFM, and SEM measurements. The amount of protein participating in the formation of the microspheres, bound to cotton and polyester fabrics, was determined by a NanoDrop 1000 spectrophotometer.

2. Experimental Section

To remove some impurities from the cotton and polyester fabrics, the samples were washed with 2 g L^{-1} of a non-ionic agent, Lutensol AT 25 (10 g L^{-1}), during 40 min at 60 °C.

2.1. Attaching Micro/Nanospheres to Fabrics Using Ultrasound Radiation

Three different kinds of PMs were attached to cotton and polyester bandages. The following proteins were used: 1) BSA (albumin, bovine fraction v, Sigma), 2) f-BSA (fluorescein isothiocyanate-conjugated bovine serum albumin, Sigma), 3) casein (casein sodium salt, Sigma-Aldrich). In order to attach proteinaceous micro/nanospheres to cotton or polyester fabrics or bandages, dodecane (20 ml, 98.0% Fluka) was layered over 30 ml of a 5% w/v aqueous solution of protein, and a piece (5 × 5 cm) of cotton or polyester fabric was placed in the sonication beaker. The solution was sonicated during 3 min with a high-intensity ultrasonic probe (Sonic and Materials, VC-600, 20 kHz, 0.5 in. Ti horn, at 41% amplitude). The bottom of the high-intensity ultrasonic horn was positioned at the aqueous–organic interface, employing an acoustic power of ≈61.5 W cm^{-2} with an initial temperature of 22 °C in the reaction cell. The sonication lasted for 3 min at 22 °C, using an ice-cooling bath to maintain the low temperature. The separation was accomplished within a few minutes, due to the lower density of the microspheres as compared to water. After separation, the bandage was washed 3 times with 5 ml of water to remove the residue of the unbounded microspheres.

2.2. Preparation of Coated Fabrics for AFM, SEM, and Microscopic Analysis

The cotton or polyester bandages coated with protein micro/nanospheres were prepared for electron microscopy analysis by secondary cross-linking with gluteraldehyde. 5 ml of a 2.5% water solution of glutaraldehyde was added to the washed bandage. The glass test tube in which the preparation was carried out was placed in a refrigerator (4 °C) for 2 h, after which the cross-linked coated fabric was separated from the glutaraldehyde solution and washed with 5 ml of distilled water. The cross-linked samples were placed on a glass slide and dried on a hotplate (40 °C). The product was then microscopically analyzed by AFM and SEM. For optical microscopy analysis the wet fiber (fiber coated with microspheres), without any fixation with glutaraldehyde, was placed on a glass slide and then microscopically analyzed.

The morphology of the product was determined using scanning electron microscopy (JSM-840, JEOL). The sample preparation for the SEM measurements included fixation with glutaraldehyde, and drying and coating with gold. To further substantiate the results, a f-BSA (fluorescein isothiocyanate-conjugated bovine serum albumin) protein was used and the bandage was analyzed by light microscopy (Apo-Tome AxioImager.z1 microscope).

2.3. Determining the Amount of the Protein Bonded to the Fabric

The amount of protein bonded to the bandages was measured using a NanoDrop 1000 spectrophotometer at 280 nm. The amount of protein attached to the fabric was determined by subtracting the amount of the "free" protein (protein in micro/nanospheres that are not attached to bandage) and the protein in the residue phase (the lower phase in the separation flask) from its total amount in the precursor solution.

2.4. Dyeing, Washing, and Desorption Tests

Two sets of experiments were performed to determine the strength of the bonding of the PM to the fabric. In the first set, coated fabrics were dyed with a 2% solution of Coomassie Brilliant Blue G dye (Merc; Acid Blue 90, C.I. 42655). For the other set of experiments, coated fabrics were dyed with Coomassie Brilliant Blue G dye after secondary cross-linking with glutaraldehyde. The dyeing tests were performed in a Rotawash machine (90 min, 60 °C, 40 rpm). In order to remove unbonded dye, the fabrics were washed with Lutensol AT 25 according to the ISO 105-CO3-1978 standard (60 min, 40 °C, 40 rpm). Washing with water was done under the same conditions. No other chemicals

were used in the washing process. Proteinaceous spheres on the fabrics were measured by the modified Lowry method.[25–26] K/S values (color staining levels) at 620 nm were measured with an ACS Chroma Color Reflectance Spectrometer.

3. Results and Discussion

The morphology of the cotton and polyester bandages coated with proteinaceous spheres was determined by light microscopy. Figure 1a presents the image of an uncoated piece of cotton. The fibrous nature of thes yarn is clearly observed. In Figure 1b and 1c we observe the presence of BSA and casein microspheres attached to the cotton fibers that are located in the center of the image. We couldn't see clearly the spheres attached to the two fibers next to the central fiber. This is because of the focus of the illuminating beam on the central fiber. However, when the beam is shifted to the other fibers, the microspheres attached to this fiber were detected. Figure 1d, and Figures 1e and 1f, show an uncoated polyester fiber and a coated polyester fiber, respectively. The big spheres attached to polyester yarn are presented in Figures 1e and 1f in order to show the attachment of the spheres in a better way. Similar results were observed for the three kinds of proteinaceous microspheres attached to fabrics (BSA, f-BSA, and casein microspheres). The light microscopy images present the wet coated and uncoated yarns of fabrics without any fixation with glutaraldehyde.

We have also determined the morphology of the microspheres attached to the bandages by using scanning electron microscopy (SEM). Figure 2a presents the image of an uncoated cotton fiber. In Figure 2b we observe a few microspheres attached to the cotton fibers. Four microspheres are shown in Figure 2b, three of which are clearly embedded in the yarn. The fourth microcapsule is most probably also embedded in the yarn, but it is difficult to be conclusive on this matter since the fiber hides it from the observer. For the three embedded microspheres, most of the volume of the microspheres is implanted in the fabric and only a small part protrudes to the surface. The sizes of microspheres attached to cotton fiber, which are presented in Figure 2(b), are (1) 2.66 μm, (2) 8.33 μm, (3) 1.67 μm, and (4) 6 μm. The white powdery substances on the surface of the cotton yarn (Figure 2b) that is not seen in the uncoated fabric (Figure 2a) are the residues of the protein which was not concerted into the spheres. In Figure 2c, an uncoated polyester fiber is presented. Figure 2d

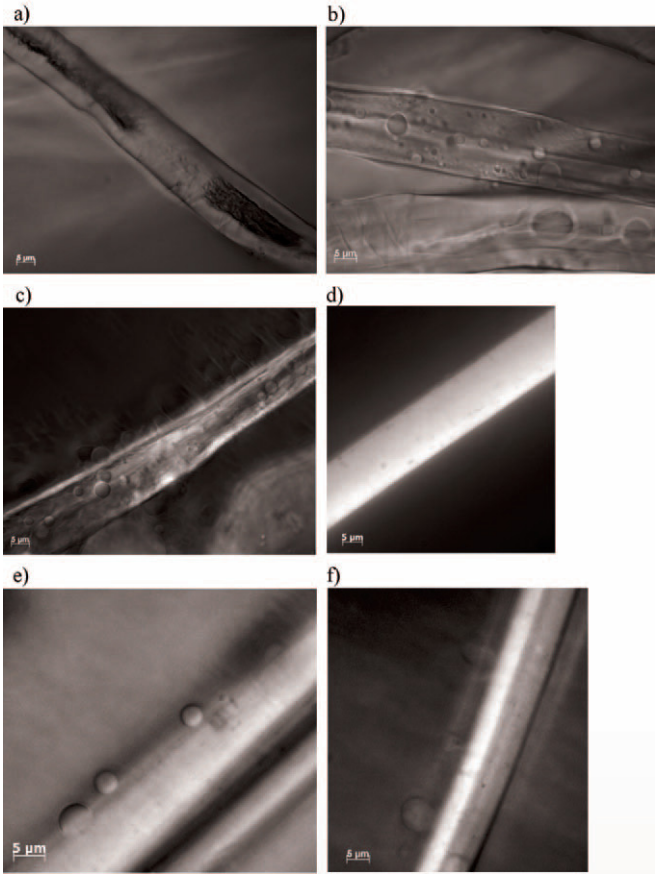

Figure 1. a) An Apo-Tome image of a pristine wet cotton fiber; b) Apo-Tome image of a wet cotton fiber coated with BSA microspheres; c) Apo-Tome image of casein spheres on cotton surface; d) Apo-Tome image of a pristine wet polyester fiber; e) Apo-Tome image of a wet polyester fiber coated with BSA spheres; f) -Tome image of casein spheres on polyester surface. For optical microscopy analyses the cross-linking agent gluteraldehyde was not used. Scale bar = 5 μm.

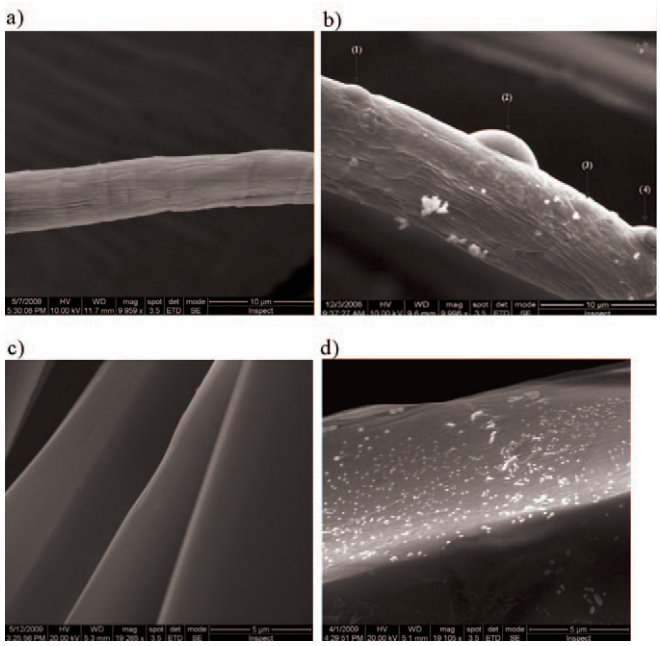

Figure 2. a) An image of a pristine piece of cotton; b) coated cotton. The sizes of attached microspheres are (1) 2.66 μm, (2) 8.33 μm, (3) 1.67 μm, and (4) 6 μm. c) An image of pristine polyester yarn; d) coated polyester. The average size of microspheres attached to the polyester yarn is about 64 nm.

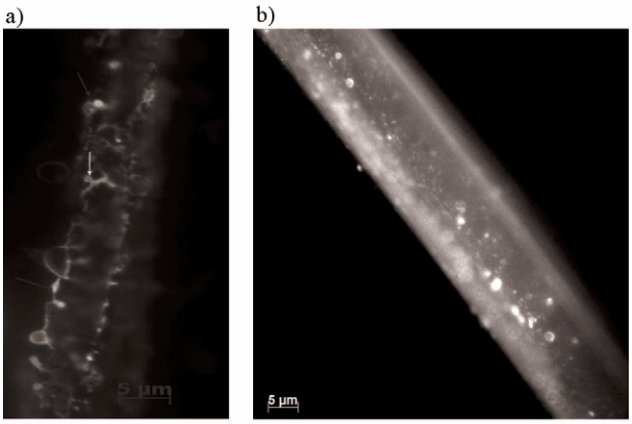

Figure 3. a) Apo-Tome image of f-BSA microspheres attached to a cotton fiber; b) Apo-Tome image of f-BSA microspheres attached to a polyester fiber.

shows the polyester yarn coated with PM. The average size of the microspheres attached to the polyester yarn is about 64 nm.

To better exhibit the presence of the microspheres on the fabrics, we have carried out experiments with f-BSA proteins. Figures 3a and 3b show Apo-Tome images of cotton and polyester fibers, respectively coated with f-BSA microspheres. The wires (marked with an arrow) that are coating a cotton fiber in Figure 3a consist of small f-BSA microspheres attached to a cotton fiber. We could detect the small microspheres comprising the wire under a higher magnification. However, there is also a possibility that some amount of protein can coat the fabric without formation of the spheres. In order to check it, the water solutions of f-BSA protein with a piece of cotton or polyester fabric were sonicated for 3 min. The samples (fabrics) then were washed and analyzed with light microscopy. No green fluorescent signal on the surface of the textiles was detected. The results show that sonication of water solution of protein and fabric doesn't cause the attachment of protein to the surface of fabric. In Figure 3a we observed a few small (marked with arrow) microspheres filled with a green color. This color emanates from the fact that some out-of-focus spheres are located behind these "green" microspheres, creating an illusion of microspheres filled with a green color. Figure 3b shows small microspheres attached to the polyester fiber as well.

The average sizes of PM anchored to cotton and polyester fabrics have been calculated by using the "Scion" image analysis program. The average sizes of microspheres attached to cotton and polyester bandages are ~973 nm and ~64 nm, respectively. While the cotton coating exhibits PMs that are very similar in size to regular PM prepared without a fabric in the sonication cell, the size is drastically reduced for the PM anchored to the polyester fabric. On the other hand, the PMs were much smaller on polyester, in the range of 60–100 nm (see also the AFM results below). These dramatic differences in size on the two fabrics were detected for all three proteins. A possible explanation is suggested based on the AFM results, which exhibit a much more dense coating of the smaller PM on the polyester fabric. We attribute this higher concentration of PM on polyester to the better bonding of the protein to the polyester, which forms many centers around which the polymerization continues. The many seeds distributed upon the fabric continue to grow, and since the amount of protein is spread over a larger quantity of seeds, smaller PMs are formed. The surface of coated polyester bandage was analyzed by atomic force microscopy (AFM). The polyester surface is the most suitable for this kind of analysis because of its lesser roughness, as compared with cotton. We couldn't analyze the surface of the coated cotton bandage because of its excessive roughness. Figures 4a and 4b show AFM microtome images of pristine polyester fabric and coated polyester fabric, respectively. The fibrous nature of the polyester yarn is clearly observed in Figure 4a. In Figure 4b we observe the surface of polyester yarn coated with PM. The size of the PMs is similar to those measured by optical microscopy.

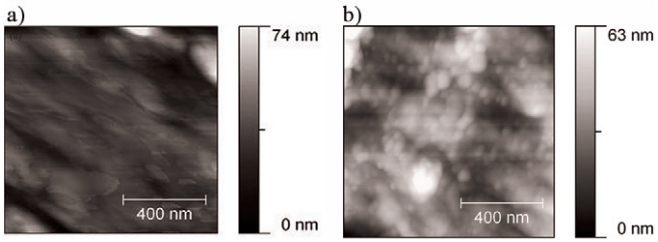

Figure 4. a) Microtome image of pristine polyester fabric; b) microtome image of polyester fabric coated with BSA microspheres.

The stability of microspheres bonded to cotton and polyester bandages was also checked. Pieces of coated bandages (5 × 5 cm) were placed in a closed vial and checked periodically by light microscopy. The vial was kept at the ambient conditions of the laboratory. After three months only ~70% of the microspheres remain bonded to the fabrics; the remaining 30% were destroyed. After five months ~50% of the spheres were destroyed, and 50% remained bonded to bandages. After seven months only ~20% of the spheres remained on the bandages. Studies of the microsphere coating of the fabrics shows the linear relationship between the amounts of microspheres bonded to fabrics vs. time. The percentage of the bonded spheres decreases with time.

We have also examined the amount of protein attached to the textiles by spectrophotometric analysis (at 280 nm). First, the amount of protein (BSA or casein) left in the aqueous solution after sonication was subtracted from the total amount of protein introduced into the aqueous solu-

tion. The results indicate that the total amount of protein converted to microspheres is ~97%, which includes PM bonded and non-bonded to the fabric. To determine the amount of protein bonded to the fabrics, we placed the aqueouos solution with the unbonded microspheres in a glass vial and heated the solution for 4 days at 45–50 °C. Heating the solution completely destroyed the microspheres in the solution. After calculating the amount of the destroyed PM, the results showed that 34.8% of the PM of BSA and 47.3% of PM of casein protein were anchored to the polyester fabric, and 43.5% of PM of BSA and 31.6% PM of casein were attached to the cotton fabric. It is worth noting that when four pieces of 5 × 5 cm. cotton or polyester bandages were sonicated with the precursor solution, all four pieces were coated with PM. Thus, we have found that a maximum of four bandages could be coated simultaneously in our sonication cell.

These amounts of PM bonded to fabrics would be interesting if protein (microsphere) binding were be stable under ambient conditions of use and wearing of cotton/polyester fabrics. Therefore, coated fabrics were dyed and washed under the usual testing conditions in a Rotawash machine (60 min, 40 °C, 40 rpm). The modified Lowry method is supposed to measure the stability of the coated fabrics. We have measured the bond strength between proteins and fabrics by this technique. The principle behind the Lowry method of determining protein concentrations lies in the reactivity of the peptide nitrogen[s] with the copper [II] ions under alkaline conditions, and the subsequent reduction of the Folin–Ciocalteay phosphor-molybdicphosphotungstic acid to hetero-polymolybdenum blue by the copper-catalyzed oxidation of aromatic acids. Although the Lowry method[24] has the distinction of being the most referenced assay in the biochemical literature, and has become the standard for protein quantization, it is also well known for its deficiencies. The results show that proteinaceous microspheres bound to cotton or polyester increased dye affinity, especially for acid dyes such as Coomassie Brilliant Blue G. The gluteraldehyde (GA) cross-linked microspheres bound to fabrics showed an increase in dye affinity, as compared to PM-coated fabrics without GA. This results from a better protein fixation on the fabrics' surfaces when GA is used. Proteinaceous microspheres on the fabrics were measured by the modified Lowry method.[25] The results of the K/S values (color staining levels) at 620 nm are presented in Figure 5.

Figure 5 shows the staining levels (K/S) of BSA/casein PM coated on cotton and polyester fabrics, compared to K/S of PM coated on cotton and polyester fabrics treated with GA. The comparisons for the GA treated and non-treated fabrics were performed after dyeing and washing. An increased dye affinity relative to the untreated (without GA) fabrics means that PMs are found at the fiber's surface after repeated washing in a washing machine,

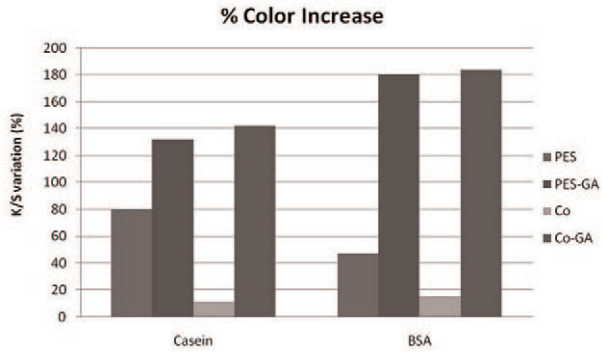

Figure 5. Staining levels (K/S) of cotton and polyester fabrics coated with BSA and casein microspheres, dyed with Coomassie Brilliant Blue G, after washing in a Rotawash machine (60 min, 40 °C, 40 rpm): PES — PM coated on polyester fabric, Co — PM coated on cotton fabric, PES-GA — PM coated on polyester fabric treated with GA, Co-GA — PM coated on cotton fabric treated with GA.

whereas the unbound spheres, or the not strongly bonded spheres, are removed from the fabric. The results in Figure 5 indicate the significant increase in K/S levels, mainly for polyester. For cotton fabrics, only a small quantity of PMs were found on the fiber's surface after repeated washings in a washing machine. The strong adhesion of the PM on PE might be due to the hydrophobic nature of polyester fiber, which strongly interacts with hydrophobic amino acids side chains of the BSA/casein PM. The further treatment of the cotton and PE PM-coated with glutaraldehyde results in the cross-linking of the amino groups on BSA and casein to these fabrics. The interaction with GA leads to high levels of coating/entrapment of microspheres on the surface of both cotton and polyester fabrics.

The understanding of the mechanism of the bonding of PM to these fabrics raises a few questions. The first is, where are the PM formed, in the solution or on the fabric? If we claim that the PM is formed in the solution, then it is well known that the after-effects of the collapse of the acoustic bubble near a solid surface are microjets and shock waves directed towards the solid surface. Sonochemistry was shown recently as an excellent coating technique for the deposition of nanoparticles on ceramics,[26] polymers,[27] glass,[28–29] textiles,[30] metals, and paper. Thus, if the microsphere is indeed created in the solution, it will be thrown by the microjets onto the fabric. That is the reason why, at first hand, we would interpret the results along these steps. However, the results indicate that the microspheres are formed on the fabric. The following arguments support this interpretation. 1) PMs were not formed when wool was used as a substrate. 2) The sizes of the PMs are strongly dependent on the substrate, being 0.8–1.0 microns on cotton and 60–120 nm on PE. If the PMs are formed in the solution, why should they vary that much in size? On the other hand, Figure 2b shows that the bubble is well embedded in the fabric. This is

more difficult to explain when the bubble is created on the surface, unless we argue that after its formation the bubble is further pushed by the microjets to the surface of the fabric. The explanation for the different sizes is as follows: In another study we have found that the microspheres of BSA contain free amine groups on their surface. These functional groups interact with the carbonyl groups of the polyester, creating an amide bond, while a similar interaction with OH groups of the cotton are not as favorable. As a result of these interactions, many more seeds leading to the formation of microspheres occur on of the polyester, and fewer seeds happen on the cotton. When the bonded proteins form microspheres on the surface these many bonding sites will result in smaller microspheres, while the few bonding places on cotton lead to the full growth of 0.8–1.0 micron spheres.

The reason why the bubble does not grow on wool is due to an interaction between the cystein's S–H groups on the wool and the S–H of the BSA, and the formation of S–S bonds. This process inhibits the formation of S–S bonds between the BSA molecules.

4. Conclusion

Using sonochemical radiation, we have succeeded, for the first time, in attaching a proteinaceous (BSA and/or casein) microsphere to cotton and polyester fabrics by a one-step process. The BSA PMs were found to be stable for more than 9 months on cotton and polyester surfaces. The sizes of microspheres anchored to cotton and polyester fabrics are different: 800–1000 nm on cotton and 60–120 nm on polyester. This could be explained by the difference in the chemical structure of the fabrics. The stability of bonded spheres under ambient conditions of using and wearing the textiles was measured by using dyeing and washing under tests (modified Lowry method). By this technique we have measured the bond strength between proteins and fabrics. The results show that proteinaceous microspheres bound to polyester remain bound to the fabric even after repeated washings in a washing machine. In regard to cotton, only a small amount of PMs were found on the fiber surface after repeated washings. Using glutaraldehyde will keep the microspheres attached to cotton, as well as polyester, even after repeated washings. It is therefore suggested these coated bandages can be used either for one-time application or for repeated use.

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