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Experimental studies of the deformation of a synthetic capsule in extensional flow

By K. S. CHANG† AND W. L. OLBRICHT
School of Chemical Engineering, Cornell University, Ithaca, NY 14853, USA

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Experiments are described to study the motion and deformation of a synthetic, liquid-filled capsule that is freely suspended in hyperbolic extensional flow. The capsule is a composite particle consisting of a viscous liquid drop surrounded by a thin polymeric membrane. The method used to fabricate capsules suitable for macroscopic flow experiments is described. The deformation of the capsule is measured as a function of strain rate for an extensional flow generated in a four-roll mill. The data agree well with results from small-deformation theory developed by Barthes-Biesel and co-workers, provided the deformation of the capsule is not too large. Using the theory to correlate the experimental data produces an estimate for the elastic modulus of the membrane that agrees reasonably well with the elastic modulus obtained by an independent technique. However, for sufficiently large strain rates, the membrane exhibits strain hardening and a permanent change in its structure, both of which are reflected in the shape of the capsule.

1. Introduction

This paper and the accompanying one (Chang & Olbricht 1993) describe experimental studies of the motion and deformation of freely suspended capsules in homogenous flows. Capsules are composite particles consisting of a liquid or solid interior surrounded by a thin membrane. This paper deals with liquid-filled capsules and their response when they are freely suspended in flow. Naturally occurring liquid-filled capsules are ubiquitous in biological systems, and synthetic liquid-filled capsules are used in many technological applications. A prominent example of a biological capsule is the red blood cell, which consists of a viscous hemoglobin solution surrounded by a thin lipid bilayer and associated protein networks. Synthetic capsules have been developed for many applications including time-release drug delivery, immobilization of enzymes, immobilization of cells for tissue culture, synthetic cells for artificial organs, artificial blood, emulsion stabilization against coalescence, and for specialized mass transfer control based on regulation of membrane permeability. The capsules used in some of these applications often have solid interior cores, but even in these cases encapsulation and processing may take place with the core in the liquid state. In view of the variety of applications, it is not surprising that the size of synthetic capsules varies from less than a micron up to several hundred microns.

Liquid-filled capsules that are used in processes involving flow present special problems in handling, because the capsules can deform in response to hydrodynamic stresses generated by the flow. In some circumstances, the capsule may align in preferred orientations with respect to streamlines of the flow. Also, the membrane is

† Present address: Kimberly-Clark, 2100 Winchester Road, Neenah, WI 54957-0999, USA.

free to rotate about the inner contents of the capsule, a motion that is often called 'tank-treading'. The degree of capsule deformation, the orientation of the capsule in the flow, and tank-treading of the capsule membrane depend not only on the viscosities of the liquids and the kinematics of the bulk flow, but also on the mechanical properties of the capsule membrane. Furthermore, flow-induced changes in capsule shape and orientation are reflected in the bulk rheological properties of suspensions of liquid-filled capsules, which exhibit non-Newtonian characteristics such as a shear-thinning viscosity in simple shear flow.

The mechanical properties of capsule membranes can play an important role in determining the suitability of capsules for specific applications. In some applications the capsules must be able to withstand specified levels of stress without undergoing irreversible changes in the properties of the membrane that could affect capsule performance. Indeed, loss of membrane integrity and capsule breakup due to stress exposure can limit the use of otherwise viable capsule formulations. Despite its importance, the mechanical performance of a capsule or capsule membrane is rarely taken into account in the design of capsule systems, probably because measuring the properties of capsule membranes *in-situ* poses a formidable challenge.

Describing the motion and deformation of capsules in flow bears a close resemblance, at least superficially, to the corresponding problem for immiscible liquid drops, which is the subject of a rich literature in low Reynolds number hydrodynamics. Solutions of the Stokes equations for flow inside and outside an immiscible drop and the flow-induced deformation of the drop can be used to derive exact constitutive equations for dilute emulsions. Experimental studies of drop deformation and breakup test the theoretical results, address problems that cannot be solved analytically, and are useful in developing correlations for multiphase process design, modelling, and scale-up. However, the results for liquid drops and emulsions cannot be applied directly to capsules and capsule suspensions, because of the membrane surrounding the capsule. The capsule membrane can support normal and shear stresses and, depending on its composition, may exhibit a rate-dependent response to an imposed strain.

An analysis of the motion and deformation of capsules suspended in flow has been presented in a series of papers by Barthes-Biesel and coworkers (Barthes-Biesel 1980; Barthes-Biesel & Chhim 1981; Barthes-Biesel & Rallison 1981; Barthes-Biesel & Sgaier 1985) and Brunn (1983). The development is based on a perturbation solution of the Stokes equations that lead to exact solutions of the motion and shape of a slightly deformed capsule in a general unbounded linear flow. The calculation follows methods that were used previously to determine the shape of an immiscible liquid drop in the limit of small deformations (e.g. Barthes-Biesel & Acrivos 1973*a*, *b*). The results for the capsule problem give its deformation and orientation as a function of certain constitutive properties of the capsule and of the parameters describing the flow. However, the constitutive properties of the capsule membrane are not known *a priori* and are difficult to measure in many instances of practical importance. Therefore, it seems appropriate to ascertain whether the relationships between capsule motion and membrane properties derived from small-deformation theory can be used to measure the properties of the membrane. For example, results from theory for a capsule suspended in simple shear flow (Barthes-Biesel & Sgaier 1985) suggest that experimental measurements of the capsule shape can be used to deduce precisely defined constitutive parameters of the capsule membrane. However, there are scant data available to corroborate predictions or to ascertain the practical limits of validity of the small-deformation theory. We are aware of no systematic studies that explore the response of a capsule for large deformations outside the limits of the asymptotic theory. By

comparison, the predictions of small-deformation theory for liquid drops have been tested extensively, and they have shown to be reasonably accurate even for highly deformed drops near breakup. We have conducted a series of experiments to evaluate critically the applicability of theoretical results to synthetic capsules formulated in our laboratory. The experiments employ large-scale model capsules of sufficient size, stability, and uniformity that their motion and shape in flow can be measured accurately. One of the goals of the experiment is to determine whether the measured shape of the capsules in flow can be used to determine the constitutive parameters of the capsule membrane. To do this without ambiguity, the values of constitutive parameters deduced from the flow experiment are compared with values obtained for the same capsule by a separate measurement based on a different experimental technique. Conditions are chosen intentionally to press the limits of the theory and to explore the response of the model capsules for large deformations where the theory is not expected to hold.

This paper focuses on model capsules in hyperbolic extensional flow generated in a four-roll mill. Experimental and theoretical results have demonstrated that extensional flows are especially efficient at deforming flexible particles. For example, an immiscible liquid drop of given size and composition undergoes a greater deformation in hyperbolic extension than it does in simple shear flow for the same nominal rate of deformation (Taylor 1934; Acrivos & Lo 1978; Barthes-Biesel & Acrivos 1973*a*, *b*; Hinch & Acrivos 1979, 1980; Rallison 1980, 1981; Rallison & Acrivos 1978). Furthermore, the deformation rate required to break liquid drops is smaller in extensional flow than in flows containing vorticity, such as simple shear flow. Indeed, for a viscosity ratio greater than about 4, a liquid drop does not break in simple shear flow regardless of the magnitude of the shear rate. However, drops with a viscosity ratio greater than 4 break in hyperbolic extensional flow for modest values of the dimensionless strain rate.

It seems reasonable to expect that similar considerations apply to the deformation of flexible capsules in linear flows. Of course, the most important difference between capsules and drops is the presence of the capsule membrane, which can rotate about the inner contents of the capsule. The motion of the membrane and the stress exerted on it depend in part on the kinematics of the bulk flow. For example, in simple shear flow, the capsule membrane rotates about the inner fluid with an angular speed that depends on the bulk shear rate. However, in a steady, purely extensional flow, the major axis of the deformed capsule aligns in the direction of the principal strain axis. Once the capsule is aligned in this direction, rotation of the membrane is impossible, owing to the symmetry of the flow. In both flows, simple shear and pure extension, the capsule may achieve a steady-state shape. However, which constitutive properties of the membrane influence the steady-state shape of the capsule depend on whether or not the membrane rotates. The small-deformation theory (Barthes-Biesel & Sgaier 1985) shows that in simple shear flow, the steady-state shape of a capsule with a viscoelastic membrane depends on the membrane viscosity, because the tank-treading motion of the membrane dissipates energy. The motion of the model capsules suspended in simple shear flow is examined in the accompanying paper (Chang & Olbricht 1993). The membrane viscosity plays no role in steady extensional flow because the membrane is stationary.

The experiments described in this paper are similar to those carried out by Barthes-Biesel (1991) and coworkers for a synthetic capsule, but the composition and characteristics of the capsule used in that experiment differ substantially from those of the capsules used here. A comparison of the results for the different capsules will help

illustrate how the response of the capsule in extensional flow can be used to interpret qualitative differences in the material properties of different capsule formulations, especially with respect to nonlinear responses of capsule membranes. Effects of nonlinear elastic behaviour of the capsule membrane have been investigated for small deformations by Barthes-Biesel (1980) and Barthes-Biesel & Chhim (1981). Li, Barthes-Biesel & Helmy (1988) extended these results numerically to large deformations in uniaxial extensional flow. Pozrikidis (1990) considered a similar problem for elastic membranes that preserve area during deformation in uniaxial extensional flow.

The studies cited above are motivated, at least in part, by an interest in the rheology of blood cells and blood cell suspensions. New experimental techniques developed to probe the mechanical properties of cellular membranes have shown that the red cell membrane exhibits an unusual combination of viscoelastic properties. Perhaps the most detailed information comes from experiments involving the aspiration of cells into micropipettes. Results show that the red cell membrane has a small elastic shear modulus, but it resists strongly any increase in its surface area. The membrane viscosity exhibits a two-stage behaviour. The cell advances into the pipette rapidly at first, implying a relatively low viscosity. However, the rate of advance then slows, suggesting that the viscosity for long times is much larger than its value early in the experiment. The rheology of the red cell membrane has been correlated with the physicochemical structure of the protein network that is intimately associated with the lipid bilayer.

Although this experiment is a prototype, insofar as it uses large-scale model capsules that are not intended for a specific technological application, the predicted relationships between capsule shape and membrane properties are expected to apply to broad classes of synthetic liquid-filled capsules. If these relationships can be corroborated for the model capsules, then it is likely that they could also be used to determine the membrane properties of technologically important capsule formulations, including micron-sized capsules in suspension, where deformation could be measured using polarized light techniques such as birefringence or dichroism.

2. Fabrication of the model capsules

The model capsules used in the experiments described here and in the accompanying paper must satisfy several requirements. The capsules must be sufficiently large that the time-dependent motion, shape, and orientation of an individual capsule can be measured accurately. The density of the capsule must be as close as possible to the density of the outer-phase fluid to minimize sedimentation during the experiment. If the capsules formed by some chemical reaction differ from each other in their material properties, then the flow experiments and any auxiliary experiments to measure membrane constitutive properties must be performed on the same capsule. This requires a capsule that is sufficiently robust to survive each experiment and handling between experiments. There must be no osmotic swelling of the capsule, which could alter its response in flow and could cause it to burst. Finally, the capsule properties must not depend on the chemical composition of the liquid in which the capsule is suspended.

The capsule fabrication process we have used is a modification of techniques described by Chang, MacIntosh & Mason (1966), Gutcho (1976), Thies (1982), Finch (1985), Mathiowitz & Cohen (1989*a*, *b*), and MacRitchie (1990), among others, to form capsules with a membrane composed of nylon and nylon derivatives. The capsule membrane is formed by an interfacial polymerization reaction on the surface of a liquid drop suspended in an immiscible liquid. Polydimethylsiloxane (silicone oil) was chosen

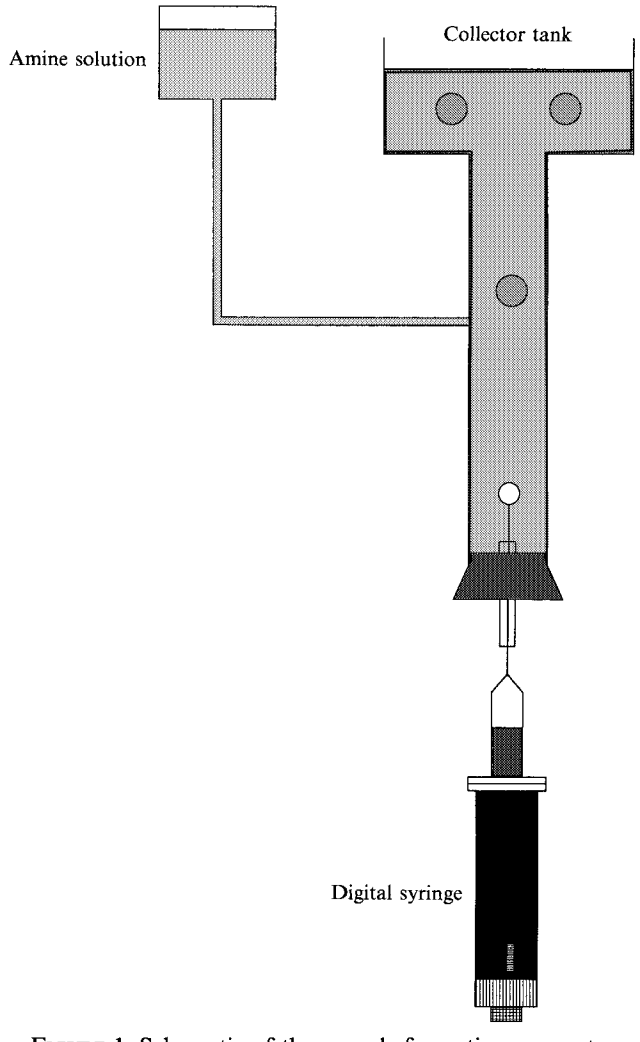

FIGURE 1. Schematic of the capsule formation apparatus.

as the drop liquid, because it is Newtonian over a large range of shear rate and its viscosity can be adjusted by mixing readily available grades of the oil. Deionized water is used as the outer-phase liquid. To conduct a polymerization reaction that is confined to the interface between the fluids, the drop liquid and the outer phase liquid are seeded with complimentary monomers. The monomer used in the drop fluid is sebacoyl chloride dissolved in iso-octane and carbon tetrachloride, which is blended with the silicone oil. The concentrations of iso-octane and carbon tetrachloride are chosen to guarantee that the capsule is neutrally buoyant in the outer-phase liquid for the experiments described in §§3 and 4. The complementary monomer in the external fluid (water) phase is diethylene triamine. Sodium carbonate and sodium bicarbonate are added to the water phase so that hydrochloric acid condensates are neutralized at a pH of 9.8.

When the monomer in the droplet phase contacts the monomer in the outer phase, a polymerization occurs at the interface between the phases to form a thin membrane. The reaction is quenched by the membrane, because it acts as a mass transfer barrier

preventing further contact between the complementary monomers. The properties and viability of the membrane depend not only on the monomers used in the reaction, but also on the solvents used and other conditions in the reactor.

Diethylene triamine is used as the water-phase monomer to improve the durability of the capsule membrane. The condensation reaction with diethylene triamine apparently promotes extensive cross-linking that improves the durability of the membrane. When other amines, such as 1,6 hexanediamine, are used, the condensation reaction forms a linear polymer with only a small degree of cross-linking, which results in a membrane that is too fragile for our purposes. Other monomers that were tested are mentioned in Chang (1991).

Figure 1 is a schematic of the capsule formation apparatus, which consists of a tubular glass reactor of length 101 cm and inner diameter 2.54 cm. The needle of a micrometer syringe is inserted into the reactor tube through a septum in the bottom of the reactor. Diethylene-triamine solution is delivered to the reactor through a fixture placed near the top of the reactor tube. The capsule formation process starts by injecting a known amount of the drop phase through the micrometer syringe into the bottom of the reactor tube. Because the density of the drop fluid is less than that of the aqueous outer phase, the drop rises slowly through the reactor tube. Conditions are chosen to keep the terminal velocity of the drop small, so that it remains nearly spherical at all times. This guarantees that the final capsule has a spherical shape at rest, i.e. in the absence of flow. When the drop travels past the port through which the diethylene-triamine solution enters the reactor vessels, the interfacial reaction begins. A nylon membrane is formed before the drop reaches the top of the reactor tube. The polymerized capsules are collected from the top end of the tubular reactor.

The diameter of the capsules ranges between 2 and 4 mm and can be measured to within ± 0.05 mm. Depending on conditions in the reactor vessel, the membrane thickness varies between 5 and 9 μm, but most capsules used in this study had a membrane thickness of 7 μm. In every case the membrane thickness is small compared with the capsule radius.

3. Four-roll mill experiments

The experiments were run using the four-roll mill at the California Institute of Technology in the laboratory of Professor L. G. Leal (now at UC Santa Barbara). A detailed description of the four-roll mill and its operation is given by Bentley (1985) and Bentley & Leal (1986*a*, *b*).

Figure 2 shows a top view of the flow cell. The main components are four cylinders that are 10.16 cm in diameter and 15.5 cm in length. The centres of the cylinders are placed at the corners of an imaginary square, which has sides 25.4 cm in length. The cylinders are immersed vertically in a tank filled with Pale 4 oil (oxidized castor oil). The sides of the tank are 49.5 cm in length, and the tank is 17.5 cm in height. The cylinders are rotated by DC stepping motors, and the rates of rotation are controlled by a PDP 11/23 computer.

By varying the rotation rates of the four rollers, the entire set of two-dimensional flows can be generated. In the vicinity of the centre of the flow, the velocity gradient tensor ∇v is given approximately as

$$\nabla v = \tfrac{1}{2}G\begin{bmatrix} 1+\alpha & 1-\alpha & 0 \\ -1+\alpha & -1-\alpha & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{1}$$

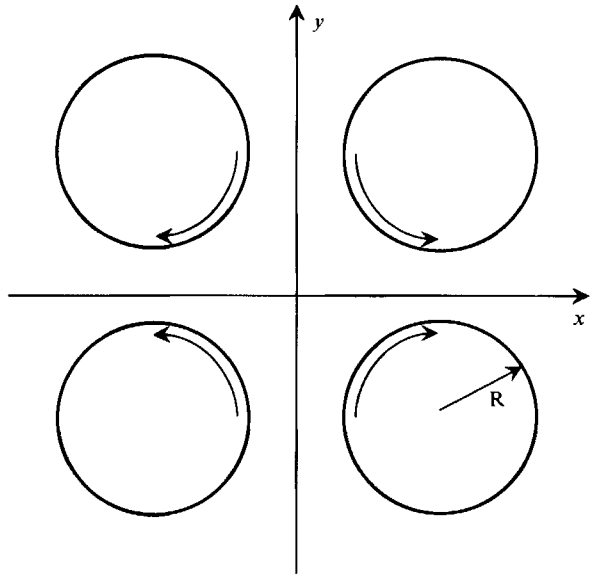

FIGURE 2. A top view of the flow cell.

where v is the undisturbed velocity, G is the strain rate, and α is a parameter that determines the flow type. For the experiments described here, $\alpha = 1$, which corresponds to hyperbolic extensional flow. Other values of α are considered by Chang (1991).

One of the difficulties with the four-roll mill is that the flow contains a stagnation point at the centre of the flow. When a particle such as a drop or capsule is suspended in the flow, the translational velocity of the particle is zero only at the stagnation point. However, the position of a drop or capsule is unstable at the stagnation point, because any small displacement causes it to move onto streamlines that carry it away from the stagnation point and out of the central part of the flow. To keep the particle near the stagnation point so that its deformation can be observed as long as possible, it is necessary to adjust the roller speeds when the particle begins to move away from the stagnation point. For reasonably large deformation rates, adjustments have to be made more rapidly than can be done manually, so computer control is employed.

A collimated beam illuminates the suspended capsule in the centre of the flow. The capsule shape is photographed by a video camera, and an on-line microcomputer digitizes the image and locates the centre of the drop. Using the known location of the drop centre, a controller adjusts the roller speeds automatically to keep the capsule in the centre of the flow.

To start the experiment, a capsule is placed in the four-roll mill and moved slowly into the field of view of the camera by rotating the cylinders manually. This motion is done carefully to avoid deforming the capsule before the experiment starts. Once the capsule is in the field of view, the computer automatically rotates the cylinders to move the capsule to the stagnation point of the undisturbed flow.

The strain rate is first set to the smallest value that can be maintained in the device, which is about 0.05 s^{-1}. The cylinders are then set into motion and the deformation of the capsule is recorded. Sufficient time is allowed for the capsule to achieve a steady-state shape. Then, a photograph is taken, and the deformation rate and time are recorded. From the capsule shape and the known deformation rate, the elastic modulus of the capsule can be determined from small-deformation theory. The deformation rate

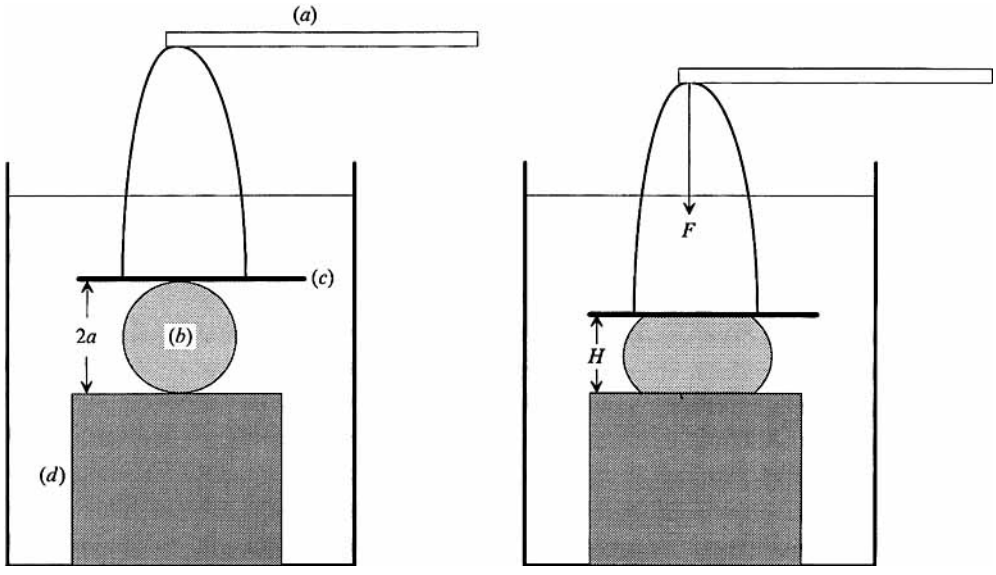

FIGURE 3. A schematic of the apparatus used to measure the elastic modulus of the capsule membrane. The drawing on the left shows the capsule before it is deformed. A rigid bar (*a*) is connected to the torsion wire of the tensiometer (not shown). The capsule (*b*) is positioned between a flat plate (*c*) suspended from the bar and a Lucite block (*d*). The drawing on the right shows the capsule under an applied load *F*.

is then increased to the next larger value, and the procedure is repeated. Preliminary tests showed that with the apparatus under complete computer control, the maximum deformation rate that can be attained while keeping the capsules stationary is about 1 s^{-1}. At higher shear rates, capsules can be held near the stagnation point by making certain manual adjustments of the controller during the experiment. At shear rates above 2 s^{-1}, the capsule oscillates about the stagnation point until it moves away from the central part of the flow.

4. Auxiliary measurement of the capsule membrane elastic modulus

To provide an independent measurement of the membrane elastic modulus, we used an experiment based on squeezing a single capsule between two parallel flat surfaces under a known load. By measuring the shape of the capsule for a given load, an elastic modulus can be determined using the analysis of this problem by Feng & Yang (1973) and by Lardner & Pujara (1977, 1978, 1980).

Figure 3 is a schematic of the apparatus used to carry out the measurement. The capsule is placed in a Lucite box that is filled with Pale 4 oil, the same oil used in the four-roll mill so that the capsule need not be rinsed when transferred between the two experiments. The composition of the liquid mixture inside the capsule has been chosen so that the capsule is neutrally buoyant in the Pale 4 oil. A small Lucite block, which is fixed to the bottom of the fluid-filled box, acts as the lower flat surface for the capsule deformation. The upper flat surface is a copper plate that is suspended from above by a thin wire.

The capsule is deformed between the copper plate and Lucite block under a known load. A modified DuNuoy ring tensiometer was employed to deform the capsule and,

simultaneously, to measure the applied load. For this purpose, the important feature of the tensiometer is that a known load can be applied to the copper plate. This is accomplished by suspending the copper plate from the beam of the tensiometer, which is fixed to the tensiometer torsion wire. The copper plate assembly replaces the circular ring that is suspended from the beam for use in conventional surface tension measurements. The weight of the copper plate is supported by the torsion wire. To apply a load the torsion wire is rotated in the direction that partially releases its support of the copper plate.

The capsule is placed on the top of the Lucite box, and the copper plate is brought nearly into contact with the top of the capsule, thereby trapping it between the two surfaces. At this point the tensiometer indicator is set to its reference mark, the tensiometer scale reading is recorded, and a photograph or video recording of the capsule is taken to determine its undeformed radius. The upper plate is then brought into contact with the capsule, and a force is applied by rotating the tensiometer torsion wire, while keeping the indicator at the reference mark. The capsule deforms slowly, and its membrane takes up the applied load. After sufficient time to guarantee that the system is at equilibrium, a recording of the deformed capsule is taken. The difference between the tensiometer reading and the initial tensiometer reading is used to determine the applied load. This is repeated for three consecutive incremental loads to complete a single run. Once the deformations and applied forces have been determined, the theory developed by Lardner & Pujara (1980) can be used to calculate the Young's modulus of the capsule membrane. Although the deformation is appreciable, it does not appear to cause any permanent change in the capsule, which returns to its rest shape after the load is released.

This procedure was repeated two or three times for each capsule used in the experiment. Variations in the resulting values for the modulus among runs for the same capsule are due to the uncertainty in the force measurement, which is comparable in magnitude to the uncertainty that occurs when the tensiometer is used in conventional surface tension measurements, and to the uncertainty in the displacement measurements, which is a consequence of the limited depth of field of the capsule photographs.

Lardner & Pujara (1977, 1978, 1980) solve this problem for two separate regions, the plate–capsule contact region and the non-contact region, and match the two solutions. The capsule membrane constitutive behaviour is described by a Mooney–Rivlin strain energy function for an isotropic, three-dimensional incompressible (rubber-like) material. Their analysis gives the relationship between the force applied to the capsule and its deformation. The results are expressed in terms of a dimensionless force Y defined as

$$Y = 6F/Eha\lambda_s^2, \tag{2}$$

where F is the dimensional force applied to the plates, E is the Young's modulus, h is the undeformed capsule membrane thickness, a is the undeformed capsule diameter, and λ_s is a so-called inflation parameter. For a thin membrane, the modulus appearing in (2) is the surface elastic modulus Eh, which will also be determined from the flow experiment. We assume that the pressure difference across the membrane of the undeformed capsule is zero, i.e. the capsule is not inflated at rest, which corresponds to $\lambda_s = 1$. The non-dimensional deformation X is given by

$$X = 1 - H/2a\lambda_s, \tag{3}$$

where H is the distance between the plates that squeeze the capsule. The relationship

between Y and X is calculated numerically, and the result is given in Lardner & Pujara (1980). The modulus Eh can be found from measurements of F, H, and a. The deformation X is calculated based on the measured deflection H at the pole of the capsule. In most of the experiments, the three values of the force applied to the capsule ranged from about 30 to 90 dyn, and they produced corresponding dimensionless deflections $H/2a$ from 0.8 to 0.5. Since F is known for each value of X, the elastic modulus Eh can be determined. Owing to the errors in measuring F and H, the uncertainty in the resulting modulus value is about 20% for most of the cases in this experiment.

As an example, we consider the results for a particular capsule with a diameter 0.38 cm. The viscosity of the inner fluid is 0.50 P, and the squeezing test is carried out with the capsule suspended in liquid with a viscosity of 0.52 P. The measured value of Eh is 890 dyn/cm, which is on the same order of magnitude of most of the capsules used in this experiment. The reproducibility of the experiment is difficult to ascertain precisely because only three or four readings could be taken for any single capsule for fear of damaging the capsule or altering its membrane properties before it is used in the flow experiment. For the majority of capsules, the readings for each capsule fell within $\pm 20\%$ of the mean value. A few capsules were malformed and had variations in the membrane thickness. The values of Eh for these capsules sometimes differed substantially among runs, so they were not used in the flow experiment. A variation among runs of $\pm 20\%$ about the mean may seem rather large, but even for bulk polymeric materials, the corresponding variation for measurements of the elastic moduli typically is $\pm 10\%$ (Rodriguez 1982). In any event, the ultimate comparison that will be made in this experiment is between values of Eh measured by different techniques, the squeezing experiment described here and the deformation in extensional flow. When different techniques are used to measure the elastic moduli of bulk polymers, values that differ by up to 30% are not unusual (Rodriguez 1982).

The values of the elastic modulus obtained for the capsules are substantially smaller than values reported for various commercial nylons. Taking an elastic modulus Eh of 700 dyn/cm and a membrane thickness h of 7 μm, a value found by examining the capsule under a microscope after the experiment, gives an estimate for the membrane Young's modulus of 1×10^6 dyn/cm^2. This value is two or three orders of magnitude smaller than a typical elastic modulus for wet nylon 66 of 7.6×10^8 dyn/cm^2. The smaller modulus for the capsule membrane probably indicates that the cross-linked nylon membrane is in a rubbery state, and not in the glassy state that characterizes wet nylon 66. Many glassy materials have elastic moduli that are $O(10^9)$ dyn/cm^2, while rubbery materials have much smaller values, usually $O(10^6$–$10^7)$ dyn/cm^2.

5. Results

The presentation of results focuses on data for seven selected capsules whose properties are listed in table 1. The seven capsules listed in table 1 were studied both in the squeezing experiment described in §4 and in the four-roll mill. Thus, a direct comparison of two independent membrane property measurements is available for these capsules. However, the flow-induced deformation of these seven capsules in extensional flow is representative of results for many others that were examined in the four-roll mill. The capsules, labelled 1–7 for the purposes of discussion, were formed using the process discussed in §2; differences in the material properties among the capsules reflect variations in reactor conditions during formation. The viscosities of the fluid mixture inside the capsule and the Pale 4 oil outer-phase fluid, μ_i and μ_o, also are

Capsule	$2a$ (cm)	μ_i (P)	ν_o (P)	Measured values of Eh: Compression (dyn/cm)	Measured values of Eh: Four-roll mill (dyn/cm)
1	0.360	0.49	37.7	150	240
2	0.346	0.50	42.0	140	190
3	0.333	0.48	31.7	250	380
4	0.352	0.50	42.0	180	240
5(*a*)	0.342	0.48	33.6	300	290
5(*b*)	—	—	—	—	240
6	0.373	0.49	37.6	180	180
7	0.360	0.49	38.0	200	250

TABLE 1. Membrane elasticity values from compression and four-roll mill experiments for seven capsules

shown in the table. The viscosity of Pale 4 oil depends strongly on temperature, which accounts for the variation in its value among the different capsules. The fluid inside the capsule is much less sensitive to temperature variations. The viscosity ratio in every case was less than 0.02, but the viscosity ratio does not affect the steady-state deformation in extensional flow because there is no membrane motion and, hence, no flow inside the drop (Barthes-Biesel 1991).

Figure 4(*a–f*) contains photographs of the steady-state shape of capsule 4 for various values of the shear rate G up to 1.1 s^{-1}. Figure 4(*a*) shows that the capsule is essentially spherical at rest. Figure 4(*b*) shows the steady-state capsule shape for a strain rate $G = 0.20\ s^{-1}$. The shape of the capsule is an ellipsoid with its major axis coincident with the extensional axis of the undisturbed flow. The shape of the deformed capsule can be described by the Taylor deformation parameter D_{12}, which is defined as

$$D_{12} = \frac{L-B}{L+B},$$

where L and B are the major and minor axes of the deformed capsule, respectively. This is the same parameter that is used frequently to describe the shape of deformable drops, provided the deformation is not too large. The value of D_{12} for the capsule shown in figure 4(*b*) is 0.06. The deformation of the drop increases with G, and D_{12} reaches 0.33 in figure 4(*f*) for $G = 1.1\ s^{-1}$.

Figure 5 shows the steady-state value of D_{12} as a function of the dimensional strain rate for three capsules. Capsules 1 and 2 were tested for relatively small deformation rates. Figure 5 shows that the deformation parameter D_{12} for capsule 1 increases as G increases from 0.05 to 0.15 s^{-1}. A similar result is seen for capsule 2 where the deformation rate was varied between 0.11 and 0.17 s^{-1}. The uncertainty in the measurements of D_{12} is ± 0.01, which arises from the error in measuring the lengths of the major and minor axes of the capsule. To within this uncertainty, we conclude that D_{12} is a linear function of G at small strain rates. Indeed, linear regressions for the two sets of data yield slopes that are very close to each other, although the measured values of D_{12} for capsule 1 are consistently larger than those for capsule 2 for comparable values of G. The difference can be attributed to the rest shapes of the two capsules. Despite care to make capsules that are perfectly spherical in the absence of flow, the fabrication process sometimes leaves them with a small deformation at rest, corresponding to values of D_{12} of up to 0.03. The value of D_{12} at rest for capsule 2 is

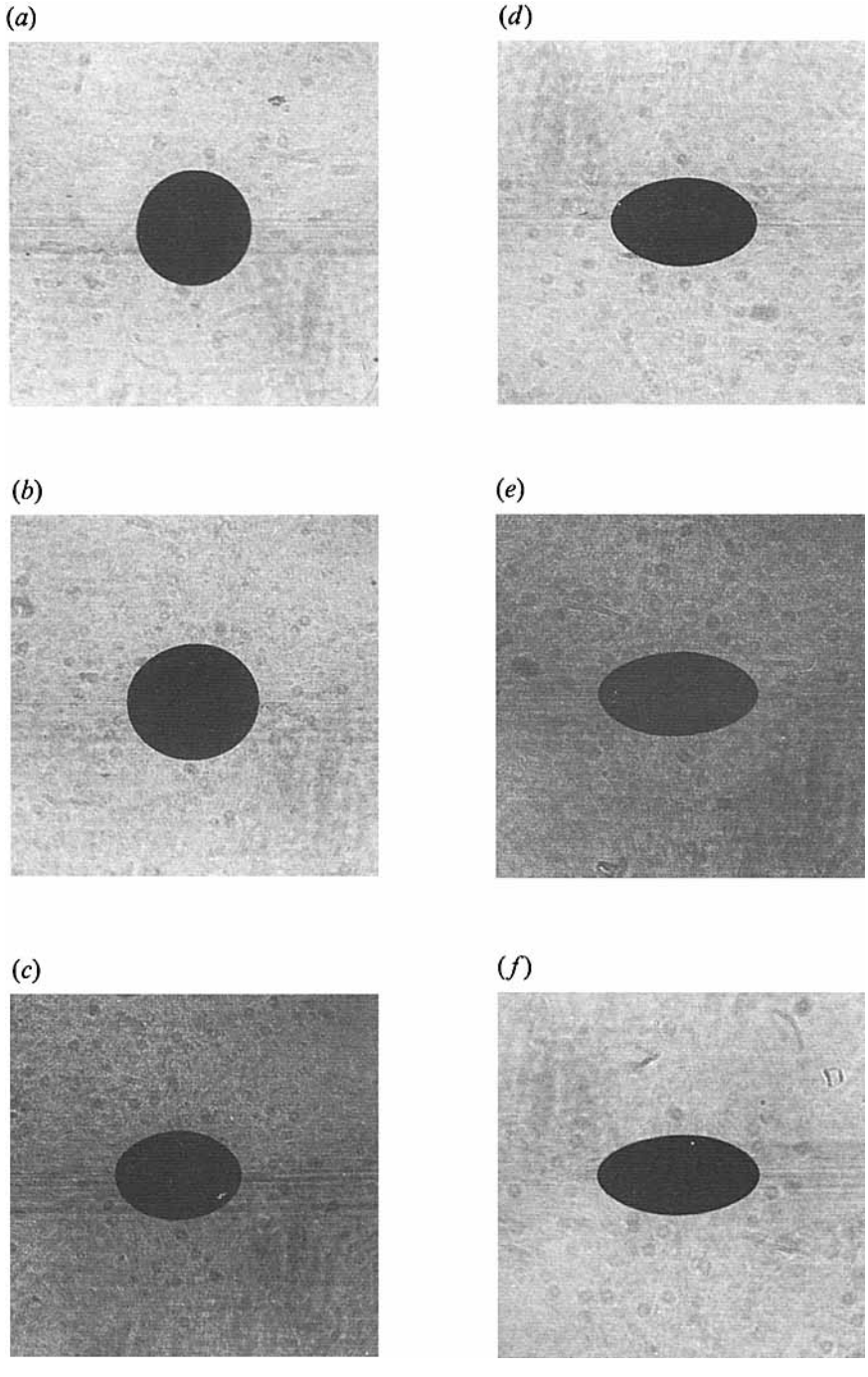

FIGURE 4. Photographs of the steady-state shape of capsule 4 for various values of G: (*a*) $G = 0$ ($D_{12} = 0.02$); (*b*) $G = 0.20\ \text{s}^{-1}$ ($D_{12} = 0.06$); (*c*) $G = 0.5\ \text{s}^{-1}$ ($D_{12} = 0.18$); (*d*) $G = 0.7\ \text{s}^{-1}$ ($D_{12} = 0.24$); (*e*) $G = 0.95\ \text{s}^{-1}$ ($D_{12} = 0.31$); (*f*) $G = 1.1\ \text{s}^{-1}$ ($D_{12} = 0.33$).

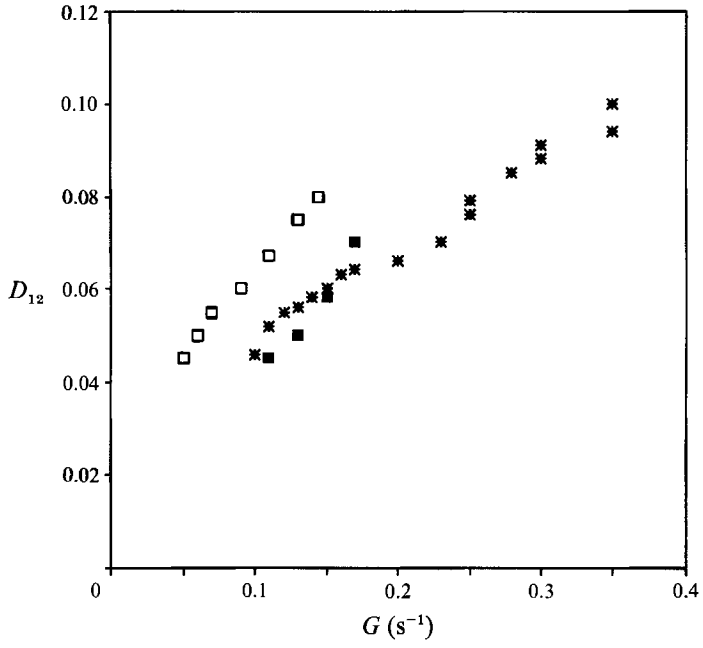

FIGURE 5. Steady-state values of D_{12} for capsules 1 (□), 2 (■), and 3 (✱) as a function of strain rate G.

zero to within experimental error, but capsule 1 is slightly non-spherical, which is reflected in a value of D_{12} of 0.03 for $G = 0$. If 0.03 is subtracted from the D_{12} values for capsule 1, the data for the two capsules are indistinguishable to within experimental error.

Figure 5 shows also the deformation parameter D_{12} for capsule 3, which was examined for larger shear rates up to 0.35 s^{-1}. The degree of deformation is a linear function of G, which was typical of all capsules examined at shear rates up to about 1 s^{-1} for the viscous solvent with values of μ_0 listed in table 1.

However, for sufficiently large deformation rates, a substantial deviation from the linear relationship between D_{12} and G was observed. This is illustrated in figure 6 which gives D_{12} for capsule 4 for values of G up to 1.5 s^{-1}. The deformation parameter varies linearly with G up to $G = 1$ s^{-1}, at which point the value of D_{12} is about 0.32. For greater strain rates, the capsule deformation appears to be limited, perhaps tending toward an asymptote at $D_{12} = 0.37$. This behaviour is shown by all the capsules that were tested for large strain rates in the four-roll mill.

To determine whether the flow-induced deformation of the capsule is reversible, we measured the shape of the capsule after the flow was stopped at the end of an experiment. For capsules 1, 2 and 3, which were exposed to strain rates up to 0.35 s^{-1}, the values of the deformation parameter D_{12} measured long after the flow was stopped were less than 0.02, which means that the capsules returned to a spherical shape within experimental error. However, capsules that were exposed to larger strain rates did not return fully to their spherical rest shape long after the flow was stopped.

The experimental protocol was modified to study this effect in more detail for capsule 4. After the capsule shape reached a steady state following a change in strain rate, the rollers were suddenly stopped and the relaxation of the capsule shape was observed. Figure 7(*a–e*) shows a series of photographs of the capsule during this

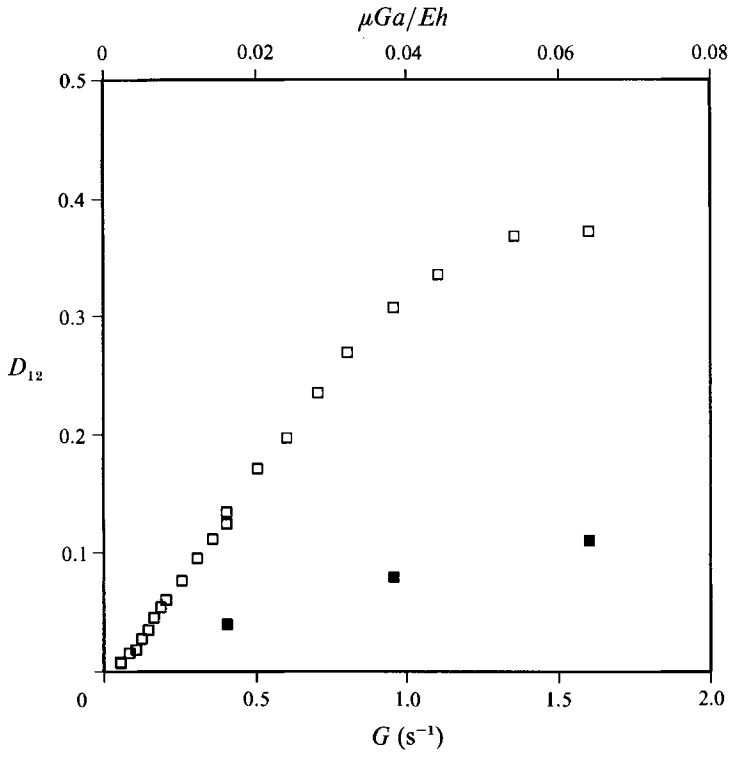

FIGURE 6. Steady-state values of D_{12} for capsule 4 as a function of strain rate. The bottom scale gives the dimensional strain rate, and the top scale gives the dimensionless strain rate based on the value of Eh determined from the squeezing experiment. Open symbols correspond to the steady-state value of D_{12}. Filled symbols correspond to the value of D_{12} that was measured long after the flow was stopped. For the filled symbols, the value of G corresponds to the strain rate just before the flow was stopped.

experiment. Figure 7(*a*) shows the steady-state shape of the capsule for a strain rate of 0.95 s^{-1} just before the flow was suddenly stopped; the steady-state value of D_{12} is 0.31. Figure 7(*b*) shows the capsule shape 0.25 s after the flow was stopped. The value of D_{12} decreased to 0.13 in this short interval. Figures 7(*c*) and 7 (*d*) show the capsule 2.40 and 10.20 s after the flow was stopped. The corresponding values of D_{12} are 0.11 and 0.10, respectively. Finally, figure 7(*e*) shows the capsule 47.50 s after the flow was stopped and no further changes in the shape were observed. The capsule remains slightly elongated in a direction that coincides with the principal straining axis of the extensional flow, and the corresponding value of D_{12} is 0.09.

The steady-state deformation and the residual deformation for capsule 4 are shown as a function of strain rate G in figure 6. The open symbols give the steady-state values of D_{12} for each strain rate G. The filled symbols show the value of D_{12} that was measured long after the flow was stopped at the strain rate shown on the abscissa. The residual deformation suffered by the capsule after the flow is stopped increases with the value of G just before the flow was stopped. In every case, the orientation of the capsule after relaxation is parallel to the principal strain axis of the flow.

Most of the change in shape took place a few seconds after the flow was stopped, and subsequent changes in D_{12} were smaller than the experimental uncertainty. It is possible that the residual deformation reflects an extremely long relaxation time for the

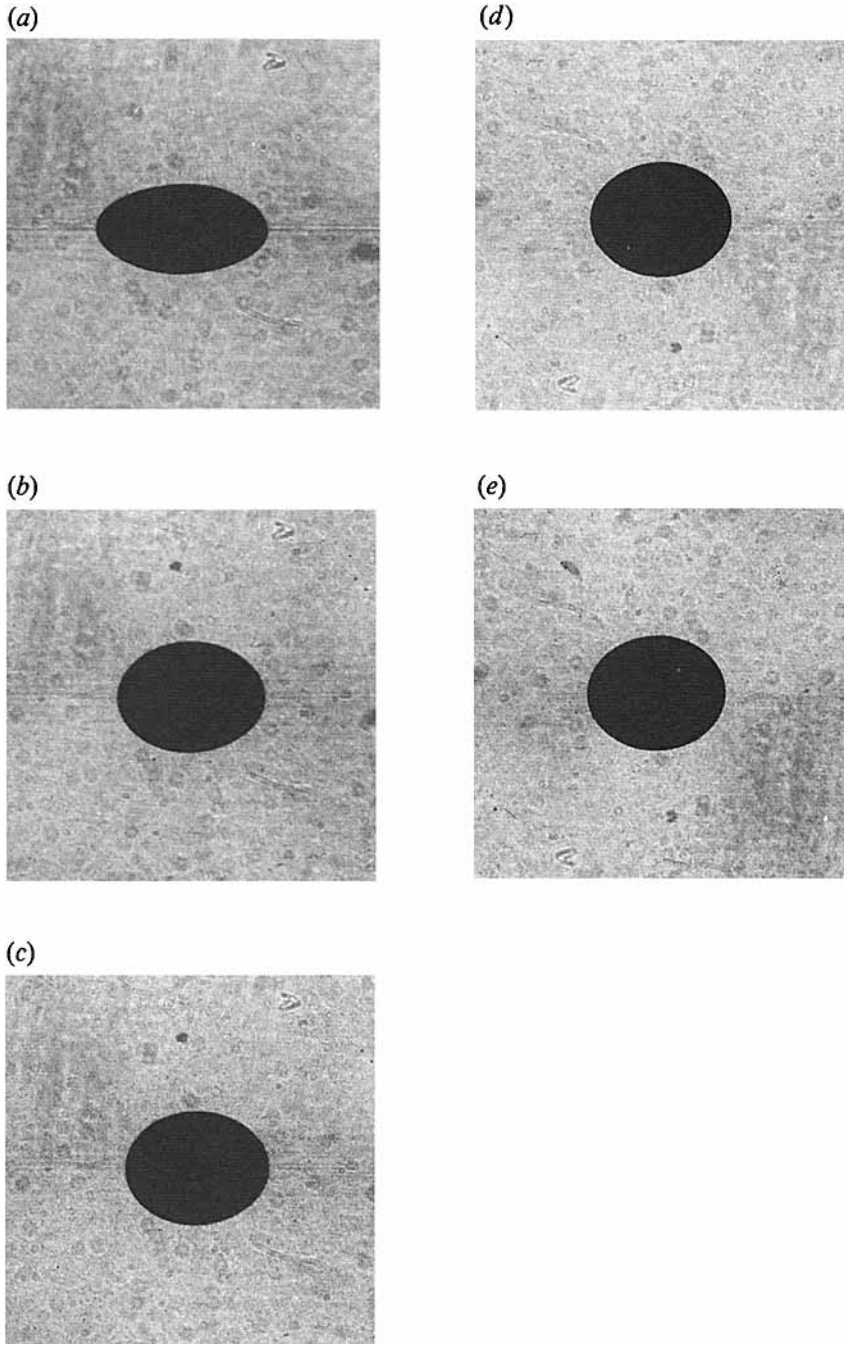

FIGURE 7. Relaxation of capsule 4 following cessation of the flow. (*a*) Capsule at steady state for a strain rate of 0.95 s^{-1}; (*b*) 0.25 s; (*c*) 2.40 s; (*d*) 10.20 s and (*e*) 47.50 s after the flow was stopped, with $G = 0$. ((*a*) $D_{12} = 0.31$, (*b*) 0.13, (*c*) 0.11, (*d*) 0.10, (*e*) 0.09.)

membrane material. If so, this relaxation time would have to be much larger than three minutes, which was the time that the capsule was observed in most runs after the flow was stopped.

It is more likely that the residual deformation of the capsule is a consequence of

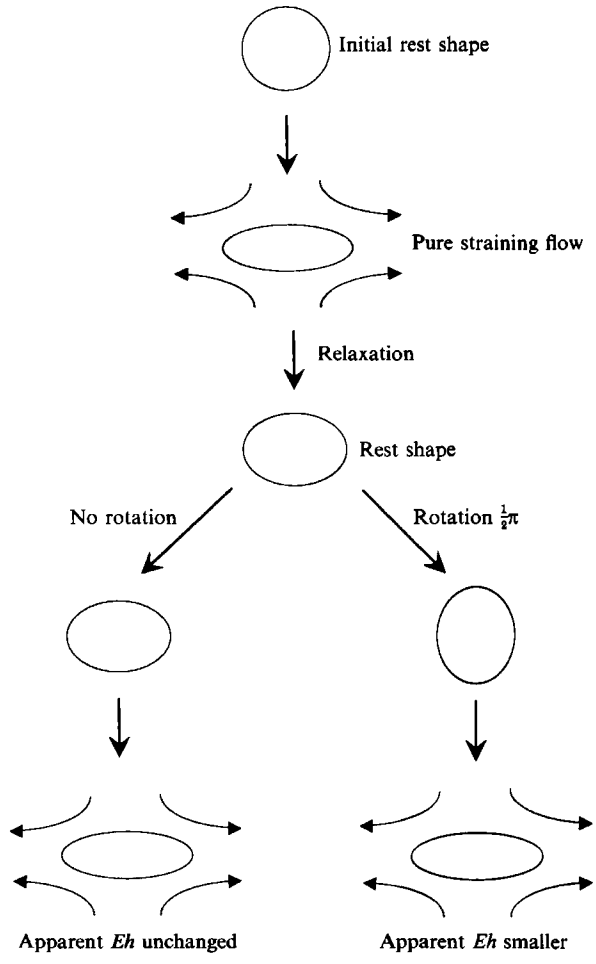

FIGURE 8. A schematic of the experimental protocol to show the effect of the anisotropy of the capsule membrane on the apparent value of *Eh*.

some rearrangement in the structure of the capsule membrane induced by exposure to high strain rates. Since the residual deformation has a preferred orientation along the principal strain axis, the supposed structural change in the membrane must be anisotropic. To test the consequences of this observation a special experiment illustrated schematically in figure 8 was run with capsule 5. The capsule was exposed to successively larger strain rates up to 0.5 s^{-1}. Then, the flow was stopped and the capsule was allowed to relax fully. The capsule had a small residual deformation with its major axis aligned in the principal strain direction of the flow. The capsule was then manually rotated 90° so that its major axis was aligned with the principal compression axis of the extensional flow. The flow was then started again, and the steady-state deformation of the capsule was observed for a series of strain rates. The measured values of D_{12} both before and after the capsule was rotated are shown in figure 9. The two sets of data have different slopes, which suggests that the effective value of the membrane elasticity depends on the orientation of the deformed capsule. The difference between the two sets of data is significant. In other cases when the deformation experiment was repeated without rotating the capsule, changes in the slope were much smaller than that shown in figure 9.

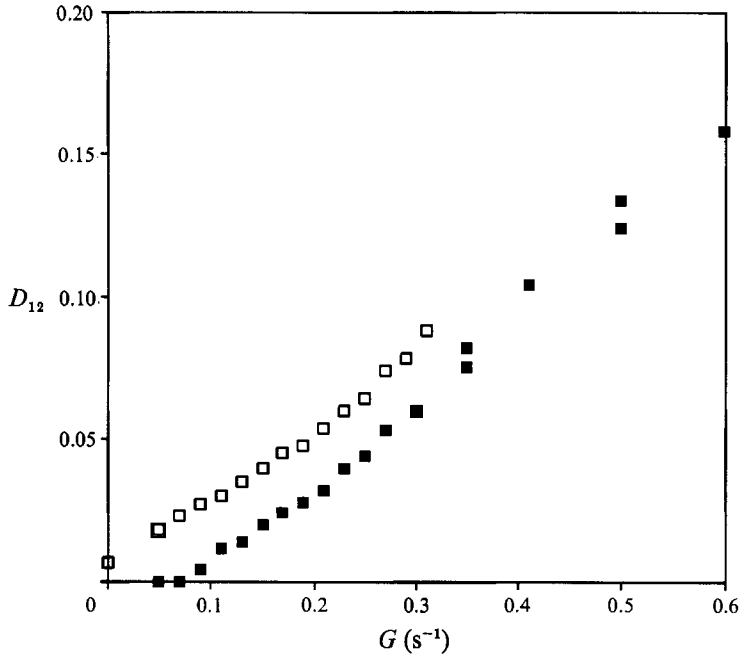

FIGURE 9. Steady-state capsule deformation as a function of strain rate in hyperbolic flow before and after capsule 5 was rotated 90°. Open symbols correspond to deformation before rotation; filled symbols correspond to deformation after rotation.

The residual deformation of the capsule at rest could be partially reversed by exposing the deformed capsule to a flow with a small amount of vorticity, which induces rotation of the membrane. For example when a capsule with a residual deformation was exposed to a flow with $\alpha = 0.8$ for $G = 0.1\ \mathrm{s}^{-1}$, the residual deformation of the capsule after the flow was stopped decreased substantially.

6. Comparison with theory and discussion

The small-deformation theory for capsules follows closely the theory for the deformation of liquid drops. The inner and outer fluids are assumed to be Newtonian, and the capsule Reynolds number, defined as $\rho G a^2/\mu$, where ρ is the outer fluid density, is small. On the capsule surface, the velocity of the membrane matches the fluid velocity. The jump in the stress vector across the membrane is balanced by the force exerted by the membrane on the fluids. The stress within the membrane depends on the membrane constitutive behaviour.

Barthes-Biesel & Sgaier (1985) solved the Stokes equations to obtain the shape of a capsule with a viscoelastic membrane. The membrane is assumed to obey a Kelvin–Voigt model, insofar as the stress in the membrane is given by the sum of elastic and viscous contributions. The viscous contribution plays no role in determining the steady-state shape of a capsule in a purely extensional flow because the membrane is stationary, i.e. it does not tank-tread. Chang & Olbricht (1993) show that the viscous contribution is significant for the sample capsules studied here when they are immersed in simple shear flow. Barthes-Biesel & Sgaier assume that the elastic response of the membrane is governed by a Mooney–Rivlin constitutive model. If the membrane is regarded as a thin sheet of a three-dimensional, isotropic, incompressible material, then

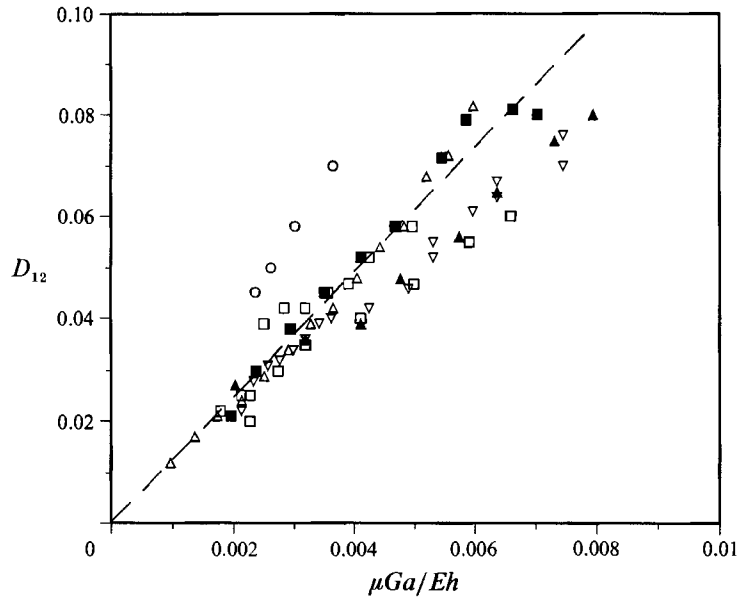

FIGURE 10. Steady-state values of D_{12} as a function of the dimensionless shear rate $\mu Ga/Eh$ for capsules 1 (■), 2 (□), 3 (▲), 4 (△), 5 (●), 6 (○), 7 (▼). the dashed line is the small-deformation theory prediction.

the appropriate elastic modulus is Eh. The shape of the capsule is computed as a regular perturbation about the rest shape. For hyperbolic flow the results predict a linear increase in the degree of deformation with G:

$$D_{12} = \tfrac{25}{2}\mu Ga/Eh + O(\mu Ga/Eh)^2, \tag{4}$$

where the dimensionless group $\mu Ga/Eh$ gives the ratio of viscous stress exerted on the capsule membrane to the elastic force that resists deformation. It plays a role analogous to that of the capillary number for the deformation of liquid drops, except that Eh replaces the interfacial tension for liquid drops.

The experimental data for the capsules follow (4) qualitatively, insofar as the deformation D_{12} is a linear function of shear rate for shear rates smaller than 1 s^{-1}. To make a quantitative comparison between data and theory, the measured values of D_{12} for all of the capsules are plotted in figure 10 as a function of the dimensionless shear rate $\mu Ga/Eh$, where Eh is the value of the elastic modulus determined from the squeezing experiment. Some of the capsules have rest shapes that are slightly non-spherical. To remove the effects of the rest shapes on the comparison between data and theory, the measured value of D_{12} at rest for each capsule has been subtracted from the measured values of D_{12} for every value of $\mu Ga/Eh$. According to (4) all of the data should fall on a line with slope $\frac{25}{2}$. The figure shows that the data for each capsule have a slope that is close to the theoretical prediction, especially for smaller values of $\mu Ga/Eh$ covered in the figure.

The deviations between data and theory can be summarized by fitting the data to (4) and deducing an effective value of Eh for each capsule. The results are shown in table 1, which gives the values of Eh deduced by fitting the four-roll mill data to (4) and compares them with the values measured for the same capsules using the capsule squeezing technique. Two values are reported for capsule 5, 290 and 240 dyn/cm, the first corresponding to the original set of data and the second corresponding to the data

obtained after the capsule was rotated, as described above. The difference between the two values is significant, because it is much larger than the variation in Eh for cases when the flow experiment was repeated without rotating the capsule.

In most cases, the values of Eh determined from the squeezing experiment are smaller than the corresponding values determined from the extensional flow experiment, and, in some cases the difference between the values is slightly larger than the experimental error. Nevertheless, the comparison shown in table 1 demonstrates that measurements of the steady-state capsule shape can be used to estimate the membrane elasticity Eh, at least for the capsules used in this study and for relatively small deformations.

Furthermore, the results are consistent with the relaxation experiment illustrated in figure 7 for capsule 4. Following cessation of the flow, the capsule shape relaxes over a time given by μ^s/Eh, where μ^s is the viscous modulus of the membrane. The membrane viscosity was not measured in the present experiment, but Chang & Olbricht (1993) show that its value for capsules similar to those used here is about 100 P cm. This value implies a relaxation time of 0.5 s for the capsule, which is similar to the time over which most of the change in shape takes place following the cessation of flow.

For larger deformations, the capsule shape presumably is influenced by nonlinear constitutive membrane properties that are not taken into account in the constitutive equation used in the theory. The data in figure 6 show the dimensionless deformation rate $\mu Ga/Eh$ required to observe nonlinear effects. The value of Eh from the squeezing experiment was used to compute values on the abscissa (top scale). The predicted linear relationship between D_{12} and $\mu Ga/Eh$ holds up to about $\mu Ga/Eh = 0.04$, at which point D_{12} is about 0.3. However, when $\mu Ga/Eh$ is increased to 0.06, there is little additional deformation of the capsule. Furthermore, figure 6 shows that the capsules undergo a residual deformation after the flow is stopped after exposure to dimensionless strain rates as small as 0.018.

It may be surprising that the relationship between D_{12} and $\mu Ga/Eh$ satisfies the prediction of small-deformation theory, even when the deformation of the capsule is not small. However, this is the case also for the shape of deformable liquid drops in extensional flow, which can achieve values of D_{12} up to 0.3 while still satisfying the predictions of a small-deformation analysis (Bentley 1985).

The shape of a capsule in extensional flow can be compared with the shape of a liquid drop having the same viscosity ratio. The appropriate dimensionless strain rate for the drop problem is the capillary number $\mu Ga/\gamma$, where γ is the interfacial tension. For $\mu Ga/\gamma = 0.04$ the value of D_{12} for a liquid drop with $\lambda = 0.001$ is 0.08 (Barthes-Biesel & Acrivos 1973*a*; Bentley 1985), whereas the measured value of D_{12} for $\mu Ga/Eh = 0.04$ is 0.30. The flow-induced deformation of a liquid drop is smaller than that of a capsule for identical dimensionless strain rates, because the stress exerted by the outer phase liquid is partially reduced by circulation of liquid inside the drop. The analogous stress-relieving mechanism for a capsule is membrane rotation, but that cannot occur in extensional flow.

The same qualitative comparison between capsules and drops in hyperbolic flow was shown by Barthes-Biesel (1991) for a capsule with a composite membrane formed by a polymerized polylysine layer coated with an alginate film. However, there are some qualitative differences between the responses of the polylysine–alginate capsules and those used in this study. For the polylysine–alginate capsules, the deformation of the capsule D_{12} is a linear function of the dimensionless shear rate. However, the polylysine–alginate capsules form pointed ends which eventually rupture. The

dimensionless shear rate is about 0.02 and D_{12} is about 0.2 when the membrane bursts. For comparable values of the dimensionless shear rate the nylon capsules in this study do not form pointed ends, and they withstand shear rates significantly larger than 0.02 without bursting.

Li *et al.* (1988) computed numerically the shape of a capsule with a purely elastic membrane in uniaxial extensional flow for large deformations. They found that there is a critical dimensionless strain rate above which no steady solution for the capsule shape can be found. Instead, the membrane tension grows in time without bound, presumably until the membrane fails and the capsule bursts. For a capsule with a spherical rest shape the critical value of $\mu Ga/Eh$ in uniaxial extension is 0.08, which is only slightly above the maximum deformation exhibited by the capsules in our experiments for hyperbolic extension. However, the deformation of the capsules in this experiment appears to reach a limiting value at modest shear rates. Since membrane viscosity plays no role in steady extensional flow, the deformation of the capsules probably is limited by strain hardening of the capsule membrane. Li *et al.* (1988) and Barthes-Biesel (1991) showed that if strain hardening is included in the membrane constitutive equation, the capsule deformation can be limited and breakup can be prevented.

The behaviour of the capsules in this study can be interpreted qualitatively in terms of the membrane chemistry. Most nylons are formed from monomers with two functional groups such as hexamethylene diamine, which assures end-to-end polymerization and a crystalline material. However, the capsule membrane in this experiment is formed from diethylene triamine which has three functional groups. The third amine group promotes cross-linking of the polymer chains and the formation of an amorphous material. Indeed, the capsules exhibit rubber-like behaviour characteristic of an amorphous polymer above its glass-transition temperature. The glass-transition temperature of the membrane is unusually low because the membrane contains a substantial amount of water, which was detected by differential scanning calorimetry measurements. Still, the fact that the capsules undergo a permanent deformation suggests that the material is far from ideal, which is probably a consequence of incomplete cross-linking and, possibly, hydrogen bonding between adjacent chains.

The strain-hardening behaviour exhibited by the membrane is not surprising for an amorphous polymeric material. When an amorphous polymer is stretched in a pure straining flow, polymer chains in the membrane become oriented and stretched in the direction of the principal strain axis. If the strain rate is sufficiently large, both the finite extensibility of the chains and strain-induced crystallization (Rodriguez 1982; Aklonis & MacKnight 1983) of individual chains could cause substantial increases in the effective modulus of the material and restrict further stretching of the membrane.

7. Conclusions

The shape of a synthetic capsule with a nylon-derivative membrane freely suspended in hyperbolic extensional flow follows the predictions of small-deformation theory worked out by Barthes-Biesel and co-workers provided that the deformation of the capsule is not too large. For the capsules used in this experiment, the degree of deformation is a linear function of $\mu Ga/Eh$ up to values of $\mu Ga/Eh$ of about 0.08. Indeed, the comparison between experiment and theory show that the value of the elastic modulus deduced from the small-deformation theory agrees reasonably well with measurements obtained by a completely different method, viz. by deforming the

capsule between parallel plates under a known load. This means that, at least in principle, the membrane properties of suspensions of microcapsules can be determined from any technique that can probe the deformation of the capsules in flow. Optical techniques such as birefringence or dichroism could be used to obtain this information for capsule suspensions by a non-invasive measurement.

Certain nonlinear characteristics of the capsule membrane also were observed from the observations of capsule shape. For sufficiently large deformations, the capsule membrane exhibits strain hardening, which can limit the deformation for high strain rates and prevent breakup. Also, the experimental capsules do not return completely to their rest shapes following a sufficiently large deformation, which suggests that the membrane undergoes some permanent anisotropic structural change.

The results obtained for hyperbolic extensional flow are compared with those in simple shear flow in the accompanying paper (Chang & Olbricht, 1993).

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