KRÜSS

Application Report

Adhesion Energy and Interfacial Tension

Application report: AR232e

Industry section: All (Packaging, automotive, printing, electronics, medical)

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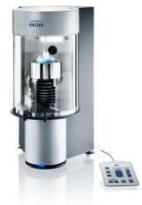
Drop Shape Analysis System DSA10



Force Tensiometer – K100

Method: SFE

Keywords: Interfacial tension, surface free energy, fishing line, coating, adhesion, hotmelt, cardboard

Adhesion Energy and Interfacial Tension

Two Related Coating/Substrate Interfacial Properties

Which is More Important for Your Application, and Why?

Background

Amongst our customers, the major reason for determining surface energy and surface polarity values is as a basis for modification of either a substrate or a coating (paint, ink, or adhesive) to improve wetting, spreading, and/or adhesion. When improved adhesion is the primary goal, two important, guiding, interfacial parameters are gained from surface energy and surface polarity characterization: physio-chemical **adhesion energy,** and coating/substrate **interfacial tension**.

Assuming a simple two component (geometric mean) surface energy approach, such as Fowkes or Owens/Wendt, the predicted adhesion energy (Ψ_{SL}) between a coating and a substrate is given by the Fowkes/Dupre expression:

$$\Psi_{SL} = 2\,(\sigma_S^D\,\sigma_L^D)^{1/2} + 2\,(\sigma_S^P\,\sigma_L^P)^{1/2}$$

wherein: σ_S^D and σ_S^P = the dispersive and polar components, respectively, of the substrate, and σ_L^D and σ_L^P = the dispersive and polar components of the coating. The total surface energy of either material equals the sum of the polar and dispersive surface energy components. And, the surface polarity is the percentage of the overall surface energy which is due to the polar surface energy component.

The interfacial tension (γ_{SL}) between the coating and the substrate is given by Good's expression:

$$\gamma_{SL} = \sigma_S + \sigma_L - 2\,(\sigma_S^D\,\sigma_L^D)^{1/2} - 2\,(\sigma_S^P\,\sigma_L^P)^{1/2}$$

wherein σ_S = overall surface energy of the substrate, σ_L = overall surface tension of the coating.

For further details on the theoretical backgrounds and developments of these equations, I recommend readers begin with either Kruss Technical Note #306 (available for download at www.kruss-scientific.com).

Adhesion Energy or Interfacial Tension?

The two properties, adhesion energy and interfacial tension, are closely related – particularly when a two-component (polar and dispersive) surface energy characterization is employed. In fact, the two equations above can be combined to show that adhesion energy (Ψ_{SL}) simply equals the difference between the sum of the energies of the two surfaces being brought together, less the interfacial tension that remains in the bond which is formed between them. $\Psi_{SL} = \sigma_S + \sigma_L - \gamma_{SL.}$ Perhaps for this reason, many researchers, and quality control engineers, have focused more heavily on the quantitative value for adhesion energy, and tended to ignore substrate/coating interfacial tension – most often noting only that "the interfacial tension should be low for the adhesion energy to be maximized".

In lithographic printing, for example, much focus has been placed on determining adhesion energy values for the print paste/ink, to the print and non-print surfaces on the print plate, to the blanket, and to the final print substrate. Using such adhesion energy information, various competitive adsorption and transfer energies can be understood, and controlled, to provide for good rapid printing. In particular, in high speed printing operations it is useful to understand the dynamic adhesion energy between the ink and the print surface on the print plate, as related to line speed – because the most rapid line speed at which printing can successfully occur is usually determined by comparing these values to the cohesion energy of the ink at that same line speed.

And, on a broader scale, the usefulness of quantitative adhesion energy characterizations has led to the evolution of many highly generalized quality control specifications for adhesion energy in various other industries. As examples: 70 mJ/m^2 of adhesion energy is considered adequate for most latex paint applications to surfaces, 65 mJ/m^2 is often quoted as adequate for organic coatings applications to metals, while 60 mJ/m^2 is adequate for printing on sized paper and many polymer films, and a 10 mJ/m^2 gap in adhesion energy is desired to allow transfer of coatings from one roller to another in roll coating operations.

However, such focus on adhesion energy has also led researchers to ignore substrate/coating interfacial tensions as useful characterization values. This is not a good idea. Despite being inherently and mathematically linked, adhesion energy and interfacial tension are different parameters. Interfacial tension values provide different, sometimes even more pertinent, information than adhesion energy values do – depending on the application at hand.

The difference is this: Adhesion energy, $\Psi_{SL} = \sigma_S + \sigma_L - \gamma_{SL}$, tells you how energetically favorable the initial formation of an interface (coating/substrate bond) is. In forming a bond, you sacrifice substrate (solid) surface and coating (liquid) surface, and you create an interface. Thus, the form of the original adhesion energy equation of Dupre, as sited immediately above. Dupre's definition pre-dates the current concepts of multi-component (polar and dispersive, or acid, base, and dispersive, or even more complicated) surface energy theories, which we make use of today. All of the current theories support this fundamental definition, but the fundamental definition itself pre-dates the theories.

Interfacial tension, on the other hand, has less to do with the original surface energies of the substrate (solid) and the coating (liquid) which form the interface. It is, of course, influenced by those surface energies, as well as the compatibility of the two materials in terms of surface polarity. However, interfacial tension is, fundamentally, a property of the bond after it is formed. Two materials have come together, sacrificing their surfaces to form an interface. Adhesion energy describes the energetic favorability of this interface formation process. Whereas, interfacial tension describes the incompatibility which is inherently left over after the interface is formed (i.e. the propensity of the bond to break in the future, if a stress is applied).

If an analogy helps here, the best one is probably marriage. Adhesion energy = the driving force (the excitement) which two people have for getting married. Interfacial tension = those underlying incompatibilities, which can later lead to divorce (given the right external stressors). You probably know of marriages started by very high "adhesion energy", but which also have very high "interfacial tension". Most of these, like poor coating/substrate bonds, were chosen for formation because people ignored the high "interfacial tension", since the "adhesion energy" looked so favorable.

Now, getting back to title topic of this paper… For your application – be it applying a paint, adhesive, ink, or other coating to an interface – how do you know which parameter is more important to you, adhesion energy or interfacial tension? The answer is you should consider both, including what stressors may be applied to the interface after its formation. Here are two examples, based on work performed in our laboratory over the last few months, of interfacial tension being more important than adhesion energy.

Example 1 – Coated Fishing Line

We recently had a customer making high strength, Kevlar® based, fishing line. They apply an organic coating to the line to give it color, and also to allow it to cast more effectively (with lower friction). The problem they were having was that the coating kept wearing off of the fishing line after 40 to 50 casts in water.

We initially investigated the adhesion energy between the line and the coating and determined it to be 59.53 mJ/m^2, based on the following line and coating properties:

	Kevlar® Based Line	Organic Coating
Overall Surface Energy (mJ/m^2)	34.52	26.53
Polar Component (mJ/m^2)	1.11	3.33
Dispersive Component (mJ/m^2)	33.41	23.20
Surface Polarity (%)	3.23	12.56
Adhesion Energy to Coating (mJ/m^2)	**59.53**	N/A
Interfacial Tension with Coating (mN/m)	**1.52**	N/A

The Kevlar® line data is based on average measured contact angles for diiodomethane and water of 51.6° and 89.2° respectively, on the line, by the bundled fiber ("straw") method on a Kruss Tensiometer K100. The coating characterization is based on pendant drop analysis of the overall surface tension (energy) of the coating and contact angle analysis of the coating against a model poly(tetrafluoroethylene) (PTFE) surface. These experiments were performed using a Kruss Drop Shape Analysis System DSA10. Average contact angle for the coating on PTFE was 57.3°.

In addition to the adhesion energy of 59.53 mJ/m^2, one can also estimate that the interfacial tension left in the fishing line/coating bond is 1.52 mN/m in this case. Based on this information, the customer decided to try to enhance the adhesion energy between the coating and the line. This was done by plasma treating the line prior to coating application. Seemingly, this was a good idea. Plasma treatment compatibilized the line and the coating in terms of surface polarity, increased the adhesion energy between the line and the coating to 64.54 mJ/m^2, and diminished the interfacial tension to 1.24 mN/m. As shown below:

	Plasma Treated Kevlar® Based Line	Organic Coating
Overall Surface Energy (mJ/m^2)	39.25	26.53
Polar Component (mJ/m^2)	4.88	3.33
Dispersive Component (mJ/m^2)	34.37	23.20
Surface Polarity (%)	12.43	12.56
Adhesion Energy to Coating (mJ/m^2)	**64.54**	N/A
Interfacial Tension with Coating (mN/m)	**1.24**	N/A

New data is based on average measured contact angles for diiodomethane and water of 49.8° and 76.1° respectively, on the plasma treated line, by the bundled fiber ("straw") method on a Kruss Tensiometer K100.

<u>However, in application it actually made the situation worse! The coating now started to come off the line after less than 10 casts!!</u> What did the customer do wrong? He forgot about interfacial tension, with regards to the bond breaking stresses involved in the application. During fishing line use, the bond between the line and the coating is being subjected to the stresses and strains of being cast, and it was being exposed to water routinely. The stresses and strains of casting cause microchasms (minute cracks) in the coating – which there is little chance to completely avoid. Once these cracks develop, water has a chance to find the surface of the line, under the coating, and replace the coating at the surface.

The extent to which the water acts to remove the coating is dependent on the ratio of the water's affinity for the surface versus the coating's affinity for the surface. In other words, the ratio between the interfacial tension that water would have on the line's surface versus the interfacial tension that the coating has on the line's surface. If we properly consider this aspect of the application, and calculate the respective ratios of interfacial tensions, as shown below:

	Untreated Kevlar® Based Line	Plasma Treated Kevlar® Based Line
Overall Surface Energy (mJ/m^2)	34.52	39.25
Polar Component (mJ/m^2)	1.11	4.88
Dispersive Component (mJ/m^2)	33.41	34.37
Surface Polarity (%)	3.23	12.43
Adhesion Energy to Coating (mJ/m^2)	**59.53**	**64.54**
Interfacial Tension with Coating (mN/m)	**1.52**	**1.29**
Interfacial Tension with Water (mN/m)	**33.54**	**21.71**
Ratio by which Coating/Line Interface is Preferred to Water/Line Interface	**22.06**	**17.48**

The key to how we made our coating adhesion worst, in this application, is in the last few of values in the table above. Water, which has an overall surface energy of 72.8 mN/m with 63.7% surface polarity has a much lower interface tension against the plasma treated line (21.71 mJ/m^2) than it does against the untreated line (33.54 mJ/m^2). So, while it seems a good idea to plasma treat the line, in order to raise overall surface energy, surface polarity, and the adhesion energy to the coating, the customer has also inadvertently given water a better chance of displacing the coating than it had before he treated the line. You see, it's not just about adhesion energy! You have to consider interface tension, against other options a surface may have to create and interface.

The solution to this particular problem was to discontinue plasma treatment of the line, and rather reformulate the coating somewhat, in order to provide for a more favorable resistance to water displacement of the coating from the untreated line. A coating with the following properties was evidentially used to solve the problem:

	Newly Formulated Coating
Overall Surface Energy (mJ/m^2)	26.40
Polar Component (mJ/m^2)	1.55
Dispersive Component (mJ/m^2)	24.85
Surface Polarity (%)	5.89
Adhesion Energy to Untreated Line (mJ/m^2)	**60.25**
Interfacial Tension with Untreated Line (mN/m)	**0.67**
Untreated Line/Water Interfacial Tension (mN/m)	**33.54**
Ratio by which Coating/Line Interface is Preferred to Water/Line Interface	**50.14**

This new coating is found to be successful in staying bound to the line after more than 250 casts, even though it offers lower adhesion energy than the plasma treated line/old coating combination. Why? Because, it offers better resistance to water displacement of the coating (ratio of water interfacial tension to coating interfacial tension of 50.14, versus only 17.48 for the plasma treated/old coating combination, and 22.06 for the original problematic case).

Example #2 – Hot Melts Adhesives – Keeping Boxes Closed Until You Open Them

Another, perhaps more broad based industry, which has recently come to understand the importance of the difference between adhesion energy and interfacial tension, is the hot melt adhesives industry. Hot melts adhesives are used to close many common food boxes (cereal, crackers, etc.). The goal: Keep the box closed, as it is transported and distributed often in a wide variety of climates (temperatures and humidities). But, at the same time, allow the box to be opened easily and neatly at the adhesive/sized cardboard interface (without fiber pullout from the cardboard), when the customer wishes to eat.

Hot melts adhesives vary in surface tension from about 20 mN/m to 33 mN/m and in surface polarity between 2% and 30%. They can also vary quite a bit in either property just from lot-to-lot, even from the same supplier. If you're a box maker, choosing the right one for your application (given the surface properties of the sizing on your cardboard), often involves considering interfacial tension, as well as adhesion energy.

For example, last summer we had a customer who was seeing far too many "pops" (box openings in high humidity conditions). His bond failure was occurring between his adhesive and a sized cardboard surface having a surface energy of 36.52 mJ/m^2 with 26.6% surface polarity. The problem was fixed by changing adhesives as highlighted quantitatively below. The surface tension values given are for the adhesive tested at 130°C, using a Kruss high temperature pendant drop system.

	Problematic Hot Melt	Better Hot Melt
Number of Box Top "Pops" per 1000 Boxes Stored One Month at 95% RH and 40°C	**124**	**17**
Overall Surface Tension (mN/m)	26.34	25.36
Polar Component (mN/m)	2.70	4.68
Dispersive Component (mN/m)	23.64	20.68
Surface Polarity (%)	10.26	18.46
Sized Cardboard /Hot Melt Adhesion Energy (mJ/m^2)	**60.60**	**60.58**
Sized Cardboard/Hot Melt Interfacial Tension (mN/m)	**2.26**	**1.30**
Sized Cardboard/Water Interfacial Tension (mN/m)	**13.67**	**13.67**
Ratio by which Sized Cardboard/Hot Melt Interface is favored over Sized Cardboard/ Water Interface	**6.05**	**10.51**

The change of hot melts had little effect on the adhesion energy to the cardboard, and thus would not be expected to change the effort it takes a customer to open the box. However, by using a hot melt which is more closely matched, in surface polarity, to the sizing on the cardboard, the interfacial tension in the bond has been decreased. So, the interfacial tension is further below the interfacial tension that water has with the sized paper. This gives ambient moisture less of a chance to break the bond prematurely. Our customer, a box manufacturer, has now set a specification on incoming adhesive lots that they must have interfacial tensions of less than 1 mJ/m^2 on his sized cardboards. This maximizes his interfacial tension advantage for his boxes to stay closed in humid environments.

Neither of these problems have obvious solutions when only adhesion energy, and not interfacial tension, is considered. So, please remember to consider your own applications in terms of both, whenever possible.

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