

Temperature Dependence of Contact Angles on Elastomers

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SYNOPSIS

Contact angle measurements with three different liquids were performed on: (i) butyl rubber PB 101-3 (Polysar Ltd.) and (ii) Dow Corning 236 dispersion. Contact angles were measured at different temperatures within the range from 23°C (room temperature) to 120°C. The surface tensions, γ_{SV} , of the polymeric coatings at each temperature were calculated from the contact angles. The temperature coefficients of the surface tensions, $d\gamma_{SV}/dT$, i.e., the surface entropies, were established for the temperature range covered.

INTRODUCTION

The contact angle and surface tension properties of elastomers and coating materials are known to be important parameters in predicting adhesion. Many industrial processes either require strong adhesion or no adhesion at all. Adhesion to the inner walls of a reactor vessel during polymerization is just one example. Contact angles are readily measured on solid surfaces, and it is generally believed that contact angle measurements is the best approach to the determination of solid surface tensions.

The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of the three interfacial tensions: solid/vapor, γ_{SV} , solid/liquid, γ_{SL} , and liquid/vapor, γ_{LV} . The equilibrium relation is known as Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_E \quad (1)$$

where θ_E is the equilibrium contact angle. This equation yields a single, unique contact angle. In practice, however, the contact angle made by an advancing liquid (θ_A) and that made by a receding liquid (θ_R) are not identical; almost all of the solid surfaces exhibit contact angle hysteresis (the difference between the advancing and receding contact

angles). Contact angle hysteresis is usually due to roughness and heterogeneity of a solid surface.¹ If roughness is the primary cause, then the measured contact angles are meaningless in terms of Young's equation. On rough surfaces contact angles are observed to be larger, leading to absurdly low values of the corresponding surface tension, which do not reflect material properties of the surface; rather, they reflect morphological ones. The effect of the surface roughness is a significant one: Surface scratches as small as¹ 0.1 μm can readily influence the measurement of the true contact angle. On the other hand, if heterogeneity is the main cause of hysteresis, then both the advancing and receding angles are thermodynamically significant and can legitimately be used in eq. (1).¹ In this case, the advancing contact angles are a measure of the wettability of the low energy portions of the solid surface, while the receding angles are a measure of the higher energy sites. Conventionally, the advancing contact angle is measured and taken as being indicative of the surface properties of low energy solids, such as polymers,¹ in this case, elastomers. It is, therefore, of utmost importance to ensure that the observed contact angles are, indeed, the maximum metastable angle (advancing angle), and that the solid surface is as smooth as possible.

Moreover, there are as yet no general criteria to answer the question of how smooth is *smooth*; one may accept the contact angle data as correct (or at least as thermodynamically significant) if they predict γ_{SV} values virtually independent of the liquids used. Another possibility of checking whether the measured contact angles may be significant and

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compatible with Young's equation (1) is to scrutinize the values of $d\gamma/dT$. Surface entropies, $d\gamma/dT$, for most liquids are known to fall within a narrow range, from say 0.05 to 0.15 mJ/m² °C, with polymeric liquids near the lower end of the scale. There is no apparent reason for the surface entropies of solids to behave in a significantly different fashion.

Many techniques have been devised to produce smooth surfaces for the purpose of measuring thermodynamically significant contact angles. Such techniques as polishing,¹ heat pressing,^{2,3} and solvent casting^{4,5} have been found suitable for producing smooth surfaces. For elastomers these techniques, in principle, can be used; however, not all techniques are readily adaptable. Polishing or pressing an elastomer might add strains to the surface, thus further complicating the interpretation of the contact angles. The solvent casting method of producing smooth surfaces is one technique that can be extended to elastomers. The dip-coating technique (see Methods: Surface Preparation) has been found to produce elastomer surfaces that are of sufficient quality for contact angle measurements, i.e., the surfaces are smooth. The purpose of the work presented was fourfold: First, to produce elastomer surfaces on which thermodynamically significant contact angles can be measured. Second, to obtain contact angle data, θ_A , over a temperature range of nearly one hundred Celsius degrees. Third, to calculate the surface tension, γ_{SV} , of the coating substances from the contact angles measured at each temperature. Finally, to establish the temperature coefficient of the surface tension, i.e., the surface entropy, $d\gamma_{SV}/dT$, for the selected coating materials.

MATERIALS AND METHODS

Surfaces and Surface Preparation

Two elastomers were characterized for this study: butyl rubber PB 101-3 produced by Polysar Ltd. and Dow Corning 236 dispersion.

The butyl rubber films were prepared by dip-coating clean microscope glass slides in a 10% (wt/v %) solution of butyl rubber dissolved in toluene bp 110.6°C or in a mixture of hexane isomers with a boiling temperature range between 68.2 and 69.6°C (Fisher Scientific Co.).

Dip-Coating Technique

A dip-coating technique was employed to form thin films of the elastomers. The apparatus for the dip-coating consists of a small dc motor (variable speed)

with a turning rod attached, a string with a clip, and a container for the coating solution. The rod winds or unwinds a length of string, from which a smooth and clean substrate, e.g., a microscope glass slide, can be suspended. Immersion and emersion (withdrawal) rates of 0.2–1.6 mm/min were found to provide optimal coating results.

In order to generate a smooth elastomer surface, the bulk elastomer material was dissolved in a suitable solvent and subsequently resolidified in the form of a thin film on a suitable smooth flat plate. This technique is somewhat similar to that of film casting which has been used to produce polymer films^{4,5} as well as bitumen films⁶ for the purpose of contact angle measurements.

Solvents with low-boiling points, e.g., hexane and toluene, are used to dissolve the elastomer. The solvent quickly evaporates, leaving an elastomer film on the substrate which is suitable for contact angle measurements. Most of the solvent was removed during the film casting process; residual solvent can be removed by using a suitable drying procedure. The dip-coating technique produces films of uniform thickness since the substrates are withdrawn at a constant rate. The thickness of the film is dependent on the rate at which the substrate is withdrawn and also on the concentration of the coating solution.

Procedure

The glass slides were first soaked in chromic acid for at least 12 h, then sonicated in distilled water, and finally dried under a heat lamp in a dust free environment. These slides were then coated with butyl rubber and placed into a desiccator (with no desiccant present), which was evacuated, using a water aspirator vacuum pump for approximately 2 h.^{4,5} The slides were then stored in the same desiccator, slightly evacuated, until they were used for measuring contact angles.

The surface morphology of the two different butyl rubber castings obtained from solution of toluene or hexanes, respectively, were studied under a light microscope. It was observed that both castings contained small solid particles which protruded through the butyl rubber surface. Surfaces casted from butyl rubber-hexane solutions contained on average less particles than the toluene-dissolved surfaces. The surface protrusions increase the surface roughness which may influence contact angle measurements, i.e., increase contact angle hysteresis (see Results and Discussion). For the temperature dependence study surfaces prepared from butyl rubber dissolved in the mixture of hexane isomers were used.

The Dow Corning 236 dispersion layer was also obtained by the dip-coating method. Clean glass slides dipped into the Dow Corning dispersion solution (as obtained) were air-dried for 4 h at room temperature in a closed chamber, maintaining a relative humidity of approximately 70% in the chamber.[‡] After drying, the Dow Corning specimens were stored in the same manner as the butyl rubber surfaces.

Liquids for Contact Angle Measurements

The contact angles of different liquids on the above two surfaces were investigated within a wide temperature range; the highest temperature applied was 120°C. Thus, the liquids used for θ measurements were carefully selected to satisfy the following criteria. (a) a relatively high boiling point (higher than 120°C); (b) a liquid surface tension γ_{LV} higher than the surface tension of the elastomers over the temperature range investigated; otherwise the liquid would completely wet the elastomer, i.e., one would observe contact angle of 0°; (c) low vapor pressure to eliminate or at least minimize evaporation and hence spreading pressure; and (d) nonsolvents for the elastomers. The liquids that satisfied the above criteria and were selected for the experiments are glycerol (Fisher Certified ASC Grade), ethylene glycol (Fisher Certified Grade), and diethylene glycol (J. T. Baker Reagent Grade). Double distilled water was also used for measurements at room temperature. The boiling point and the surface tensions, γ_{LV} , measured by the Wilhelmy plate technique at 23°C are given in Table I. The literature values of the temperature coefficients of the surface tensions, $d\gamma_{LV}/dT$ for the selected liquids are also included in Table I.

Contact Angle Measurements

Advancing contact angles, θ_A , were measured by the sessile drop method. First, the contact angle measurements were performed at room temperature on (a) surfaces casted from butyl rubber-toluene solutions and (b) surfaces casted from butyl rubber-hexanes solutions. Subsequently the measurements were performed on butyl rubber surfaces casted from butyl rubber-hexane solution at 23, 30, 40, 50, 60, 70, 80, and 100°C and on Dow Corning 236 dispersion surfaces at 23, 40, 60, 80, 100, and 120°C.

The experimental setup for the sessile drop

Table I Properties of Liquids Used for Contact Angle Measurements

Liquid	Boiling Point (°C)	γ_{LV} Measured at 23°C (mJ/m ²)	$d\gamma_{LV}/dT$ (Lit.) (mJ/m ² °C)
Glycerol	290	63.90	-0.0879 ¹²
Ethylene Glycol	198	48.35	-0.0890 ¹³
Diethylene Glycol	245	45.08	-0.0880 ¹³
Water	100	72.40	-0.1477 ¹²

method consists of a horizontal stage, a source of illumination, and a telescope equipped with a goniometer eyepiece. Details of the sessile drop method, as used in this laboratory, were described by Neumann and Good.⁷ For measurements at elevated temperatures, the horizontal stage, on which the specimen is mounted, is located in an oven with a glass front door. Also located in the oven, behind the stage, is a polished steel mirror, adjustable by magnet. The mirror reflects the light provided by a light source which is located in front of the oven. The telescope is mounted in front of the glass door of the oven so that it can be moved left to right relative to the stage.

Prior to the contact angle measurement, the specimen was placed inside the oven, and the oven was heated up to the measuring temperature. After reaching the desired temperature, 6 to 12 individual drops were formed on the surface of each elastomer film. The liquid drops were produced with the aid of a 2-mL micrometer syringe with a 12-cm, 30-gauge Teflon needle. The contact angles on both sides of each drop were measured to assure symmetry. At each measuring temperature three different coated slides were used, one for each measuring liquid. For each slide the mean and the 95% confidence limits of the resulting 12-24 individual contact angles were then calculated.

Solid Surface Tension, γ_{SV}

Young's equation (1) relates four surface quantities. Of the four quantities only two can be readily determined experimentally, the contact angle and the liquid-vapor surface tension. The interfacial tensions γ_{SL} and γ_{SV} , on the other hand, cannot be measured directly but have to be derived. It has been shown by thermodynamic considerations that an equation of state type relation

$$\gamma_{SL} = \gamma_{SL}(\gamma_{SV}, \gamma_{LV}) \quad (2)$$

[‡] The drying procedure was specified by the manufacturer.

Table II Contact Angles of Water and Ethylene Glycol on Butyl Rubber PB 101-3 Measured at Room Temperature^a

	Contact Angle (°)	
	Water	Ethylene Glycol
Dissolved in Toluene	113.3 ± 2.6	84.6 ± 2.2
Dissolved in Hexanes	110.8 ± 1.4	84.4 ± 1.3

^a The error limits are the 95% confidence limits.

exists.⁸ An explicit formulation of eq. (2) has not yet been achieved analytically. Using experimental contact angles and liquid-vapor interfacial tensions, eq. (2) has, however, been formulated explicitly by Neumann et al.⁹ The equation is implemented as a computer program,⁹ or in the form of tables.¹⁰ The input parameters for this program are the contact angle and the liquid surface tension.

The γ_{SV} of each elastomer was calculated by means of this equation of state relation. The calculated mean contact angle measured at each temperature and the liquid surface tension relevant to each measuring temperature were used to calculate the solid surface tensions. The liquid surface tension values for the elevated temperatures were obtained by using the temperature coefficient, $d\gamma_{LV}/dT$, of each liquid from the data given in Table I.

RESULTS AND DISCUSSION

The results obtained from the above experiments will be presented in two sections. First, the contact angles measured on the differently prepared butyl

rubber surfaces will be reported. In the second part, the temperature dependence of contact angles of butyl rubber and Dow Corning 236 dispersion will be discussed.

Contact Angles on Butyl Rubber at Room Temperature

Table II presents the average contact angles measured at room temperature with ethylene glycol and water on butyl rubber cast from two solutions, i.e., butyl rubber dissolved in toluene and hexane. The contact angles measured on the butyl rubber casted from toluene solution are slightly larger than on the butyl rubber casted from hexane solution for both liquids. This slight difference in the measured θ can be attributed to either (a) morphological differences in the toluene and hexane recast butyl rubber, (b) surface roughness, (c) dissimilar heterogeneities present in the casted film, or (d) a combination of the above. The fact that the microscopic observations of the casted surfaces (see Materials and Methods: Procedures) revealed that the toluene-cast surfaces were rougher leads us to believe that the difference in the contact angles are a mere reflection of surface roughness. Experimentally, advancing contact angles increase with increase in surface roughness.¹¹ The calculated confidence limits of θ for the toluene casted surfaces are also larger, indicating a larger scatter in the measured θ , which is caused by the presence of surface imperfections.

The main intent of this paper is to investigate the temperature dependence of the contact angles on the elastomer surfaces. For that reason, only contact angles measured on surfaces formed by film casting from hexane solution were selected for further investigation.

Table III Advancing Contact Angles θ_A , the Temperature Dependence of the Contact Angles, $d\theta/dT$, and the Calculated Solid-Vapor Surface Tension γ_{SV} , of Butyl Rubber PB 101-3 at Various Temperatures

Temperature (°C)	Contact Angle θ_A (°)			Surface Tension γ_{SV} (mJ/m ²)		
	Glycerol	Ethylene Glycol	Diethylene Glycol	Glycerol	Ethylene Glycol	Diethylene Glycol
23	99.7 ± 1.3	84.4 ± 1.3	81.7 ± 1.6	17.5 ± 0.7	17.1 ± 0.6	17.1 ± 0.9
30	99.2 ± 1.3	83.2 ± 0.9	81.8 ± 2.0	17.8 ± 0.6	17.9 ± 0.4	17.0 ± 0.8
40	99.2 ± 1.3	85.4 ± 0.8	80.7 ± 1.1	15.7 ± 1.0	16.7 ± 0.3	17.0 ± 0.4
60	101.9 ± 1.1	86.3 ± 0.9	81.0 ± 0.9	14.1 ± 0.4	15.4 ± 0.4	16.1 ± 0.4
80	100.9 ± 1.7	88.8 ± 1.1	81.8 ± 1.4	13.5 ± 1.0	13.7 ± 0.4	15.0 ± 0.5
100	105.5 ± 1.1	86.9 ± 0.8	82.3 ± 0.8	12.0 ± 0.5	13.7 ± 0.3	14.0 ± 0.8
120	106.4 ± 0.9	87.4 ± 0.9	84.2 ± 0.9	11.1 ± 0.4	12.8 ± 0.3	12.6 ± 0.3
$d\theta/dT$ (°/°C)	0.062	0.021	0.022			

Table IV Advancing Contact Angles θ_A , the Temperature Dependence of the Contact Angles, $d\theta/dT$, and the Calculated Solid-Vapor Surface Tension γ_{SV} , of Dow Corning 236 Dispersion at Various Temperatures

Temperature (°C)	Contact Angle θ_A (°)			Surface Tension γ_{SV} (mJ/m ²)		
	Glycerol	Ethylene Glycol	Diethylene Glycol	Glycerol	Ethylene Glycol	Diethylene Glycol
23	99.8 ± 1.3	86.0 ± 1.3	82.4 ± 2.2	17.5 ± 0.7	17.1 ± 0.6	17.1 ± 0.9
40	102.2 ± 1.4	85.4 ± 0.8	80.7 ± 1.1	15.7 ± 1.0	16.7 ± 0.3	17.0 ± 0.4
60	104.0 ± 0.9	86.3 ± 0.9	81.0 ± 0.9	14.1 ± 0.4	15.4 ± 0.4	16.1 ± 0.4
80	103.7 ± 2.2	88.8 ± 1.1	81.8 ± 1.4	13.5 ± 1.0	13.7 ± 0.4	15.0 ± 0.5
100	105.5 ± 1.1	86.9 ± 0.8	82.3 ± 0.8	12.0 ± 0.5	13.7 ± 0.3	14.0 ± 0.8
120	106.4 ± 0.9	87.4 ± 0.9	84.2 ± 0.9	11.1 ± 0.4	12.8 ± 0.3	12.6 ± 0.3
$d\theta/dT$ (°/°C)	0.062	0.021	0.022			

Table V Temperature Dependence of Surface Tensions of Polymers Reported in the Literature

Polymer	Temperature Dependence of Surfaces Tensions $d\gamma_{SV}/dT$ (mJ/m ² °C)
PTFE ¹⁴	-0.064
Polyethylenes ¹⁵ (melt)	-0.060
Polyisobutylene ¹⁶ (melt)	-0.064
Poly(vinyl acetate) ¹⁶ (melt)	-0.066
Polydimethylsiloxane ¹⁷ (melt)	-0.048
Polybutene ¹⁷ (melt)	-0.066
Polypropylene ¹⁷ (melt)	-0.056

Temperature Dependence of Contact Angles and Surface Tension

The averaged values of the advancing contact angles together with the calculated surface tension γ_{SV} of butyl rubber and Dow Corning 236 dispersion with three liquids (glycerol, ethylene glycol, and diethylene glycol) at various temperatures are given in Tables III and IV, respectively. Also included in the tables are the calculated temperature dependence of the contact angles, $d\theta/dT$, for the three liquids. The errors given represent 95% confidence limits. The mean value of the solid surface tensions obtained for each liquid was calculated at each temperature. These mean values are plotted as a function of temperature in Figure 1 for both dip-coated surfaces. The straight lines drawn through the points represent least-squares fits of the data; the error bars represent 95% confidence intervals. The temperature coefficient of γ_{SV} for both elastomers is linear over the temperature range investigated. An r value (the correlation coefficient) of better than 0.96 was

attained for both curves. The calculated temperature coefficient of γ_{SV} for butyl rubber then is -0.0676 and -0.0526 mJ/m² °C for the Dow Corning 236 dispersion.

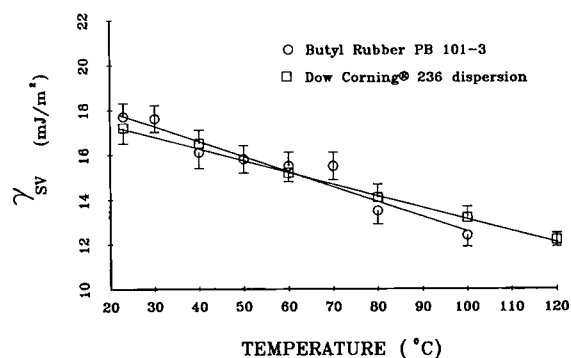


Figure 1 Temperature dependence of the surface tension γ_{SV} of Butyl Rubber PB 101-3 and Dow Corning 236 dispersion at ambient and elevated temperatures as calculated from contact angles measured with glycerol, ethylene glycol, and diethylene glycol.

Table VI Surface Tension γ_{SV} , at 20°C and the Surface Entropy, $d\gamma_{LV}/dT$, of Butyl Rubber PB 101-3 and Dow Corning 236 Dispersion

Solid Surfaces	γ_{SV} at 20°C (mJ/m ²)	d_{SV}/dT (mJ/m ² °C)
Butyl rubber PB101-3	17.9	-0.0676
Dow Corning 236 dispersion	17.3	-0.0526

The above values of the calculated surface entropy are well within the range that others have measured for a solid polymer and polymer melts. Some results of the temperature dependence of the surface tensions measured for polymers, polymer melts, and elastomers are presented in Table V. The fact that the measured surface entropy for both butyl rubber and Dow Corning 236 dispersion are in the same range as other polymers further support our contention that the measured contact angles are representative of the solids, and are not artifacts, e.g., due to roughness. Summarizing our results we present the surface entropies and the values of γ_{SV} at 20°C for the two elastomers in Table VI.

CONCLUSIONS

Contact angles of glycerol, ethylene glycol, and diethylene glycol on well-prepared surfaces of butyl rubber PB 101-3 and Dow Corning 236 dispersion increase with temperature. The surface entropies calculated from the temperature dependence of the contact angle fall well within the range of entropies obtained by direct surface tension measurements on polymer melts and other solid polymers. It is concluded that the contact angles reported here are significant in the sense that they satisfy the Young equation.

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