

Microencapsulation and Fabrication of Fuel Pellets for Inertial Confinement Fusion

R. L. NOLEN, Jr., and L. B. KOOL*

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Abstract □ Various microencapsulation techniques were evaluated for fabrication of thermonuclear fuel pellets for use in existing experimental facilities studying inertial confinement fusion and in future fusion-power reactors. Coacervation, spray drying, *in situ* polymerization, and physical microencapsulation methods were employed. Highly spherical, hollow polymeric shells were fabricated ranging in size from 20 to 7000 μm . *In situ* polymerization microencapsulation with poly(methyl methacrylate) provided large shells, but problems with local wall defects still must be solved. Extension to other polymeric systems met with limited success. Requirements for inertial confinement fusion targets are described, as are the methods that were used.

Keyphrases □ Fuel pellets—fabrication and microencapsulation, various microencapsulation techniques, glasses, and polymers compared □ Polymers—shell fabrication, fuel pellets, various microencapsulation techniques compared □ Microencapsulation—symposium, various microencapsulation techniques compared, glass and polymeric shells, microencapsulation of fuel pellets

The use of high-energy pulsed lasers to compress matter to extremely high densities (e.g., 1000 times its solid density) has been studied for some time (1). By compression of deuterium and of deuterium and tritium mixtures, thermonuclear fusion reactions are expected to be initiated for practical, commercial energy production. In principle, extremely high compression, with consequent heating, initiates fusion. Further heating by alpha-particles (whose range is drastically reduced by the compressed fuel) increases the reaction rates of deuterium and tritium to sustain and enhance the burn. High-energy (14.1 Mev) neutrons generated by these deuterium-tritium fusions become available as a usable source of nuclear energy to be exploited by capture in a heat-transfer medium such as lithium or by radionuclear chemistry for direct production of gaseous fuels such as hydrogen or methane.

DISCUSSION

Large-scale release of fusion energy has occurred on earth but only in the uncontrolled action of thermonuclear weapons. In attempts to employ high compression for the controlled release of thermonuclear energy, confinement difficulties arise because the material being compressed escapes before useful work can be performed. These confinement difficulties are diminished if compression is accomplished rapidly to take advantage of inertial confinement.

Experiments were conducted in these laboratories utilizing implosion experiments with spherical pellets. In a laser-driven implosion, the pellet surface is heated by the laser and ablated away while the cold inner surface is driven inward, thereby conserving momentum and causing compression of the fuel and subsequent thermonuclear fusion.

Target pellets are produced by filling hollow spherical shells of glass or polymer with deuterium or a deuterium-tritium mixture, taking advantage of the shell's permeability to hydrogen at elevated temperatures. Since these pellets are microcapsules, utilization and extension of existing microencapsulation technology are desirable to solve problems in the fabrication of microscopic, highly spherical, hollow shells that fulfill the stringent requirements of inertial confinement fusion.

Glass Shells—Glasses and polymers, because of uniquely suitable properties, are the principal shell materials chosen for inertial confinement fusion targets. Although considerable progress has been made in utilizing these properties, many areas for improvement remain. Glasses have extremely high tensile strengths, $\sim 7 \times 10^2 \text{ kgf/mm}^2$ ($\sim 1,000,000$

psi), when formed under carefully controlled experimental conditions. Therefore, one could expect to make glass shells of high tensile strength, $\sim 1.4 \times 10^2 \text{ kgf/mm}^2$ ($\sim 200,000$ psi) or higher.

A most important quality of glasses is the extremely low permeability at ambient temperature, which allows gas retention times in targets ranging from hours for silica to years for soda lime glasses. Permeability increases exponentially with temperature, however, allowing relatively rapid filling to equilibrium pressure at elevated temperatures (~ 10 hr

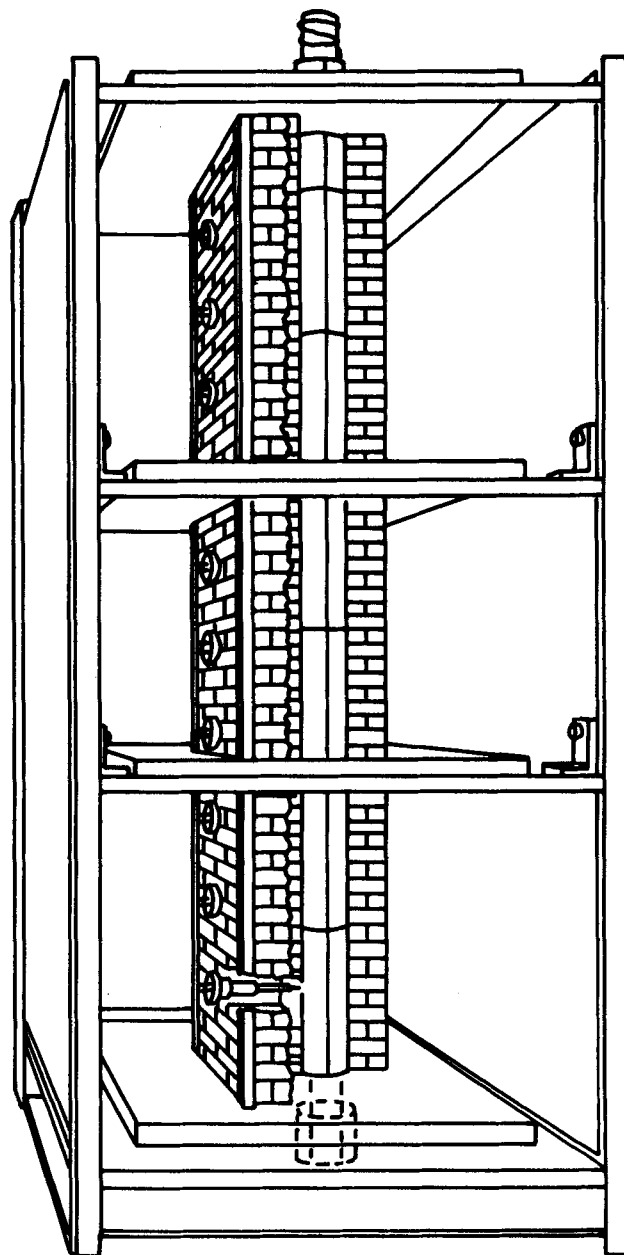


Figure 1—Glass-shell-blowing tower furnace. Coiled wire resistors in clamshell heaters surround an inner mullite tube (7.0 cm i.d. \times 2.1 m long). The tube end is terminated in a container of water. Temperature maximum was $1250^\circ (\pm 10^\circ \text{ for } 1.3 \text{ m})$.

for soda lime at 673 °K). The amorphous nature of glass permits easy fabrication of hollow shells. The large range of viscosities through which a glass proceeds helps to control the formation and freezing of the glass to produce a hollow shell configuration.

Another important property of glass is its ability to withstand low-energy ionizing radiation (such as tritium beta-particles) for extended periods without serious loss of strength.

Gel Synthesis—Microscopic glass shells suitable for use in targets for inertial confinement fusion research can be produced by at least two techniques. The first method utilizes the phenomenon known as glass reboil. Reboil can occur in glass that was manufactured to contain dissolved gases or gas-generating species that are produced or released when the glass is reheated to temperatures above its original forming temperature. For bulk glass, the resultant product of such a treatment is a foamed structure. If the glass is in particulate form, the reboil phenomenon can result in the formation of glass shells (2).

The second technique uses a solution-derived dried gel as the glass shell starting material. A blowing agent is incorporated in the solid gel during the solution stage prior to gelation. As described in a patent (3), a gel, derived from a water-glass-type solution, first is converted into particulate form and subsequently is heated in a furnace where glass shells are formed. The preparation of such gels from water or water-alcohol solutions of chemicals convertible to metal oxides was probably first reported by Roy (4) who employed them as precursors for glasses and synthetic minerals. The gel approach to glass manufacture is costly compared to conventional glass-forming techniques, but its unique characteristics make it attractive as the basis for additional research on glass shells (5, 6).

The gel is cured by heating for 14 hr at ~55°. The product then is air dried to remove most solvents and reaction by-products and finally is vacuum dried at 100°. The resulting particles, 0.1–1.0 cm in size, are crushed and sieved. This crushed and sieved material will be referred to as "metal-organic gel."

The gel technique and the dried particulates it provides have disadvantages as well as advantages. The disadvantages include: (a) restrictions on glass composition arising from incompatibility of certain metal-organic reagent combinations; (b) the metastable state of the solutions, which requires careful control of reaction parameters to obtain homogeneous gels instead of precipitates with their accompanying segregation of glass precursor components; and (c) the presence of residual organic groups, which can result in the production of carbon in the glass shell, which is not removed during fabrication.

Important advantages are: (a) the variability of glass composition through any of three variations of the basic technique; (b) the capability of combining all glass precursors in a solution and thus achieving mixing on a molecular scale, an important consideration when producing individual gel particles weighing only nanograms; and (c) the homogeneous incorporation of a blowing agent. Carbon, converted to carbon dioxide in the drop tower, is the likely source of the blowing agent in the gel technique. Homogeneous distribution of carbon throughout the dried gel seems highly probable since the carbon undoubtedly arises from residual ethoxy groups trapped in the silicon-oxygen-silicon network during gelation.

Glass shells are fabricated in a vertical tubular furnace or tower furnace (Fig. 1). The bottom of the mullite tube is sealed by immersion in water. This arrangement effectively prevents undesirable updrafts in the furnace tube and serves as a convenient collection medium for glass shells produced in the tube.

The shell fabrication procedure involves adding 20–30 mg of metal-organic gel at the top of the tower intermittently. Time intervals are varied from 0.25 to 1.0 min, depending on gel size. Shells formed in the furnace are collected and subsequently washed with water, washed and floated in isopropyl alcohol, and then dried.

Polymeric Shells—Glass shells are the most commonly used fuel containers because their physical properties are nearly ideal. Glass exhibits very low permeability, high tensile strength, optical clarity, a high melting point, abrasion resistance, and chemical durability, and it can be formed easily into shells.

Polymeric shells offer the following alternatives in physical properties that could be useful in the design of future laser fusion targets:

1. Organic polymers are considerably less dense than glass or metal.
2. Polymers can be copolymerized and blended to produce a wide range of physical properties and compositions.
3. Polymers offer the potential for low cost, high volume fabrication of shells.

A polymer must satisfy a number of prerequisites to be useful as a container for inertial confinement fuel. Since a target must contain the

gaseous fuel until illumination by the driver, low permeability to hydrogen isotopes is essential. Permeability coefficients range from 1.4×10^{-14} mole (standard temperature and pressure) $m^3/m^2 \cdot \text{SPa}$ for poly(propylene) to 3.0×10^{-2} mole (standard temperature and pressure) $m^3/m^2 \cdot \text{SPa}$ for silica (7). Some polymers exhibit characteristics similar to those of glass, but only a few exhibit permeability coefficients that approach those of glass [silica is ~100 times less permeable than poly(vinyl alcohol) at 293 °K].

Since shells usually are pressurized with 10 atm (1 MPa) of gaseous fuel, the shell material must have sufficient tensile strength to withstand the stress of high internal pressure. The tensile strength of poly(methyl methacrylate), representative of most common plastics, is 7 kgf/mm²; that of heat-treated poly(vinyl alcohol) is 110 kgf/mm² (8).

Elongation is another important property affecting the selection of polymers because of its relation to the dimensional stability of pressurized pellets. Elongation values range from 4% for poly(methyl methacrylate) to 600% for poly(vinyl alcohol) with water present. Typically, the elongation of fully hydrolyzed poly(vinyl alcohol) is 250%; however, with proper heat treatment, its elongation can be held to <2% (8). Typical glass elongation is 3% at break (8). Thus, heat-treated poly(vinyl alcohol) shells kept at a relative humidity of <5% can have elongations comparable to glass shells.

The ideal polymer must satisfy the conditions of high strength, low permeability to hydrogen, and low elongation. Poly(vinyl alcohol) satisfies these criteria better than any polymer investigated. Although most experiments have used poly(vinyl alcohol), considerable research has been devoted to chemical synthesis of new monomers and subsequent polymers such as polymethylol¹. Polymethylol has certain properties and characteristics superior to those of poly(vinyl alcohol); but since polymethylol is not soluble in useful solvents, it is not suitable for established shell fabrication methods. Some polymers cannot be spray dried or microencapsulated, and polymethylol appears to be one of them.

Two techniques to fabricate polymer shells were developed. These two techniques, spray drying and *in situ* polymerization microencapsulation, will be described.

Spray Drying—The spray-drying method of polymer shell fabrication involves spraying a solution of polymer and volatile solvent into a large, heated chamber. This method was developed initially to produce minute solid particles and was modified to produce hollow shells. Shell formation involves atomizing a polymer solution, thus forming droplets which, upon heating, concentrate and encapsulate a mixture of solvent, air, and atomizing gas. These various encapsulants form the inner cavity but diffuse through the shell wall upon expansion of the capsule when heated. Mass spectral analysis of the residual gas in polymer shells revealed only trace quantities of the solvent vapor.

The drying chamber consists of a square box (3.66 m high \times 1.22 m \times 1.22 m) constructed of galvanized steel sheet and insulated with 10.2 cm of fiber glass. Sixteen 1.5-m long electrical resistance heaters are affixed at regular intervals along the inside walls and supply heat to the chamber. Thermocouples are positioned at three different locations within the chamber to record the temperature profile. The 3.66-m chamber is of sufficient height to provide time for falling droplets within the size range of interest to be dried.

The atomizer² utilizes a high-velocity jet of gas as the atomization medium. The polymer solution is fed into the gas stream, which imparts shearing force to the solution to form droplets. This atomizer is designed to provide maximum variability in atomizing solutions over a wide range of viscosities. Interchangeable atomizer heads were employed in this study to accommodate the large range of viscosities and to produce droplets of predictable and reproducible size. The atomizer uses compressed gas to form the high velocity atomizing jet. The flow rates of the solution and gas are variable. Various polymers have been spray dried, of which nine have produced acceptable shells. Table I lists these polymers, their characteristic sizes, and their gas retention times.

Because the physical properties of polymers vary greatly, shells were produced under unique conditions for each polymer. Poly(methyl methacrylate) and polycarbonate, for example, form high quality shells quite readily. Both are hard, glassy, amorphous polymers, which form solutions of moderate viscosity in low boiling solvents. Poly(vinyl alcohol) and carboxymethylcellulose sodium form shells only under precisely controlled temperature and solution composition. Both polymers are water soluble, and their solutions are difficult to atomize because of high

¹ Polymethylol is poly(vinyl alcohol) with a hydroxyl group on each carbon atom.

² The atomizer is a modified version of the A-CUADF automatic airbrush manufactured by Paasche Airbrush Co.

Table I—Spray-Dried Polymeric Shells

Polymer ^a	Mean Diameter, μm	Mean Wall Thickness, μm	Maximum Diameter, μm	Maximum Aspect Ratio	R_t^b , hr	Gas ^c
PVA (10 lots)	56–116	1.2–2.9	182	134	32.0 28.0	D ₂ DT
PMMA (two lots)	96–567	1.6–2.0	744	402	<0.5	D ₂
CMC	83	2.2	108	78	35.0 15.0	D ₂ DT
VAVB	85	2.2	132	55	<0.5	D ₂
SAL	90	4.6	112	25	<0.5	D ₂
PVF	98	4.0	124	49	<0.5	D ₂
PC	112	2.4	142	71	<0.5	D ₂
PVB	90	2.7	116	59	<0.5	D ₂
HPM	67	1.2	92	85	<0.5	D ₂
PS	123	3.9	184	54	<0.5	D ₂

^a PC = polycarbonate. PVA = poly(vinyl alcohol). PMMA = poly(methyl methacrylate). CMC = carboxymethylcellulose sodium. VAVB = poly[(vinyl alcohol)-co(vinyl butyral)], 80% of which is butyral. SAL = poly[(styrene)-co(allyl alcohol)]. PVF = poly(vinyl formal). HPM = poly(2-hydroxypropyl methacrylate). PS = polystyrene. ^b Time for pressure to drop to 80% of $P_0 = 1 \text{ MPa}$. ^c D₂ = deuterium, and DT = deuterium-tritium mixture.

viscosity. Furthermore, water is difficult to remove quickly because of its high heat capacity and heat of vaporization.

A polymer solution that is too dilute forms solid beads or thin, collapsed shells. If a polymer solution is too concentrated or if the polymer has a high molecular weight (>100,000), the shear forces provided by the atomizing gas are insufficient, and long filaments result. For example, when high molecular weight poly(methyl methacrylate) is sprayed from dilute solution, only very fine fibers are obtained because of the high viscosity of the solution. If the atomized polymer is very crystalline, the polymer precipitates when sprayed, and no hollow particles are formed. When a solution of low molecular weight polyethylene in toluene is sprayed, opaque solid beads are formed. This polyethylene is highly crystalline and precipitates instead of forming a film.

The parameters of shell formation involved in spray drying a variety of polymers were investigated. The method can produce shells ranging from 20 to 740 μm . The size of a shell produced from a given droplet can be estimated (9):

$$D_2 = D_1 \left(\frac{d}{\rho d_s} \right)^{1/3} \quad (\text{Eq. 1})$$

where D_2 is the droplet diameter, D_1 is the capsule diameter, d is the capsule density, d_s is the solution density, and ρ is the weight fraction of the polymer solution.

The spray-drying method is versatile, and a broad range of shell sizes can be fabricated from numerous polymers. Many shells can be fabricated easily in a short time. The hardware is relatively safe to operate and easy to maintain, and the equipment and process can be integrated into an automatic system.

Coacervation Microencapsulation—Microcapsules containing a liquid internal phase have been considered both as possible fusion pellets and as expandable precursors of hollow shells. The patent literature is replete with descriptions of microencapsulation systems that produce liquid-containing microcapsules using coacervation microencapsulation.

Coacervated microcapsules generally exhibit sphericity and surface finish that are unsatisfactory for fusion pellets. Extensive experimentation with a urea-formaldehyde coacervation system has not yielded acceptable sphericity or surface finish.

In Situ Polymerization Microencapsulation—Another patent (10) described a process for producing thermoplastic microcapsules containing a liquid blowing agent. Heating of the microcapsules causes them to expand and form hollow particles. In this method, a solution is prepared consisting of a monomer, a free radical polymerization initiator, a low boiling liquid (used in the internal phase and as a solvent for the monomer and initiator), and additives (for tailoring molecular weight by chain transfer). This solution is added to an immiscible aqueous phase containing surfactants and a colloidal antiagglomerating agent.

Upon mechanical agitation, the monomer solution is dispersed as suspended droplets in the aqueous medium. The initiator causes the monomer to polymerize as a film on the outer surface of the droplet, thus forming a thin wall. As polymerization continues, the film thickens and grows internally while the internal phase is encapsulated. This process

continues, and the capsule wall thickens until all of the monomer and/or initiator is consumed.

After the polymerization process, the capsules are separated from the aqueous phase, washed, and sorted. When a capsule is heated above the glass transition point of the polymer, the capsules expand to form hollow shells due to the liquid-gas transition of the internal phase. The gaseous vapors of the internal phase escape by permeation as the wall thickness decreases and are replaced by air shortly after expansion, as verified by mass spectroscopy of the shell contents.

EXPERIMENTAL

All *in situ* polymerization microencapsulation experiments were run in a 1-liter resin kettle equipped with a variable-speed impeller, condenser, and nitrogen inlet. The resin kettle was immersed in a constant-temperature water bath.

The aqueous phase consisted of 300 ml of distilled water, 0.5 g of colloidal silica³, 3 g of 5% surfactant⁴, and 1 g of 2.5% sodium dichromate. The pH was adjusted to 4 with dilute hydrochloric acid.

The oil phase consisted of 100 g of methyl methacrylate, 35 g of neohexane (internal phase), 0.5 ml of dichlorodimethylsilane, and 1.42 g of free radical polymerization initiator⁵. This mixture was maintained at 35° in a constant-temperature bath.

The two phases were mixed vigorously at ~5000 rpm for 1 min; then agitation was stopped. After 2 hr, the reaction temperature started to rise because of autoacceleration. Ice was added to the kettle, and gentle agitation was provided to maintain a temperature below 37°. After 8 hr, capsules were isolated by filtration and washed several times. Capsules expanded upon heating in an oven at 175° for 5 min and then were placed in a 100° oven for several hours to allow out-permeation of the internal phase vapor.

RESULTS

The experimental procedure produced shells of 100–7000 μm . The size and wall thickness were controlled by the size of the stable droplet formed in the aqueous solution and the relative amounts of monomer and internal phase.

A narrow distribution of stable droplet sizes is obtained by using limited coalescence (10). In limited coalescence, colloidal particles, which are dispersed in the aqueous phase, collect on the surface of the suspended droplets. Droplets that are substantially covered by colloids are stable to coalescence. In a given droplet dispersion, the total droplet surface area is a function of the total volume of the dispersed liquid and the diameter of the droplets. In limited coalescence, the nonaqueous phase is dispersed as small droplets until they reach a critical limiting size, which depends on the amount of colloid present. The average size of a stable droplet is related directly to the aqueous phase composition by (10):

$$D = \frac{\pi dt V}{kW} \quad (\text{Eq. 2})$$

where D is the average diameter of the stabilized droplets in centimeters, t is the colloidal particle thickness in centimeters, V is the volume of the droplet phase in cubic centimeters, k is the swelling ratio of the colloid, d is the dry density of the solid colloid in grams per cubic centimeter, and W is the weight of solid colloid suspending agent in grams.

A more useful scaling relationship is (10):

$$D_1 W_1 = D_2 W_2 \quad (\text{Eq. 3})$$

This equation means that if a weight (W_1) of colloid producing capsules of average diameter (D_1) has been determined experimentally, the procedure can be tailored to produce capsules of another diameter (D_2) simply by adjusting the amount of colloid in the aqueous phase to an amount (W_2) in accordance with the ratio of diameters.

Early successful *in situ* polymerization microencapsulation experiments produced shells with poor inner surface uniformity. Upon microscopic examination, there appeared to be small polymer particles that were not incorporated into the wall. Apparently, a high molecular weight polymer formed late in polymerization after the capsule wall had appreciably hardened and thus could not merge with the wall. This hypothesis was supported in experiments with dichlorodimethylsilane, a potent polymerization chain transferring agent. With this agent, the amount of inner surface roughness decreased appreciably. Further im-

³ Ludox, DuPont.

⁴ Hyonic LA-90, Diamond Shamrock.

⁵ VaZo 33W, DuPont.

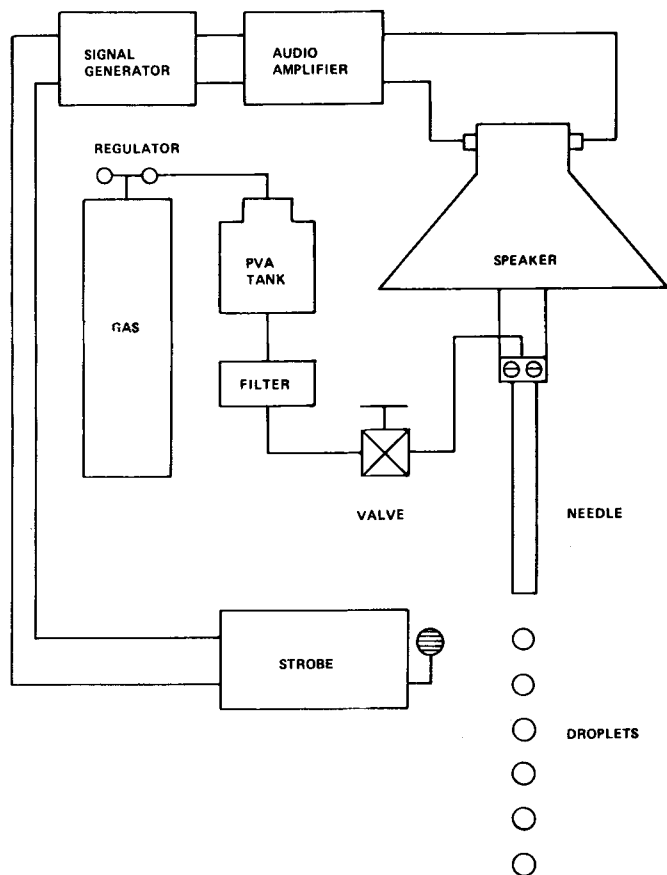


Figure 2—Schematic diagram of droplet generator. [PVA = poly(vinyl alcohol).]

provements may be achieved by modifying the polymerization kinetics.

Further polymeric shell research will be aimed at improving sphericity and increasing sizes. To this end, a device known as an acoustically modulated fluid jet has been designed and built (Fig. 2.) It is capable of producing uniformly sized droplets of polymer solution or melt. The solution to the problem of producing large (5 mm), hollow, spherical polymeric pellets will likely be solved through an understanding of uniform droplet production.

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Long-Term Studies of Microencapsulated and Adsorbed Influenza Vaccine Nanoparticles

JÖRG KREUTER ^{*} and EKKE LIEHL [‡]

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Abstract □ Incorporation of antigens into nanometer-sized polymer particles was recently shown to lead to a good adjuvant effect. An optimal antibody response with killed influenza virus antigens was achieved with 0.5% poly(methyl methacrylate). Long-term experiments showed prolonged antibody response of polymer adjuvants with incorporated or adsorbed influenza virus. Adsorption also yielded an optimal adjuvant effect with 0.5% poly(methyl methacrylate). The antibody response was accompanied by protection of the mice against infection with mice-adapted influenza virus. In addition, the polymer vaccines were more stable against temperature inactivation than were vaccines with aluminum hydroxide or without adjuvants.

Keyphrases □ Vaccine, influenza—virus antigen incorporated into and adsorbed onto polymer nanoparticles, vaccines with and without adjuvant compared for protection in mice and against heat inactivation □ Polymers—poly(methyl methacrylate) and aluminum hydroxide used as adjuvants in influenza vaccine, effect of polymer on protection against influenza in mice and heat inactivation □ Microencapsulation—symposium, incorporation of influenza virus antigens into polymer nanoparticles compared with their adsorption onto polymer nanoparticles, vaccines with and without adjuvant evaluated for protection against influenza in mice and heat inactivation

Nanocapsules or nanoparticles, first described a few years ago (1-4), are nanometer-sized delivery systems for biologically active materials. This biologically active material may be totally or partially encapsulated, or it may be attached to these particles by adsorption or through chemical bonding.

At present, there are three distinctly different methods for nanoparticle production (1). The first method is micelle polymerization (2). In this process, polymerization is carried out in micelles or micelle-like structures in which the biologically active material and the polymerizable material are present.