TOWARDS QUANTIFICATION OF ADHESION AND WATER STRIPPING IN BITUMINOUS MATERIALS USING MODERN SURFACE ENERGY THEORY

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ABSTRACT

Establishing adhesion between bitumen and aggregate is a fundamental prerequisite to good performance of asphalt mixtures. Debonding of bitumen from aggregate due to displacement by water is known as stripping. Although stripping can be largely attributed to interfacial relations between the component materials, attempts to place this on a quantitative level have had limited success. This paper introduces a thermodynamic approach, based on modern surface energy theory, with the potential to quantify adhesion and water stripping of bituminous materials as part of a more fundamental materials design process. The theory developed by van Oss, Chaudhury and Good forms the basis of this approach. The importance of identifying efficient and reliable techniques for surface energy characterization is emphasized and several techniques are briefly discussed. Apart from techniques that have been investigated, the authors recommend a research focus on microcalorimetry, dynamic vapor sorption, and electrophoreses. Furthermore, three potential areas of application are highlighted and illustrated, including: selection of compatible materials; evaluation of stripping potential; and the use of surface energy properties as part of the performance modelling process. Although this approach offers many advantages, the current theory needs further evaluation and possible modification for application to bitumen-aggregate systems.

1. INTRODUCTION

Loss of adhesion between bitumen and aggregate, and the detrimental effect of water is a well-known cause of failure in bituminous composites. Evaluation, however, of adhesion between these materials has largely remained phenomenological, and subjective.

Adhesion between bitumen and aggregate is a complex phenomenon, mainly due to the complexity of the materials involved. Moisture damage in general cannot be attributed to a single mechanism, but may be caused by several mechanisms at work simultaneously (Little and Jones, 2003). Hefer et al. (2005a) present a synthesis of theories and mechanisms of bitumen-aggregate adhesion and identify the thermodynamic theory as a universal approach, encompassing several mechanisms associated with different theories. Since the early years of the previous century, researchers have known that stripping in bitumen-aggregate systems is the exhibition of interfacial tension relations between these materials in the presence of water. Surface tension, more specifically surface free energy, is central to the application of the thermodynamic theory in the description of adhesion at interfaces.

The objective of this paper is to introduce a thermodynamic approach, based on modern surface energy theory, with the potential to quantify adhesion and water stripping of bituminous materials as part of a more fundamental materials design process. Different surface energy characterization techniques are briefly discussed and some of the promising applications of this approach to bitumen-aggregate systems are highlighted. The current status of research is presented, and future research needs are discussed.

2. BASIC THERMODYNAMIC CONCEPTS

Thermodynamics is the study of energy changes. The balance between two natural tendencies, namely enthalpy and entropy, dictates the spontaneous occurrence of a process. In order to relate enthalpy (H) and entropy (S), Gibbs free energy (G) is defined so that at constant temperature (T) and constant pressure,

$$\Delta G = \Delta H - T\Delta S \qquad\qquad (1)$$

A change in the Gibbs free energy represents the difference between the initial and final energy state of a system and predicts whether a process will or will not occur. Enthalpy (ΔH) is the total energy given off or absorbed during this process, while entropy (ΔS) is the energy expended during internal molecular motion which is dependant on the temperature of the system. Entropy (TΔS) is subtracted form total energy of the system in order to determine the energy available to perform work (ΔG). For ΔG < 0, energy will be released to perform work and the process will occur spontaneously. If ΔG > 0, then energy will have to be absorbed from the environment or the process cannot occur. For ΔG = 0, the process is in equilibrium. In the context of adhesion, the Gibbs free energy is the excess free energy of a system associated with an interface.

3. MODERN SURFACE FREE ENERGY THEORY

The fundamental surface forces that take part in adhesion can be attributed to the fact that atoms and molecules at the surface usually possess significantly different reactivity than in the bulk of the material. In the bulk phase, a unit experiences a uniform force field due to interaction with neighbouring units. However, if a surface is created by dividing the bulk phase, the forces acting on the unit at the new surface are no longer uniform. Due to the missing interactions, the units are in an energetically unfavourable condition, i.e. the total free energy of the system is increased. This increase in energy is termed the "surface free energy" or more accurately the "excess surface free energy". In order to restore equilibrium, molecules and atoms at the surface of liquids tend to contract, known as surface tension. Solids may direct some of the forces inward with consequent orientation adjustment of the crystal lattice, and/ or may attract contaminants to satisfy broken bonds.

Many fundamental forces exist of which a few are of practical significance in the adhesion process. Although the concept of dividing surface energy into components that represent different fundamental forces is not a new concept, the physical chemistry relationship between surface energy components and the free energy of adhesion proposed by van Oss, Chaudhury, and Good (1988), is widely used by adhesion scientists today. Three basic components are considered, namely, the Lifshitz-van der Waals component (γ^{LW}), acid (electron acceptor, γ^+), and base (electron donor, γ^-) component of surface energy. The γ^{LW} component represents non-polar interactions, which are non-specific in nature, including Keesom orientation forces, Debye induction forces, and most importantly, London forces. The γ^+ and γ^- components, sometimes referred to as the acid-base component (γ^{AB}), represent polar interactions that are specific by nature and in this

context, donor-acceptor interactions related to hydrogen bonding. The relationship proposed by van Oss, Chaudhury, and Good is given as Equation (2).

$$\Delta G_{12}^a = -2\left(\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right)$$ (2)

The subscripts 1 and 2 represent the two material phases under consideration. While Equation (2) is used to calculate the free energy of adhesion in the dry state, it can be extended to calculate this quantity in the presence of a third medium. Three additional surface energy components for the third medium are then included, and the relationship then becomes:

$$\Delta G_{132}^a = 2\begin{bmatrix} \sqrt{\gamma_1^{LW}\gamma_3^{LW}} + \sqrt{\gamma_2^{LW}\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \gamma_3^{LW} \\ + \sqrt{\gamma_3^+}\left(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-}\right) \\ + \sqrt{\gamma_3^-}\left(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+}\right) \\ - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+} \end{bmatrix}$$ (3)

The importance of Equation (3) is that the free energy of adhesion, or bonding energy, can be calculated in the presence of water.

The original relationship proposed by van Oss and his colleagues expressed the free energy of adhesion in terms of contact angles, known as the Young-Dupré Equation.

$$W_{LS}^a = \gamma_{LV}\left(1 + \cos\theta\right) = -\Delta G_{LS}^a$$ (4)

The work of adhesion, W, is often used in lieu of ΔG, and differs only in sign. The subscripts, L and S, represent the liquid in contact with a solid, respectively. The contact angle (θ) which forms when a liquid is in contact with a solid is a measurable, macroscopic quantity. If Equations (2) and (4) are considered simultaneously, the following significant observations can be made:

- If three liquids with selected, known characteristics, i.e. known surface energy components, are used to obtain contact angles on the surface under consideration, then the three unknown surface energy components can be determined.
- This approach is not limited to the measurement of contact angles, but applies to any measurable parameter that can be used to quantify the free energy of adhesion.
- This theory can be used to calculate the free energy of adhesion in the presence of water, provided that the surface energy components of water are known.

4. SURFACE ENERGY CHARACTERIZATION

Measurement of liquid surface tension is common and well-described in classic texts on surface chemistry, such as Adamson and Gast (1997). Many of the classic techniques are mechanically based and not suitable for characterization of the surface energy components of materials. The theory by van Oss, Chaudhury, and Good (1988) can be used to characterize the surface energy of an "unknown" material by measuring its interaction with at least three substances of known surface energy characteristics. Efficient and reliable measurement of surface energy is an important prerequisite for successful implementation of this technology. Techniques that have been used to characterize

bitumen or aggregate are briefly introduced in the following paragraphs. In addition, candidate techniques are identified for future research.

4.1 Contact Angles

The Wilhelmy plate technique (Elphingstone, 1997; Cheng, 2002; and Hefer, 2004) and Sessile Drop technique (Bose, 2002) are both techniques that have been used to measure contact angles of different liquids on bitumen surfaces. The Wilhelmy plate technique measures dynamic contact angles, while the Sessile Drop technique produces static contact angles. In both techniques, a thin film of hot bitumen is coated onto a micro cover glass slide and allowed to cool before contact angle measurement.

4.1.1 Wilhelmy Plate Technique

The coated glass slide is suspended from the hook of a micro balance. A liquid with known surface energy characteristics is placed in a glass beaker on the motorized stage. By upward and downward movement of the stage at rate of approximately 10 to 20 microns per second, the coated glass slide advances and recedes in and out of the liquid substance. By knowing the difference in applied force due to the interaction of the bitumen with the liquid, the contact angle can be calculated through consideration of force equilibrium. The advancing and receding contact angles produced in this way are known as dynamic contact angles. Hefer et al. (2005b) describe a refined experimental and analysis approach for the use of this technique to determine bitumen surface energies.

4.1.2 Sessile Drop Technique

A liquid drop is dispensed from a micro syringe onto the horizontally positioned coated glass slide. Nowadays, optical imaging systems are available that can be used to capture and analyze the shape of the drop. In this technique, the contact angles of the drop are obtained when the drop has reached an "equilibrium" state.

Recent research by the authors suggests that coating of a thin film of bitumen onto a plate produces a surface that lacks important bitumen functional groups that takes part in the adhesion process. Polymer-like materials exhibit "potential surface energy", which is dictated by the surface it contacts. Molecular orientation is responsible for this phenomenon. The authors recommend that a "substitute" technique be considered where an orientation medium is induced that produces a more representative polar surface energy. Although this approach has been used to determine surface energy components of aggregate, polishing aggregates to produce smooth surfaces limits the practicality of this approach and creates an unnatural surface.

4.2 Vapor Sorption

In the presence of vapour, the energy of solid surfaces is reduced. This reduction of surface energy in the presence of vapour is termed equilibrium spreading pressure. Similar to contact angles, equilibrium spreading pressure (π_e) allows one to calculate the free energy of adhesion between vapour and a solid surface. Vapour sorption techniques are especially suited to characterize the surfaces of solids with peculiar and irregular shapes. These techniques are commonly used in the industry, such as the pharmaceutical industry, to determine specific surface area of powders. Different devices are available for this purpose. Li (1997), Cheng (2002), and Hefer (2004) used a static vapor sorption technique, while Hefer (2004) also identified dynamic vapor sorption as an alternative approach.

4.2.1 Vacuum Static Vapour Sorption

The equipment used in static vapour sorption experiments normally includes a highly sensitive magnetic suspension balance and a sample chamber that is separated from the balance. This type of equipment is often used in experiments where corrosive gases are involved. An aggregate sample with a mass of approximately 20g, and comprised of the fraction larger than 2.35-mm and smaller than 4.75-mm is suspended from the measuring hook in a basket fabricated from fine aluminium mesh. Each of the selected liquid substances has a unique saturation vapour pressure, which is arbitrarily divided into a number of pressure levels. Vapour is gradually introduced into the sample chamber until equilibrium is reached before proceeding to the next pressure level. This process is repeated until the saturation vapour pressure is reached for the liquid substance under consideration. In this way, a so-called adsorption isotherm is constructed, i.e. the amount of gas adsorbed at a pre-determined pressure level. Such an isotherm is the basic data required to calculate equilibrium spreading pressure for each vapour adsorbed onto the aggregate sample.

4.2.2 Dynamic Vapour Sorption

Similar to the static process, aggregate is suspended in a basket from the measuring hook of a microbalance. In this case, however, vapours are washed over the sample and no vacuum is required. These techniques could be considered more user friendly, and forgiving, since vacuum techniques are more sophisticated and demand a higher level of control. In addition, temperature control is easier in dynamic systems due to the presence of a carrier gas medium. While inert gases are most commonly used as the carrier gas, air could also be used. The use of air as a carrier gas is attractive in that sample pre-conditioning should be closer to what would be expected in asphalt plants. Fully automated dynamic vapour sorption devices are commercially available. This technique needs to be investigated more closely.

4.3 Inverse Gas Chromatography

Inverse gas chromatography involves elution of a known liquid or gas through a column packed or lined with an unknown material. While columns packed with small particles, or "packed columns" is the traditional method used in analytical chromatography, the use of "capillary columns" is the modern approach.

Small injections of selected organic probe molecules are eluted through a column with constant flow of an inert carrier gas. Retention time (t_R) of the molecules through the column are related to retention volume (V_R), which in turn is related to the free energy of adhesion (or adsorption). A series of n-alkanes (non-polar organics) represents the non-specific interactions, while selected acidic and basic mononpolar molecules represent specific interactions.

While the packed column approach is commonly used to analyze powders, attempts to apply this approach to small aggregates were not too successful. Heterogeneity and highly energetic surfaces of aggregates cause distortion of retention time peaks and elution of gases can be problematic when strong interactions occur. The Western Research Institute (WRI) in Wyoming, USA, has used inverse gas chromatography since the 1960s to investigate the interaction of selected organics with bitumen. Hefer (2004) adapted the WRI capillary column technique and applied an appropriate analysis procedure to determine bitumen surface energies. Because columns are prepared by coating a thin film of bitumen onto the inside of a capillary column, one would expect that polar interactions

will be small, perhaps questionable, due to limited orientation of molecules at the interacting surface.

4.4 Force Microscopy

While most techniques characterize adhesion indirectly through parameters such as contact angles, equilibrium spreading pressure, and retention time, atomic force microscopy (AFM) quantifies adhesion directly. Essentially, AFM consists of a flexible cantilever of a few hundred micrometers equipped with a tip that can vary in size from tens of a nanometre up to a few micrometers. The cantilever deflects when surface forces "grab" the tip. The cantilever is raised and the tip is pulled-off the surface. The pull-off force is a direct measurement of adhesion and is related to the free energy of adhesion. WRI has applied AFM to measure surface energies of bitumen solvent cast onto glass substrates. In order to obtain surface energy components, chemically functionalized tips are required. An inherent difficulty with this approach is that bitumen coats the tip after a few oscillations. The application of AFM to aggregate surfaces requires a polished surface. The author does not envision the use of such a technique on a routine basis for characterization of bitumen or aggregate surfaces due to practical limitations and level of sophistication.

4.5 Microcalorimetry

Microcalorimetry is a relatively simple technique used to measure sorption heats directly. Essentially, aggregates are brought into contact with bitumen and the energy released during interaction, and over time, is measured with a sensitive microcalorimeter. This approach essentially characterizes enthalpy, i.e. the total energy involved. Although it would be possible to measure this property using liquids of different polarities, determining the free energy of adhesion (or adsorption) would require quantification of the entropy term, as defined in Equation (1). Such an experiment involves a series of supplementary tests at different temperatures. This technique could be considered should the entropy term prove to be negligible at the temperatures under consideration.

4.6 Electrophoreses

The study of charge particles in motion in an electric field is called electrophoreses.

Electrophoreses has been applied to bitumen-aggregate systems in the past to explain moisture damage, or stripping (Labib, 1992). Zeta potential, essentially surface charge, is the main property derived from these experiments. The authors consider this approach valuable, and perhaps one of a few fundamental approaches, to study the effect of pH (of the interface water) on bitumen-aggregate adhesion. Hefer (2004) emphasizes the importance of this phenomenon and explored ways to include the pH effect in the current theory utilizing electrophoreses data. The use of electrophoreses to characterize surface energy should be explored.

5. APPLICATION

Surface energy is generally defined as the energy required to create a new surface. In light of this definition, the relationship between fracture and surface energy becomes clear, i.e. two new surfaces are formed in each of these modes of distress. Proposed applications related to bituminous materials are discussed in the following paragraphs.

5.1 Materials Selection

Despite the role played by external factors (environmental, and wheel loads), the significance of the surface chemistries of the materials involved is the key in establishing fundamental adhesion. A direct application of bitumen and aggregate surface energy values is the ability to assess the compatibility of different bitumen-aggregate combinations. Table 1 is an example of free energy of adhesion calculated between two aggregate types and two bitumen types in the dry state (Equation 2) and in the wet state (Equation 3). The bitumen types AAD-1 and AAM-1 were used during the Strategic Highway Research Program (SHRP) in the late 1980s early 1990s and were selected for this study based on the data on these binders and the very different characteristics of these binders.

An important observation from the values reported is that all bitumen-aggregate combinations produce negative bond strengths in the absence of water, and positive bond strengths in the presence of water. While larger negative numbers indicate resistance to fracture, larger positive numbers suggest that water has a greater affinity for the aggregate surface than bitumen and therefore promotes adhesive fracture. These figures suggest that bitumen AAM-1 produces the strongest bond with both granite and limestone. The data further suggest that not one of the bitumen-aggregate combinations can successfully stand up to the detrimental effect of water. Based on relative numbers, AAD-1 with limestone seems to be the most water susceptible material combination.

It should be noted that the objective of showing these data is illustrative of a concept and that more work is required in order to validate actual numbers. Surface energy values used to calculate ΔG were obtained from contact angle and vacuum static vapor sorption experiments for bitumen and aggregates, respectively.

Table 1: Application of Surface Energy in the Material Selection Process (Adapted from Lytton, 2004)

Aggregate	Bitumen	ΔG_{dry}	ΔG_{wet}
Georgia Granite	AAD-1	-152.9	48.3
	AAM-1	-198.6	30.0
Texas Limestone	AAD-1	-141.8	66.9
	AAM-1	-250.2	30.9

5.2 Quantification of Stripping

Stripping of bitumen from aggregate surfaces is traditionally evaluated based on subjective tests, such as boil tests. In addition to material related factors, mechanisms induced by traffic loading exist, including pore pressure effects and hydraulic scouring (Fromm, 1974). The percentage of the surface area of an aggregate that has been exposed to water (P) can be used as an index to quantify the level of adhesive fracture.

$$\Delta W = W_{12}^a(1-P) + W_{132}^a P \qquad (5)$$

Where ΔW^a is the net work of adhesive fracture; W_{12}^a (see Section 3 for definitions) is the work of adhesion in the absence of water; (1-P) is the percentage of the aggregate surface area that is not exposed to water; W_{132}^a is the work of adhesion in the presence of water, and P is the percentage of the aggregate surface area exposed to water. Under cyclic compression loads, the reduction in stiffness at loading cycle N, under wet conditions, can

be computed as the ratio of the net work of adhesive fracture in the presence of water and the work of adhesion in the dry state.

$$\frac{E_{wet}}{E_{dry}} = \frac{(\sigma/\varepsilon)_{wet}}{(\sigma/\varepsilon)_{dry}} = \frac{\varepsilon_{dry}}{\varepsilon_{wet}} = \frac{W_{12}^a(1-P) + W_{132}^a P}{W_{12}^a} \qquad (6)$$

Where E_{wet} and E_{dry} are the compressive stiffness in the wet and dry conditions, respectively; σ is the compressive stress; ε is the permanent strain, induced either in wet or dry conditions; and other terms as defined above.

Figure 1 illustrates the aggregate-water-exposure phenomenon for the asphalt mixtures under cyclic loading.
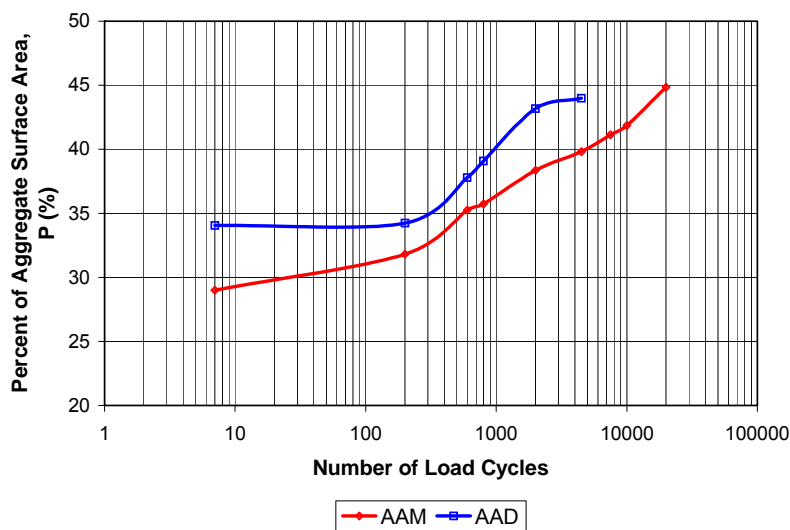

Figure 1: Percent of aggregate surface wetted by water as a function of number of load cycles for bitumen AAM and AAD mixed with limestone, respectively (Cheng, 2002; Lytton, 2004, Hefer et al., 2005a)

It is interesting that initial P-values exist for both mixtures. This premature damage is attributed to diffusion of water through the bitumen to the interface during moisture preconditioning. The data indicates that the percentage of stripped area generally increases with increase in number of load cycles. Furthermore, the P-value for the AAD mixture remains higher than the value for the AAM mixture throughout the test. The graph indicates that a point exists on the wetting line where a sudden increase in the slope occurs. This point (or knee) on the wetting line corresponds to the number of cycles to accelerated damage, or adhesive fracture. The slope of the line represents the rate of adhesive fracture.

5.3 Performance Modeling

It should be realized that surface energy represents only one of a number of variables that influences asphalt mix performance. Although important, these thermodynamic properties should be used together with other simple physical material properties to appreciate moisture damage in general. The thermodynamic approach is, however, universal due to its energy basis. The surface energy concept has played an important role in discoveries of the rules that govern microfracture and healing in bitumen-aggregate mixtures. Based on the fundamental laws of fracture, the classical crack growth theory for brittle materials

(Griffiths crack growth theory) was extended to viscoelastic materials. These fundamental relationships of fracture were applied to asphalt mixtures by Lytton and his colleagues (Lytton, 2000; Lytton, 2004)

Dedicated validation studies are currently being conducted at Texas Transportation Institute at Texas A&M University under the National Cooperative Highway Research Project (NCHRP) 9-37. This project not only considers the role of surface energy in performance modelling, but also focuses on evaluation of several candidate techniques for surface energy characterization of both bitumen and aggregate.

6. QUO VADIS?

- Establishment of good adhesion between bitumen and aggregate is of fundamental importance in the production of high quality asphalt mixtures. It is envisioned that modern surface energy theory can be implemented on a practical level in the material selection process and to assess stripping potential quantitatively.
- The physical chemistry theory developed by van Oss, Chaudhury, and Good use surface energy characteristics of the materials involved to estimate the adhesive bond strength dry or in the presence of water. Although promising, the ability of this theory to incorporate factors such as the pH of interface water and representation of chemical bonds known to form in bitumen-aggregate systems, requires further consideration.
- Establishing an efficient and reliable surface energy measuring technique is critical for successful implementation of this technology. The use of dynamic vapour sorption, microcalorimetry, and electrophorese deserves further investigation.
- The thermodynamic approach is based on the universal energy concept that allows integration of physical and chemical factors at the root of distress mechanisms that dictate bituminous material failure. A national study in the USA, NCHRP 9-37, is currently being conducted and will provide further guidance to the application and implementation of this approach.

7. ACKNOWLEDGEMENTS

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