

The Surface Tension of Viscous Polymers at High Temperatures

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INTRODUCTION

A measurement of the surface tension of molten polyamides was required as part of a general study of their spreading upon surfaces. The method had to be suitable for opaque liquids of viscosities up to 500 poises at temperatures up to 300°C. Because many polyamides suffer pyrolytic and oxidative degradation on prolonged heating, the method had to be fairly rapid. Various methods have been described in the literature especially for molten glasses. Mitchell et al.¹ have reviewed the methods which have been used in the glass industry and concluded that the maximum bubble pressure, the dipping cylinder, and the pendant drop methods were most useful. The application of the maximum bubble pressure method has been described in more detail by several authors.²⁻⁷ This method was used in this work with molten polyamides, but modifications were necessary because of their opacity and thermal instability. Measurements were also carried out on silicone oils at room temperature and on molten polyethylene.

The results obtained have not been particularly precise but were useful in the study of the spreading of molten nylon. They are presented here because they may have much wider interest.

THE APPLICATION OF THE MAXIMUM BUBBLE PRESSURE METHOD TO VISCOUS OPAQUE LIQUIDS

The maximum bubble pressure method of Jaeger⁸ for measuring surface tension is well known. The maximum pressure P that can be maintained in a bubble at the tip of a tube of radius r at a distance h below the surface of a liquid of surface tension γ and density ρ is given by

$$P = h\rho g + (2\gamma/r)$$

If this maximum pressure is exceeded, the bubble will expand and break away from the tube. Knowing r and ρ , the surface tension can be determined if P and h can be measured.

For opaque liquids, the measurement of h presents some difficulty. Sugden⁹ overcame this by using two capillary tubes of different radii set at the same depth in the liquid. This method was tried for molten polymers but was discarded, since it required a larger sample which was difficult to heat uniformly. Jaeger's method was found to be satisfactory for opaque liquids when the capillary tube was placed a known distance below the surface by the method described by Parmalee et al.⁴

With mobile liquids, the maximum bubble pressure P is usually recorded on a manometer when a slow stream of gas is passed through the capillary tube. The system acts as a valve and releases some gas as soon as the maximum pressure is exceeded. This method is not successful with viscous liquids, since to blow bubbles into the liquid at this rate requires an excess pressure to overcome viscous resistance as well as the bubble surface forces plus the hydrostatic pressure. If any pressure greater than the maximum bubble pressure is set in the system containing a viscous liquid, a bubble will eventually be blown. The time for the bubble to form will depend upon the excess of pressure and upon the viscosity of the liquid. Parmalee et al.⁴ allowed 15 min. at each pressure for the formation of a bubble and gradually increased the pressure set in the system until a bubble was formed. In this work, mainly with molten polyamides, this process had to be shortened because of their poorer thermal stability.

EXPERIMENTAL

The Apparatus

Measurements were made on molten polymers with the apparatus shown (Fig. 1). Tube S contained the sample, which was heated by the vapor jacket in which the pressure could be regulated. The glass tube C rapidly tapered to a capillary orifice. Many tubes were drawn and cut near the wide part. The orifices were reduced in size by

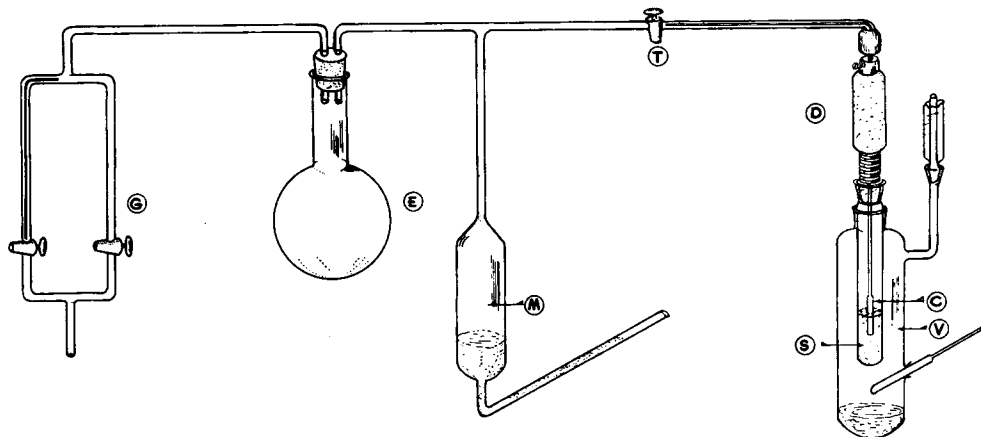


Figure 1.

heating them gently in a small flame. They were ground with carborundum to give flat surfaces, which were examined under the optical microscope. Two capillaries of circular orifices and radii 0.018 and 0.0093 cm., respectively, were selected and used for all this work. The screw thread device D was used to adjust the position of the capillary orifice in the melt. The pressure in the system was measured on the manometer inclined at an angle of 30° to give greater sensitivity. The 2-l. thermostatted flask E stabilized the pressure adequately. The capillary tap T was used to control the size of the bubble formed in the melt. Capillary tubing was used from tap T to the bulb at the end of tube C.

Procedure

The apparatus was flushed with nitrogen which had been passed over hot copper to remove traces of oxygen. The sample of dried polymer chip was introduced quickly to tube S and heated in the vapor jacket. The melt attained a steady temperature $0.5^\circ\text{C}.$ below that of the vapor bath after 15 min. The temperature of the vapor bath was always adjusted to be $0.5^\circ\text{C}.$ above the required temperature. Eight minutes after adding the polymer, the capillary tube C was located at the surface of the melt in the following way. A slow stream of gas was passed from the system through the tube C placed just above the surface of the melt. The tube was lowered slowly. When the tip just touched the surface, the flow of gas stopped so that a pressure increase was immediately recorded on the manometer. The capillary tip was then set at the required depth by rotating the tube the appropriate number of revolutions by use of the screw thread

device D. The capillary tip was always set near the bottom of the container tube so that any bubbles formed by gaseous products of thermal degradation did not affect the mass of polymer above the tip of the tube. Since the tube C displaced a considerable volume of polymer, the number of revolutions was calibrated with a cathetometer against the depth of the capillary tube, when immersed in a transparent liquid, e.g., a silicone oil.

A nitrogen pressure above the expected maximum bubble pressure was then set in the system. To prevent a large volume of gas being released into the system when the maximum pressure was exceeded, the capillary tap T was closed as soon as the bubble commenced to expand, as indicated by a sudden drop in pressure recorded on the manometer. Even with opaque polymers, the tap T could be closed before a large bubble was formed, even though the bubble itself was invisible.

A succession of slightly lower pressures were then set in the system until a pressure was obtained at which no bubble was formed within 3 min. This pressure was taken as the maximum bubble pressure.

RESULTS

Viscous Silicone Oils at Room Temperature

Silicone oil (viscosity 300 poises) was used to test the method on viscous substances at room temperature since repeat determinations could be taken at any desired interval. Consistent results were obtained for surface tension measurements when the maximum bubble pressure was determined by (a) three different experimenters when the tube had been placed in position at a known depth,

(b) after removing and resetting the capillary tube at this depth, and (c) after setting the tube at varying depths.

The mean value of eleven determinations of the surface tension of this silicone oil at room temperature was 21.9 dynes/cm. with a standard deviation of 0.2 dynes/cm. A value of 21.1 dynes/cm. for the surface tension of a similar silicone oil of this viscosity was obtained by Dow Corning workers using a Du Nuoy tensometer with extremely slow movement of the ring.¹⁰

Molten Nylon 66

Many independent determinations of the surface tension of molten nylon 66 containing 0.03% titanium dioxide at 285° C. were made. The value 1.02 g./cm.³ was used for the density of molten nylon 66 at 285°C.¹¹ The room temperature calibrations of *h* and *r* were used directly. A calculation showed that the error involved in ignoring the effect of the expansion of the glass on these values was less than 0.1%. For six determinations, an experienced operator obtained a mean value of 35.1 dynes/cm. with a standard deviation of 0.7 dynes/cm. A greater standard deviation of 2.1 dynes/cm. on a mean of 35.4 dynes/cm. from eight determinations was found by a less experienced operator.

Other Molten Polymers

The surface tensions of other molten polymers were measured by the same method at a temperature approximately 20° C. above the melting point as shown in Table I. The density of each molten polyamide was taken as 1.02 g./cm.³. A value of 0.85 g./cm.³ was used for molten polyethylene at 150° C.

TABLE I
Surface Tension of Other Molten Polymers

Polymer	Temperature, °C.	Surface tension, dynes/cm.
Nylon 6	265	36.1
Nylon 610	265	37.0
Nylon 11	225	22.6
Polyethylene	150	22.8

DISCUSSION

The surface tension of a substance arises from the unbalanced attractions on a molecule or molecular aggregate in the surface by those immediately

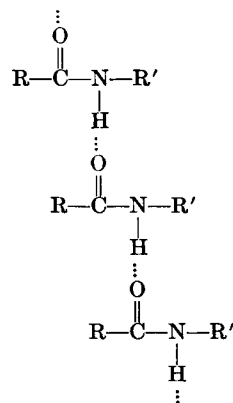
adjacent and within the body of the material; hence, the surface tension is a guide to the existence and order of intermolecular (or interatomic) attraction.

Organic compounds generally have surface tensions in the range 25–40 dynes/cm. Compounds which show molecular association give the higher values in this range. Although fatty acids exist in dimeric form, this association is limited, and surface tensions are about 25–30 dynes/cm. Amides generally have higher values (Table II).¹²

TABLE II
Surface Tension of Simple Organic Compounds

Compound	Temperature, °C.	Surface tension, dynes/cm.
Formamide	20	58.2
Acetamide	85	39.3
Acetanilide	120	35.6
Glycerol	150	51.9
Glycerol tristearate	130	24.7

The association of amides can take an extended form:



and it is this particular feature of association which appears to give rise to high surface tension.

Fused salts give very high values for surface tension. Polyhydroxy compounds (e.g., glycerol) also give high values. The much greater effect on surface tension of associating groups compared with that of long chains is illustrated by the surface tension values for glycerol and glycerol tristearate (Table II).

The value obtained for the molten polyamide is what would be expected of a liquid amide with association between C=O and NH groups. Much lower values were obtained for the surface tension of molten polyethylene and nylon 11, in which

little or no chain interaction should occur. The surface tension values for the silicone oil, polyethylene, and nylon 11 melts show that long molecular chains do not necessarily involve large energy changes in molecular movement to produce the increased surface area. We therefore attribute the higher values obtained for the polyamides containing more amide groups to greater interaction between the polyamide chains in the melt.

Other evidence for association between polyamide molecules persisting in the molten state has been presented by Holliday¹³ and by Cannon¹⁴ from examinations of frequency shifts in the infrared spectra and by Slichter¹⁵ from x-ray diffraction patterns of quenched fibers. Cannon¹⁶ has also shown similar association in polyamides in concentrated *m*-cresol solutions.

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Synopsis

The maximum bubble pressure method for the determination of surface tension has been modified for use with thermally unstable, viscous, opaque polymers at high temperatures. A value of 35.1 dynes/cm. was obtained for nylon 66 at 285° C. The order of this value and those for other polymers has been compared with the values for simpler compounds. Further evidence for the persistence of association between polyamide molecules in the molten state is presented.

Résumé

La méthode de pression de bulle maximum, pour la détermination de la tension superficielle, a été modifiée pour pouvoir l'employer dans le cas de polymères opaques, visqueux et thermiquement instables, à de hautes températures. On a obtenu une valeur de 35,1 dynes/cm pour le nylon 6,6 à 285°C. L'ordre de cette valeur et ceux dans le cas d'autres polymères ont été comparés avec les valeurs obtenues pour de plus simples composés. On a acquis une évidence ultérieure de la persistance de l'association entre les molécules de polyamide, à l'état fondu.

Zusammenfassung

Die Blasendruckmethode zur Bestimmung der Oberflächenspannung wurde zur Verwendung bei thermisch instabilen, viskosen, undurchsichtigen Polymeren bei hohen Temperaturen modifiziert. Ein Wert von 35,1 dyn/cm wurde für Nylon-66 bei 285°C erhalten. Die Grösse dieses Wertes sowie Werte für andere Polymere wurde mit den Werten einfacherer Verbindungen verglichen. Es werden weitere Ergebnisse mitgeteilt, welche auch für den geschmolzenen Zustand das Vorhandensein einer Assoziation zwischen den Polyamidmolekülen beweisen.

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