Application Report

Coating of fibers

Application report: AR245e
Industry section: Textiles
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Date: 2005

Force Tensiometer – K100

Drop Shape Analysis System DSA10

Method:

Keywords: fiber coating, composite, non-woven, adhesion energy, surfactant, interfacial tension, coating thickness, wear resistance, Marangoni effect, critical micellar concentration CMC

The role of surfactants, adhesion energy and interfacial tensions in fiber coating applications

Abstract

Fibers affect all of us in one way or another during our daily lives. They may be used in the form of a composite material, a woven or non-woven technical textile or even in reinforced concrete structures. The surface properties of these fibers play a key role in delivering the performance required by a particular process or final product. To impart the fiber with the appropriate surface properties, surface treatments or coatings are applied and most often serve to protect, functionalize, lubricate, color code and sometimes decorate the surface. This article focuses upon two important aspects of the surface chemistry related to fibers: the influence of surfactant concentration in coating formulations upon the coating thickness and the optimization of finished coating performance through the exploitation of fiber-coating adhesion energy and interfacial tension values calculated from contact angle and surface tension measurements.

Surface tension, CMC and coating thickness on fibers

Generally, coating is achieved by drawing a fiber at a given speed through a bath containing the coating liquid. As the fiber traverses the liquid air interface, a thin layer of coating is deposited onto it. Early work on film coating problems was carried out by Landeau and Levich [1] and Derjaguin [2] who determined the relationship between substrate geometry (fiber) and speed (U) in the low capillary number limit,

$$C = \frac{\mu U}{\gamma} << 1$$

where C is the capillary number, μ is the fluid shear viscosity and γ is the fluid surface tension.

This so-called LLD relationship for the fiber coating film thickness for Newtonian fluid in the absence of surfactant was found to be:

$$\frac{h}{b} = 1.34C^{2/3}$$

Where h is the coating thickness and b is the fiber radius.
The wetting of fibers with surfactants at different concentrations both below and above the CMC has been the subject of a number of studies. It has been generally been observed that the presence of surfactant in a solution at concentrations below the CMC leads to a thickening of the film-coating compared to that of the pure solution.
The reason for this is illustrated in Figure 1.

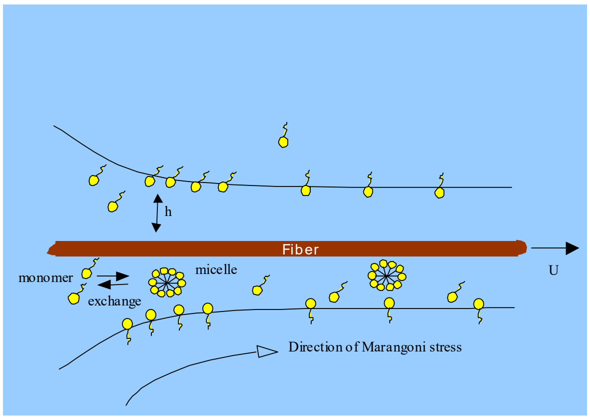

Fig. 1: Diagram of a fiber being drawn through a liquid bath in the presence of surfactant.

The mechanism for the observed film thickening with a surfactant solution is due to stretching of the interface as it is dragged out from the meniscus by the fiber. This stretching alters the concentration of surfactants, which results in a surface tension gradient along the interface. Stress along the film resulting from this surface tension gradient is commonly referred to as the Marangoni effect. In the case of a fiber being coated by a surfactant solution, the Marangoni stress is caused by a difference in the concentration of surfactant between the meniscus and the continuous film region along the fiber. This results in an additional traction along the direction of pull towards the film and leads to a thickening of the film.

The influence of surfactants is not restricted to a simple increase of the film thickness with increased surfactant concentration. In fact, for surfactant concentrations close to and above the CMC, the film thickness can decrease with increasing surfactant concentration. This has been reported for both surfactant solutions of SDS [3],[4] and Triton X100 [4].

This effect can be explained as follows. As the surfactant concentration reaches and exceeds the value of CMC, micelles form in the solution. As these micelles are in constant dynamic equilibrium with free surfactant monomer in the bulk, monomers are being constantly exchanged with micelles. In this way, micelles close to the interface can act as reservoirs of free monomer that can adsorb at the interface resulting in a more uniform distribution of surfactant at the surface compared with bulk surfactant concentrations below the CMC. Consequently, the Marangoni effect is reduced and in turn the film thickness decreases. This effect has been referred by Stebe et al [5],[6] as surface re-mobilization.

The extent to which the presence of surfactant affects the film thickness has been described as the thickening factor [4] and is given by:

$$\alpha = \frac{h}{h_{LLD}}$$

where h is the measured film thickness of the surfactant solution and h_{LLD} is the thickness predicted by the previously mentioned LLD relation. In the case of sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$), α increases from a value of 1 at zero concentration to a first maximum $\alpha \cong 2$ at a concentration of 0.4 x CMC. As the bulk concentration surpasses the CMC, α begins to decrease with increasing concentration. This decrease is consistent with the surface re-mobilization effect described above.

When the concentration reaches 10 x CMC, the film starts to thicken again and reaches a second maximum at 25 x CMC at a value again of $\alpha \cong 2.0$ followed by a further decrease to $\alpha \cong 1.6$. These fluctuations in film thickness are a result of the changing kinetics of micelle-monomer exchange with increase bulk concentration of surfactant. In other words, the stability characteristics of micelles – and thus their ability to exchange monomers to the interface – are dependent upon the bulk concentration of surfactant. These kinetics and the stability characteristics of micelles will of course vary for different surfactants or mixtures of surfactants. Consequently the variation in film thickness with bulk concentration of surfactant will also exhibit different behavior.

Keeping the coating on. Adhesion energy or interfacial tension?

In fiber coating applications, the aim is typically to improve the wetting and adhesion between the fiber and the coating liquid. This can be achieved by modifying the surface characteristics of the fiber surface or by adjusting the formulation of the coating liquid. In either case, this will lead to a change in the surface energy (and probably the surface polarity) of the respective phase. These changes can be calculated from contact angle and surface tension data measured on the respective phases. From these surface energy values, two important, guiding, interfacial parameters are gained: physico-chemical adhesion and coating/substrate interfacial tension. These are described as follows.

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

$$\Psi_{SL} = 2(\gamma_S{}^D \gamma_L{}^D)^{1/2} + 2(\gamma_S{}^P \gamma_L{}^P)^{1/2}$$

where γ_S^D and γ_S^P are the disperse and polar components, respectively, of the substrate and γ_L^D and γ_L^P are the disperse and polar components of the liquid. The total surface energy of either material equals the sum of the disperse and polar surface energy components. The surface polarity is given by the percentage of the overall surface energy that is due to the polar surface energy component.

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

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S{}^D \gamma_L{}^D)^{1/2} - 2(\gamma_S{}^P \gamma_L{}^P)^{1/2}$$

where γ_S is equal to the total surface energy of the substrate and γ_L the total surface tension of the coating.

A more detailed treatment of the theoretical backgrounds and developments of these equations has already been reported [7].

The two properties, adhesion energy and interfacial tension are closely related. By combining the two previous equations we can show that adhesion energy (Ψ_{SL}) simply equals the sum of the energies of the two surfaces being brought together, less the interfacial tension which remains in the bond which is formed between them.

$$\Psi_{SL} = \gamma_S + \gamma_L - \gamma_{SL}$$

Researchers very often tend to focus solely upon the adhesion energy value simply noting that the interfacial energy should be low for the adhesion energy to be high. This is not always a good idea, as we will illustrate below. Despite being inherently linked mathematically, adhesion energy and interfacial tension are different parameters. Depending upon the application in question, interfacial tension values can provide different and sometimes more pertinent information than adhesion energy. The difference between the two is this: Adhesion energy tells you how energetically favorable the initial formation of an interface (fiber/coating) is. In forming a bond, you sacrifice substrate (fiber) surface and coating (liquid) surface and you create an interface.

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 (though it is influenced by these surface energies). It is fundamentally a property of the bond after it is formed. When two materials come together, they sacrifice their surface energies to form an interface. Adhesion energy describes the energetic favorability of interface formation whereas interfacial tension describes the incompatibility which is left over once the interface is formed (the tendency for the bond to break if stress is applied).

The usefulness of both these parameters is nicely illustrated by the following example. It involves the manufacture of a high-strength fishing line that is coated to add color and to allow it to cast more efficiently. In this case the problem was that the coating wore off the fishing line after just 40 to 50 casts. The surface energy values of the Kevlar® line were calculated from the contact angle values of water and diiodomethane measured with a K100 tensiometer using the bundled fiber (straw) method [8]. Having determined the surface energy values of the coating and line, the adhesion energy and the interfacial tension between line and coating were determined to be 59.53 mJ/m^2 and 1.52 mN/m respectively (Table 1).

	Organic coating	Untreated Kevlar® Line	Plasma treated Kevlar® Line
Overall surface Energy (mJ/m^2)	26.53	34.52	39.25
Polar component (mJ/m^2)	3.33	1.11	4.88
Disperse Component	23.20	33.41	34.37
Surface Polarity (%)	12.56	3.23	12.43
Adhesion energy to coating	N/A	59.53	64.54
Interfacial tension with coating (mN/m)	N/A	1.52	1.24
Interfacial tension with water (mN/m)	N/A	33.54	21.71
Ratio by which coating/line interface is preferred to water/line interface.	N/A	22.06	17.48

Table 1

In an attempt to increase the adhesion energy, the line was plasma treated before being coated. This treatment made the line more compatible with the coating in terms of its surface polarity resulting in an increase in adhesion energy to 64.54 mJ/m^2 (Table 1). The interfacial tension value decreased to 1.24 mN/m. By increasing the adhesion energy and reducing the interfacial tension between line and coating one would expect to observe an improvement in performance. In reality, performance was worse with the coating now coming off after just 10 casts!

So what could explain this unexpected behavior? The answer lies in the interfacial tension with respect to the bond breaking stresses experienced by the line during its usage. As the line is cast during fishing, the stresses and strains associated with this action, cause minute cracks on the coating surface which are difficult to prevent. Any water present can now penetrate under the coating via these cracks, to reach the line surface and replace the coating. The extent to which the water does this, is dependent upon the ratio of the water's affinity to the line's surface versus the coating's affinity to the line's surface. This can also be expressed as a ratio of the interfacial tension that water has on the line's surface to the interfacial tension that the coating has on the line's surface. The greater this number, the less likely is the chance that the water will replace the coating at the fiber's surface. These values for interfacial tension and water/coating interfacial tension ratios are shown in table 1 for the untreated and treated lines.

Although the plasma treatment of the line has increased the adhesion energy between line and coating from 59.53 to 64.54 mJ/m^2, it has also reduced the water-line interfacial tension from 33.54 to 21.71 mJ/m^2. This now gives water a better chance of displacing the coating with the plasma treated line than with the untreated line and results in poorer overall performance. The final solution to this problem was to abandon plasma treatment of the Kevlar® line in favor of reformulation of the coating to give a more favorable resistance to coating displacement by water. This resulted in the adhesion energy and interfacial tension values against the untreated line as indicated in Table 2.

	Reformulated organic coating
Overall surface Energy (mJ/m^2)	26.40
Polar component (mJ/m^2)	1.55
Disperse Component	24.85
Surface Polarity (%)	5.89
Adhesion energy to untreated line	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

Table 2

Even though the adhesion energy is lower than that with the plasma treated line, casting performance has improved (>250 casts). This can be explained by an improved resistance to water displacement of the coating, indicated by an increase in the ratio of water interfacial tension to coating interfacial tension to 50.14 mJ/m^2 compared with 17.48 mJ/m^2 for the plasma treated line/old coating combination and 22.06 for the untreated line/old coating. So, as we stated at the beginning, simply focusing on adhesion energy does not always solve problems. They sometimes also require careful consideration of the interfacial tensions involved in all processes related to the application.

Summary

The presence of surfactant in a fiber coating solution at concentrations below the CMC leads to a thickening of the film-coating compared to that of the pure solution. This increase can be explained by the Marangoni stresses caused by a difference in the concentration of surfactant between the meniscus and the continuous film region along the fiber. At concentrations close to and above the CMC a decrease in film thickness can be observed as micelles close to the interface reduce the Marangoni stresses by supplying surfactant monomer to the interface resulting in a more uniform distribution of surfactants.

In coating applications, improved fiber to coating adhesion can be achieved by modifying either the surface characteristics of the fiber surface or by adjusting the formulation of the coating liquid. Both of the important interfacial parameters – interfacial tension and physico-chemical adhesion energy should be taken into consideration when evaluating the effect of these changes. Exclusive focus on an increase in the adhesion energy between fiber and coating through surface treatment of the fiber can lead to undesirable competing processes such as water penetration to the fiber surface. In this case, careful analysis of interfacial tension can lead to more appropriate measures such as reformulation of the coating solution as a means of optimizing adhesion whilst at the same time minimizing the affinity of water to the fiber.

Literature

[1] L. Landau and B. Levich, “Dragging of a liquid by a moving plate” Acta Physicochim. URSS 17, 42 (1942).

[2] B. Derjaguin, “On the thickness of the liquid film adhering to the walls of a vessel after emptying” Acta Physicochim. URSS 20, 349 (1943).

[3] D. Quéré, A. de Ryck, and O. Ou Ramdane, “Liquid coating from a surfactant solution” Europhys. Lett. 37 305 (1997).

[4] A. Q. Shen, B. Gleason, G. H. McKinley and H. A. Stone, "Fiber Coating With Surfactant Solutions ", Physics of Fluids, 14(11) 4055—4068 (2002).

[5] K. J. Stebe, S. Lin, and C. Maldarelli, “Remobilizing surfactant retarded fluid particle interfaces. I. Stress-free conditions at the interfaces of micellar solutions of surfactants with fast sorption kinetics” Phys. Fluids A 3, 3 (1991).

[6] K. J. Stebe and C. Maldarelli, “Remobilizing surfactant retarded fluid particle interfaces. II Controlling the surface mobility at interfaces of solutions containing surface active components” J. Colloid Interface Sci. 163, 177 (1994).

[7] “So You Want to Measure Surface Energy? By Dr Christopher Rulison. ” Krüss technical note #306 available at www.kruss.de.

[8] “Contact Angle Determination by the "Straw" Method and Packed Cell Method”, by Dr Christopher Rulison. Krüss technical note #206 available at www.kruss-scientific.com

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