# Some Thermodynamic Aspects of Polymer Adhesion

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## Synopsis

Recently developed techniques permit the estimation of the surface free energy of polymers and the separation of this free energy into dispersion and hydrogen-bonding components. These techniques have been used to calculate the thermodynamic reversible work of adhesion of a vinylidene chloride copolymer coating to propylene film. The changes in work of adhesion upon immersion of the coated polypropylene in water and surfactant solutions were calculated. When the calculated work of adhesion was negative, spontaneous separation of the coating from the polypropylene occurred upon immersion in all cases. When the calculated work of adhesion was positive, no separation was observed in agreement with theory.

## INTRODUCTION

Many important uses of polymers require that they adhere strongly to one another under a variety of environmental conditions, e.g., coatings on films for packaging applications. These coatings are generally applied to film substrates either from solution or from dispersion, and adhesion after evaporation of the solvent or dispersing medium frequently occurs entirely through the operation of secondary or van der Waals forces (and hydrogen bonding if the polymers are polar). Often, however, polymers that exhibit strong adhesion when dry fail completely when exposed to water vapor, liquid water, or aqueous solutions.

Fowkes[1] has advanced the simple but illuminating hypothesis that the free energy of a liquid, $\gamma_{LV}$, is the sum of the surface forces due to various types of molecular attraction such as dispersion forces, $\gamma_L^d$, and hydrogen bonding forces, $\gamma_L^h$, in the case of water. Thus the surface free energy of water can be expressed as follows:

$$\gamma_{LV} = \gamma_L^d + \gamma_L^h. \tag{1}$$

He then proposed that the attractive force across the interface between immiscible liquids was due to the interaction of like forces; unlike forces are assumed not to interact. He then developed an expression for the interfacial free energy between two liquids based on dispersion forces alone. Owens and Wendt[2] have expanded Fowkes' equations to include the hy-

drogen bonding term.    Thus, the interfacial free energy $\gamma_{BC}$ between two liquids B and C is given by

$$\gamma_{BC} = \gamma_B + \gamma_C - 2\left(\sqrt{\gamma_B{}^d\gamma_C{}^d} + \sqrt{\gamma_B{}^h\gamma_C{}^h}\right). \tag{2}$$

With liquids, the interfacial free energy between immiscible pairs is a measure of the degree to which the liquids interact with one another. When the interfacial free energy is high, as between aliphatic hydrocarbons and water, the interaction is low.    The reason for this high interfacial free energy between hydrocarbons and water is that the hydrogen bonding component of free energy of water cannot interact with the hydrocarbon and appears at the interface as a free energy.    Another measure of the attraction across an interface is the reversible work of adhesion, $W_A$.    This quantity is given by eq. (3), the familiar Dupré relationship, and its equivalent in terms of surface energy components,

$$W_A = \gamma_B + \gamma_C - \gamma_{BC} = 2\left(\sqrt{\gamma_B{}^d\gamma_C{}^d} + \sqrt{\gamma_B{}^h\gamma_C{}^h}\right), \tag{3}$$

and is the work required to separate B and C thereby creating unit areas of B and C surface at the expense of a unit area of B–C interface.    In the case of a liquid L on a solid, the work of adhesion can also be expressed in terms of the contact angle $\theta$:

$$W_A = \gamma_L(1 + \cos\theta). \tag{4}$$

Although these concepts have been developed for liquids, there is no a priori reason why they are not equally applicable to solid–solid interfaces. Difficulties arise, however, because it is not possible to measure directly the surface and interfacial free energies of solid systems.    These difficulties have been largely overcome by Owens and Wendt[2] who have described a simple contact angle method whereby the components of surface free energy of a solid due to dispersion and hydrogen bonding forces may be estimated. For the solid surface, the total free energy should then be the sum of the dispersion and hydrogen bonding components by analogy with eq. (1). With these values, a theoretical interfacial free energy between two solids can be calculated by eq. (2).

Let B represent the substrate film and C the coating.    If a coating–substrate interface is immersed in a liquid L, the expression for the reversible work of adhesion becomes

$$W_A = \gamma_{BL} + \gamma_{CL} - \gamma_{BC} \tag{5}$$

where the appropriate solid surface free energies are replaced by solid–liquid interfacial energies.    If the interfacial free energy $\gamma_{BC}$ between the solids is high, and if the liquid interacts strongly with B or C or both so that $\gamma_{BL}$ and $\gamma_{CL}$ are low, then it is possible for the calculated work of adhesion to be negative.    Under these circumstances, the separation of B and C is favored and will occur spontaneously since the free energy of the

system is reduced thereby.   The condition for spontaneous separation may be written as follows:

$$\gamma_{BC} > \gamma_{BL} + \gamma_{CL}. \tag{6}$$

If the work of adhesion is positive, it means simply that work must be done on the system to separate the solids, and separation will not be spontaneous.

## EXPERIMENTAL

To evaluate the validity of these concepts, biaxially oriented polypropylene film coated with an aqueous polymer dispersion was used.   The dispersion was applied to the film at 30% solids and dried with hot air to give a coating approximately 5 $\mu$m thick.   The coating polymer was a copolymer of 80 parts vinylidene chloride and 20 parts methyl acrylate and contained 4% (based on the weight of the other two components) acrylic acid.[3]   The polymer was made in a surfactant-free system using persulfate–bisulfite initiator.[4]   The surface of the polypropylene film was oxidized by flame treatment,[3] and the surfaces of the coating and the polypropylene film were characterized by the contact angle method of Owens and Wendt.[2]   The solutions in which the coated films were immersed were characterized for components of surface energy by measuring their surface tensions by the ring method with the usual corrections and by measuring interfacial tension between the solution and $n$-hexadecane also by the ring method.[5]   The components of surface energy of the surfactant solutions were then calculated from surface and interfacial tension measurements through the use of eq. (2).   Since $n$-hexadecane does not hydrogen bond, the $\sqrt{\gamma_B{}^h\gamma_C{}^h}$ term of eq. (2) is zero.   The hydrogen-bonding component of the surfactant solution is found by difference through eq. (1).

## RESULTS

Table I lists the surface properties of the substrate film and the coating. Before flame treatment, the polypropylene film exhibits no hydrogen-bonding component of surface free energy as would be expected from its hydrocarbon structure.   The value of total surface free energy of 30.2 ergs/cm$^2$ is somewhat higher than the value of 28 ergs/cm$^2$ reported elsewhere based on extrapolation of molten surface tension data.[6]   Flame treatment has the effect of creating a polar component of surface free energy

TABLE I
Surface Properties of Adherends

| Solid | $\gamma_s{}^d$ | $\gamma_s{}^h$ | $\gamma_s$, ergs/cm$^2$ |
|---|---|---|---|
| Untreated polypropylene | 30.2 | 0.0 | 30.2 |
| Flamed polypropylene | 33.5 | 4.1 | 37.6 |
| Copolymer coating | 38.9 | 14.7 | 53.6 |

presumably due to oxidation of the film surface. The coating polymer is quite polar, having a hydrogen-bonding component of free energy of 14.7 ergs/cm². This doubtless is due to the presence of the acrylic acid as well as the presence of the acrylate ester groups in the polymer.

The properties of the liquids in which the films were immersed are shown in Table II. The concentration of each surfactant solution was chosen to be above the critical micelle concentration where the thermodynamic properties of the solution are no longer dependent on solute concentration. The major effect of adding surface-active agents to water appears to be that of masking the hydrogen-bonding component of the water. Indeed, some of the more powerful surface-active agents such as the sulfosuccinate esters adsorb to give an interface which thermodynamically resembles a hydrocarbon rather than water. It also appears from Table II that the interfacial tension between alkanes and aqueous solutions arises solely from the unsatisfied hydrogen-bonding components of the aqueous phase, since the dispersion force components of all the solutions except sodium isobutyl-sulfosuccinate are low and nearly equal to the surface tension of $n$-hexadecane.

TABLE II
Properties of Solutions

| Solution | Concn, % | $\gamma_{IF}{}^a$ | $\gamma_L{}^d$ | $\gamma_L{}^h$ | $\gamma_L$, ergs/cm² |
|---|---|---|---|---|---|
| Water | — | — | 21.8 | 51.0 | 72.8 |
| Sodium $n$-octyl sulfate | 3.5 | 14.8 | 26.6 | 14.8 | 41.4 |
| Sodium $n$-decyl sulfate | 1.0 | 11.5 | 28.0 | 11.5 | 39.5 |
| Sodium $n$-dodecyl sulfate | 0.5 | 8.2 | 29.0 | 8.2 | 37.2 |
| Sodium $n$-tetradecyl sulfate | 0.2 | 8.6 | 28.1 | 8.6 | 36.7 |
| Sodium $n$-hexadecyl sulfate | 0.05 | 7.2 | 28.8 | 7.2 | 36.0 |
| Triton X-405[b] | 1.0 | 13.0 | 29.4 | 13.0 | 42.4 |
| Sodium diisobutyl sulfosuccinate | 1.0 | 28.0 | 16.6 | 26.7 | 43.3 |
| Sodium diisoamyl sulfosuccinate | 1.0 | 2.0 | 23.7 | 1.9 | 25.6 |
| Sodium di(2-ethylhexyl) sulfosuccinate | 1.0 | 1.2 | 24.7 | 1.1 | 25.8 |

[a] Interfacial tension of solution versus $n$-hexadecane, $\gamma_{LV} = 27.4$ ergs/cm².

[b] Octylphenol–ethylene oxide (40 moles) condensate.

These conclusions agree completely with those of Becher.[7] From these data, $W_A$ between coating and substrate was calculated to be 3.5 ergs/cm², and $W_A$ between coating, substrate, and liquids can be calculated as shown in Table III. Table III also shows the experimental results of immersing the coated film in the solutions listed. In every case where $W_A$ upon immersion in the liquid is negative, the coating spontaneously separated from the substrate, becoming completely detached. Where $W_A$ was positive, spontaneous separation did not occur. Where separation occurred between coating and substrate, it did so within 15 min. The films that did not show separation were left immersed for six months. At the

TABLE III
Work of Adhesion of Coating to Polypropylene[a]

| Liquid | $\gamma_{CL}$ | $\gamma_{BL}$ | $W_A$, ergs/cm$^2$ | Immersion test[b] |
|---|---|---|---|---|
| Dry | — | — | +87.7 | — |
| Water | 13.3 | 27.4 | +37.3 | NS |
| Sodium n-octyl sulfate | 1.1 | 3.7 | +1.4 | NS |
| Sodium n-decyl sulfate | 1.0 | 2.1 | −0.3 | S |
| Sodium n-dodecyl sulfate | 1.6 | 0.9 | −0.9 | S |
| Sodium n-tetradecyl sulfate | 1.7 | 1.0 | −0.7 | S |
| Sodium n-hexadecyl sulfate | 2.0 | 0.6 | −0.8 | S |
| Triton X-405 | 0.7 | 2.6 | −0.1 | S |
| Sodium diisobutyl sulfosuccinate | 6.4 | 12.8 | +15.8 | NS |
| Sodium diisoamyl sulfosuccinate | 7.9 | 1.2 | +5.7 | NS |
| Sodium di(2-ethylhexyl) sulfosuccinate | 9.3 | 1.6 | +7.5 | NS |

[a] $\gamma_{CB} = 3.5$ ergs/cm$^2$.
[b] S = Spontaneous separation; NS = did not separate.

end of this time, they still were not separated, and some effort was required to remove the coatings from the films.

## SUMMARY AND CONCLUSIONS

Implicit in this investigation of adhesion are certain simplifying assumptions. It is assumed that the coating and substrate are immiscible so that the interface between them is sharp and that adhesion takes place entirely through the operation of secondary forces and hydrogen bonding. It is further assumed that the surfactant solutions behave as simple liquids, having the properties shown in Table II. This last assumption may appear unwarranted in the light of what is known about the nature of surfactant solutions, but it is consistent with the experimental results. In this work, only the surface and interfacial properties of the solution are considered. These are perhaps less complex than the bulk of the solution, which contains micelles as well as molecularly dispersed surfactant. At the air–liquid or solid–liquid interface, one expects to find an excess of surfactant present as a monolayer whose degree of orientation and close packing is a function of the constitution of the surfactant molecule. The hydrocarbon portion of the molecule will be oriented away from the water in the systems under consideration. The physical picture of the surface of a surfactant solution is then that of a water surface partly covered with a hydrocarbon where the amount of exposed water is determined by the ability of the surfactant to form a close-packed monolayer. Surface and interfacial tension measurements then give an average of the contributions from the hydrocarbon and the exposed water.

In order for a liquid to displace two adhering solids from one another, it must interact fully with both solids so that the liquid–solid interfacial

energies are low and separation of the solids results in a net decrease of the free energy of the system. Since the components of surface free energy due to dispersion and hydrogen-bonding forces appear to interact with like forces in a contacting solid or liquid but not with unlike forces, a liquid of low hydrogen-bonding ability cannot interact fully with a surface that has a high hydrogen-bonding ability, nor can a liquid of high hydrogen-bonding capacity interact fully with a surface having low hydrogen-bonding capacity. This concept explains the experimental observation that there is a range of liquid surface tensions outside of which spontaneous separation of the adhering solids does not occur. It also explains the rather surprising observation that the most efficient surfactants in terms of surface tension lowering do not cause spontaneous separation of the coating and substrate. These surfactants mask the hydrogen-bonding component of the aqueous phase so completely that the hydrogen-bonding components of free energy in the coating and substrate are not satisfied and interfacial free energy between coating, substrate, and liquid is high. The same is true at high values of surface tension where the large hydrogen-bonding component of the liquid is not satisfied by the like component of the coating and substrate, and again a substantial interfacial free energy results. In cases where spontaneous separation does not occur upon immersion in the liquid, there is nonetheless a reduction in the reversible work of adhesion of the system, and a reduction in the actual adhesive force between the coating and the substrate would be expected. Because of the well-known difficulties of measuring the actual adhesion between substances, no attempt was made to measure this reduction in adhesive strength where separation was not clearly spontaneous. With suitable control of external variables, it may be possible in the future to evaluate the reduction in actual adhesion from calculations of $W_A$ in cases where spontaneous separation does not occur.

## References

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