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Polymer surfaces

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Polymer surfaces

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Preface

As polymers come to be used in ever more critical engineering applications, it becomes more important to understand the properties of their surfaces. Mechanical stress cannot be put into a material other than by means of stress transfer through its surface, and thus efficient utilisation of the properties of a material demands an understanding of the interactions which may take place at an interface. This is the prime reason for this study of polymer surfaces.

Historically, phenomena associated with the surfaces of polymers have been studied in a range of disciplines from physical chemistry to mechanical engineering, often from different viewpoints and usually with different terminologies, so that a chemist and an engineer working on the same system may have considerable difficulty communicating with each other. One object of the present book is therefore to try and present a logical development of the subject which spans most of the subject. Thus the book starts with a look at molecular interactions and surface thermodynamics, and then goes on to see how these control the chemistry of wetting and hence a major portion of adhesive technology. The strength of adhesive joints is controlled by the fracture mechanics of interfacial systems and the production of surfaces by rupture, and so an attempt is made to show how the surface chemistry of an adhesive system may influence the fracture mechanics of the system. Since some frictional phenomena involve the same molecular forces as adhesion, two chapters on friction attempt to show how the description of surface interactions developed in the earlier chapters explains these frictional phenomena. Wear is allied to friction, and the book concludes with a brief introductory treatment of this expanding subject.

A preface is the traditional place in which an author acknowledges the contribution made by others to the production of his work. Any book on this subject must depend heavily on the earlier books by Kaelble, by Wake and by Bowden & Tabor. I hope that I have given due credit where credit is due. Various colleagues have been prevailed upon to read and comment on various chapters, Bill Wake and John Griffiths have been responsible for major improvements in the text, and Ian Ward's reading of the whole book has gone far beyond the line of duty of a series editor. Thanks are due to the ladies who typed the script, Mrs Guthrie, Mrs Palmer and Mrs Fry, and to Julie Frazer who did a magnificent job photographing diagrams. To my wife and family, thanks are due for their forbearance

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during the protracted production of the book, and to Fricka, apologies for much neglect during the last two years.

B. W. Cherry

Melbourne
December 1979

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1 Polymer surfaces

1.1 Introduction

This book is concerned with surfaces and with interfaces. The term interface will be used whenever we are concerned with phenomena which result from the interaction of substances which are on each side of the interface; the term surface will be used whenever we are concerned with phenomena resulting from the interactions of material which is only on one side of the interface. This chapter will be concerned with polymer surfaces: in fact these surfaces will always be in contact with a vapour phase but, because the concentration in the vapour phase is so low, in this chapter the presence of the vapour phase will be neglected.

The objective of this chapter is to define the thermodynamic variables which characterise the properties of a surface, to indicate how these properties may be determined experimentally, and then to relate those thermodynamic variables to the molecular properties of the material, both for solid and liquid surfaces. The most useful parameters for the discussion of surfaces are the Helmholtz free energy and the entropy, and so most of the discussion will be concerned with these quantities.

1.2 Basic thermodynamics of surfaces

Surface variables

Those atoms or molecules of a material which are situated close to its surface are subjected to different intermolecular forces from those to which molecules in the bulk of the material are subjected. Consequently the total energy of the system differs from the value which it would have had in the absence of the surface. It seems logical therefore to define a surface variable as the excess of that variable associated with the system due to the presence of the surface. The surface internal energy E^σ is thus given by the expression

$$E^\sigma = E - E^\beta, \tag{1.1}$$

where E is the total internal energy of the system and E^β is the total internal energy which the system would have had if all the material had been present in the unperturbed bulk state. In the same way it is possible to define a surface entropy (S^σ) and a surface Helmholtz free energy (A^σ) by means of the expressions

$$S^\sigma = S - S^\beta,$$
$$A^\sigma = A - A^\beta.$$

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In general the Helmholtz free energy is a more useful variable in surface studies than the more commonly used Gibbs free energy, because nearly all surface studies are carried out at constant volume. A surface by geometrical definition has location and area but no volume, and so changes in the total amount of surface present can take place at constant volume.

Surface quantities are, of course, associated with a certain area of surface, Ω. The thermodynamic quantity per unit area is then given a lower case symbol and often termed a 'specific' surface variable. Thus the specific surface internal energy $e^\sigma = E^\sigma/\Omega$ and the specific surface entropy $s^\sigma = S^\sigma/\Omega$. The specific surface Helmholtz free energy is sometimes loosely termed the surface energy and given the symbol $a^\sigma = A^\sigma/\Omega$.

Surface tension and surface energy

A system possesses excess surface energy because the molecules in the surface are subjected to a different environment from those in the bulk. Because the molecules in the surface, unlike the molecules in the bulk, are subject to intermolecular attractions from one side only, the packing at least will differ from surface to bulk. If we now consider a line in the surface of the body and imagine the body divided into two by means of a plane perpendicular to the surface and containing the line, then similar arguments can be applied to the forces parallel to the surface across the dividing plane. Because of the difference in the molecular packing between the surface and the bulk, there will be a difference in the force acting across the dividing plane. The excess force per unit length of the line in the surface is termed the surface tension and is given the symbol γ; it is reckoned positive if it acts in such a direction as to contract the surface.

The surface tension may be related to the surface energy by considering the changes in the thermodynamic quantities which accompany a small change in a surface-containing system. Considering first a system which does not contain a surface, if N_i is the number of moles of the ith component which are present in the system, the chemical potential μ_i may be written as $\mu_i = (\partial A/\partial N_i)_{V,T,N_j}$. Consequently if $\mathrm{d}q$ is a small heat input to the system

$$\mathrm{d}E = \mathrm{d}q - \mathrm{d}\omega + \sum_i \mu_i\,\mathrm{d}N_i, \tag{1.2}$$

where $\mathrm{d}\omega$ is the work done by the system.

However, if the system contains a surface, work can be done on the system by extending the surface against surface tension forces, i.e.

$$\mathrm{d}\omega = P\mathrm{d}V - \gamma\mathrm{d}\Omega.$$

Hence writing $T\mathrm{d}S$ for $\mathrm{d}q$

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \gamma\mathrm{d}\Omega + \sum_i \mu_i\,\mathrm{d}N_i. \tag{1.3}$$

Now by definition

$$A = E - TS$$

so that

$$\mathrm{d}A = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T.$$

Hence, substituting from (1.3)

$$\mathrm{d}A = \gamma \mathrm{d}\Omega - P\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \,\mathrm{d}N_i$$

or

$$\gamma = \left(\frac{\partial A}{\partial \Omega}\right)_{V,T,N_i} \tag{1.4}$$

The surface tension (a force per unit length) is thus equal to the change in Helmholtz free energy of the *whole system* associated with unit increase of surface area (an energy per unit area). It is not necessarily equal to the surface energy, which is the change in Helmholtz free energy of the *surface* associated with unit increase of surface area. The relationship between the surface tension and the surface energy may be derived as follows. The force necessary to extend the surface of an isotropic solid is γ per unit length, and so the work done in extending a surface by $\mathrm{d}\Omega$ is $\gamma\mathrm{d}\Omega$. The work done must equal the increase in total surface energy $\mathrm{d}A^\sigma$. Therefore,

$$\gamma \mathrm{d}\Omega = \mathrm{d}A^\sigma = \mathrm{d}(\Omega a^\sigma),$$

i.e.

$$\gamma = \frac{\mathrm{d}}{\mathrm{d}\Omega}(\Omega a^\sigma)$$

$$\gamma = a^\sigma + \Omega\left(\frac{\mathrm{d}a^\sigma}{\mathrm{d}\Omega}\right). \tag{1.5}$$

For a liquid, any attempt to extend the surface will usually result in more molecules flowing into the surface, whose composition is thereby unchanged, i.e. $(\mathrm{d}a^\sigma/\mathrm{d}\Omega) = 0$. For a liquid, therefore, the surface tension γ equals the surface energy a^σ. For a solid, however, as the surface is stretched the surface density of molecules changes and so $(\mathrm{d}a^\sigma/\mathrm{d}\Omega) \neq 0$, and in general for a solid the surface tension and the surface energy are different.

Surface entropy and surface internal energy

The general expression

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

may be written for a surface in the form

$$\frac{\partial}{\partial T}(\Omega\gamma) = -S^\sigma$$

or

$$-S^\sigma = \Omega\left(\frac{\partial \gamma}{\partial T}\right)_V + \gamma\left(\frac{\partial \Omega}{\partial T}\right)_V. \tag{1.6}$$

In general the coefficient of thermal expansion of a surface is small compared with the thermal coefficient of the free energy, and so the second term on the right-hand side of equation (1.6) may be neglected. Consequently the specific surface entropy is given by the expression

$$s^\sigma = -\left(\frac{\partial\gamma}{\partial T}\right)_V, \tag{1.7}$$

and the specific surface internal energy by the expression

$$e^\sigma = \gamma - T\left(\frac{\partial\gamma}{\partial T}\right)_V. \tag{1.8}$$

1.3 Experimental methods for the determination of polymer surface energies

Many of the methods available for the determination of the surface tension of low molecular weight liquids can be adapted for the determination of the surface tension and hence the surface energy of liquid polymers. The determination of the surface tension of solid polymers will be dealt with in section 1.5. In this section techniques which have been used for liquid polymers will be discussed and the techniques will arbitrarily be divided into those which involve the determination of the shape of a polymer surface and those which involve a determination of the load on a polymer surface.

The shapes of a liquid polymer surface

The shape of any liquid surface is governed (Aveyard & Haydon, 1973, p. 59) by Laplace's capillary equation

$$\Delta P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \tag{1.9}$$

where ΔP is the pressure difference across a curved surface and r_1 and r_2 are the principal radii of curvature of the surface. So determination of the relationship between r_1, r_2 and ΔP therefore simply yields a value for the surface tension. Methods based on this technique include the sessile drop or bubble, the pendant drop, the maximum bubble pressure and the capillary rise.

The sessile bubble technique was used by Sakai (1965) for the determination of the surface tension of polyethylene melts. If a bubble in a liquid is trapped beneath a horizontal surface, as in figure 1.1, then if the bubble is large enough the lower surface becomes planar and horizontal.

Equation (1.9) can then be applied to either of the curved surfaces in the section through the drop shown in figure 1.1. The radius of curvature r_1 in the plane perpendicular to the paper is so much larger than the radius of curvature in the plane of the paper that $1/r_1$ can be neglected by comparison with $1/r_2$. Hence, since $\Delta P = (\rho_l - \rho_v)gz$, where ρ_l and ρ_v are the densities of the liquid and the vapour respectively and z is the distance above the planar polymer surface at 0,

$$\frac{\gamma}{r_2} = (\rho_l - \rho_v)gz. \tag{1.10}$$

The radius of curvature of any curve is given by

$$r = \frac{[1 + (\mathrm{d}z/\mathrm{d}x)^2]^{3/2}}{\mathrm{d}^2z/\mathrm{d}x^2},$$

so that writing q for $\mathrm{d}z/\mathrm{d}x$ and substituting in (1.10) yields

$$\frac{\gamma q\,\mathrm{d}q}{(1 + q^2)^{3/2}} = (\rho_l - \rho_v)gz\ \mathrm{d}z,$$

which can be integrated using the fact that at $z = h$, $q = \infty$ to give

$$\frac{\gamma}{(1 + q^2)^{1/2}} = \frac{(\rho_l - \rho_v)\,g\,(h^2 - z^2)}{2}.$$

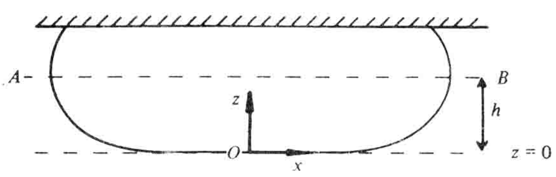
Then since $q = 0$ when $z = 0$ at the bottom horizontal surface and ρ_v can usually be neglected by comparison with ρ_l,

$$\gamma = \tfrac{1}{2}\rho_l g\,h^2,$$

and a determination of the depth of the drop below the equatorial plane *AB* will suffice to determine the surface tension and the surface energy of the liquid. Correction factors to modify the simple theory detailed above have been tabulated by Porter (1933) and Staicopolus (1962). Precisely the same theory applies to a drop of molten polymer on a flat plate (Cherry, el Mudarris & Holmes, 1969).

The basic theory of the pendant drop technique for the determination of the surface tension of a liquid was formulated by Andreas, Hauser & Tucker (1938), and adapted to systems which would solidify and retain their shape on cooling to room temperature by Davis & Bartell (1948). This method involves determining the shape of a liquid drop which hangs from the bottom of a vertical tube. If d_e is the equatorial diameter of a pendant drop, then by a similar operation to that which led to the equation for a sessile bubble, the relationship

Fig. 1.1. The sessile bubble.



$$\gamma = (\rho_l - \rho_v) g\, d_e^2 / H$$

may be derived, where H is a correction factor which varies with the shape of the drop and values for which have been tabulated by Adamson (1967). This method has been used by Wu (1969) and Roe (1968) for the determination of the surface tension of a range of polymer melts.

In the maximum bubble pressure method, bubbles are formed at a fine tip under the surface of the liquid. The radius of curvature of the bubble is a minimum, and hence the pressure in the bubble is a maximum when the bubble forms a hemisphere on the tip as diameter. Under these circumstances equation (1.9) leads to the result

$$\Delta P = 2\gamma / r_c,$$

where r_c is the radius of the capillary. However, the pressure across the surface will vary with the depth below the surface of the liquid and so the bubble will not be entirely hemispherical at the point of detachment. This leads to a small correction factor being applied to give (Edwards, 1968), for a tip which is situated at the surface of the fluid,

$$\gamma = \tfrac{1}{2} \Delta P r_c \left[1 - 2a(\rho_v - \rho_l) g / 3\Delta P\right].$$

With viscous polymeric liquids the pressure which is measured will, unless the rate of application of the pressure is infinitely slow, include a component which is utilised in overcoming the forces of viscous deformation. In order to overcome this, the technique which has to be adopted is that bubbles are blown at successively lower pressures, with correspondingly longer periods to the bubble breaking away from the tip of the capillary. It is then possible to find the pressure at which the bubble will just not separate from the tip. Using this technique Edwards (1968) was able to determine the surface tension of a range of liquid polyisobutylenes.

The application of equation (1.9) to the rise of a liquid polymer in a capillary tube leads, assuming a zero contact angle for the polymer on the surface of the tube and neglecting any deviations from sphericity in the meniscus, to the expression

$$\gamma = \tfrac{1}{2} (\rho_l - \rho_v) h r_c g,$$

where h is the rise in the capillary tube.

Schonhorn, Ryan & Sharpe (1966) developed a technique based on the determination of the capillary rise for their measurement of the surface tension of a liquid polychlorotrifluorethylene. Instead of the more usual technique of using a cathetometer to determine the difference in heights of the capillary rise in tubes of different radii, Schonhorn *et al.* located the position of the meniscus by probing with a very finely pointed wire attached to a micrometer screw. The instant of contact could be very easily seen and this technique was claimed by the authors to provide an accurate value for the height of the liquid in the capillary and to eliminate sources of error involved in the use of two capillary tubes.

Determination of surface tension by force measurements

Although a determination of the force required to stretch a polymer surface would seem an attractive proposition as a method of determining the surface tension, problems arise because during the stretching process energy has also to be expended in bringing about viscous deformation of the liquid, and whilst this second mechanism of energy dissipation is negligible for lower molecular weight liquids it may be considerable in the case of highly viscous polymer liquids. Two methods have, however, been developed which overcome this problem by using very carefully controlled rates of deformation; they are modifications of the du Nuouy ring technique and the Wilhelmy plate technique, which have been used for less viscous liquids. The du Nuouy ring technique, in which the force required to detach a horizontal ring from a liquid surface is measured, was used by Schonhorn & Sharpe (1965) to determine the surface tension of molten polyethylene. The elementary theory of the method suggests that just before detachment of the ring from the surface, the weight of liquid which is lifted out of the surface is entirely supported by the surface tension of the liquid acting vertically on either side of the ring. The mass of liquid W which is supported by the wire ring just before detachment should therefore be given by

$$Wg = 4\pi a_r \gamma, \tag{1.11}$$

where a_r is the radius of the ring. Schonhorn & Sharpe used an Instron tensile testing machine in their work. By utilising the moving cross head of the machine to withdraw the ring at a series of standard rates, and the load cell to measure the force required for detachment, they could, by extrapolation, determine the detachment force at zero rate of withdrawal when the viscous forces would be non-existent. The simple theory represented by equation (1.11) is seriously in error due to curvature of the polymer surfaces, but correction factors calculated using equation (1.9) have been published by Harkins & Jordan (1930).

The modification to the Wilhelmy plate technique which was used by Dettre & Johnson (1966) to determine the surface tension of molten polyethylene is illustrated in figure 1.2.

If the tip of the plate just touches the surface of the molten polymer, then for zero contact angle the force due to surface tension is $p\gamma$, where p is the perimeter of the plate. Then if ΔWg is the difference between the weight of the plate in air and its weight at equilibrium in contact with the surface but at zero immersion,

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