



CHAPTER III EXPERIMENTAL

3.1 Materials

The materials used in this study were polydimethylsiloxanes, PDMS, at viscosity value of 30,000 centiStoke (Viscasil 30M, donated by General Electric International Operations Company Inc.) as the matrix phase and a polybutadiene, PBd (Ricon 150, donated by Chemical Innovation), as the dispersed phase. The properties of the blend components are listed in Table 3.1. High-molecular-weight polybutadiene ($M_w \sim 841,000$, $M_w/M_n \sim 1.20$ purchased from Fluka Chemical Corp.) was used as a high molecular weight polymer component additive to the Ricon 150 to make a “Boger” fluid [Binnington (1977)] with significantly higher elasticity but with only a slight shear thinning behavior. The polymer blend systems are listed in Table 3.2.

Table 3.1 Polymers used

Polymers	Supplier	Mn	Specific gravity
Low Mw PBd	General Electric International Operations Company Inc.	3,900	0.89
High Mw PBd	Aldrich Chemical Company, Inc.	702,000	1.2
PDMS 30M	Chemical Innovation	91,700	0.976

Table 3.2 Polymer blend systems

Blend systems	Blend components	Temperature (°C)
A	PBd/PDMS 30M	20, 33, 67
B	High MW + low MW PBd/PDMS 30M	25

3.2 Sample Preparation

PDMS's were used as received. Because of volatile components in PBd as received, it had to be vacuum dried at 50 °C until all volatile components were driven off and the weight loss discontinued. The disperse phase in System B was prepared by completely dissolving a ten percent of high molecular weight PBd into chloromethane. The solution was mixed with low molecular weight PBd at room temperature to obtain a "Boger" fluid (Boger and Binnington, 1977). The mixture was left for five days to obtain a homogenous solution. The chloromethane and other volatile components were removed by vacuum dried at 50 °C.

3.3 Rheological Characterization

The storage modulus (G') and loss modulus (G'') of each blend component were measured by a cone and plate rheometer (Rheometrics Scientific, model ARES, NJ), with 25-mm plate diameter with cone angle of 0.04 rad. Because of the difference in temperature dependence of the viscosities of PBd and PDMS, the equiviscosity condition, the desired viscosity ratio and G'' ratio can be obtained by adjusting the operating temperature. Each polymer was molded into a cone and plate fixture with a gap of 0.051 mm. From the rheological properties of pure polymers at various temperatures, the desired pairs of polymers and operating temperatures were selected for further study. The rheological properties are shown in Appendix A. In this study, we investigated the system 1 at G'' ratios equal to 0.16, 1 and 3 and the corresponding G' ratios are 0.16, 1.0 and 3.0 at the temperatures of 67, 33 and 20 °C, respectively. Since $G'' \gg G'$ at all frequencies and all temperatures investigated, the blend system 1 can be considered a pure viscous fluid containing nearly zero viscosity.

Table 3.3 Effect of viscosity ratio

Blend system	Blend components	T (°C)	Γ (mN/m)	G''_r	Wi_d	f (Hz)	τ_{rel} (sec)	τ_{osc} (sec)	Time scale ratio (τ_r)
A1	PBd /PDMS 30M	67	3.5	0.16	0.0006-0.006	0.35	0.585	2.857	0.2
A2	PBd /PDMS 30M	33	2.9	1.0	0.0034-0.034	0.3	1.9	3.33	0.2
A3	PBd /PDMS 30M	20	2.67	3.0	0.0092-0.092	0.04	5.1	25	0.2

Table 3.4 Effect of time scale ratio ($\tau_r = \tau_{rel}/\tau_{osc}$)

Blend system	T (°C)	Γ (mN/m)	G''_r	Wi_d	f (Hz)	τ_{rel} (sec)	τ_{osc} (sec)	Time scale ratio (τ_r)
A2	33	2.9	1.0	0.0034-0.034	0.1	1.9	10	0.2
A2	33	2.9	1.0	0.0045-0.045	0.3	1.9	3.33	0.57
A2	33	2.9	1.0	0.0057-0.057	0.52	1.9	1.9	1.0

Table 3.5 Effect of elasticity

Blend system	Blend Components	T (°C)	Γ (mN/m)	G''_r	Wi_d	f (Hz)	τ_{rel} (sec)	τ_{osc} (sec)	Time scale ratio (τ_r)
A2	PBd /PDMS 30M	33	2.9	1.0	0.0034-0.034	0.1	1.9	10	0.2
B1	0.02% High PBd Sol ^{II} /PDMS 30M	27	3.0	1.0	0.006-0.068	0.099	2.02	10.1	0.2
B2	0.05% High PBd Sol ^{II} /PDMS 30M	25	3.02	1.0	0.018-0.186	0.087	2.30	11.5	0.2

3.4 Observation of an Isolated Droplet in Shearing Flow

3.4.1 Shearing Apparatus

To observe the droplet behaviors in an oscillatory shear flow, we used a flow cell (Linkam CSS 450, Linkam Scientific Instruments Ltd., UK) consisting of two transparent quartz parallel disks mounted on an optical microscope (Leica DMRPX, Leica Imaging Systems Ltd., Cambridge, England), and connected to a CCD camera (Cohu 4910, Cohu Inc., CA). In addition, the images were analyzed on a computer using the Scion image software (U.S. National Institutes of Health, www.scioncorp.com). In case of isolated droplets, the PDMS matrix phase was first loaded into the flow cell. The PBD disperse phase, an isolated single droplet, was inserted into the matrix phase by using a microsyringe. To prevent the droplet from migrating away from the wall, the droplet at the center of the gap was chosen for the study.

3.4.2 Droplet Shape Relaxation Time

Here, we determined the interfacial tensions of various systems studied. The samples were loaded into the flow cell, and the temperature was adjusted to obtain a desired G'' ratio. We selected the droplet with the initial size of around 200 ($\pm 10\%$) μm . The step strains that we imposed to the sample were 0.5-20% with the shear rates of 1, 2 and 3 rad/s. The deformation of the isolated droplet shape after a step strain was recorded and the deformation parameters (Def, Eq. 1.3) were determined to obtain a time series of the retracting droplet deformation Def* vs. time, which has been known to decay exponentially as [Lucinia *et al.* (1997)]:

$$Def = Def_o \exp\left(-\frac{t}{\tau}\right) \quad (3.1)$$

The characteristic relaxation time for a single isolated droplet (τ) can be derived from semi-logarithmic plots of droplet deformation versus relaxation time. The slope of the straight line fitted to the data in the linear relaxation regime [Luciani *et al.* (1997), Mo *et al.* (2000), Xing *et al.* (2000)]. By equating this characteristic relaxation

time to that predicted by the Paliarne model (Eq. 3.2) [Paliarne (1990) and Graebling *et al.* (1993)], the interfacial tension was then calculated from the following relation:

$$\tau = \frac{(3 + 2\eta_r)(16 + 19\eta_r)r_o\eta_{m,o}}{40(1 + \eta_r)\Gamma} \quad (3.2)$$

where $\eta_r = \eta_d/\eta_m$ is the ratio between the dispersed phase viscosity and the matrix phase viscosity, Γ is the interfacial tension and r_o is the radius of the spherical drop. To obtain images of the relaxation droplet after a step strain, the desired strain was imposed onto a selected droplet in the field of view of the microscope. The droplet was then allowed to relax. Two hundred to three hundred images were then recorded (ten to twenty frames per second) while the droplet relaxed its shape to its original sphere shape.

Using the optical microscope, the droplet images were captured only from the top view, this view cannot measure the true lengths of the principle axes. However, the lengths of these axes can be determined by using the affine angle of rotation of the droplet in plane containing the flow and shear-gradient directions (Larson 1988) together with the condition of volume preservation, $D_o^3 = abc$ (Almusallam *et al.* (2000)). Although the lengths of the principle axes can be calculated by using the method mentioned above, we use the apparent lengths of the observable axes, to describe the behavior of each droplet. We can define a modified deformation parameter Def^* as:

$$Def^* \equiv \frac{a^* - c}{a^* + c} \quad (3.3)$$

where a^* and c are major and minor axis of droplet images obtain from top view. The droplet image was shown in Figure 3.1.

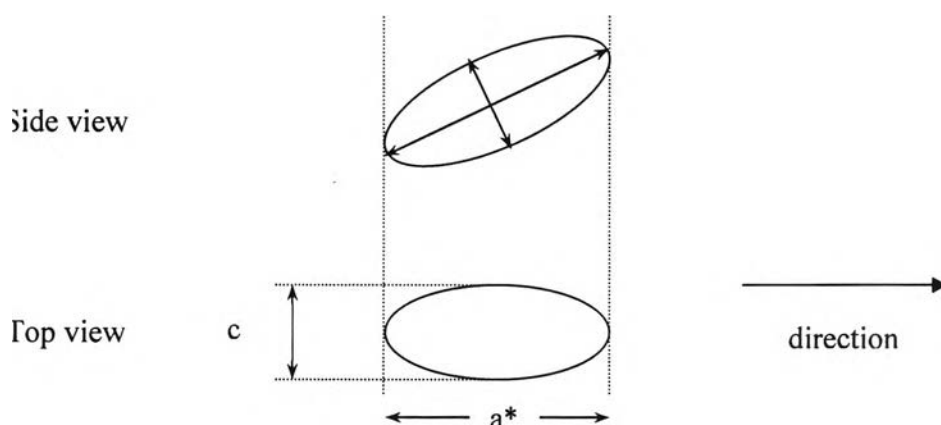


Figure 3.1 Schematic drawing of a single drop observed from the “side” and “top” view by optical microscopy, a and b : the long and short axes of the droplet in the flow-gradient plane, a^* : the a axis projected into the flow direction and c : the principal axis in the radial direction.

3.4.3 Oscillatory Deformation

This experiment is similar to the relaxation experiment, where a sample was loaded and the operating temperature and the size of the droplet were chosen. Now, the shearing mode was oscillatory. The Linkham device, which has one stationary and one moving plate, inevitably caused the droplet to move back and forth. Before we started each experiment the drop should be allowed for relax until it retained a spherical shape. Appropriate strain and frequency were then chosen.

The characteristic time scale ratio (τ_r), equal to the characteristic relaxation time scale (τ_{rel}) over the oscillatory time ($\tau_{osc} = 1/f$), was used to describe the ability to relax of drops under an oscillatory shear flow at various frequencies. For the system 1, at the viscosity ratio equal to one, we investigated τ_r equal to 0.04, 0.2 and 1 corresponding to oscillating frequencies of 0.02, 0.1, and 0.5 Hz, respectively.

For a given frequency, we increased the strain until we cannot capture the complete images during a droplet deformation cycle. For a droplet deformation, six hundred and seven hundred images were recorded; for each period of deformation the numbers of captured images were equal to or above 32 in order to track the deformation time series in details. The droplet deformation, major and minor axes were measured as function of time, frequency, strain, G'' ratio, and G' ratio.