The movement of poly(vinyl butyral) (PVB) and dibutyl phthalate (DBP) plastic solution under the influence of capillary forces was observed directly by hot-stage optical microscopy (\(T = 160°C\)). Migration of a PVB–DBP droplet within a tapered capillary was examined, allowing the surface tension of the binder system at elevated temperatures to be measured, while maintaining constant composition. Calculated surface tension values for PVB–DBP plastic at \(T = 160°C\) ranged from \(8 \times 10^{-3}\) to \(20 \times 10^{-3}\) N/m (8 to 20 dyn/cm); the large error was attributable primarily to the difficulty in measuring the radii of curvature of the leading and trailing edges of the droplet. [Key words: binders, processing, modeling, green body, plastic solution.]

Recently, the thermolysis of polymeric binder systems from ceramic greenware and powder metallurgy parts has received a great deal of attention.1,2 Often this manufacturing operation requires extensive processing, and frequently it creates defects, such as cracks, voids, and delamination. An understanding of the many physicochemical processes that occur during binder removal is necessary to optimize processing conditions and to propose improved binder systems.

The distribution of binder components in a green body can be divided into two regimes: that governed by diffusion and that governed by capillary migration.1 The relative importance of either mechanism is dictated by the physical properties of the organic material, the packing of the particles constituting the green body, and the rate at which volatile material is removed. The magnitude of the capillary force that drives binder migration is directly proportional to the surface tension of the liquid. Capillary forces move molten binder into the smallest pores of the green body; high viscosity retards the rate at which this process occurs.

Indirect evidence of capillary migration in a common binder system, poly(vinyl butyral) (PVB) and dibutyl phthalate (DBP), has been reported recently.1 The study was an investigation of the distribution of the PVB–DBP solution within partially thermalized ceramic tape and of the average pore size as a function of the amount of binder removed. It was shown that the average pore size decreases during thermolysis, indicating that binder is removed from the largest pores first. These observations are consistent with the hypothesis that capillary forces drive binder into the smallest pores during pyrolysis. The present communication is a report of (1) direct observations of the movement of a PVB–DBP solution under the influence of capillary forces and (2) a method that can provide the surface tension of common binder systems at temperatures at which these systems are molten and can maintain the binder system's composition. Frequently, binder systems such as PVB–DBP comprise many constituents with greatly varying volatilities. Some components, such as plasticizers, are very volatile and are removed from the green body at low temperatures; other components are polymers, which decompose at much higher temperatures to produce volatile products. The high volatility of certain components makes common surface tension measurement techniques difficult since the liquid composition can change over the course of measurement at the elevated temperatures of interest. Newman3 abandoned classical pendant drop measurements for molten PVB because of the polymer's tendency to cross-link during prolonged heating.

The method described herein is based on the motion of a liquid droplet in a tapered capillary (Fig. 1). The two liquid–vapor surfaces of a droplet wetting the inside surface of the capillary have different radii of curvature. The magnitude of the capillary forces in a liquid droplet is given by

\[
n = \frac{4 \gamma}{R},
\]

where \(n\) is the capillary number, \(\gamma\) is the surface tension, and \(R\) is the radius of curvature of the liquid–vapor interface.

Fig. 1 Schematic of a liquid droplet wetting the inside of a tapered capillary.
curvature, since the diameter of the capillary decreases toward one end. Surface tension acting in each surface produces a tensile force toward the center of curvature. The pressure difference across the drop is thus given by

$$\Delta P = \frac{\pi \Delta \kappa}{2(1/r_1 - 1/r_2)} \tag{2}$$

where $\Delta \kappa$ is the difference in curvature at each end of the drop, $r_1$ is the radius of curvature at the narrow end of the drop, and $r_2$ is the radius of curvature of the opposite surface. Equation (2) can be simplified to the expression $\Delta P = \frac{\pi \Delta \kappa}{r}$, which states that the pressure difference is proportional to the difference in the inverse radii of curvature. The taper in the capillary thus creates a hydrostatic pressure difference across the drop, causing the liquid to flow. The fluid moves toward the surface with greatest tensile force, which is toward the smaller end of the capillary.

The droplet’s rate of movement is a function of the pressure difference, the dimension of the drop, and the viscosity, $\mu$, of the liquid. For small tapers, one can assume the following functional relation given by Poisuiules’ law:

$$\Delta P = \frac{32\mu L u}{D^2} \tag{3}$$

where $D$ is the diameter of the capillary, $L$ is the length of the drop, and $u$ is its velocity. Equation (3) assumes that the effects resulting from capillary taper are negligible and that the fluid motion is fully developed along most of the drop’s length so that effects of fluid motion near the ends are also negligible. A discussion of the importance of corrections for these effects follows. Equating Eqs. (2) and (3) yields the following relation that can be solved for the surface tension:

$$\tau = \frac{32\mu L u}{\Delta \kappa D^2} \tag{4}$$

where $D$ represents the average diameter of the capillary. Equation (4) shows that, by this simple analysis, the surface tension of a liquid can be calculated by measuring the dimensions and velocity of a drop in a tapered capillary and by taking an independent measurement of its viscosity.

**Experimental Procedure**

The composition of the PVB–DBP plastic used in this study was chosen to represent binder compositions used in tape casting. A 33 wt% DBP** (99%, bp 340°C) in PVB\(^1\) plastic was made by adding 1.8-g DBP and 3.6-g PVB to 80 mL of toluene and stirring rapidly. After the PVB had completely dissolved, the toluene was removed through evaporation at room temperature, leaving a film 630 µm thick that could be peeled from the evaporation dish for viscosity measurements. A parallel-plate viscometer with a mechanical spectrometer, equipped with a heating unit was used to measure the viscosity of the plastic film at 160°C. The surface tension of DBP was measured using a plate tensiometer.\(^3\)

The tapered capillaries were made from 1.5-mm ID and 1.8-mm OD glass capillaries. The closed end of each capillary was first removed, then a thin region in the center of the capillary was carefully heated in a flame and stretched. The thinnest region of each taper was 200 to 300 µm in diameter. A toluene solution of PVB–DBP similar to that described earlier was pipetted into the capillary and held near one end of the taper by gravity. The capillary was dried at room temperature for several weeks, both to allow the toluene to evaporate and to leave a small amount of plastic material at one end of the taper.

Capillary migration of the plastic droplet was observed using a hot-stage microscope, in which the hot zone was between two quartz viewing windows held in place by water-cooled jackets; the temperature was measured with a small thermocouple and was controlled by a programmable microprocessor. The droplet length and position were recorded by superimposing a scale with 10-µm divisions. The temperature was increased at the rate of 15°C/min to 160°C, and then held constant for various time periods. The positions of the leading and trailing edges of the droplet, as well as the sample temperature, were recorded every 15 s. The sample was cooled to room temperature and reheated to continue the measurements as long as the droplet had not reached the narrowest region of the glass capillary.

**Discussion**

The micrographs in Fig. 2 depict the sequence of events that occur during the heat treatment of a tapered capillary containing a small amount of PVB–DBP plastic. Two general phenomena occur when the capillary temperature exceeds $\approx 150^\circ$C. First, and most obvious, is the migration of the liquid toward the narrow end of the capillary; second, the droplet volume at first appears to increase, then it reaches a steady state. Figure 3 graphs the volume of a droplet (derived from its cross-sectional area, as measured in a sequence of micrographs) as a function of time. The amount of material contained in the drop clearly is

---

\(^1\) Mallinckrodt, Inc., Paris, KY.
\(^2\) Butvar B-90, Monsanto Co., St. Louis, MO.
\(^3\) Rheometrics, Inc., Piscataway, NJ.
\(^4\) Rosano surface tensiometer using a Roller-Smith precision balance, Biolar Corp., North Grafton, MA.
\(^5\) Kimax-51, Kimble Division, Owens-Illinois, Inc., Toledo, OH.
\(^6\) Linkam TMS-90, Marcon Instruments Co., Inc., Norwood, MA.
seen to increase rapidly to a steady-state value. The walls of the capillary are initially coated with a thin layer of PVB-DBP, which is drawn from the walls and consolidated in the droplet as the capillary is heated. This phenomenon does not result from dewetting, since the contact angle between the liquid in the capillary, which has a curvature of $1/r$ and only one radius of curvature. Thus, the tensile force at the droplet's surface is greater than that on the film which coats the wall, and liquid consequently flows toward the droplet (Fig. 4). Measurements of the drop velocity were taken after the capillary had been heated sufficiently for the drop to reach equilibrium.

Figure 2 shows that the true boundaries of the sample in the tube are somewhat ambiguous because of optical effects created by the lighting in the optical microscope. This issue was resolved by cooling the capillary to room temperature and filling one end with a fine powder. Observing this capillary the lighting in the optical microscope ensured a correct assessment of the drop's radius of curvature. Thus, the tensile force at the droplet's surface is greater than that on the film which coats the wall, and liquid consequently flows toward the droplet (Fig. 4). Measurements of the drop velocity were taken after the capillary had been heated sufficiently for the drop to reach equilibrium.

The PVB-DBP mixture was found to possess a viscosity that decreased from 4916 to 3855 Pa·s as the shear rate was increased from 0.0396 to 0.3962 s$^{-1}$. Shear-thinning behavior is common for most molten polymers; thus, viscosity measurements should properly be taken over the entire range of shear rates that are of interest. The shear rates observed in the capillary experiment were on the order of 0.004 s$^{-1}$—that is, an order of magnitude less than the shear rate used in the viscosity measurements. The derived values of the viscosity were, however, taken as an order of magnitude approximation since over the next decade the viscosity changed by 20%.

For the experiments discussed here, an error of 0.0017 cm in a radius measurement suggests that this phenomenon plays a role in determining the distribution of binder in a ceramic green body.

The critical surface tensions at 20°C reported for PVB, PVB with residual poly(vinyl ester) mers; thus, viscosity measurements should properly be taken over the entire range of shear rates that are of interest. The shear rates observed in the capillary experiment were on the order of 0.004 s$^{-1}$—nearly an order of magnitude less than the shear rate used in the viscosity measurements. The derived values of the viscosity were, however, taken as an order of magnitude approximation since over the next decade the viscosity changed by only 20%.

The radius of curvature of each edge of the drop could be measured from photomicrographs of the capillary at various times during heat treatment. These values, plus the length of the drop, its velocity, and its average diameter, permit the application of Eq. (4). This calculation results in estimates of surface tensions between $8 \times 10^{-3}$ and $20 \times 10^{-3}$ N/m (8 and 20 dyn/cm) for the PVB-DBP solution at 160°C.

This range in surface tension values is attributable to the difficulty in measuring the radius of curvature of the leading and trailing edges of the drop; the error of the radius measurement is estimated to be 17 μm. The surface tension calculation is quite sensitive to this error and can be shown to be quantitatively related by the following equation:

$$\sigma = \frac{2T_0}{\Delta R} \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

where $r_1$ and $r_2$ are the radii of curvature of the leading and trailing edges, respectively, and $\sigma_0$ and $\sigma$ are the errors in the radius and in the surface tension, respectively. For the experiments discussed here, an error of 0.0017 cm in a radius measurement amounts to a 30% to 40% error in the calculated surface tension.

The reported surface tensions for polymers are most often determined by observing the spreading behavior and contact angle of a series of related liquids of decreasing surface tension. These values are referred to as "critical surface tensions" and are, by necessity, for the solid polymer. Critical surface tensions at 20°C reported for PVB, PVB with residual poly(vinyl alcohol), and poly(vinyl alcohol) are $28 \times 10^{-3}$ N/m (28 dyn/cm), $24 \times 10^{-3}$ to $25 \times 10^{-3}$ N/m (24 to 25 dyn/cm), and $37 \times 10^{-3}$ N/m (37 dyn/cm), respectively. The surface tension of DBP at 23°C was found to be 34.1 dyn/cm. This value com-
pares well with that reported for diethyl phthalate \((37.5 \times 10^{-2} \text{ N/m}} (37.5 \text{ dyn/cm})\), which is structurally similar to DBP. These values are all much higher than those observed in the mixture at 160°C, a fact which is to be expected because the surface tension of most liquids decreases with increasing temperature.\(^9\)

Several other sources of error in the present study result from assumptions about the flow dynamics as the droplet moves. Equation (3) describes the viscous losses in a straight tube and also assumes that the flow is fully developed. For tubes with only a slight taper, the first assumption can be relaxed by a lubrication approximation,\(^9\) which simply modifies Eq. (3) by a multiplicative factor. This correction increases the required pressure gradient for a given flow rate by as much as 80% for the tapered tubes used in this study. The assumption of a fully developed flow is much more difficult to relax and can only be properly addressed by a finite-element calculation. One way to eliminate these difficulties would be to perform static experiments, in which the drop is prevented from moving by an applied gas pressure difference across the drop.\(^*\) Measurement of the applied pressure would thus reveal the exact difference in capillary tensile stress between the two ends. Unfortunately, the slow steady-state migration observed for the very viscous solution studied here would make determining the point at which the drop stops moving very difficult.

**CONCLUSION**

In conclusion, the motion of viscous binder systems under the influence of capillary forces was directly observed. The motion of the drop could be used to reveal the approximate surface tension of the binder and further confirm the origin of the drop motion. The surface tension of the PVB-DBP solution at 160°C was estimated to be \(8 \times 10^{-2} \text{ to } 20 \times 10^{-2} \text{ N/m} (8 \text{ to } 20 \text{ dyn/cm})\). The real-time motion of the viscous binder under the relatively small capillary pressure gradient found in the large capillaries used in this study suggests that the effect would be even more important in the fine capillaries of ceramic greenware.

---

\(^{*}\)As suggested by Dow Chemical, Midland, MI.
