Research Results Digest 316

Using Surface Energy Measurements to Select Materials for Asphalt Pavements

DETAILS

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USING SURFACE ENERGY MEASUREMENTS TO SELECT MATERIALS FOR HMA PAVEMENTS

This digest summarizes key findings from NCHRP Project 9-37, "Using Surface Energy Measurements to Select Materials for Asphalt Pavements," conducted by the Texas Transportation Institute, College Station, Texas. The project final report was authored by the principal investigator, Dallas N. Little, and Amit Bhasin of Texas Transportation Institute. The complete final report is available on the TRB website as *NCHRP Web-Only Document 104* (http://www.trb.org/news/blurb_detail.asp?id=7359).

INTRODUCTION

The surface energy of an aggregate particle determines its affinity for both inorganic and organic binders as well as for water. The surface energy of an asphalt binder affects its ability to adhere to an aggregate particle surface and, thus, the long-term strength and stability of the composite material. Interactions among aggregate particles, binders, and water can also influence the development and longevity of binder adhesion, most notably, in the stripping of asphalt binder from aggregate by moisture. Therefore, the ability to characterize asphalt binders and aggregates by measurement of their surface energies may lead to improved performance of hot mix asphalt (HMA) pavements through development of (1) application-specific materials selection criteria, (2) project-specific matching of the characteristics of binders and aggregates, and (3) identification of additives or treatments that improve binder-aggregate compatibility.

A micromechanics model developed at the International Center for Aggregates Research (ICAR) at Texas A&M University explains fatigue damage in HMA through the interaction of two competing processes: (1) crack formation and (2) microcrack healing. Both processes are theoretically described by the principles of viscoelastic fracture first set forth by Schapery in 1984. Further, Schapery hypothesized that both fracture and healing are strongly affected by cohesive (within the mastic) surface energy and adhesive (between the aggregate and the asphalt binder or mastic) surface energy.

Research at ICAR sponsored by the Federal Highway Administration produced a methodology for measuring the surface energies of aggregates, asphalt cement, and mastic (asphalt cement with mineral dust, other additives, or both). The surface energy of asphalt binders is measured by the Wilhelmy plate method. For aggregates, an extremely sensitive and precise magnetic suspension balance is used in conjunction with a chamber in which the material under test is allowed to sorb (i.e., adsorb, absorb, or both) dipolar, monopolar, and non-polar vapors (of water, methyl propyl ketone, and hexane, respectively). This methodology allows determination of the total aggregate surface energy as well as its components,

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including the acid and base components and the Lifshitz–van der Waals component.

This work at ICAR confirmed that the fatigue and healing potentials of HMA are directly and strongly related to the surface energies of the components and their compatibility. Because they have better fracture and healing properties, asphalt binders that have high acid or base surface energies are more resistant to fatigue than those with low acid or base surface energies. The adhesive surface energy between asphalt binder and aggregate is a more complex process and is just as important, if not more important, than the cohesive surface energies of the asphalt binder or mastic. Testing of a wide range of aggregates at ICAR revealed that aggregate surface energy is influenced not only by the source and mineralogy of the aggregate, but also by the level of processing and surface treatments.

NCHRP Project 9-37 was an investigation of the effectiveness and practicality of surface energy measurement as a tool for routine screening and selection of materials for optimum performance of HMA pavements. The specific objective of the project was to develop and conduct limited validation of the surface energy measurement methodology developed by ICAR for characterization of aggregates, asphalt binders, and additives.

This digest summarizes the findings and conclusions of the project and presents three proposed test methods for determining surface energy (reproduced from the AASHTO-formatted appendices of the project final report, *NCHRP Web-Only Document 104*). There are two test methods proposed for determining the surface energy of asphalt binders (Appendices B and D, *NCHRP Web-Only Document 104*) and one for determining the surface energy of aggregates (Appendix C, *NCHRP Web-Only Document 104*). These proposed test methods are recommendations of NCHRP Project 9-37 and have not been approved by NCHRP or AASHTO. The final report with 10 appendices is available in its entirety as *NCHRP Web-Only Document 104* (http://www.trb.org/news/blurb_detail.asp?id=7359). The information in this digest will be of interest to materials engineers in the public and private sectors.

FINDINGS

For surface energy measurements to be used routinely to select materials for better-performing HMA pavements, simple, accurate, and reliable test methods to measure the surface energy components of asphalt binders and aggregates must be identified, and the link between surface energy and performance of HMA must be established and validated. In this study various candidate test methods to measure the surface energy components of these materials were selected based on an exhaustive literature review. These methods were evaluated based on technical criteria such as precision, accuracy, ability to provide all three surface energy components, and ability to evaluate samples representative of the material being investigated. Practical considerations such as capital outlay for the equipment required for each test method and expertise required to perform tests were also evaluated.

Four candidate methods were used to measure the surface energy components of asphalt binders. The Wilhelmy plate method and the sessile drop method, each with five probe liquids (see the first and third proposed test methods in this digest), are recommended for routine use. Some further research is required with the latter test method to improve its sensitivity to the acid and base components of the asphalt binders. Inverse gas chromatography (IGC) and atomic force microscopy (AFM) can be used as advanced material characterization tools to characterize surface properties of asphalt binders. These recommendations are based on criteria such as precision of the test method, ability to measure the three surface energy components, ability to measure a representative surface area of the sample, and practical considerations such as capital outlay and expertise and experience required from the operator to conduct each type of test.

Four candidate methods were used to measure the surface energy components of aggregates. The universal sorption device (USD) is recommended for use on a routine basis to measure the surface energy components of aggregates (see the second proposed test method in this digest). The use of a microcalorimeter to measure the surface energy components of aggregates entails making an assumption for the contribution of entropy. Further research with this test method can improve the accuracy of results and render it useful as a routine test method to measure the surface energy components of aggregates. The IGC can be used for advanced material characterization and to measure specific surface properties of aggregates and pure minerals. These recommendations are based on criteria such as precision and accuracy of the test method, ability to measure a representative area of the sample, and practical considerations such as expertise required to conduct each type of test.

Four energy parameters—based on the work of adhesion between asphalt binder and aggregate, work of debonding when water displaces binder from the aggregate, wettability, and specific surface area of the aggregate—were evaluated in this research to select materials for asphalt mixtures that are resistant to moisture damage. These energy parameters can be computed for all possible combinations of different asphalt binders and aggregates if the surface energy components of these materials are known. In general, parameters demonstrated good correlations with the moisture sensitivity of nine different asphalt mixtures measured in the laboratory.

Surface free energy of asphalt binders and aggregates and concomitant works of adhesion or cohesion are important material properties that can be used with the principles of fracture mechanics to model the crack growth behavior and healing characteristics of asphalt mastics. Other important material properties that relate to the crack growth behavior in asphalt mastic can be obtained from simple tests conducted using a dynamic mechanical analyzer (DMA). This research demonstrated that material properties derived from surface energy measurements and tests with the DMA can be used to determine the crack growth behavior in mastic samples. Limited correlation of results based on this approach with the qualitative performance of field mixes was also demonstrated.

PROPOSED TEST METHOD TO USE A WILHELMY PLATE DEVICE TO DETERMINE SURFACE ENERGY COMPONENTS OF ASPHALT BINDERS

1. Scope

1.1 This test method covers the procedures for preparing samples and measuring contact angles using the Wilhelmy plate device to determine the three surface energy components of asphalt binders.

1.2 This standard is applicable to asphalt binders that do not contain particulate additives such as crumb rubber.

1.3 This method must be used in conjunction with the manual for mathematical analysis to determine surface energy components from contact angle measurements or the computerized spreadsheets that were developed to carry out this analysis.

1.4 *This standard may involve hazardous material, operations, and equipment. This standard is not intended to address all safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to its use.*

2. Referenced Documents

2.1 AASHTO Standards
T40 Sampling of Bituminous Materials

3. Definitions

3.1 *Surface energy,* γ, or surface free energy, of a material is the amount of work required to create unit area of the material in vacuum. The total surface energy of a material is divided into three components: the Lifshitz–van der Waals component, the acid component, and the base component.

3.2 *Contact angle,* θ, refers to the equilibrium contact angle of a liquid on a solid surface measured at the point of contact of the liquid-vapor interface with the solid.

3.3 *Advancing contact angle,* within the context of this test, refers to the contact angle of a liquid with the solid surface as the solid surface is being immersed into the liquid.

3.4 *Receding contact angle,* within the context of this test, refers to the contact angle of a liquid with the solid surface as the solid surface is being withdrawn from the liquid.

3.5 *Probe liquid,* within the context of this test, refers to any of the pure, homogeneous liquids that do not react chemically or dissolve with asphalt binders and are used to measure the contact angles with the binder. The three surface energy components of the probe liquid must be known at the test temperature from the literature.

3.6 *Mixing temperature,* within the context of this test, refers to the temperature at which the viscosity of the asphalt binder is approximately 0.170 Pa's, or any other temperature that is prescribed or determined by the user for use as the mixing temperature with aggregates to prepare hot mix asphalt.

4. Summary of Method

4.1 A glass slide coated with the asphalt binder and suspended from a microbalance is immersed in a probe liquid. From simple force equilibrium conditions, the contact angle of the probe liquid with the surface of the asphalt binder can be determined. The analysis to obtain the contact angle is performed using software accompanying the Wilhelmy plate device.

4.2 Contact angles measured with different probe liquids are used with equations of work of adhesion to determine the three surface energy components of the asphalt binder.

4.3 Figure 1 presents a schematic of the Wilhelmy plate device.

5. Significance and Use

5.1 Surface energy components of asphalt binders are important material properties that are related to the performance of hot mix asphalt. Surface energy components of asphalt binders can be used to determine the total surface energy and cohesive bond strength of this material. The cohesive bond strength of asphalt binders is related to the work required for microcracks to propagate within the asphalt binder in an asphalt mix, which is related to the fatigue cracking characteristics of the mix.

5.2 Surface energy components of asphalt binders also can be combined with the surface energy components of aggregates to compute the work of adhesion between these two materials and the propensity for water to displace the asphalt binder from the asphalt binder-aggregate interface. These two quantities are related to the moisture sensitivity of the asphalt mix.

6. Apparatus

6.1 The Wilhelmy plate device comprises a microbalance with a motor-controlled stage that can be raised or lowered at desired speed to immerse a slide with asphalt binder in the probe liquid in advancing mode and to withdraw the slide from the probe liquid in receding mode.

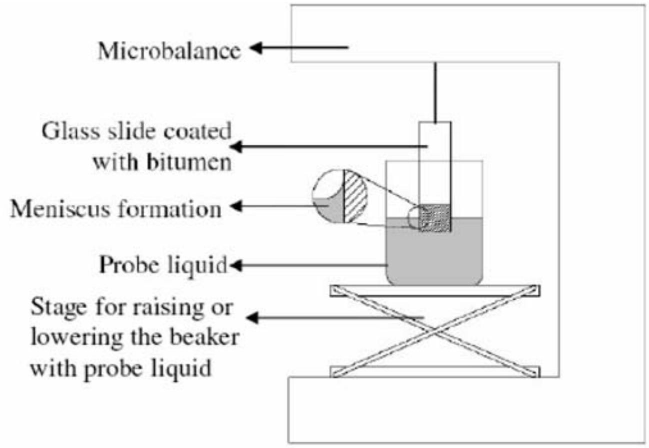


Figure 1 Schematic of the Wilhelmy plate device.

6.2 Data acquisition and analysis software is required to collect the data and determine the contact angles.

6.3 An oven capable of heating up to 150°C is required to heat asphalt binders for sample preparation. Microscope glass slides (24 mm × 60 mm No. 1.5) are required to serve as substrates for the asphalt binder, and a vernier caliper is required to measure the dimensions of the slide. A heating plate with temperature control is required for maintaining the temperature of the asphalt binder during the sample preparation process.

6.4 The tests are conducted at 25±1°C. If the room temperature is significantly different from the test temperature, then an appropriate environmental chamber may be required to house the apparatus.

6.5 A slotted slide holder is required to hold the finished asphalt binder slides.

7. Sampling

7.1 Obtain a representative sample of the asphalt binder according to procedure T40. Approximately 50 g of asphalt binder stored in a small metallic container is required for this test.

8. Preparation of Test Samples

8.1 Heat the container with asphalt binder in an oven to the mixing temperature for about 1 h and place it over a heating plate. Set the temperature of the heating plate so that the asphalt binder remains at the mixing temperature. Stir the liquid asphalt binder from time to time throughout the sample preparation process.

8.2 Pass the end of the glass slide intended for coating through the blue flame of a propane torch six times on each side to remove any moisture (Figure 2). Dip the slide into the molten asphalt binder to a depth of approximately 15 mm (Figure 3). Allow excess binder to drain from the slide until a very thin (0.18 to 0.35 mm) and uniform layer remains on the slide. The thickness of asphalt binder must be uniform on both sides of the slide throughout its width and for at least 10 mm from the edge that will be immersed in the probe liquid. A thin coating is required to reduce variability of the results. Turn the slide with the uncoated end downward (Figure 4)

Figure 2 Glass slide dried before immersion by passing it over a propane flame.

and carefully place it in the slotted slide holder (Figure 5). If necessary, the heat-resistant slide holder with all the coated slides is placed in the oven for 15 to 30 s to obtain the desired smoothness. Place the binder-coated slides in a desiccator overnight.

9. Procedure

9.1 The user must ensure that the microbalance is calibrated in accordance with the manufacturer specifications before the start of the test.

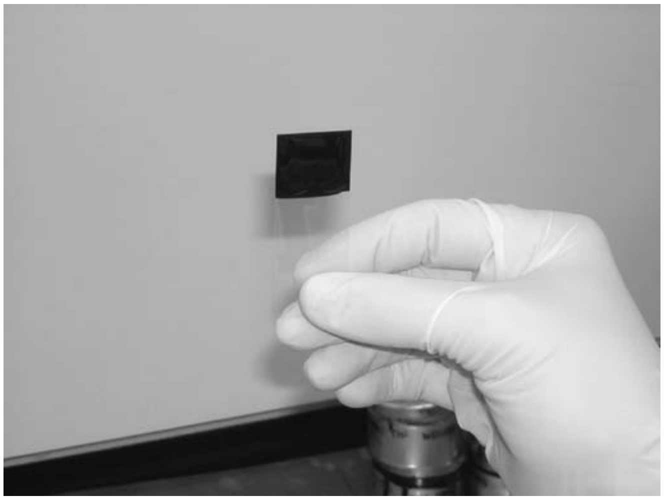


Figure 4 Glass slide coated with asphalt binder for testing with the Wilhelmy plate device.

9.2 Remove one asphalt binder–coated slide from the desiccator at a time. Measure the width and thickness of the asphalt binder slide to an accuracy of 0.01 mm to calculate its perimeter. The measurements must be made just beyond 8 mm from the edge of the slide to avoid contamination of the portion of coating that will be immersed in the probe liquid.

9.3 Suspend the glass slide coated with asphalt binder from the microbalance using a crocodile clip. Ensure that the slide is horizontal with respect to the base of the balance. Fill a clean glass beaker with the probe liquid to a depth of at least 10 mm and place it on the balance stage. Raise the stage manually to bring the top of the probe

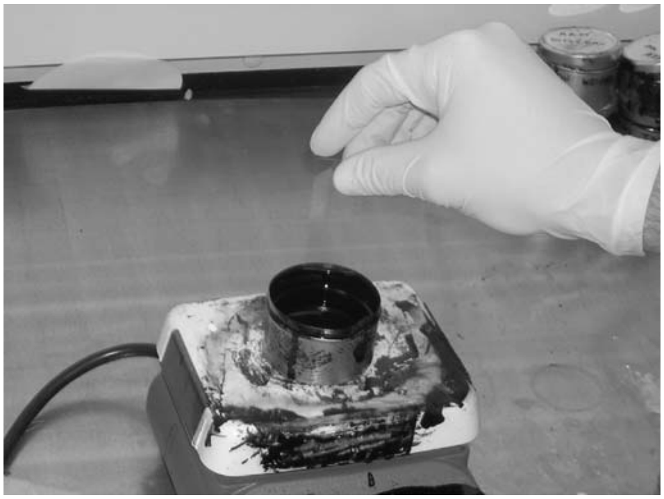


Figure 3 Clean glass slide dipped in molten asphalt binder to create coating.

Figure 5 Finished slides stored on slotted holder in desiccator before testing.

liquid in proximity to the bottom edge of the slide (Figure 6).

9.4 During the test, the stage is raised or lowered at the desired rate via a stepper motor controlled by the accompanying software. A rate of 40 micrometers/s is recommended to achieve the quasi-static equilibrium conditions for contact angle measurement. Set the depth to immerse the sample in the probe liquid to 8 mm. Larger depths up to 15 mm may be used if the thickness of asphalt coating on the slide is uniform. The weight of the slide measured by the microbalance is recorded continuously by the software accompanying the device during the advancing (stage is raised to dip the slide) and receding (stage is lowered to retract the slide from the liquid) process.

9.5 At least five probe liquids should be used with this test. These are water, ethylene glycol, methylene iodide (diiodomethane), glycerol, and formamide. All reagents must be high-purity grade (>99%). Contact angles must be measured for at least three replicates with each probe liquid for each asphalt binder.

Figure 6 Asphalt binder sample suspended from microbalance for immersion in probe liquid.

9.6 Because methylene iodide is a light-sensitive material, the beaker containing methylene iodide must be covered with black tape to reduce the effect of light.

9.7 Dispose of the probe liquid in the beaker after testing three asphalt binder slides, and use a fresh sample of the probe liquid for each different type of binder. Store all probe liquids in airtight containers and do not use probe liquids after they have been exposed to air in open-mouthed beakers for prolonged periods.

9.8 Tests must be completed within 24 to 36 h from the time of preparation of the slides.

10. Calculations

10.1 From simple force equilibrium considerations, the difference between weight of a slide measured in air and partially submerged in a probe liquid (ΔF) is expressed in terms of buoyancy of the liquid, liquid surface energy, contact angle, and geometry of the slide. The contact angle between the liquid and surface of the slide is calculated from this equilibrium as:

$$\cos\theta = \frac{\Delta F + V_{im}\left(\rho_L - \rho_{air} g\right)}{P_t \gamma_L^{Tot}} \tag{1}$$

where

θ = the dynamic contact angle between the asphalt binder and the liquid,
V_{im} = the volume immersed in the liquid,
ρ_L = the density of the liquid,
ρ_{air} = the air density,
g = the local acceleration due to gravitation,
P_t = the perimeter of the asphalt binder–coated plate, and
γ_L^{Tot} = the total surface energy of the liquid.

The accompanying software requires the density of the liquid, total surface tension of the liquid, dimensions of the sample, and local acceleration due to gravity as inputs to compute the contact angle using the force measurements from the microbalance.

10.2 Buoyancy correction based on slide dimensions and liquid density can introduce unwanted variability into the resulting contact angles. To eliminate these effects, the accompanying software performs a regression analysis of the buoyancy line and extrapolates the force to zero depth. The user must select a representative area of the line for regression analysis (Figure 7). The software reports the advancing and receding contact angles based on the area selected using the aforementioned equation.

10.3 If the force measurements are not smooth (i.e., if sawtooth-like force measurements are observed because of slip-stick behavior between the probe liquid and the asphalt binder), then report this along with the advancing and receding contact angles.

10.4 The typical standard deviation of the measured contact angle for each pair of liquid and asphalt binder based on measurements with three replicate slides is less than 2°.

10.5 The contact angle of each replicate and probe liquid is used with the surface energy analysis workbook that conducts the required analysis to determine the three surface energy components of the asphalt binder and the standard deviations of these components. This workbook also verifies the accuracy and consistency of the measured contact angles and integrates data from other test methods such as the surface energy components of aggregates to determine various parameters of interest that are related to the performance of asphalt mixes.

PROPOSED TEST METHOD TO USE A SORPTION DEVICE TO DETERMINE SURFACE ENERGY COMPONENTS OF AGGREGATES

1. Scope

1.1 This test method covers the procedures for preparing samples and measuring adsorption isotherms using a sorption device with an integrated Surface Energy Measurement system (SEMS) to determine the three surface energy components of asphalt binders.

1.2 This standard is applicable to aggregates that pass through a 4.75-mm sieve (#4) and are retained on a 2.36-mm sieve (#8).

1.3 This method must be used in conjunction with the manual for mathematical analysis to determine surface energy components from spreading pressures or the computerized spreadsheets that were developed to perform this analysis.

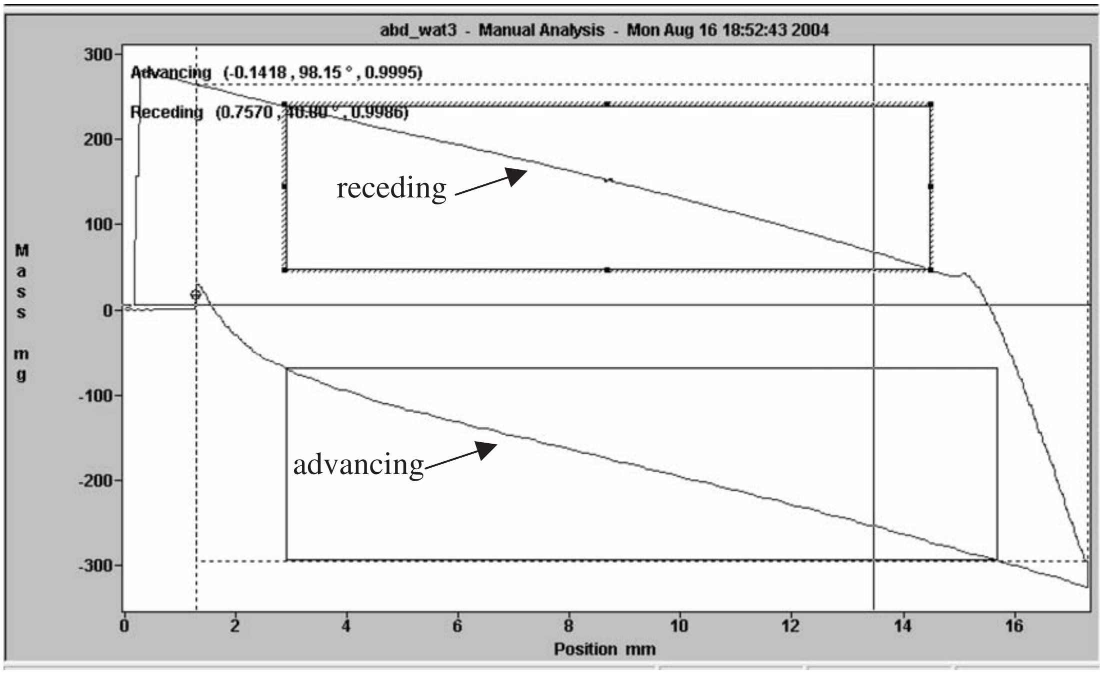


Figure 7 Selection of representative area to determine advancing and receding contact angles.

1.4 *This standard may involve hazardous material, operations, and equipment. This standard is not intended to address all safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations before its use.*

2. Referenced Documents

2.1 AASHTO Standards
T2 Practice for sampling aggregates

3. Definitions

3.1 *Surface energy,* γ, or surface free energy, of a material is the amount of work required to create unit area of the material in vacuum. The total surface energy of a material is divided into three components: the Lifshitz–van der Waals component, the acid component, and the base component.

3.2 *Equilibrium spreading pressure,* π_e, is the reduction in surface energy of the solid due to adsorption of vapors at its saturation vapor pressure on the surface of the solid.

3.3 *Probe vapor,* within the context of this test, refers to vapors from any of the pure, homogeneous liquids that do not chemically react or dissolve with aggregates and are used to measure the spreading pressure with the aggregate. The three surface energy components of the probe vapor must be known at the test temperature from the literature.

3.4 *Relative vapor pressure,* within the context of this test, refers to the ratio of the pressure of the vapor to its saturation vapor pressure and can vary from 0 (complete vacuum) to 1 (saturation vapor pressure).

3.5 *Adsorption isotherm* of a vapor with an aggregate is the relationship between the equilibrium mass of vapor adsorbed per unit mass of the aggregate and the relative vapor pressure of the vapors at a constant temperature.

4. Summary of Method

4.1 Clean aggregate samples are degassed under high temperature and vacuum in an airtight sorption cell. Vapors of probe liquids are introduced into the sorption cell in controlled and gradually incremental quantities to achieve different relative pressures. The equilibrium mass of the vapor adsorbed to the solid surface is recorded for each relative pressure to obtain the adsorption isotherm. The adsorption isotherm is used to compute the equilibrium spreading pressure of the probe vapor with the aggregate.

4.2 Equilibrium spreading pressure with different probe vapors is used with equations of work of adhesion to determine the three surface energy components of the aggregate.

5. Significance and Use

5.1 Surface energy components of aggregates are important material properties that are related to the performance of hot mix asphalt. Surface energy components of aggregates can be combined with the surface energy components of asphalt binders to quantify the work of adhesion between these two materials and the propensity for water to displace the asphalt binder from the asphalt binder-aggregate interface. These two quantities are related to adhesive fracture properties and moisture sensitivity of the asphalt mix.

6. Apparatus

6.1 A sorption device is integrated with the SEMS comprising an airtight adsorption cell, a magnetic suspension balance that measures the mass of the sample in the sorption cell in non-contact mode, a manifold with vacuum pump, temperature control, probe liquid containers with appropriate valves and controls to regulate the flow of vapors into the sorption cell, and associated software for test control and analysis (Figure 8). The microbalance must have a precision of 10 µg with a capacity to weigh at least 50 g.

6.2 Temperature of the sorption cell, the piping that carries vapors, and the buffer tank is maintained using a water bath that is automatically controlled by the SEMS software.

6.3 An oven capable of heating up to 150°C is required to prepare aggregate samples before testing.

7. Sampling

7.1 Obtain a representative sample of the aggregate according to procedure T2. Sieve the sample to

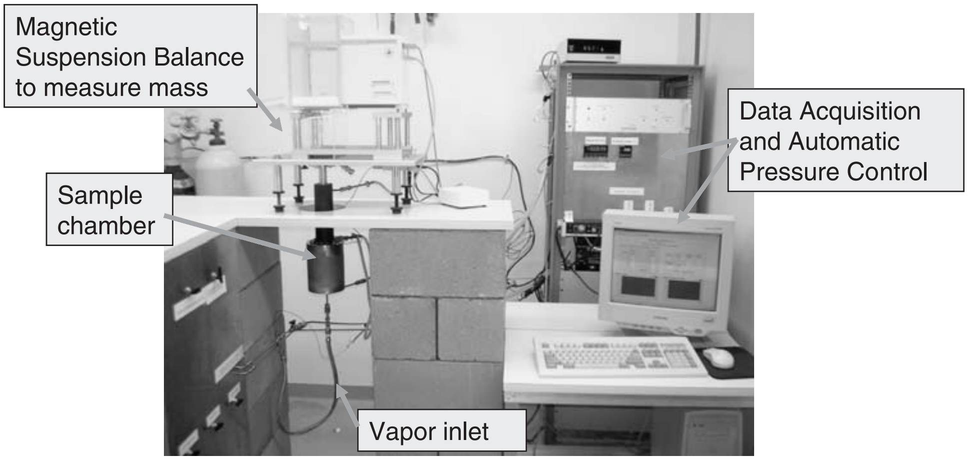


Figure 8 Universal sorption device.

obtain about 100 g of aggregates passing a 4.75-mm sieve (#4) and retained on a 2.36-mm sieve (#8).

8. Preparation of Test Samples

8.1 Thoroughly wash about 25 g of the aggregate in a 2.36-mm sieve with deionized or distilled water. The quality of water used for cleaning of aggregates must be comparable to the quality of water used for gas chromatography. Place the clean aggregate sample in an oven at 150°C for 8 h, and thereafter transfer it to a desiccator at room temperature for at least 8 h before testing.

9. Procedure

9.1 The samples are held in a wire mesh basket during the test. Rinse the basket with acetone and air dry. Transfer the aggregate sample to the basket (Figure 9) and suspend the basket from the hook underneath the suspension balance (Figure 10). Seal the sorption cell, the coupling, and the suspension balance using a Viton® O-ring (Figure 11). A metal jacket connected to a water bath is used around the sorption cell to maintain temperature (Figure 12).

9.2 To obtain stable and consistent readings with the magnetic suspension balance, the sample basket and magnetic suspension coupling must be in vertical and horizontal alignment with each other. Activate and deactivate the magnetic suspension coupling repeatedly until stable and consistent readings are observed. This is an indication that the basket is aligned. This process, referred to as centering of balance, also can be automatically executed with the horizontal centering module of the SEMS software (Figure 13).

9.3 Degas the sample and the test manifold by drawing vacuum from the system using a mechanical vacuum pump. After the first 2 h of degassing at 70°C, reduce the temperature of the manifold to 25°C (test temperature) and continue degassing for another 4 h. The pressure in the cell must be maintained below 20 millitorr during the last 4 h of degassing. The temperature and degassing times can be controlled manually or automatically using the degassing module of the SEMS software (Figure 14). Monitor the

Figure 9 Basket with aggregate sample for testing with the USD.

Figure 10 Sample basket suspended from the magnetic suspension balance.

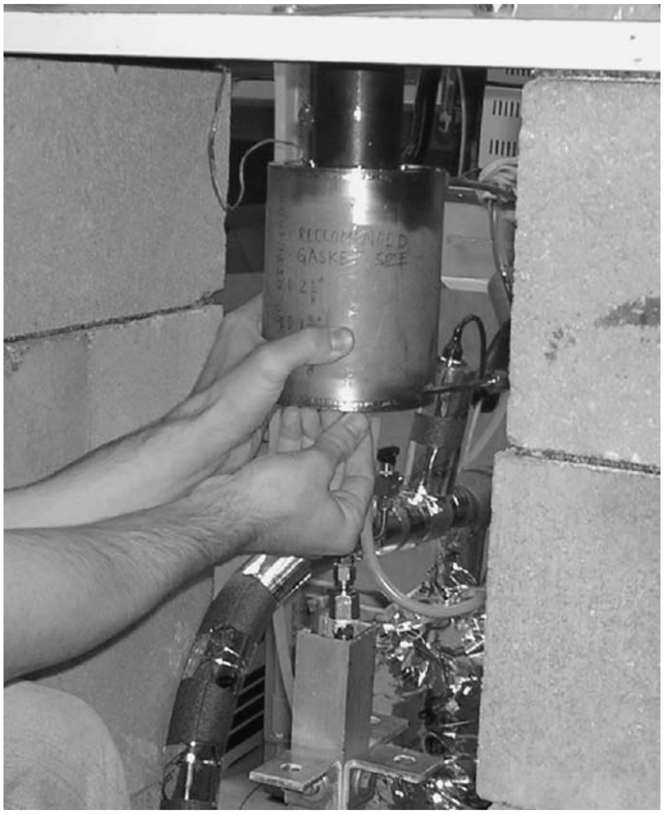


Figure 12 Temperature jacket raised to cover adsorption cell.

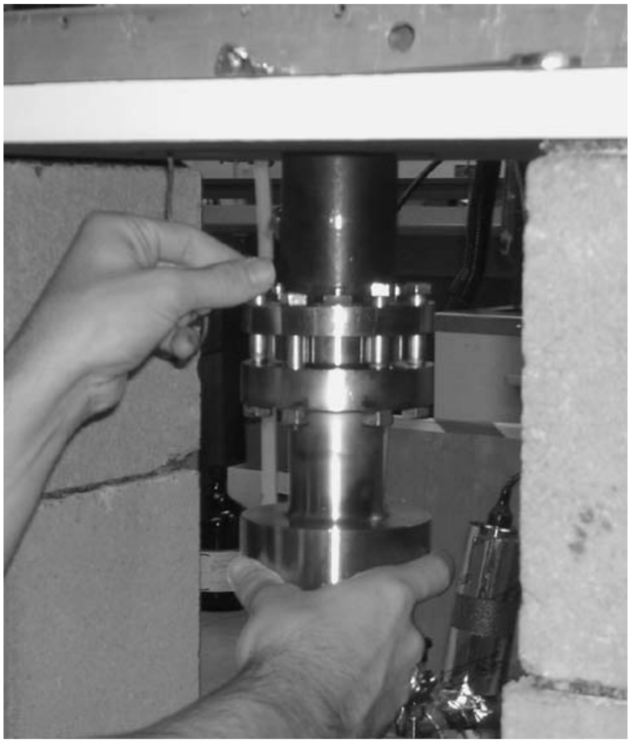
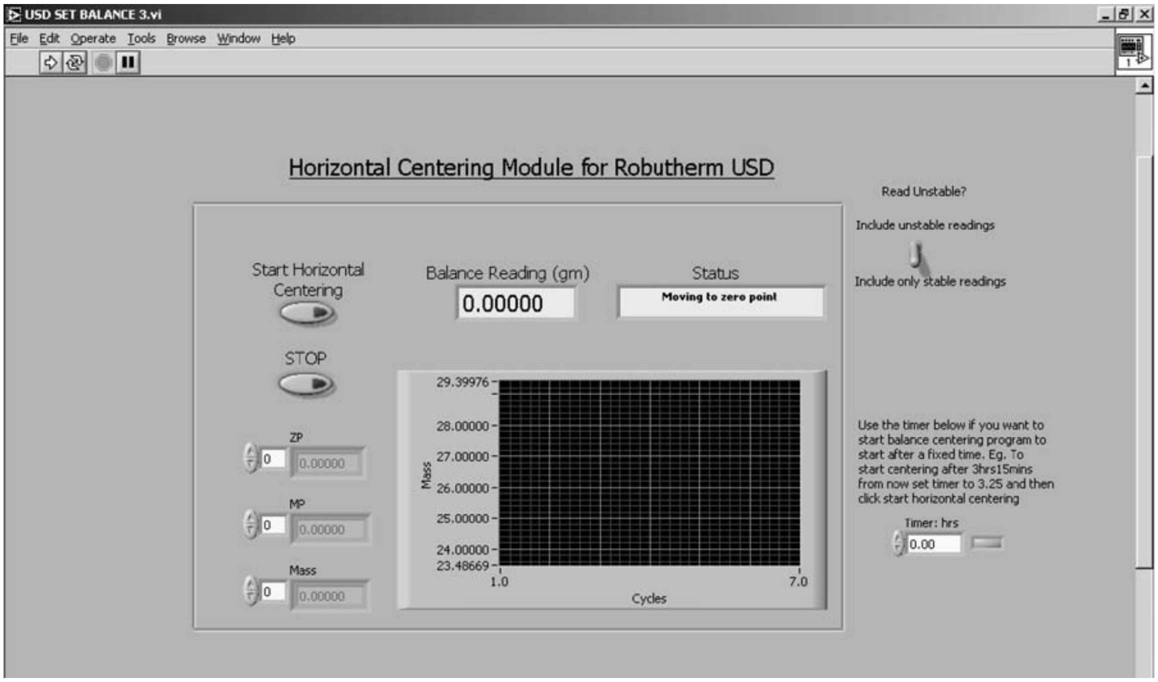


Figure 11 Adsorption cell raised and sealed with sample basket inside.

mass of the sample for the last 1 h of the degassing time to ensure that it is stable. If the mass continues to decrease, the sample is still losing physically adsorbed particles from its surface and more degassing time is required.

9.4 After completion of degassing, isolate the vacuum pump from the adsorption system. Monitor the pressure of the system for a few minutes to ensure that there is no significant leak. Typically, a leak that allows the system pressure to increase by more than 40 millitorr/h is unacceptable. In such cases, retighten or replace the seal with the sorption cell and repeat the degassing process.

9.5 Activate the adsorption test module of the SEMS software to control and execute the adsorption test (Figure 15). Provide the necessary inputs to the software, such as volume of aggregate (computed by dividing the mass of the aggregate by its density) and probe vapor to execute the test. Other inputs such as name and description of the sample, name and location of the file for saving results, and minimum equilibrium time for each increment



Horizontal Centering Module for Robutherm USD

Start Horizontal Centering

STOP

Balance Reading (gm): 0.00000

Status: Moving to zero point

ZP: 0 0.00000

MP: 0 0.00000

Mass: 0 0.00000

Read Unstable?

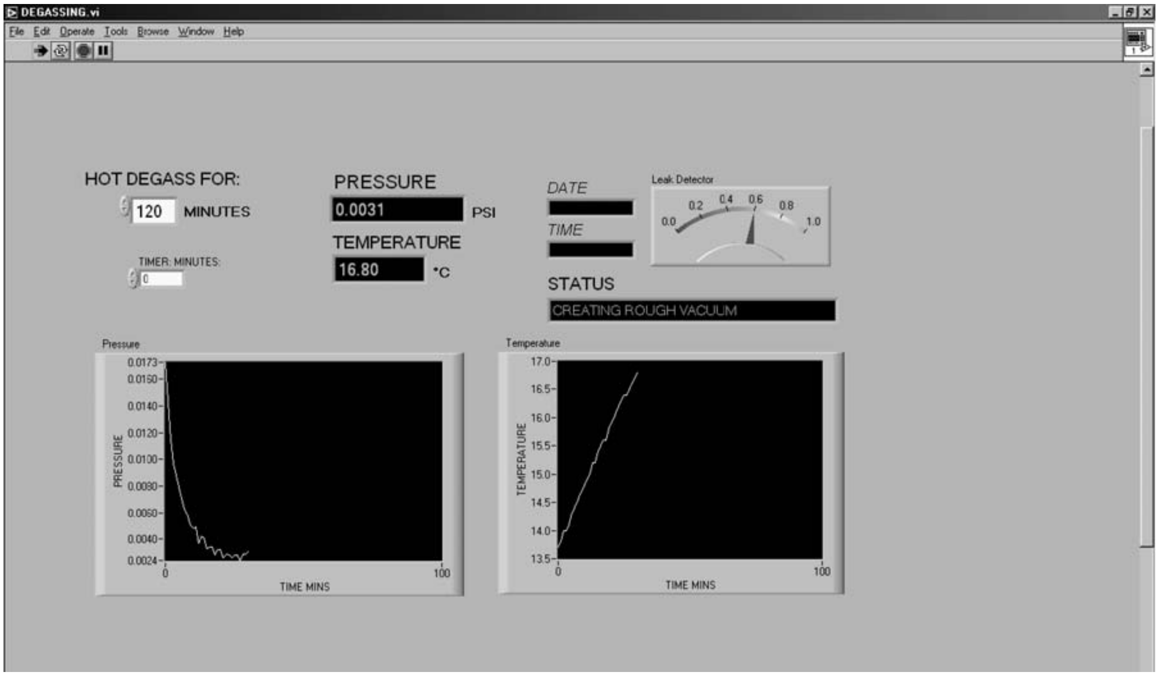
Include unstable readings

Include only stable readings

Use the timer below if you want to start balance centering program to start after a fixed time. Eg. To start centering after 3hrs15mins from now set timer to 3.25 and then click start horizontal centering

Timer: hrs: 0.00

Figure 13 Horizontal centering module in SEMS software.



HOT DEGASS FOR: 120 MINUTES

TIMER: MINUTES: 0

PRESSURE: 0.0031 PSI

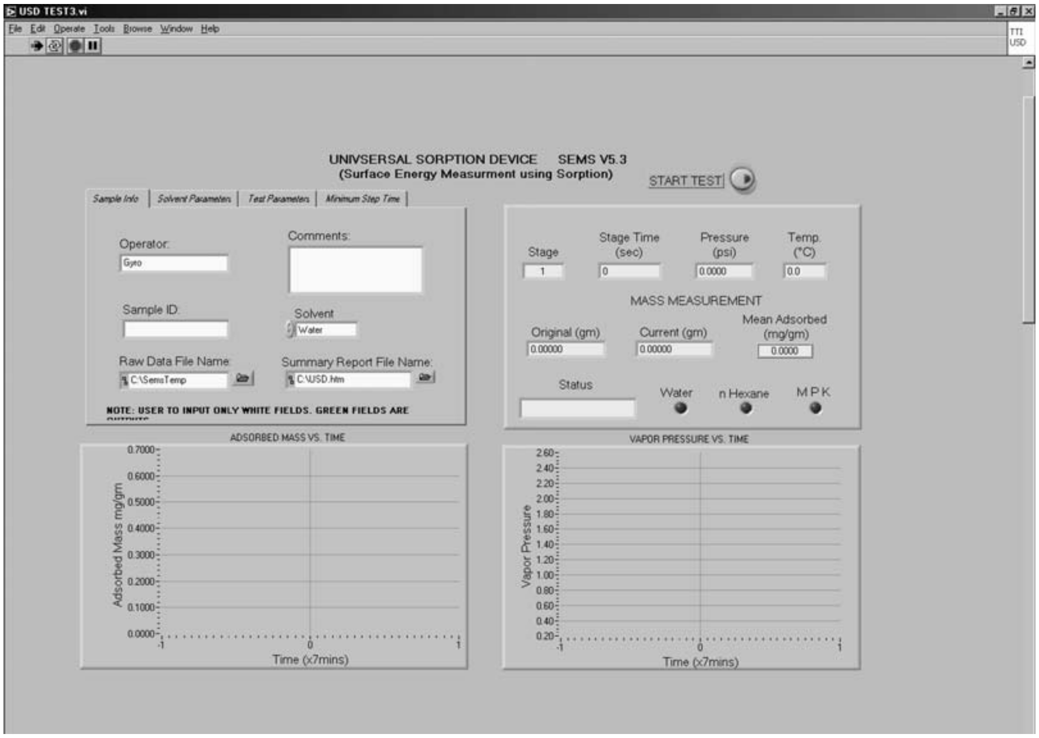
TEMPERATURE: 16.80 °C

DATE

TIME

STATUS: CREATING ROUGH VACUUM

Figure 14 Degassing module in SEMS software.



UNIVSERSAL SORPTION DEVICE SEMS V5.3
(Surface Energy Measurment using Sorption)

Operator: Gyro
Comments:
Sample ID:
Solvent: Water
Raw Data File Name: C:\SemsTemp
Summary Report File Name: C:\USD.htm

NOTE: USER TO INPUT ONLY WHITE FIELDS. GREEN FIELDS ARE

Stage: 1
Stage Time (sec): 0
Pressure (psi): 0.0000
Temp. (°C): 0.0
Original (gm): 0.00000
Current (gm): 0.00000
Mean Adsorbed (mg/gm): 0.0000
Status:

Figure 15 Adsorption test module in SEMS software.

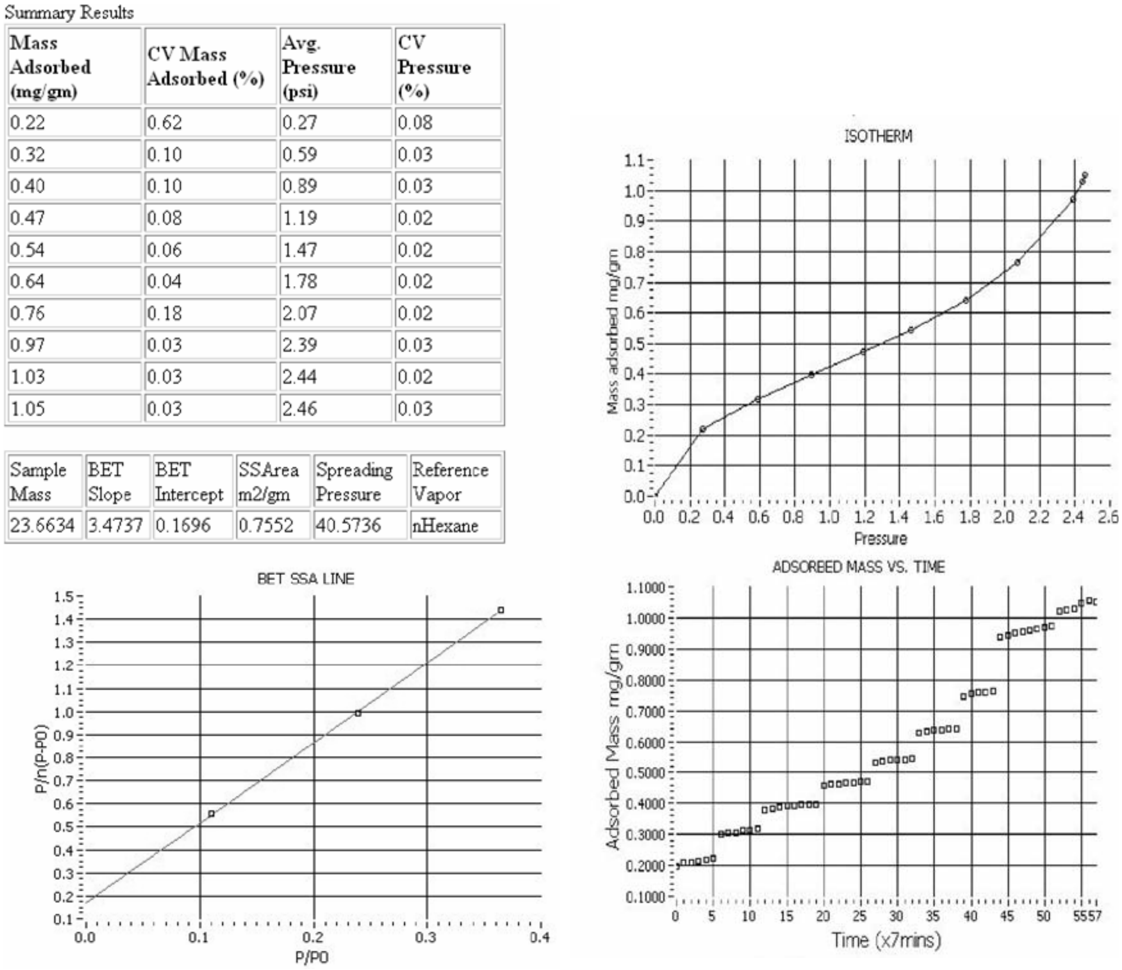
of relative pressure are also required. A minimum time of 15 min for equilibrium of each increment is recommended. Start the test from the SEMS software. A mechanical isolation valve is used between each of the probe liquid tanks and the system to prevent accidental exposure of the system to the probe vapors. Open the valve corresponding to the probe vapor for the test. Close this valve after completion of the test and before changing or degassing samples.

9.6 The test is controlled and data are acquired using the SEMS software. The software regulates valves to dose probe vapors into the system in 10 steps to achieve an increment of 0.1 in the relative pressure with each step. The mass of the sample is continuously acquired during this process by the SEMS software. The software computes the mass of vapor adsorbed in real time as the difference in the mass of sample at any time from the mass of the sample in vacuum after applying for corrections due to buoyancy. The software also corrects for any drift in the measurements due to the magnetic suspension coupling. Each increment of relative pressure is applied by the software after the mass of the sample comes into equilibrium due to adsorption of vapors from the previous increment, or after the minimum time for equilibrium is achieved, whichever is later. The test is complete after the saturation vapor pressure of the probe liquid is achieved in 10 increments and the equilibrium mass of vapor adsorbed is recorded for each increment.

9.7 Three probe vapors are recommended for this test. These are water, methyl propyl ketone (MPK), and hexane. All reagents must be high-purity grade (>99%). After filling the respective liquid tanks in the manifold for the first time, degas the tanks to remove any air trapped during the process of refilling. Typically, 100 ml of n-hexane lasts for approximately 15 tests, and 100 ml of MPK and water last for 60 tests.

10. Calculations

10.1 After completion of all 10 increments in vapor pressure, the software reports a summary of final results that includes the adsorption isotherm, specific surface of the aggregate with Brunauer-Emmett-Teller (BET) equations, and spreading pressure based on the specific surface area and the adsorption isotherm (Figure 16).


Summary Results

Mass Adsorbed (mg/gm)	CV Mass Adsorbed (%)	Avg. Pressure (psi)	CV Pressure (%)
0.22	0.62	0.27	0.08
0.32	0.10	0.59	0.03
0.40	0.10	0.89	0.03
0.47	0.08	1.19	0.02
0.54	0.06	1.47	0.02
0.64	0.04	1.78	0.02
0.76	0.18	2.07	0.02
0.97	0.03	2.39	0.03
1.03	0.03	2.44	0.02
1.05	0.03	2.46	0.03

Sample Mass	BET Slope	BET Intercept	SSArea m2/gm	Spreading Pressure	Reference Vapor
23.6634	3.4737	0.1696	0.7552	40.5736	nHexane

Figure 16 Results reported by SEMS software.

10.2 The typical coefficient of variation (standard deviation / average) for the spreading pressure for each pair of probe vapor and aggregate based on three replicate measurements is about 15%.

10.3 Although the SEMS software reports specific surface areas and spreading pressures for each test, certain corrections must be applied to obtain the correct specific surface area and spreading pressures that can be combined to determine the three surface energy components. Therefore, the adsorption isotherms for each of the three probe vapors reported by SEMS are used with the surface energy analysis workbook that conducts the required analysis to determine the specific surface area and the three surface energy components of the aggregate and the standard deviations of these components. This user-friendly workbook also integrates data from other tests such as the surface energy components of asphalt binders to determine various parameters of interest that are related to the performance of asphalt mixes.

PROPOSED TEST METHOD TO USE A SESSILE DROP DEVICE TO DETERMINE SURFACE ENERGY COMPONENTS OF ASPHALT BINDERS

1. Scope

1.1 This test method covers the procedures for preparing samples and measuring contact angles using the sessile drop method to determine the three surface energy components of asphalt binders.

1.2 This standard is applicable to asphalt binders that do not contain particulate additives such as crumb rubber.

1.3 This method must be used in conjunction with the manual for mathematical analysis to determine surface energy components from contact angle measurements or the computerized spreadsheets that were developed to carry out this analysis.

1.4 *This standard may involve hazardous material, operations, and equipment. This standard is not intended to address all safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to its use.*

2. Referenced Documents

2.1 AASHTO Standards
T40 Sampling of Bituminous Materials

3. Definitions

3.1 *Surface energy,* γ, or surface free energy, of a material is the amount of work required to create unit area of the material in vacuum. The total surface energy of a material is divided into three components: the Lifshitz–van der Waals component, the acid component, and the base component.

3.2 *Contact angle,* θ, refers to the equilibrium contact angle of a liquid on a solid surface measured at the point of contact of the liquid-vapor interface with the solid.

3.3 *Probe liquid,* within the context of this test, refers to any of the pure, homogeneous liquids that do not react chemically or dissolve with asphalt binders and are used to measure the contact angles with the binder. The three surface energy components of the probe liquid must be known at the test temperature from the literature.

3.4 *Mixing temperature,* within the context of this test, refers to the temperature at which the viscosity of the asphalt binder is approximately 0.170 Pa's, or any other temperature that is prescribed or determined by the user for use as the mixing temperature with aggregates to prepare hot mix asphalt.

4. Summary of Method

4.1 A probe liquid is dispensed over a smooth horizontal surface coated with asphalt binder. The image of the drop of liquid formed over the surface of the binder is captured using a camera. Contact angles are obtained by analyzing the image manually or using software.

4.2 Contact angles measured with different probe liquids are used with equations of work of adhesion to determine the three surface energy components of the asphalt binder.

4.3 Figure 17 presents a schematic of the sessile drop device.

5. Significance and Use

5.1 Surface energy components of asphalt binders are important material properties that are related to the performance of hot mix asphalt. Surface energy components of asphalt binders can be used to determine the total surface energy and cohesive bond strength of this material. The cohesive bond strength of asphalt binders is related to the work required for microcracks to propagate within the asphalt binder in an asphalt mix, which is related to the fatigue cracking characteristics of the mix.

5.2 Surface energy components of asphalt binders also can be combined with the surface energy components of aggregates to compute the work of adhesion between these two materials and the

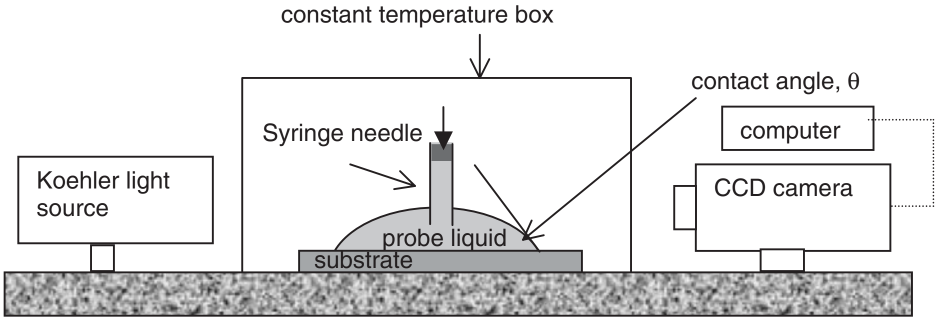


Figure 17 Schematic of the sessile drop method.

propensity for water to displace the asphalt binder from the asphalt binder-aggregate interface. These two quantities are related to the moisture sensitivity of the asphalt mix.

6. Apparatus

6.1 A sessile drop system comprises a microsyringe and a CCD (charge-coupled device) camera to create and capture images of sessile drops, respectively.

6.2 Image analysis software is required to determine contact angles from captured images. Alternatively, contact angles can also be determined from manual measurements on the drop images.

6.3 An oven capable of heating up to 150°C is required to heat asphalt binders for sample preparation. Glass slides or thin aluminum sheets are required to serve as substrates for the asphalt binder.

6.4 An environmental control system using a thermoelectric module is optional to conduct tests at temperatures other than room temperature.

7. Sampling

7.1 Obtain a representative sample of the asphalt binder according to procedure T40. Heat the asphalt binder to the mixing temperature, stir it thoroughly, and transfer it to smaller containers approximately 50 mL in capacity. Fifteen containers of the asphalt binder are required to test three replicates with five probe liquids. These containers will be heated only once more to prepare samples for testing.

8. Preparation of Test Samples

8.1 Clean the surface of the glass slide or aluminum sheet that is used as a substrate for the asphalt binder.

8.2 Heat the container with asphalt binder in an oven to the mixing temperature. Stir the liquid asphalt binder in the container and pour a small quantity on the substrate. The quantity of asphalt poured must be adequate to form an area of approximately 5 cm × 5 cm in size.

8.3 This binder sample is stored in a desiccator and allowed to cool to room temperature.

9. Procedure

9.1 Place the substrate with the asphalt binder between the light source and the camera. If a thermoelectric temperature control module is used, then place the sample over the module, which is fixed at the proper location between the light source and the camera. A transparent glass cover also may be used to reduce thermal flow to the atmosphere. Set the temperature of the module to the test temperature and allow the sample to remain at this temperature for at least an hour before starting the test.

9.2 Rinse the microsyringe with the probe liquid. Position the tip of the microsyringe needle approximately 5 mm away from the top of the sample. Dispense a small drop of the probe liquid from the syringe. As more volume of the probe liquid is added, the drop on the asphalt binder surface expands to a point when its interfacial boundary with the binder surface just begins to expand. Stop addition of probe liquid at this point and capture an image of the drop using the CCD camera.

9.3 At least five probe liquids are recommended for use with this test. These are water, ethylene glycol, methylene iodide (diiodomethane), glycerol, and formamide. All reagents must be high-purity grade (>99%). Contact angles must be measured for at least three replicates with each probe liquid for each asphalt binder.

9.4 When methylene iodide is used as a probe liquid, cover the light source with a red film because methylene iodide is a light-sensitive material and must not be exposed or stored in light for prolonged duration.

9.5 Store all probe liquids in airtight containers and do not use probe liquids after they have been exposed to air for prolonged duration.

10. Calculations

10.1 Analyze each sessile drop image to obtain two contact angles (Figure 18). Report the

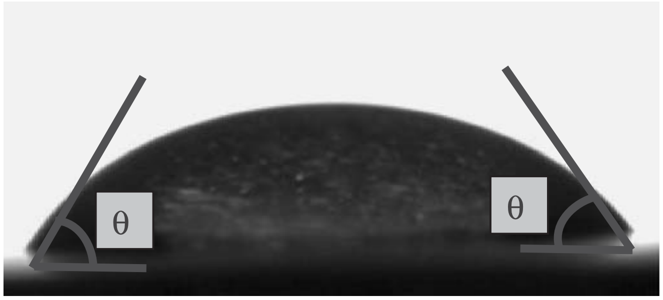


Figure 18 Typical image of sessile drop for contact angle measurement.

average of these two contact angles as the contact angle for that specific replicate and probe liquid combination.

10.2 The typical standard deviation for the contact angle measured for each pair of probe liquid and asphalt binder based on tests with three replicates is less than 5°.

10.3 The contact angle of each replicate and probe liquid is used with the surface energy analysis workbook that conducts the required analysis to determine the three surface energy components of the asphalt binder and the standard deviations in these components. This workbook also verifies the accuracy and consistency of the measured contact angles and integrates data from other test methods such as the surface energy components of aggregates to determine various parameters of interest that are related to the performance of asphalt mixes.

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