

EGDM Foam Shell Status Report (TAT 95-049)

**S. Lambert
G. Overturf
B. Cook
D. Schroen-Carey**

June 27, 1995



This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (615) 576-8401, FTS 626-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Date: June 27, 1995 TAT 95-049
To: Distribution
From: Stephen Lambert - STI
George Overturf, Bob Cook - LLNL
Diana Schroen-Carey - WJSA
Subject: EGDM Foam Shell Status Report

Summary:

We have completed an investigation of a low density foam made from ethylene glycol dimethacrylate (EGDM). We are confident that we have attained foam properties similar to those reported by Osaka, such as foam density (~60 mg/cc) and visibility of optical interference fringes. However, the material undergoes significant shrinkage during supercritical CO₂ drying which hinders additional target fabrication steps. We also discuss issues related to preparing shells using a droplet generator and overcoating this material with hydroxyethyl cellulose.

Introduction

The work reported here concerns our investigation of a new methacrylate-based foam shell material made from ethylene glycol dimethacrylate (EGDM). This work was motivated by reports from Osaka that the EGDM foam has a significantly improved interference fringe visibility compared to previous foams.^{1,2} The improved fringe visibility could potentially provide enough optical access to allow characterization of either liquid or solid D₂ or DT layers. Additionally, a method for overcoating methacrylate-based foam shells developed at Osaka has been used successfully at LLNL.³ There are two significant differences between this new formulation and that used in previous methacrylate based foams. The first is the choice of polymerizable monomer. EGDM is a difunctional monomer; previous foams were prepared from trimethylol propane trimethacrylate (TMPTMA), a trifunctional monomer. The second is that the polymerization initiation chemistry has been changed to an oxidation reduction system that operates at room temperature opposed to the previously used thermally activated AIBN.

This report is organized as follows: The section titled **Foam Preparation** describes the methods used to prepare foam samples. Compared to the TMPTMA foam, there are several differences involving solvents and water-phase reagents in addition to the change in monomer and initiator chemistry. In addition, however, the EGDM foam material has some inherent problems, most notable of which is significant shrinkage during CO₂ drying. The section titled **Foam**

¹Takagi, M., T. Norimatsu, Y. Izawa, and S. Nakai, "Development of Low Density, Low Atomic Number Foam Shell with Gas Barrier for Laser Fusion Target," MRS Meeting, Boston, MA, October 1994.

²Takagi, M., T. Norimatsu, Y. Izawa, and S. Nakai, "Development of Low Density, Low Atomic Number Foam Shell for Laser Fusion Target," 10th Target Specialists Meeting, Taos, NM, February 1995.

³Overturf, G., S. Buckley, R. Cook, D. Schroen-Carey, "Foam Shell Project Progress Report," August 22, 1994, TST 94-100.

Characterization describes the properties of the resulting foam material. Foam samples were prepared in the form of bulk cylinders, wedges and beads and characterized with respect to density, foam morphology, optical properties, and surface morphology (i.e., skinning). The section titled **Encapsulation Issues** describes process modifications in order to make shells by encapsulation using a droplet generator. The section titled **Overcoating** describes our results when we attempted to overcoat beads and shells with hydroxyethyl cellulose (HEC). The shrinkage which occurs during CO₂ drying appears hamper the ability to consistently overcoat this material. Lastly, the **Conclusions** section summarizes the accomplishments of this work and discusses the significant obstacles that would have to be overcome in order to produce a useful overcoated foam shell using this material.

Foam Preparation

The method we used to prepare the EGDM foam is similar to that used by Osaka.^{1,2} Bulk EGDM foam samples, in the form of cylinders and wedges, were prepared from a 3 wt% solution of EGDM dissolved in diethyl phthalate (DEP). Rather than using a thermal initiator at 70-90 °C, room-temperature redox-initiators were used at concentrations of 0.64 wt% benzoyl peroxide (BP) and 0.32 wt% N,N-dimethylaniline (DMA) (1:1 mole ratio of BP to DMA). DMA is a reducing agent of BP and facilitates the generation of free radicals at reduced temperatures.⁴ These concentrations represent a 5:1 mole ratio of monomer to initiator. Mixtures were rigorously degassed before and after the addition of DMA to the mixture of DEP, BP and EGDM to remove any dissolved oxygen. After degassing, the mixture was placed in ampoules or wedge molds where it gelled in 15-20 minutes. After as little as an hour or as long as overnight, solvent exchanges with ethanol were started. Afterwards, the ethanol was replaced with liquid CO₂ and subsequently removed as a supercritical fluid to leave the dry foam.

EGDM foam beads were prepared using a droplet generator without injection of an inner water phase. The gel phase consisted of essentially the above mixture, except that a 50:50 mixture (by weight) of DEP and dibutyl phthalate (DBP) was used as the solvent to more closely duplicate Osaka's formulation. Before the addition of DMA and the second degassing, the mixture was filtered to 0.2 μm using a syringe filter. The aqueous stripping fluid consisted of 1.5 wt% PVA as a stabilizer for the organic-phase droplets and, in some cases, water-soluble redox initiators. The water-phase redox initiators consisted of ammonium peroxydisulfate (APS) and its reducing agent, sodium bisulfite (SBS), at concentrations of 1.36 wt% and 0.64 wt%, respectively (1:1 mole ratio SBS:APS). In addition to reducing APS to form free radicals, SBS also removes dissolved oxygen.⁵ Organic-phase droplets were delivered from the generator into a beaker containing approximately 500 mL stripping solution and agitated using a stir blade. Since polymerization of the EGDM begins with the addition of DMA, the amount of time the organic phase can be run through the droplet generator is limited. Although the "bulk" organic phase (that does not come in contact with any aqueous phases) gels in about 15 minutes, beads in contact with the water phase took considerably longer, typically 45-90 minutes. After the beads fully gelled, the stripping solution was decanted off and the beads were washed with large amounts of distilled water and then placed in ethanol. The 300-1500 μm diameter beads were dried in the same manner as the bulk samples.

⁴Bamford, C.H., "Redox Initiators," Ch. 9 in *Comprehensive Polymer Science*, Vol. 3, Oxford: Pergamon Press, 1989, pp. 123-27.

⁵Braun, D, H. Cherdron, W. Kern, *Techniques of Polymer Syntheses and Characterization*, New York: Wiley-Interscience, 1971, pp. 129-31.

The preparation of EGDM foam shells is discussed in the section on Encapsulation Issues.

Foam Characterization

Density

Bulk samples made from 3 wt% EGDM mixtures resulted in foam densities of 48-52 mg/cc, whereas foam beads had somewhat higher densities of 60-70 mg/cc. This spread in foam density reflects variations both within a batch and between batches. The density of the Osaka EGDM material was reported to be 59 mg/cc. In all cases, the final foam density is significantly higher than the formulation density which is 35 mg/cc. The greatest shrinkage occurs during the CO₂ drying step. This was ascertained by measuring the diameters of selected beads before (i.e., in ethanol) and after drying. Bead diameters were observed to decrease by ~20-25%, corresponding to volume reductions of about 48-58%. Hence, the observed shrinkage accounts for the discrepancy between observed and formulated foam density.

The source of the observed shrinkage is unclear; it can be caused by collapse of the foam structure (i.e., reduction in cell size) and/or deswelling of the fibrous interconnected solid-polymer material. Additionally, it is unknown whether the shrinkage occurs during the exchange of ethanol with liquid CO₂, or during depressurization when CO₂ is removed as a supercritical fluid.

Since we are still within the range of useful foam densities (<100 mg/cc) we prepared beads with an increased formulation density of ~65 mg/cc by increasing the monomer concentration to 6 wt%. Initiator concentrations were increased to keep the mole ratio of monomer to initiator at 5:1. The resulting beads had densities of 85-95 mg/cc and volume reductions of 38-42%. Hence, the higher density foam still shrinks significantly, but to a less extent than the lower density foam.

SEM analysis indicates that the morphology of the EGDM foam is similar to that of TMPTMA, as shown in Figure 1. However, the "filament" or "strut" thickness appears finer and the cell size of the EGDM foam appears smaller than that for the TMPTMA foam.

Optical Transparency

The optical properties of the foams were tested several ways. The transmission of 641 nm light was measured through different thicknesses of foam of varying geometry. Results are summarized in Figure 2. The EGDM wedge has about the same transmittance as the TMPTMA wedge, which are both much less transparent than the RF foam. However, EGDM beads were found to be more transparent than the EGDM and TMPTMA wedges.

The transmittance through EGDM beads was measured in two ways. First, transmittance was measured through the pole of beads of different diameter. Second, the transmittance was measured at successive positions along the mid-section of a single bead. For a given foam thickness, the transmittance for the second method was found to be less than the first, most likely due to lensing effects as light passes through curved surfaces. This curvature is minimized when measured through the pole. Extrapolating the results in Figure 2, we estimate the transmission through 200 μ m of this material to be 20-40%.

Since the beads gave promising values of transmittance, a second analysis measured the extent of edge blurring through this material due to scattering by the foam. The extent to which the edge is blurred by the foam can be observed by placing a bead at the edge of a piece of aluminum

foil on top of a glass slide, illuminating from underneath and focusing on the foil edge. As illustrated in Figure 3 for a 550 μm diameter EGDM foam bead, the edge does not appear blurred to any perceptible extent. The ability to observe edges through larger foam thicknesses or higher foam densities is limited by opacity rather than by blurring.

Lastly, interference fringes were observed in foam beads under 400 μm in diameter; one such bead is shown in Figure 4. Fringes were measured by reflection, so light passes through the foam twice. If measured by a single-pass technique, the fringes would most likely be more distinguishable. However, a significant amount of fringe distortion occurs indicating foam density variations within a bead; the level of fringe distortion also varied from bead to bead.

Skinning

SEM analysis indicates that beads prepared with aqueous-phase redox initiators possess a sub-micron thick skin. Skinning does not occur in the absence of the water phase initiators, but beads produced under these conditions have extremely rough and uneven surfaces. To achieve gelation in the absence of the water-phase redox initiators, the stripping fluid had to be rigorously degassed by boiling and bubbling argon through the solution. Surprisingly, a skin forms even when only SBS is added to the stripping solution. The skin surface with only the SBS present appears smoother than that formed when both SBS and APS are used. The difference in skin morphologies can be observed while the beads are still in ethanol (see Figure 5). Upon drying, shrinkage can cause splits or cracks to develop on the bead surfaces (see Figure 6).

Encapsulation Issues

Encapsulation using a droplet generator requires a few modifications in the foam preparation method. The organic (shell wall) phase must be closely matched in density with the core fluid (water) in order to reduce P1 defects; toluene was chosen to reduce the density of the organic phase. However, the amount of toluene added (~32 wt%) reduced the viscosity of the organic phase enough to destabilize the ungelled shells which collapsed 15-20 minutes after being formed. To circumvent this problem, the solvent was changed to a mixture of toluene (~24 wt%) and DBP, and 0.1 wt% SPAN 40 surfactant was added to the organic phase.

Additional modifications were related to increasing the rate of gelation of the organic phase. First, increases in viscosity associated with gelation help stabilize the preformed shell. Second, toluene appears to be lost during the gelation period making it important to gel the shells as quickly as possible to avoid densification. We attempted to increase the gelation rate two ways: (1) by increasing the monomer concentration and (2) by increasing the initiator concentration. All shells were made from solutions containing 6 wt% monomer. The mole ratio of monomer to initiator was decreased to 3:1. Under these conditions the time to run the solution through the droplet generator is restricted further to 7-10 minutes. Shells prepared using the lower density formulation either did not gel or did not have sufficient structural integrity to survive solvent exchanges.

Despite the above modifications, the shells took considerably longer than the bulk organic mixture to gel, typically about 40 minutes. During this period the shells would initially float near the top but eventually sink, most likely due to loss of toluene. Additionally, the resulting shells had large P1 defects (see Figure 7) indicating that the shell and core phases were no longer density matched.

The composition of the core fluid was also briefly explored. When SBS (0.64 wt%) was added to water, a skin was observed to form on the inner shell surface. Shells were also made using boiled, argon-degassed water as the core fluid, and their inner walls did not appear skinned.

Overcoating

Beads

EGDM beads made from 3 wt% monomer mixtures were overcoated with HEC using the same protocol as the TMPTMA shells; we refer to a previous report for a description of the overcoating process.³ The goal of these experiments was to see how foam shrinkage effects the ability to overcoat this material. Figure 8(a) shows an EGDM foam bead with ~30 μm HEC overcoat in 1,4-dioxane. Upon drying, both the foam and overcoat shrink. X-radiographs of overcoated beads are shown in Figure 9. In a few cases, the overcoat appears conformal to the foam [Figure 9(a)], but in many cases gaps exist where the foam and overcoat have separated [see Figure 9(b)].

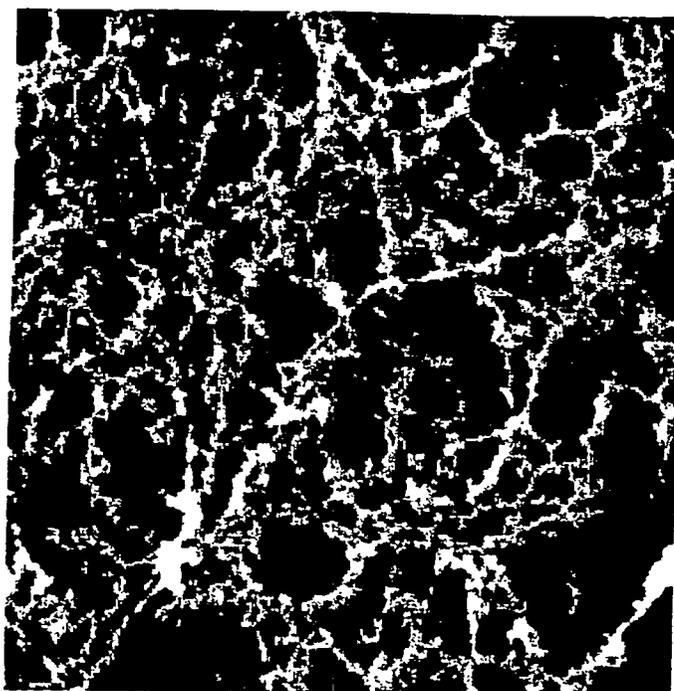
Shells

The EGDM shells made from 6 wt% monomer solutions were overcoated in the same manner as the beads. The shells were more fragile than the beads and a lot of breakage occurred. Figure 8(b) shows an EGDM shell with ~20 μm HEC overcoat in 1,4-dioxane. Upon drying, the shells behaved in a similar manner as the beads; in a few cases the foam and overcoat appear conformal [Figure 9(c)], but in most cases separation of the foam and overcoat was observed [Figure 9(d)].

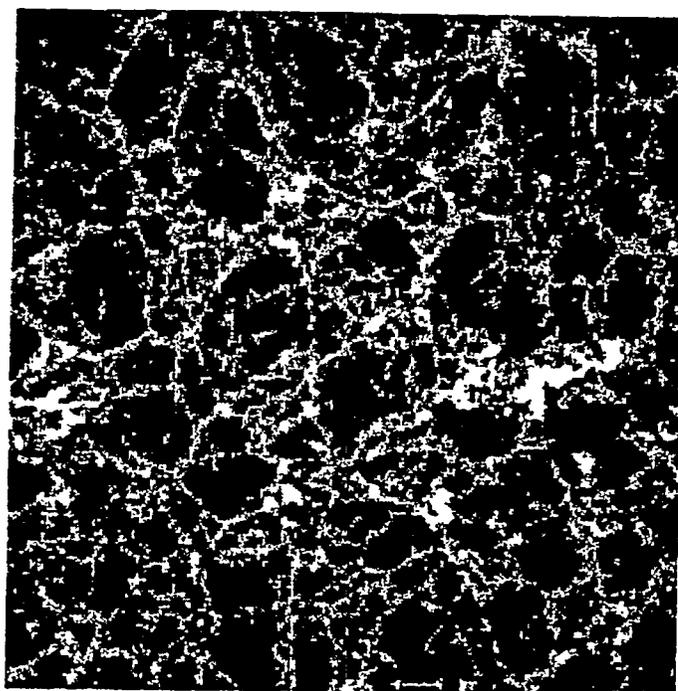
Conclusions

At this point we are confident that we have produced the EGDM foam material with properties similar to those reported by Osaka, i.e., density of ~60 mg/cc and greater optical transparency than the TMPTMA foam. Also we have investigated issues such as encapsulation using a droplet generator and overcoating, which (to our knowledge) have not yet been dealt with by Osaka.

However, there are several significant obstacles which must be overcome in order for this material to yield a viable foam shell. First, the source of the observed shrinkage must be determined and eliminated in some manner, since shrinkage appears to prevent this material from being adequately overcoated. This most likely would require a different solvent for supercritical drying. Second, although we were able to encapsulate this material, the foam shells are *not* made from the same material as the beads with the "optimal" density and transparency. Issues such as increasing the gelation rate and density matching the shell and core phases will require further investigation.



3.0 μm



3.0 μm

Figure 1. SEM micrographs comparing the foam morphology of the TMPTMA foam (top) and the EGDM foam (bottom).

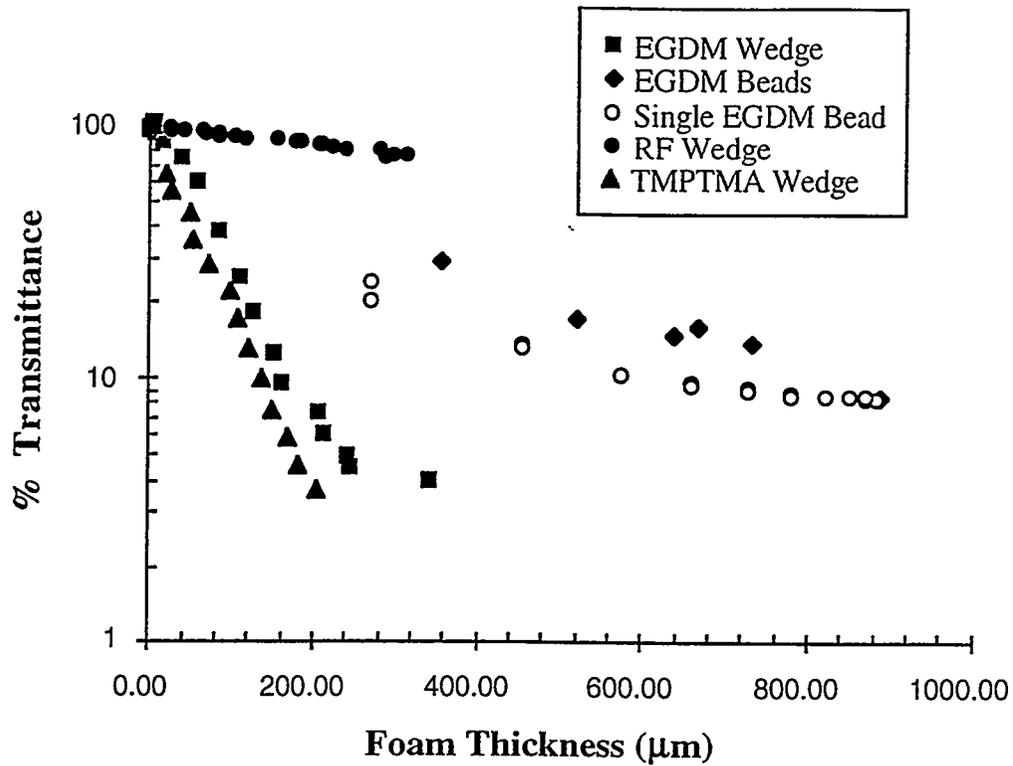


Figure 2. Transmittance (of 641 nm light) vs. thickness of various low density foam materials.



Figure 3. Determination of the amount of edge blurring through a 550 μm diameter EGDM foam bead. Although the %T through the bead pole is only about 22%, the foil edge below the bead is not greatly blurred by scattering through the foam.

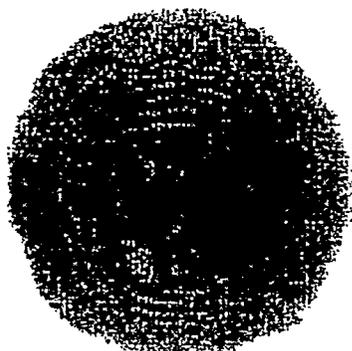


Figure 4. Interference fringes observed in a 330 μm diameter EGDM foam bead.

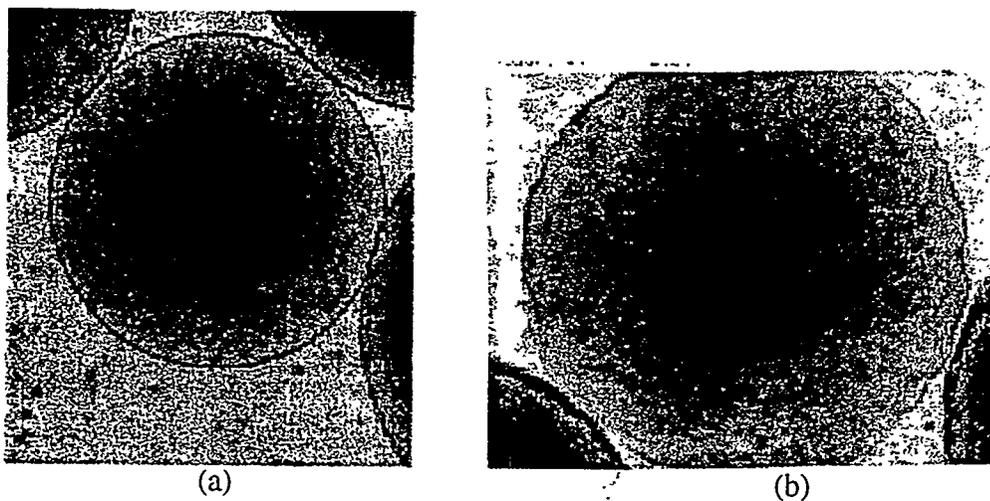
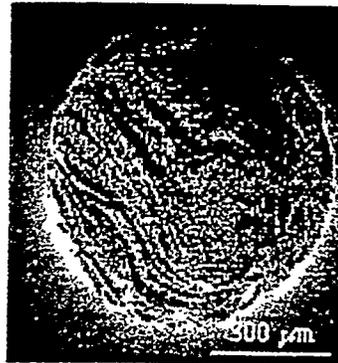
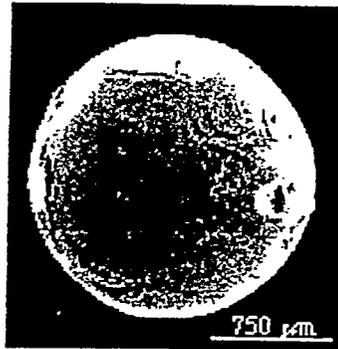


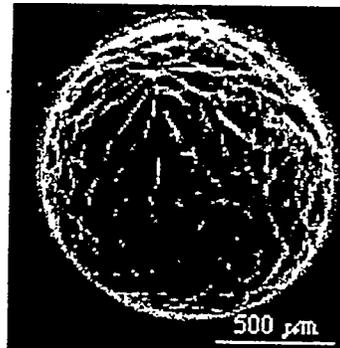
Figure 5. EGDM Beads in ethanol: (a) Prepared with only SBS in the water phase, (b) Prepared with both SBS and APS in the water phase, which appears to have a wrinkled surface.



(a)



(b)



(c)

Figure 6. SEM micrographs of the exterior surface of EGDM beads. (a) Prepared with no redox initiators in the water phase; (b) Prepared with only SBS in the water phase; (c) Prepared with both SBS and APS in the water phase.

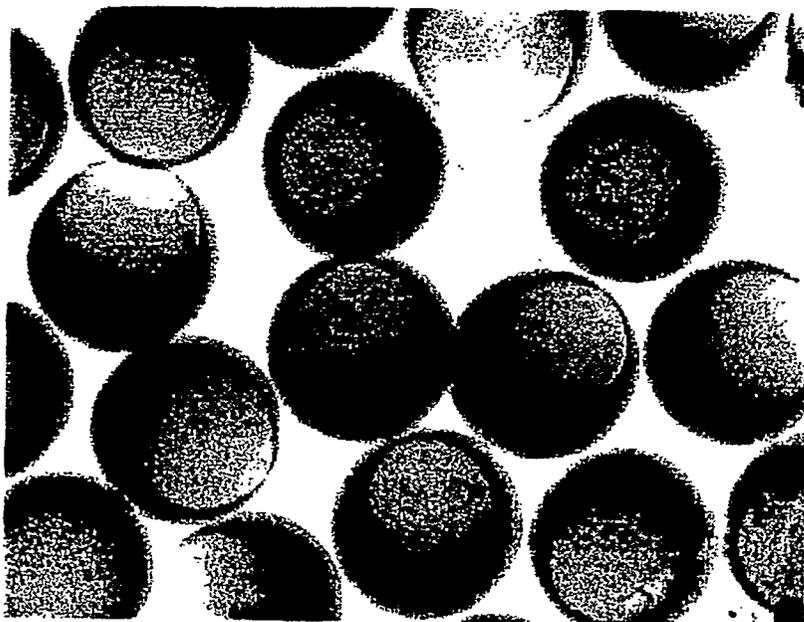


Figure 7. EGDM shells in ethanol.

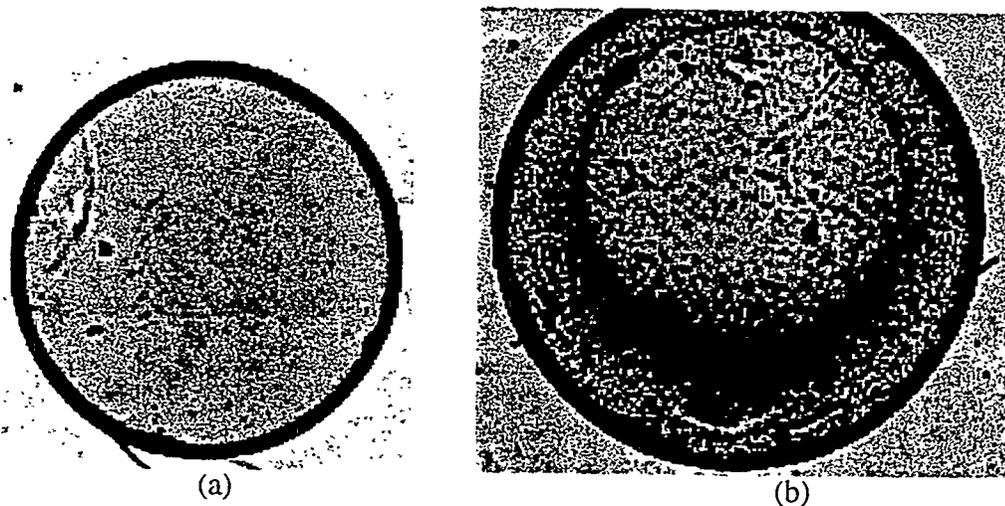


Figure 8. (a) Hydroxyethyl cellulose (HEC) overcoated EGDM bead and (b) HEC overcoated EGDM shell, both in 1,4-Dioxane.

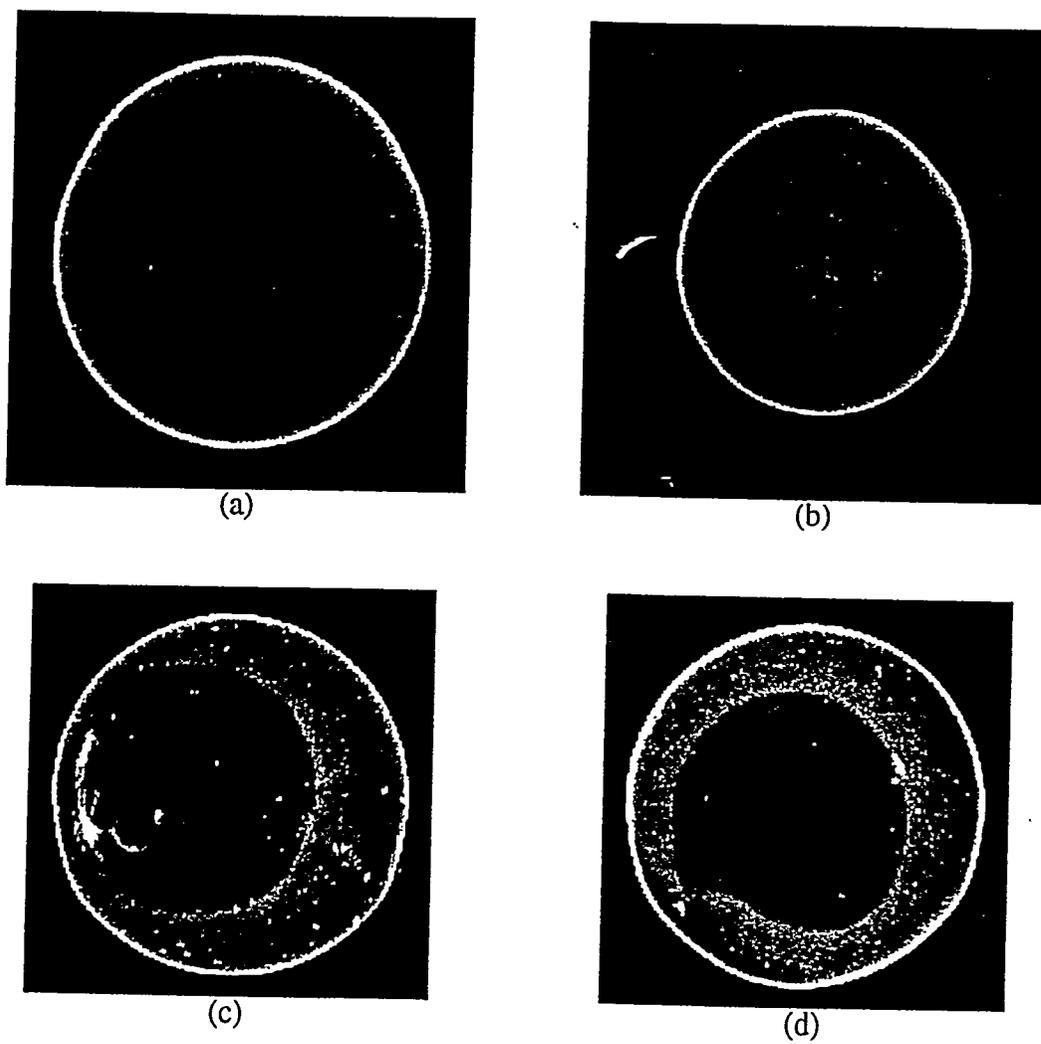


Figure 9. X-Radiographs of dry HEC overcoated (a,b) EGDM beads and (c,d) EGDM shells. In (b) and (d) gaps where the overcoat and foam have separated can be seen.