Art Conservation

DOI: 10.1002/anie.200904244

Nanoscience for Art Conservation: Oil-in-Water Microemulsions Embedded in a Polymeric Network for the Cleaning of Works of Art**

*Emiliano Carretti, Emiliano Fratini, Debora Berti, Luigi Dei, and Piero Baglioni**

Scientific[1] and technological interest[2] in microemulsions arises from the possibility of controlling through confinement the activity of hydrophilic/hydrophobic molecules in a nonpolar or polar matrix.[3] The microstructural properties of microemulsions[4] have been characterized extensively; investigations into the application of microemulsions have mainly been focused on their use as nanoreactors in catalysis[5] and biocatalysis,[6] and their use in drug delivery.[7] Our research group has explored their application for the conservation of cultural heritage and designed novel systems containing low amounts of volatile oils as low-impact cleaning tools for the removal of aged polymeric coatings from the surface of paintings.[8] In spite of the well-established importance of direct microemulsions[9] in many technological fields[10] and the ecological relevance of some environmentally friendly applications,[11] the applicative potential of oil-in-water microemulsions (o/w μE) embedded into an aqueous polymeric dispersion,[12] or bicontinuous microemulsions in which the oil phase is gelled by means of a low-molecular-weight gelator,[13] is still underestimated.

Herein we report on a previously studied *p*-xylene-in-water microemulsion (M1; see the Supporting Information for the composition) embedded in a hydrophobically modified hydroxyethylcellulose (hmHEC, 2% w/w) aqueous network. Such systems, owing to their confinement capacity and high viscosity, present many applicative advantages in the cleaning of a work of art with respect to traditional methods: 1) the penetration of the cleaning agent into the porous matrix constituting the bulk of the painted layer is minimized as a result of the very high viscosity; 2) there is a drastic decrease in environmental impact, since the microemulsion is mainly composed of water (more than 85% w/w), and the evaporation of the volatile active oil-dispersed phase (*p*-xylene) is reduced by the high retention of the hmHEC microemulsion system; 3) residues can be removed readily from the paint surface; 4) these systems are optically transparent, and the cleaning action can be monitored visually and controlled during the application.

The idea that underpinned this study was to produce a complex system in which the structure and superior performance of the microemulsion were preserved, and the diffusion of its droplets was controlled by the mesh size and viscosity of the polymeric network. With this view, we analyzed possible changes induced by hmHEC in the nanostructure of the o/w μE and studied the interactions between the microemulsion embedded in the hmHEC network (M1/hmHEC) and the organic materials to be removed from the surface of the works of art.

One-dimensional small-angle X-ray scattering (SAXS) intensity distributions were obtained as a function of the scattering vector, Q, for the polymer solution (2% w/w hmHEC in water), the microemulsion M1, and the embedded microemulsion M1/hmHEC from the azimuthally averaged 2D isotropic patterns (Figure 1). The scattered intensity for M1 shows a very well defined correlation peak typical of the paracrystalline ordering resulting from repulsive electrostatic interactions between the charged oil droplets.[14] In contrast, the scattered-intensity distribution of the aqueous hmHEC solution is consistent with the form factor of a swollen polymer chain (Figure 1).[15] When hmHEC is added to M1, the peak observed for M1 persists, and its width is almost unchanged. This result suggests that the polymer has a

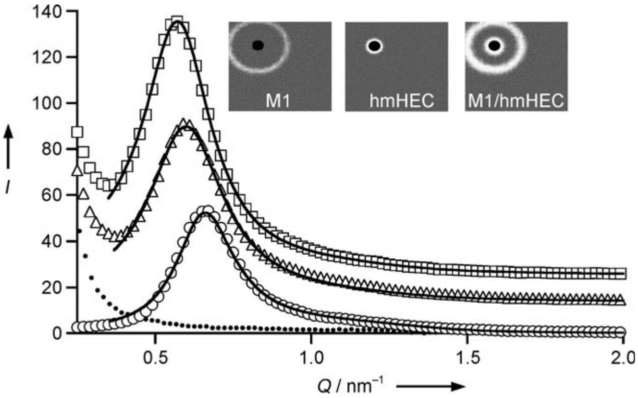

Figure 1. SAXS intensity distribution of hmHEC (2 % w/w) in water (●), the microemulsion M1 (○), the microemulsion embedded in a hmHEC aqueous matrix (M1/hmHEC, △), and M1/hmHEC enriched with poly(ethyl methacrylate-co-methyl acrylate) (p(EMA/MA, 70:30, 0.001 wt%, □). The continuous lines are the best-fitting curves obtained with a model based on polydisperse spheres with a core–shell structure. The interactions are mediated by screened Coulomb repulsions (see the Supporting Information). Images at the top: 2D SAXS intensity distribution for the microemulsion M1 (left), hmHEC (2 wt%) in water (middle), and M1/hmHEC (right).

---

[*] Dr. E. Carretti, Dr. E. Fratini, Dr. D. Berti, Prof. L. Dei, Prof. P. Baglioni
Department of Chemistry and CSGI, University of Florence
Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence (Italy)
Fax: (+39) 055-457-3032
E-mail: baglioni@csgi.unifi.it

[**] We thank Dr. B. Santi and Dr. A. Bagnoli of the "Soprintendenza per i Beni Artistici, Storici ed Etnoantropologici per le Provincie di Siena e Grosseto" and the conservators P. De Santis, S. Belle', F. Iacopini, and P. Pecorelli. Financial support from the Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase (CSGI) and MIUR is acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200904244.

negligible screening effect on the charged droplets and, more important to the aim of the present study, that the nanostructure of the microemulsion is retained. This feature is very important, because the efficacy of this system as a cleaning tool relies on the presence of nanodroplets in the microemulsion.

Further confirmation of the persistence of the main structural features of the microemulsion in the polymeric network can be deduced from differential scanning calorimetry (DSC) patterns (Figure 2). An intense peak occurs for all systems as a result of the melting of bulk water (Figure 2, top). However, two additional peaks are present for M1 and M1/hmHEC (LμE1, LμE2 and GμE1, GμE2; Figure 2, bottom) at temperatures well below 0°C. These transitions can be attributed to the melting of two different populations of water of hydration that are already present in the aqueous o/w microemulsion formulation M1. The presence of these two peaks after the addition of the polymer suggests that the nanostructure of M1 is retained in the presence of the polymeric network.

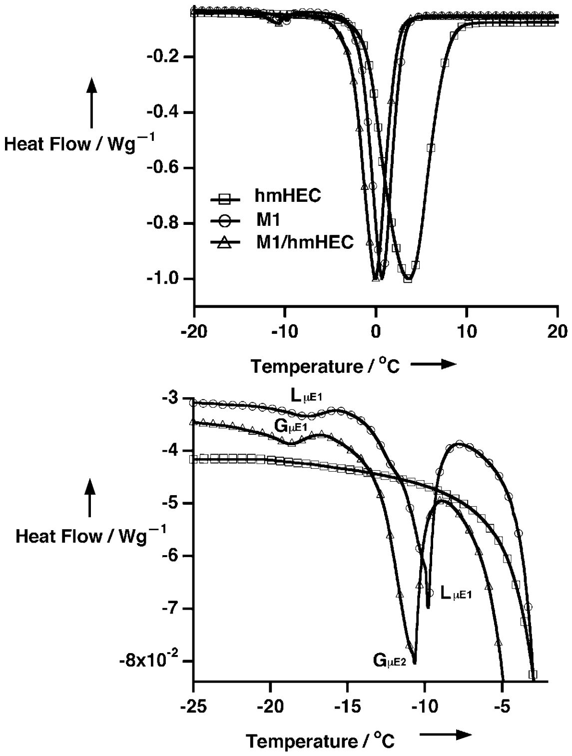

Figure 2. DSC curves obtained for M1 (○), M1/hmHEC (△), and hmHEC (2 wt %, □) in the range from −20 to 20°C (top) and −25 to −1°C (bottom).

The SAXS investigation showed that structural changes in the nanodroplets occur as a result of their confinement in the hmHEC network, as indicated by the change in the position of the peak. The shift of the peak to lower values of the scattering vector Q in the presence of hmHEC suggests a slight increase in the average interparticle spacing[16] as a result of the confinement of M1 in the hmHEC network. This behavior is clear evidence that nanodroplets and the cellulose network interact with each other at a certain level, as it was confirmed by the fitting of the SAXS curves (Table 1). The microemulsion is modeled as composed of polydisperse spheres with a core–shell structure: the core is composed of the surfactant (sodium dodecyl sulfate) and cosurfactant alkyl chains along with p-xylene, and the shell contains the polar head groups and the water of hydration (see the Supporting Information). After the loading of the liquid microemulsion in hmHEC, minor structural changes occurred. In particular, whereas the thickness of the shell remained unchanged, both the polydispersity[17] and the mean size of the core particles increased (Table 1).

Table 1: Structural parameters extracted from SAXS analysis of the microemulsion M1, the M1/hmHEC system, and M1/hmHEC with poly(ethyl methacrylate-co-methyl acrylate) (70:30, 0.001 wt %, M1/hmHEC/p(EMA/MA)).

	M1	M1/ hmHEC	M1/hmHEC/ p(EMA/MA)
core radius [nm]	2.38 ± 0.1	2.65 ± 0.1	2.77 ± 0.1
shell thickness [nm]	0.55 ± 0.1	0.55 ± 0.1	0.55 ± 0.1
polydispersity (± 0.02)	0.26	0.30	0.35
charge [*e*]	33 ± 2	32 ± 3	35 ± 1
equivalent radius [nm]	3.30 ± 0.1	3.57 ± 0.1	3.75 ± 0.1

The slight increase in the droplet size and polydispersity could be attributed to the partial inclusion of the hydrophobic side chains of the cellulose molecules into the nanodroplets (Figure 3), in analogy to previous findings for micellar solutions.[18]

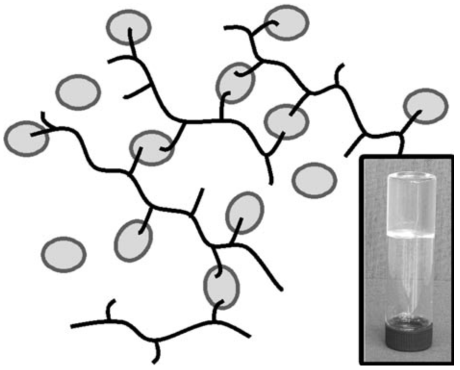

Figure 3. Schematic illustration of hmHEC (black) with o/w microemulsion nanodroplets (gray). A photograph of an equilibrated sample of M1/hmHEC is shown.

This hypothesis was confirmed by rheological analysis. The zero-shear viscosity η_0 (η_0 values were obtained by fitting the flow curves with the Cross equation;[22] see Figure 3 in the Supporting Information) of M1/hmHEC was found to be about three times that of the hmHEC system in the absence of the microemulsion; this difference confirmed the interaction of the microemulsion droplets with the polymer network (Figure 3).

Nowadays, one of the most important problems faced during the cleaning of works of art is the removal of organic materials, mainly acrylic polymers, applied in the past as consolidants or protective coatings. Unfortunately, their application induces a drastic alteration of the interfacial properties of the work of art[19] and leads to increased degradation. These organic materials must therefore be removed.

To simulate the removal of an acrylic polymer, we carried out a further SAXS investigation on M1/hmHEC in the presence of poly(ethylmethacrylate-co-methylacrylate) (p-(EMA/MA), 70:30), one of the most popular polymers in conservation.[20] At a p(EMA/MA) concentration of 0.001 wt %, no phase separation was observed. The main effects of the addition of the acrylic copolymer were an increase in polydispersity and a further shift of the size distribution of the microemulsion droplets toward higher values; the changes in these properties indicate that an interaction between M1/hmHEC and p(EMA/MA) occurs (see Figure 1 and Table 1).

The efficacy of the M1/hmHEC system as a cleaning agent was tested on a wall-painting surface (Santa Maria della Scala Sacristy, Siena, 15th century) coated with 35 year old p(EMA/MA) from a previous restoration treatment. Figure 4 shows a picture of the region of the painting in which the cleaning test was carried out. The grazing-light image (bottom right) taken after treatment with M1 embedded in hmHEC and subsequent washing with deionized water shows the complete disappearance of the glossy effect due to the presence of the copolymer film. This image indicates macroscopically that the cleaning system was appropriate for removing the aged coating. FTIR reflectance analysis of the cleaned surface (see Figure 1 in the Supporting Information) confirmed that the aged p(EMA/MA) layer had been removed.

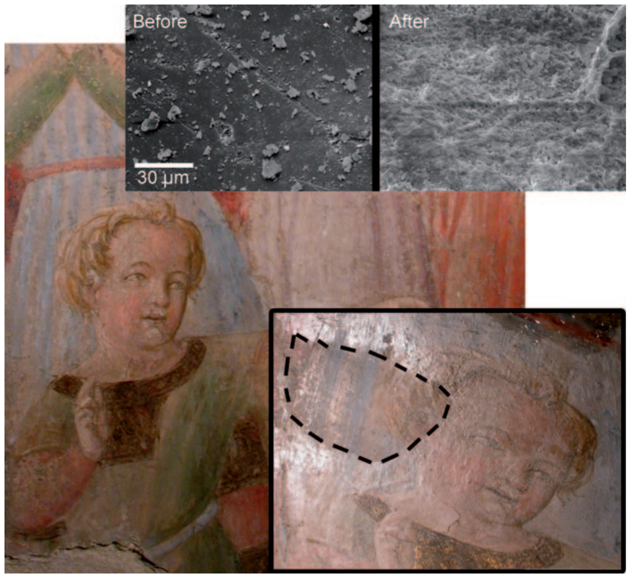

Figure 4. Detail of the wall painting (Santa Maria della Scala Sacristy, Siena, Italy) on which the removal of p(EMA/MA) with the M1/hmHEC system was tested. Bottom right: grazing-light photograph of part of the painting after the application of the cleaning system (see the region within the dashed line). Top: SEM images before and after polymer removal.

The surface morphology was also investigated by scanning electron microscopy (SEM; Figure 4). The aged polymer coating makes the surface “smooth”, with very low roughness relative to that of the cleaned surface; the texture of the cleaned surface resembles that of an original mortar (Figure 4, top right). Furthermore, energy-dispersive X-ray (EDX) analysis indicated that no traces of sodium were present; thus, surfactant residues did not remain on the surface of the work of art.

Another potential innovative application of this system is the removal of aged organic varnishes from the surface of easel paintings or gilded surfaces, as an alternative to gels traditionally used in conservation.[21] This further possibility was tested on an 18th century gilded frame with a layer of a natural aged varnish from a previous conservation treatment. The image in Figure 5 shows clearly that the surface dark patina was removed completely in the region where the test was carried out. The removal of this patina was also confirmed analytically by FTIR (see Figure 2 in the Supporting Information): a strong decrease in intensity was observed for all signals associated with the aged varnish.

Figure 5. A gilded 18th century frame with a surface layer of a degraded natural varnish (dark patina) before (left) and after (right) the application of M1/hmHEC.

We can conclude that microemulsions embedded in an aqueous polymeric network enable the complete removal of an aged p(EMA/MA) layer. This effective method is simpler and less invasive than traditional methods.[21] Microemulsions embedded in aqueous polymeric networks combine the main advantages of o/w microemulsion systems (a decrease in environmental impact owing to minimization of the quantity of the organic solvent and enhancement of detergency) with the versatility of polymer-solution technology and straightforward manipulation of the material. A further advantage offered by this approach is the broad field of application: for the first time the application of water-based cleaning systems has proved to be effective for the removal of organic materials from both wall-painting and easel-painting surfaces. For these reasons, oil-in-water microemulsions entrapped in aqueous polymeric networks can be considered to be among the most promising low-impact cleaning agents for works of art.

Experimental Section

M1/hmHEC was obtained according to a procedure described in the Supporting Information.

SAXS was performed with an apparatus described previously.[8f] SEM images were obtained with a Stereoscan S360 instrument. FTIR spectra were recorded in the microreflectance mode with a BioRad FTS-40 spectrometer equipped with a BioRad UMA500 microscope (MCT detector). DSC experiments were carried out under a nitrogen atmosphere with a TA Instruments Q1000 differential scanning calorimeter by using sealed steel pans. Rheological measurements were performed on a Paar Physica UDS 200 rheometer operating in controlled shear stress mode. For further details, see the Supporting Information.

Received: July 30, 2009
Revised: September 24, 2009

Keywords: art conservation · microemulsions · polymers · surface analysis · small-angle X-ray scattering

[1] a) G. Capuzzi, P. Baglioni, C. Gambi, E. Sheu, *Phys. Rev. E* **1999**, *60*, 792–798; b) C. Gambi, R. Giordano, M. Laurati, L. Lanzi, R. Pini, P. Baglioni, *Appl. Phys. A* **2002**, *74*, 377–379.

[2] a) M. Bonini, A. Wiedenmann, P. Baglioni, *Physica A* **2004**, *339*, 86–91; b) A. Ledo-Suárez, J. Rivas, C. F. Rodríguez-Abreu, M. J. Rodríguez, E. Pastor, A. Hernández-Creus, S. B. Oseroff, M. A. López-Quintela, *Angew. Chem.* **2007**, *119*, 8979–8983; *Angew. Chem. Int. Ed.* **2007**, *46*, 8823–8827; c) J. Eastoe, S. Gold, S. Rogers, P. Wyatt, D. C. Steytler, A. Gurgel, R. K. Heenan, X. Fan, E. J. Beckman, R. M. Enick, *Angew. Chem.* **2006**, *118*, 3757–3759; *Angew. Chem. Int. Ed.* **2006**, *45*, 3675–3677; d) M. Bonini, U. Bardi, D. Berti, C. Neto, P. Baglioni, *J. Phys. Chem. B* **2002**, *106*, 6178–6183.

[3] a) E. Ruckenstein, *Adv. Colloid Interface Sci.* **1999**, *79*, 59; b) *Handbook of Applied Surface and Colloid Chemistry* (Ed.: K. Holmberg), Southern Gate, Chichester, UK, **2002**; c) M. Bourrel, R. S. Schechter, *Microemulsions and Related Systems*, Marcel Dekker, New York, **1988**; d) M. Kahlweit, G. Busse, B. Faulhaber, H. Eibl, *Langmuir* **1995**, *11*, 4185–4187; e) P. G. De Gennes, C. Taupin, *J. Phys. Chem.* **1982**, *86*, 2294–2304.

[4] a) *Microemulsions: Background, New Concepts, Applications, Perspectives* (Ed.: C. Stubenrauch), Chichester, UK, **2009**; b) M. Gradzielski, *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 263–269; c) C. Petit, T. Zemb, M. P. Pileni, *Langmuir* **1991**, *7*, 223–231.

[5] R. Abu-Reziq, D. Avnir, J. Blum, *Eur. J. Org. Chem.* **2005**, 3640–3642.

[6] a) H. Stamatis, A. Xenakis, *J. Mol. Catal. B* **1999**, *6*, 399–406; b) T. J. Jenta, G. Batts, G. D. Rees, B. H. Robinson, *Biotechnol. Bioeng.* **1997**, *53*, 121–131.

[7] a) M. J. Lawrence, *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 826–832; b) Y. Zhu, L. Y. Zheng, *J. Drug Delivery Sci. Technol.* **2006**, *16*, 55–58; c) S. Kantaria, G. D. Rees, M. J. Lawrence, *J. Controlled Release* **1999**, *60*, 355–365; d) G. H. Desai, *Drug Dev. Res.* **2004**, *63*, 33–40.

[8] a) E. Carretti, R. Giorgi, D. Berti, P. Baglioni, *Langmuir* **2007**, *23*, 6396–6403; b) E. Carretti, B. Rosenzweig, M. Picollo, P. Baglioni, L. Dei, *Appl. Phys. A* **2006**, *83*, 669–673; c) E. Carretti, L. Dei, P. Baglioni, *Langmuir* **2003**, *19*, 7867–7872; d) E. Carretti, B. Salvadori, P. Baglioni, L. Dei, *Stud. Conserv.* **2005**, *50*, 128–136; e) M. Bonini, S. Lenz, R. Giorgi, P. Baglioni, *Langmuir* **2007**, *23*, 8681–8685; f) M. Bonini, S. Lenz, E. Falletta, F. Ridi, E. Carretti, E. Fratini, W. Albrecht, P. Baglioni, *Langmuir* **2008**, *24*, 12644–12650; g) R. Giorgi, P. Baglioni, *Soft Matter* **2006**, *4*, 293–303.

[9] E. Sheu, P. Lo Nostro, G. Capuzzi, P. Baglioni, *Langmuir* **1999**, *15*, 6671–6676.

[10] a) A. Shukla, R. H. H. Neubert, *Colloid Polym. Sci.* **2006**, *284*, 568–573; b) J. Barton, I. Capek, *Macromolecules* **2000**, *33*, 5353–5357.

[11] a) F. L. Chen, Y. Wang, F. N. Zheng, Y. Wu, W. Liang, *Colloids Surf. A* **2000**, *175*, 257–262; b) N. Garti, A. Yaghmur, A. Aserin, A. Spernath, R. Elfakess, S. Ezrahi, *Colloids Surf. A* **2003**, *230*, 183–190.

[12] R. Lapasin, M. Grassi, N. Coceani, *Rheol. Acta* **2001**, *40*, 185–192.

[13] C. Stubenrauch, R. Tessendorf, A. Salvati, D. Topgaard, T. Sottman, R. Strey, I. Lynch, *Langmuir* **2008**, *24*, 8473–8482.

[14] G. Colafemmina, D. Fiorentino, A. Ceglie, E. Carretti, E. Fratini, L. Dei, P. Baglioni, G. Palazzo, *J. Phys. Chem. B* **2007**, *111*, 7184–7193.

[15] P. Debye, *J. Phys. Colloid Chem.* **1947**, *51*, 18–32.

[16] S. H. Chen, E. Sheu, J. Kalus, H. Hoffmann, *J. Appl. Crystallogr.* **1988**, *21*, 751–769.

[17] M. Kotlarchyk, S. H. Chen, *J. Chem. Phys.* **1983**, *79*, 2461–2469.

[18] S. Panmai, R. K. Prud'homme, D. G. Peiffer, S. Jockusch, N. J. Turro, *Langmuir* **2002**, *18*, 3860–3864.

[19] E. Carretti, L. Dei, *Prog. Org. Coat.* **2004**, *49*, 282–289.

[20] a) *AA.VV. Capitolato Speciale d'Appalto per il Restauro della Cappella degli Scrovegni*, Roma, ICR, **2001**; b) O. Chiantore, M. Lazzari, *Polymer* **2001**, *42*, 17–27.

[21] R. Wolbers, *Cleaning Painted Surfaces: Aqueous Methods*, Archetype Publications, London, **2000**.

[22] H. A. Barnes, *A Handbook of Elementary Rheology*, University of Wales, Aberystwyth, **2000**, p. 56.