A METHOD TO CHARACTERIZE MATERIALS TO BE USED ON OLEOPHILIC SKIMMERS [1]

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ABSTRACT

A significant amount of effort is being devoted by scientists and industry in order to increase the efficiency of oil spill recovery equipment as it determines the impact of oil spills on coastal ecosystems as well as the time and cost of cleanup operations. One way to increase the efficiency of adhesion skimmers is to replace traditional recovery materials with polymeric materials that have the highest affinity for oil. The research conducted at the University of California Santa Barbara has shown that modern scientific equipment such as a Dynamic Contact Angle Analyzer can be used for evaluation of candidate materials and selection of materials that can be most efficiently used for oil spill cleanup. The study found that the contact angle formed between oil and test surface can be used to characterize the affinity of material to oil. The contact angle correlates well with the mass of recovered oil. For a given oil, the lower the contact angle the higher the recovered mass. The study also showed that surface roughness and oil composition have a significant effect on the results of the adhesion tests. Higher roughness results in lower contact angle and larger recovered mass, for the same oil-polymer pair.

1. INTRODUCTION

An adhesion (oleophilic) skimmer is one of the most common types of mechanical recovery equipment. It exploits the property of oil to adhere to the rotating skimmer surface in preference to remaining in the water. The rotating surface lifts the oil out of the water to an oil removal device (e.g. scraper, roller, etc.). The adhesion surface is the most critical element of the skimmer as it determines the efficiency of recovery. Various shapes of the recovery unit, such as a mop, belt, brush, disc, and drum, have been developed to increase skimmer efficiency. Despite these changes, the materials used to manufacture the surface of adhesion skimmers have remained the same. Steel, aluminum, and general-use plastics had been in use for more than 30 years. Material selection has not been based on the adhesive properties, but rather on historical practice, price and availability. Very little effort has been made to study the surface properties of the response materials and utilize this knowledge for optimization of oil spill recovery.

2. PREVIOUS RESEARCH

Over the past decade, intensive research on wettability and adhesion processes between solids and liquids has been conducted in the fields of adhesion science (Mittal, 2002), petroleum reservoirs (Drummond and Israelachvili, 2002) and polymer science (Mittal, 2000). These studies found that for the same test liquid, properties of the polymer such as composition, surface energy, hydrophobicity and surface charge, greatly affect its wetting and adhesive properties. Although polymeric materials have been tested for their affinity to water and various chemicals, their affinity to oil has barely been studied.

Numbers of tests were performed by various oil spill response agencies and equipment manufacturers in the attempt to study the effect of different belt types on skimmer performance. Although these studies tested various configurations of belts, very little or no attention was paid to the material these belts are made of and the effect it has on the recovery efficiency. To our knowledge, there have been only two studies of the dependency of oil recovery on the properties of recovery material. To determine the adhesion between oil and test material, these studies employed "dip-and-withdraw" technique, as described by Jokuty et al. (1995, 1996) and Liukkonen et al (1995). Adhesion was determined as the weight of oil remaining after withdrawal, per unit area of a test surface. Jokuty et al. (1996) tested the adhesive properties of fresh and evaporated oils with a number of materials such as steel, plastic (polyethylene), glass, Teflon, ceramic, and wood. This study indicated that oil adhesive properties differ for various oils, oil weathering degrees and surface material combinations. For certain oils, ceramic and Teflon were found to pick up two times more oil than steel. Roughness of the samples was not reported, so it is hard to conclude whether the results of the adhesion tests were predominantly determined by chemical composition of the test surface or by its roughness. A study by S. Liukkonen et al (1995) on plastics, stainless steel and ice, also found some dependence of oil recovery on surface material type and surface roughness. Only propylene-based polymers where tested in this study.

3. PROPOSED TECHNIQUE

To study the affinity of liquids, such as different crude oils, to various solid surfaces, the contact angle can be measured and used to calculate the work of adhesion. When drop of liquid is deposited on the solid surface, an angle θ is formed (Figure 1).

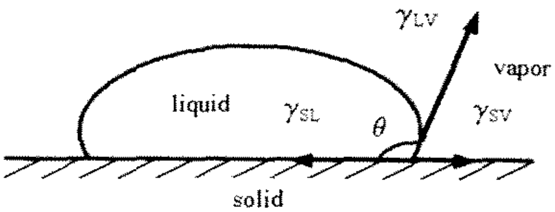

FIGURE 1. CONTACT ANGLE MEASUREMENT, SESSILE DROP TECHNIQUE.

The affinity of the solid for the test liquid increases with decreasing θ. The size of this angle is determined by the equilibrium of surface forces of liquid surface tension (γ_{LV}), solid surface energy (γ_{SV}) and surface tension at liquid-solid interface (γ_{SL}). This relation is described by Young's equation (T. Young, 1805):

$$\gamma_{lv}\cos\theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

The Young-Dupré equation (Young, 1805 and Dupré, 1869) established the relation between work of adhesion, W_A, between solid and liquid, surface tension γ_{LV} and contact angle θ of a sessile drop:

$$W_A = \gamma_{lv}(1+\cos\theta) \quad (2)$$

Work of adhesion is measured in mJ/m^2. It can be easily determined once the contact angle between liquid with known surface tension and test surface is measured. This parameter is very different from the "adhesion" measured by Jokuty et al. (1996) and Liukkonen et al (1995), who determined the adhesion as a weight of oil per unit surface area. In the latter case, cohesion between the molecules of oil film can represent a significant contribution to the amount of recovered oil. While the adhesion force between oil molecules and solid surface may be similar to that one of light oils, in the case of viscous oils, a thicker film is being formed on the test surface and a larger mass of oil is recovered. In the future, we will refer to this parameter as "recovered mass". Work of adhesion, contact angle and recovered mass can all be used to evaluate the affinity of test materials to oil.

While the theory of contact angle measurements is based on the equilibrium of an axisymmetric sessile drop on a flat, horizontal, smooth, homogeneous, isotropic, and rigid solid, it is generally found in practice that a static contact angle does not give a correct representation of the wetting process. It is believed that using the Wilhelmy plate technique and measuring a dynamic contact angle provides more accurate estimates of surface tension. The Dynamic Contact Angle (DCA) analyzer operates by holding a sample of the test surface in a fixed vertical position, attaching it to a microbalance and moving a probe liquid contained in a beaker at a constant rate up and down past the plate. A unique contact angle hysteresis curve is produced by the microbalance as it measures the force exerted by the moving contact angle in advancing and receding directions (Figure 2).

The forces acting on the plate consist of the weight of the plate, the buoyancy of the submerged part of the plate and the surface tension of liquid in contact with the plate. This can be expressed as:

$$F = (\rho_p l w t)g - (\rho_l h w t)g + 2(w+t)g_l\cos\theta \quad (3)$$

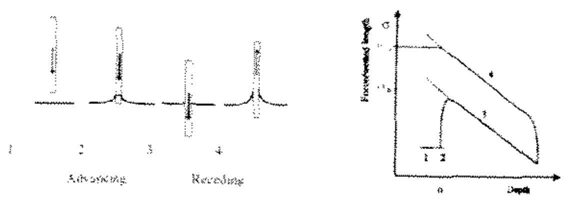

FIGURE 2. DYNAMIC CONTACT ANGLE ANALYSIS BY WILHELMY PLATE TECHNIQUE (KSV INSTRUMENTS LTD.)

where F = force, ρ_p = density of plate, w = width of plate, l = length of plate, t = thickness of plate, g = acceleration due to gravity, ρ_l = density of liquid, h = length of submerged part, γ_l = surface tension of liquid, and θ = contact angle between liquid and plate.

The first term in Equation 3 is eliminated by zeroing the balance after the plate is attached to it. The second term can be neglected because measurements are taken when the plate is withdrawn from the liquid in a way that only its lower edge is in a contact with the liquid, which eliminates the buoyancy term. Equation 3 can be simplified to:

$$F = 2(w+t)\gamma_l\cos\theta \quad (4)$$

Knowing the force needed to draw the plate out of the liquid (F) and the surface tension of the liquid, the contact angle can be expressed as:

$$\cos\theta = F / 2(w+t)\gamma_l \quad (5)$$

Equation 5 is called the modified Young's equation or Wilhelmy equation (Kaya, 2000). This equation assumes that the solid surface is smooth and nonporous. High energy solids (glass, platinum, etc.) can be used to measure surface tension of liquids. It is assumed that a test liquid forms a contact angle equal to 0 with such solids making cosθ = 1. Alternatively, if the surface tension of a liquid is known, the contact angle formed between this liquid and the new test surface can be determined using Equation 5.

The DCA overcomes the limitations of static contact angle measurements by measuring much larger surfaces on liquid solutions rather than single drops on a plate. This eliminates the risk of concentrated contaminants or incomplete profiles.

4. EXPERIMENTAL SECTION

Equipment

For the experimental component of this work, a DCA that utilizes the Wilhelmy plate technique (Cahn Radian 315, Thermo Electron Corporation) was used. This equipment is capable of estimating adhesion-related parameters such as dynamic contact angle, surface tension, surface free energy, surface polarity and amount of adhered oil. This system can be applied to many types and geometries of solid surfaces, including single fibers as small as 0.1 mm in diameter. The Cahn Radian Dynamic Contact Angle Analyzer has been successfully used in the past by other researchers studying wetting and adhesion properties of various surfaces (e.g. Lee Y. et al., 1998 and Della Bona A., 2004). Technical characteristics of DCA are presented in Table 1.

The DCA can also be used to imitate the oil spill recovery process. The system determines oil adsorption by measuring the weight increase of the test surface (plate, fiber or set of fibers) while the sample is dipped into and withdrawn from oil. Oil recovery can be measured as the weight of adhered oil per unit surface area. This mechanism most closely represents the process of oil

Table 1. Measurement characteristics of Cahn Radian DCA 315

Surface Tension Range	Contact Angle Range	Surface Tension Precision	Contact Angle Precision	Balance Precision	Max Sample Weight	Max Sample Diameter	Min Fibe Diameter
1-1000 mN/m	0-180 degrees	± 0.001 mN/m	± 0.01 degrees	1 μg	100 g	75 mm	0.1 mm

withdrawal from the water by the recovery device. This pick-up technique was used in both previous studies of oil adhesion to various materials by Jokuty (1996) and Liukkonen (1995). Recent advances in equipment will allow for automation of this standard technique, leading to more consistent and reliable results.

Materials

Three Alaskan crude oils (Point McIntyre, North Star and Endicott) were used for the experiments. Properties of these oils are summarized in Table 2.

Table 2. Properties of test oils at 15°C.

	North Star	Point McIntyre	Endicott
Density (g/ml)	0.860	0.883	0.910
Surface tension (mN/m)	27.9	28.5	29.8
Viscosity (cP)	9.06	20.2	82.5
% Asphaltenes	Less than 0.5	2.4	4

Three types of commercially available polymers were used for these tests. The test surface dimensions are 22 mm X 22 mm X 0.2 mm. All samples had very smooth surfaces, with roughness less than 10 nm. This eliminated possible error introduced by differences in sample roughness and allows a comparison of the actual adhesion properties of materials.

Methods

Experiments were performed in a temperature-controlled room at 15°C to simulate the temperature of oil spilled in the ocean. Surface tension of test oils was measured using the DCA by the Du Nouy ring method. Test surfaces were pre-cleaned using ethyl alcohol and distilled water, and then blow-dried under nitrogen flow prior every test.

After the test surface was installed in the DCA test chamber, it was automatically dipped into test oil to a depth of 10 mm with a speed of 80 microns/sec and then withdrawn. Weight change during this process was detected and contact angle was calculated using the technique and equations summarized in Section 3. Recovered mass remaining on test surface was measured at the end of each run.

To study the effect of oil recovery on roughness of the test surface, three surfaces of Polymer 2 were evaluated. One surface was used without preparation and had an initial roughness of about 10 nm. Two other surfaces were roughened using sandpaper of grades 220 and 320 to achieve a relatively homogeneous roughness of about 20 μm and 50 μm respectively. Samples were installed in the DCA test chamber, dipped into the test oil to 10 mm and then withdrawn. The contact angle and the mass of oil remaining on the surface were measured.

5. RESULTS AND DISCUSSIONS

The results of the contact angle measurements presented in Table 3 confirm that oil properties have a significant effect on the adhesion process. A more viscous oil (Endicott) forms a thicker film on the test surface allowing a larger amount of oil to be recovered. This is despite the fact that its affinity to the test material (contact angle value) is lower than the one of less viscous oil (North Star). Recovered mass is largely influenced by the cohesion of the oil film (oil-to-oil interactions) and highly depend on oil composition and properties, while the contact angle value is more closely related to interactions at the oil–test surface interface. This observation implies that comparison of materials to evaluate their oleophilicity should be done with a consistent set of oils.

The results indicate that, for a given oil, there is a relation between the amount of adhered oil and the contact angle the oil forms with the test surface. This suggests that the affinity of oil to various materials can be evaluated using contact angle data obtained with the DCA. Contact angle measurements can be performed along with measurements of recovered mass using the DCA. If one only uses the dip and withdraw technique, the results may lead to an erroneous interpretation of adhesion, because significant amount of recovered mass is concentrated in a drop attached to the test surface. The mass of this drop is not determined by the properties of test surface but rather by the properties of oil as well as the geometry and roughness of the lower tip of the test surface.

Roughness of the test material has a large effect on the amount of recovered oil and on the contact angle oil forms with the test surface. When oil is brought into contact with a rough oleophilic surface, oil tends to penetrate into the cavities due to capillary forces and forms a film of uneven thickness. Furthermore, the actual surface contact area between the oil and a rough surface is very different from its two dimensional projection. When compar-

Table 3. Contact angle measurements

	Polymer 1		Polymer 2		Polymer 3	
Oil Type	advancing angle	recovered mass (mg)	advancing angle	recovered mass (mg)	advancing angle	recovered mass (mg)
North Star	25°±1°	3	34°±1°	2.5	37°±1°	2
Point McIntyre	25°±1°	5.5	33°±1°	5	38°±1°	2
Endicott	33°±1°	12.5	42°±1°	11	45°±1°	9

ing materials with different roughness, all equations containing surface area value must be scaled by their roughness factor.

The effect of surface roughness is illustrated by the results in Table 4. The same type of polymer was used to prepare samples with increasing roughness. These data indicate that a rougher oleophilic surface recovers more oil. This is caused by the geometry and pattern of surface features and not by the higher affinity for oil. The decrease of contact angle with increased roughness confirms that oil tends to penetrate into channels and cavities. In future experiments, test materials should be divided in the groups based on their roughness and compared only within these groups. This would eliminate possible error and allow accurate comparison of their adhesive properties.

Table 4. Effect of roughness.

	Smooth (< 10 nm)	**Low roughness (20 μm)**	**High roughness** (50 (m)
Advancing contact angle	33°±1°	28°±1°	22°±1°
Recovered mass (mg)	5	8	10

6. CONCLUSION

These studies show that measurement of a contact angle formed between oil and test surface using a Dynamic Contact Angle analyzer can provide valuable information about the affinity of various materials to oil, and allow comparison between these materials. There is an inverse correlation between the mass of recovered oil and angle oil forms with the test surface. For a given oil, the lower the contact angle the higher the recovered mass. Contact angle measurements can be performed along with traditional mass recovery (dip and withdraw) tests.

Surface roughness and oil composition have a significant effect on the results of the tests. Higher roughness results in larger recovered mass and lower contact angle, for the same oil-polymer pair. More viscous oils form a thicker film on the test surface allowing larger mass to be recovered, although their affinity (contact angle) to the test surface may be similar to less viscous oils.

Hence, a thorough study of oil adhesion to a solid surface must monitor and report the following parameters:

- Oil composition and physical properties
- Chemistry of the test surface
- Shape and roughness of the test surface
- Test protocol
- Temperature of experiments

A meaningful comparison between samples can be made only if all these parameters are known and carefully monitored throughout the test.

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BIOGRAPHY

Victoria Broje is a PhD candidate at the Bren School of Environmental Science and Management at University of California Santa Barbara with more than six years of experience in oil spill research. Her research interests include fate and behavior of offshore oil spills, oil spill response techniques and petroleum chemistry.

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