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The Determination of Surface Properties of Polymers from Liquid Drop Stability on an Inclined Plane

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INTRODUCTION

In this paper is described a simple technique for studying the surfaces of solids. Liquid drops of various sizes are deposited on a horizontal surface which is tilted slowly. The angles of inclination at which the drops begin to slide are recorded. The experimental results thus obtained were analyzed and correlated by the method of Ockrent and Macdougall.[1]

The surface of polyethylene was characterized by use of the sliding drop method with an inclined platform tester. The results show correlations both with the extent of surface treatment and with the printability of the surface.

Zisman[3,4] and Allan[5] used the contact angle method extensively to study the spreading of liquids on surfaces. Allan proposed a relationship between contact angle and printability, and showed that the flame or electric corona discharge treatment of a polyethylene surface decreases the contact angle. Because of the nonuniformity of the surfaces, several measurements were made to obtain an average contact angle. The method was complicated by the use of a special microscopic technique.

THEORY

Ockrent and Macdougall[1] proposed the relation

$$\sin \alpha_S = \frac{\cos \theta_R - \cos \theta_A}{(dg/\gamma)\, A} \tag{1}$$

to relate α_S, the angle of inclination of the plane, to θ_A and θ_R, the advancing and receding "contact angles" (see Fig. 1), when movement of the drop is imminent. A is the area of the meridian section through the drop (the section cut by the plane of symmetry of the drop), d is the density of the liquid, g is the gravitational acceleration, and γ is the surface tension of the liquid.

The experimental data on which eq. (1) is based are not extensive. Its practical use is limited, since only d, g, and γ are known in advance. The area A depends on both the drop volume (an experimentally controllable quantity) and the drop shape. The latter depends on α_s, so that numerical values of θ_A, and θ_R, at incipient sliding must be determined experimentally.

Equation (1) may be put into more useful form if one writes

$$A = CV^{2/3} \tag{2}$$

where V is the volume of the drop and C is a drop shape factor. Substitution into eq. (1) gives

$$\sin \alpha_S = \frac{\cos \theta_R - \cos \theta_A}{C\,(dg/\gamma)} V^{-2/3} \tag{3}$$

If θ_R, θ_A, and C are constant, then

$$\sin \alpha_S = KV^{-2/3} \tag{4}$$

This relation was tested by placing drops of various sizes on the surface of polyethylene film and recording α_S when sliding starts. If eq. (4) is valid, a plot of $\sin \alpha_S$ versus $V^{-2/3}$ should give a straight line through the origin, whose slope K characterizes the surface.

EXPERIMENTAL

Films of Alathon (Du Pont registered trademark) 23A polyethylene resin were treated on one surface by electric corona discharge at various intensity levels. Drops of water of various sizes were placed on the films, and α_s, was determined as a function of V. As predicted by eq. (4), the data fell on straight lines passing through the origin (Figs. 2–4). The surfaces thus are characterized by the slopes of the lines, K. The data in Table I show that K is related to the ink seal

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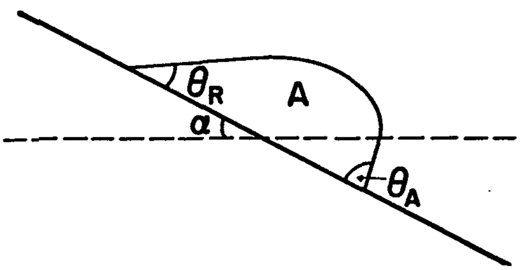

Fig. 1. Liquid drop on inclined plane.

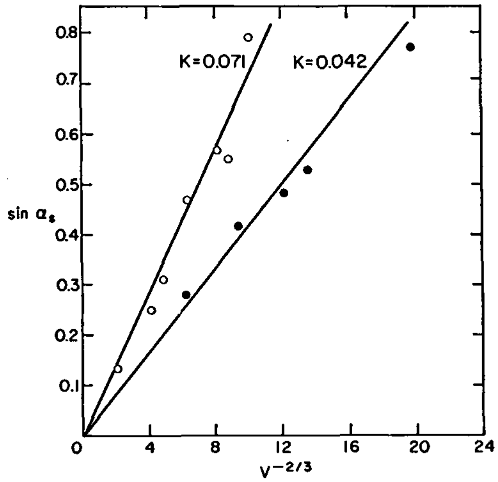

Fig. 2. Stability of water drops on treated (O) and untreated (●) sides of an Alathon 23A polyethylene film: ink seal value, 468 g./in.

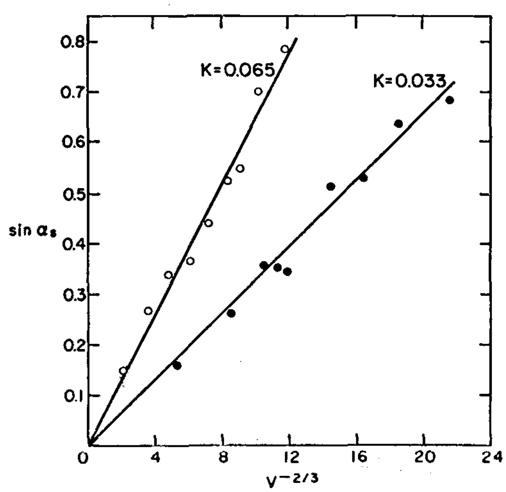

Fig. 3. Stability of water drops on treated (O) and untreated (●) sides of an Alathon 23A polyethylene film: ink seal value, 328 g./in.

value as measured by the Chapman test,[7] and that the treated and untreated sides may be distinguished from one another by their K values.

Figure 5 shows plots for liquids of various sur-

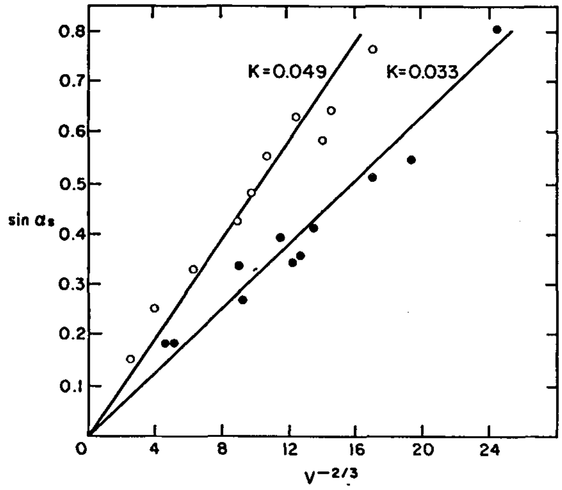

Fig. 4. Stability of water drops on treated (O) and untreated (●) sides of an Alathon 23A polyethylene film: ink seal value, 70 g./in.

face tensions sliding over a surface of Teflon (TFE) resin (Du Pont registered trade-mark). Since the factor (dg/γ) is a property of the liquid only, it is convenient to define

$$K' \doteq K(dg/\gamma) = (\cos\theta_R - \cos\theta_A)/C \quad (6)$$

Equation (6) shows the relation of K' to the advancing and receding contact angles and the shape factor These parameters are dependent on the surface tension of the liquid; the effect of surface tension on K' is shown in Figure 6. As the critical surface tension is approached, θ_R and θ_A tend toward zero, and therefore K' tends to zero. The critical surface tension derived from this point is 20.5 dynes/cm., in close agreement with Fox and Zisman's value of 18.0 dynes/cm., determined by the contact angle method. The fact that K' decreases after going through a maximum is readily understood by considering a nonwetting system such as mercury–Teflon, for which $\cos\theta_R - \cos\theta_A$ becomes again very small when sliding starts.

In polyethylene film, regular die lines usually are produced in the machine direction. The effect of surface roughness on the drop stability is shown in

TABLE I
K and the Printability Level of Alathon 23A Films

	K	
Ink seal, g./in.	Treated side	Untreated side
468	0.071	0.042
328	0.065	0.033
70	0.049	0.033

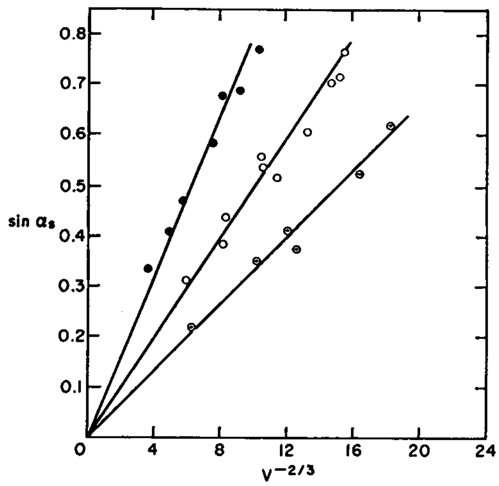

Fig. 5. Stability of drops of liquids of differing surface tensions on a Teflon surface: (●) ethylene glycol, γ = 47.5 dynes/cm.; (○) chlorobenzene, γ = 33.0 dynes/cm.; (⊙) *n*-butanol, γ = 24.4. dynes/cm.

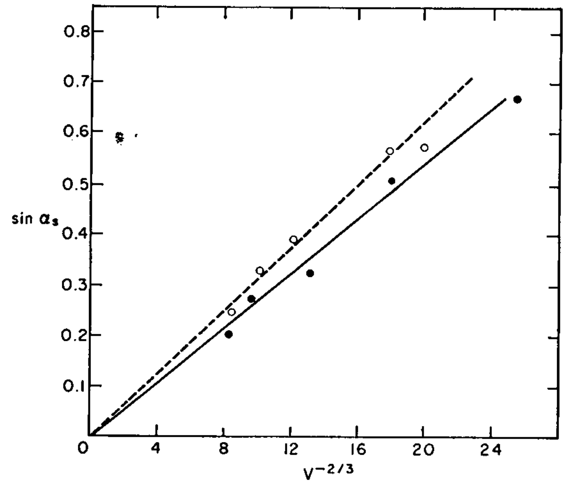

Fig. 7. Effect of roughness on drop stability: sample inclined in transverse direction (○) and machine direction (●).

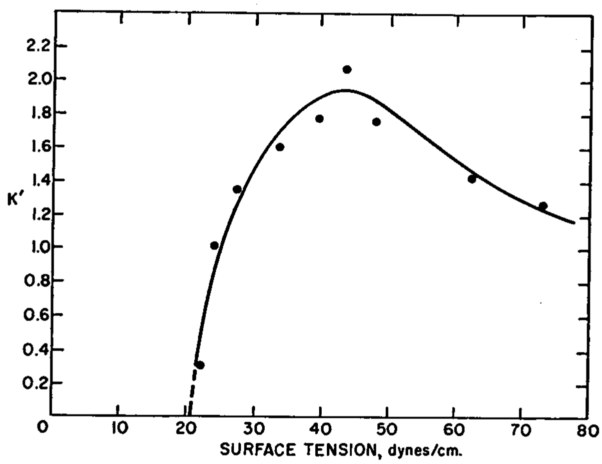

Fig. 6. The effect of surface tension on K'.

Figure 7, and the results indicate that roughness has only a minor effect on the drop stability. The major variables which control drop stability are the air–liquid, liquid–solid, and solid–air interfacial forces.

TEST METHOD

In the standard tests for determining the effect of preprinting treatments on polyethylene surfaces, the adhesion of the materials to the treated surface is measured. Two such tests rate the ability of a treated polyethylene surface to hold a flexographic ink. One of these, the cellophane tape test,[6] is a rapid, qualitative evaluation. In this test the tape is pressed against an inked surface and then removed with a quick pull. A rating is given to the amount of ink remaining on the surface. The Chapman[7] test utilizes the ink as an adhesive between two identically treated film surfaces. A recording tensile tester is then used to pull the two

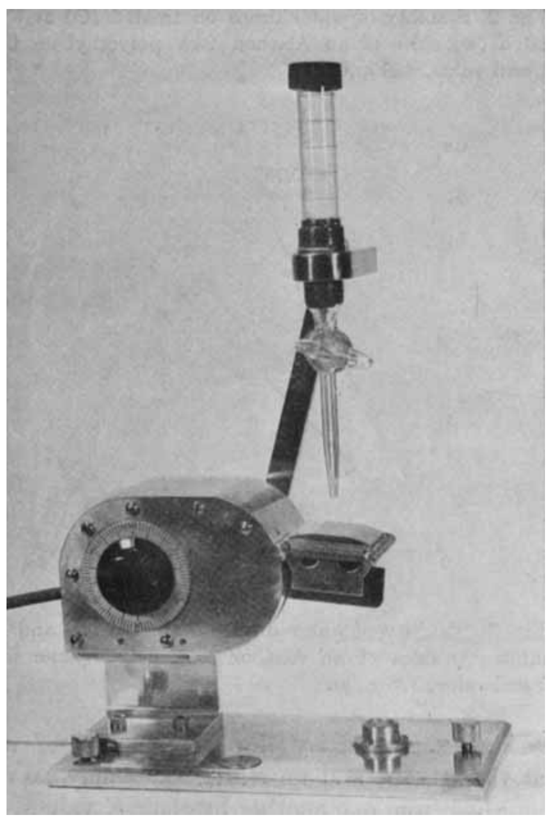

Fig. 8. Overall view of test equipment.

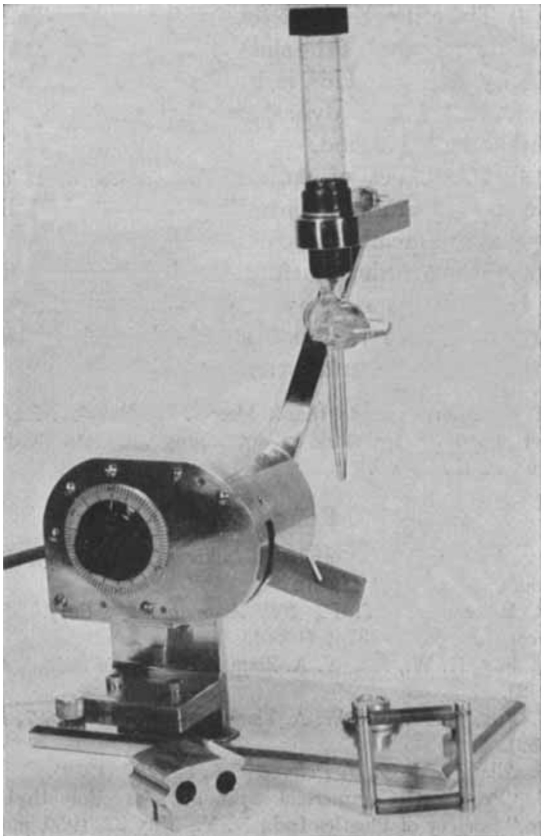

Fig. 9. Clamping arrangement for fastening specimen onto tester.

surfaces apart and register a quantitative measure of the bond strength. In another test described recently, Wechsberg and Webber[8] measured the adhesion of a special pressure-sensitive tape directly to the treated surface.

A portable instrument[2] was recently developed for measuring the surface properties of solid polymers, for example, the level of surface treatment of polyethylene film. In order to simplify the method for routine use, the drop volume was standardized at 0.04 cc. A photograph of this instrument is shown in Figure 8. The test platform upon which the sample is mounted has a flat surface serves as a support for flexible materials such as films. A test platform of different design is available for use with stiff samples such as laminates or sheeting.

In the starting position, the arm supporting the test platform must be horizontal, as shown by a zero reading on the indicating dial. The test platform can be removed from its supporting arm for mounting of the sample which is then held by a spring clip (Fig. 9). The supporting arm is driven by a small synchronous electric motor with a gear train. The arm moves at the rate of one degree per second. The indicating dial on the side of the instrument is geared to move at four times the speed of the arm so that one complete rotation of this dial corresponds to the maximum inclination, ninety degrees, the supporting arm. The indicating dial is graduated in increments of one degree.

A convenient clutch arrangement on both the supporting arm and dial gears permits manual resetting of these components. This feature adds greatly to the speed of operation of the instrument.

With the test sample and drop on the platform in the horizontal position and with the dial indicator set, the electric drive mechanism is started. The supporting arm with platform tilts at the constant rate of one degree per second until the drop begins to slide down the inclined surface (Fig. 10). At this instant the stop button is pressed, securing the entire mechanism in its inclined position. The angle of inclination from the horizontal can then be read from the indicating dial.

In order to obtain reproducible data it is important that several precautions be observed.

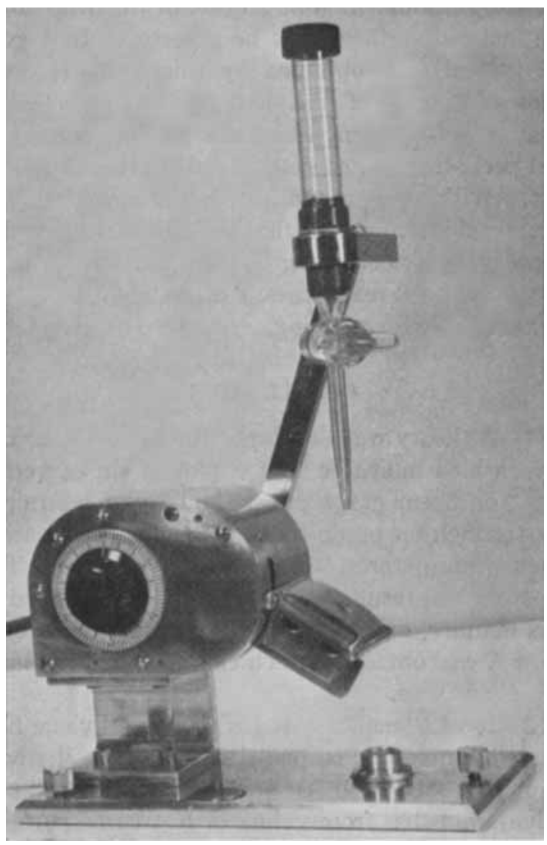

Fig. 10. Tilting of plane at constant rate for observation of drop instability.

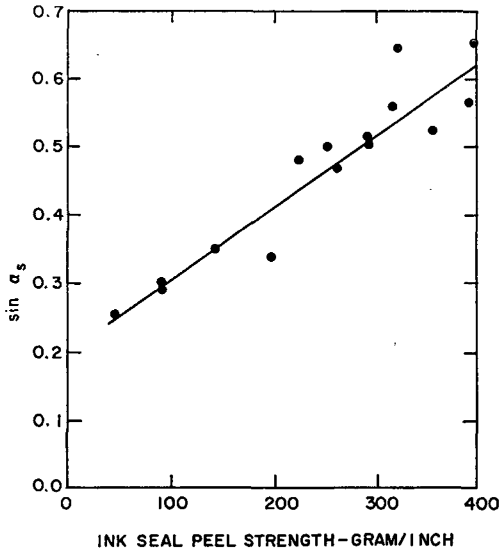

Fig. 11.

The ambient temperature and relative humidity and additives in the base resin must be controlled, and the contact of foreign material with the surface prevented. Similarly, for an accurate test the specimen must be fixed tight to the platform and the precise moment that motion of the drop down the inclined surface must be detected. In Figure 11, typical data obtained by this technique, the sines of angles of incipient sliding on corona-treated polyethylene films, are plotted versus ink seal peel strength, as determined by the Chapman test. Within the range tested, the relationship is linear and it is apparent that the sliding angle varies strongly with peel strength; thus this sliding drop test provides a ready means of distinguishing surfaces suitable for printing.

CONCLUSIONS

(1) A theory was developed for drops of various sizes, which indicated that a plot of sin α_s versus $V^{-2/3}$ on linear graph paper should give a straight line through the origin (α_s is the angle of inclination when sliding starts, V is the drop volume). The experimental results were found to be correlated in this manner, and from the slope of the line a constant K was obtained which characterized the individual surfaces.

(2) It was demonstrated with polyethylene film treated by electric corona discharge that the constant K is related to the printability level (ink seal value), and that from values of K treated surfaces may readily be distinguished from untreated surfaces.

(3) The critical surface tension for wetting Teflon was found, by use of the sliding drop technique to be 20.5 dynes/cm. This is in close agreement with the value of 18.0 dynes/cm. determined by the contact angle method.

(4) The effect of surface roughness is small. The major variables controlling the drop stability are the interfacial forces.

(5) The inclining platform test instrument which we have developed may be used by processors of polyethylene to establish standards and controls for polyethylene surface treatment.

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Synopsis

A method for studying the surfaces of solid polymers is described. Drops of various sizes were deposited on a horizontal surface; then the plane was tilted and the angles of inclination at which the drops begin to slide were recorded. A theory was developed which indicated that a plot of sin α_s against $V^{2/3-}$ on linear graph paper should give a straight line. From the slope of the line, a constant K was obtained which characterized the surface. This constant is a function of the interfacial forces and the density of the drop. The critical surface tension for wetting Teflon (TFE) resin was found to be 20.5 dynes/cm. This is in close agreement with the critical surface tension determined by contact angle measurements. Alathon 23A polyethylene film which had been treated by electric corona discharge was studied. It was shown that K is related to the printability level, and that treated and untreated surfaces may readily be distinguished from one another by their K values.

Résumé

On décrit une méthode qui étudie les surfaces de polymères solides. Des gouttes de différentes grandeurs sont placées sur une surface horizontale. Le plan était incliné et les angles d'inclinaison auxquelles les gouttes commencent à glisser ont été notées. Une théorie a été développée qui indique que le graphique de sin α_s en fonction de $V^{-2/3}$ sur un papier graphique rectangulaire doit donner une ligne droite. De la pente de la droite on peut calculer une constante K que caractérise la surface. Cette constante est une fonction des forces interfaciales et de la densité de la goutte. La tension de surface critique pour une résine mouillée de Teflon RFE fluorocarboné a été trouvée de 20.5 dynes/cm. Ceci est en bon accord avec la tension de surface critique déterminée à l aide des mesures des angles de contact. Un film de polyéthylène de Alathon 23A traité par une décharge électrique coronaire a été étudié. On a trouvé que K est en relation avec la possibilité d'impression et que l'on distingue facilement les surfaces traitées et non-traitées.

Zusammenfassung

Eine Methode zur Untersuchung der Oberfläche fester Polymerer wird beschrieben. Tropfen verschiedener Grösse wurden auf eine horizontale Oberfläche aufgesetzt. Die Fläche wurde geneigt und der Neigungswinkel, bei welchem die Tropfen zu rutschen beginnen, festgestellt. Nach der entwickelten Theorie sollte ein sin α_s gegen $V^{-2/3}$-Diagramm auf rechtwinkeligem Koordinatenpapier eine gerade Linie liefern. Aus der Neigung der Geraden wurde eine für die Oberfläche charakteristische Konstante K erhalten. Diese Konstant ist eine Funktion der Grenzflächenkräfte und der Dichte des Tropfens. Die kritische Oberflächenspannung für die Benetzung des Fluorkohlenstoffharzes Teflon TFE wurde zu 20,5 dyn/cm bestimmt, was nahe mit der aus Randwinkelmessungen erhaltenen kritischen Oberflächenspannung übereinstimmt. Alathon 23A-Polyäthylenfilm wurde nach Behandlung mit einer elektrischen Coronaentladung untersucht. Es wurde gezeigt, dass K ein Mass für die Bedrukbarkeit ist und eine leichte Unterscheidung behandelter und nichtbehandelter Oberflächen ermöglicht.

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