Construction and Building Materials 175 (2018) 448–457

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Different methods of selecting probe liquids to measure the surface free energy of asphalt binders

Dharamveer Singh *, Vinamra Mishra

Civil Engineering Department, Indian Institute of Technology Bombay, Mumbai 400076, India

HIGHLIGHTS

- The CN approach may be more reliable than Υ_L Cosθ vs. Υ_L.
- Probe liquid triplets, W-F-D, W-G-D and W-D-E are suitable to estimate binder SFE.
- Applicability of Bi-polar, Polar & Polar triplets to find binder SFE is debatable.

ARTICLE INFO

Article history:
Received 6 February 2018
Received in revised form 8 April 2018
Accepted 24 April 2018

Keywords:
Surface free energy
Condition number
Probe liquid triplets
Asphalt binder
Sessile drop

ABSTRACT

The present study evaluates two different methods for selection of probe liquids to determine the surface free energy (SFE) of asphalt binders: (i) Condition Number (CN) of probe liquids, and (ii) plot between cosine of total SFE (Υ_L Cosθ) and total SFE of probe liquids (Υ_L). Five different probe liquids, i.e. Water (W), Formamide (F), Ethylene Glycol (E), Diiodomethane (D), and Glycerol (G) were selected. Overall, ten different combinations of probe liquid triplets (W-G-F, W-G-E, W-G-D, W-F-E, W-F-D, W-D-E, G-F-E, G-F-D, F-E-D, and D-E-G) were formed to examine CN and plot of Υ_L Cosθ versus Υ_L. Three asphalt binders, namely unmodified (VG30), SBS polymer modified binder (PMB40) and crumb rubber modified (CRMB60) binders were selected for the present study. The contact angle of asphalt binders was measured using sessile drop method, and SFE of each of the selected asphalt binders was determined for all ten combinations of probe liquids. Thereafter, CN of probe liquid triplets was determined using Singular Value Decomposition (SVD) method. In addition, Υ_L Cosθ versus Υ_L plot was made for triplets using the measured contact angles of probe liquids. The CN approach and Υ_L Cosθ versus Υ_L plot were compared based on binder's total SFE to identify a better approach for selecting appropriate probe liquid triplets. CN approach was observed to be superior compared to the plot of Υ_L Cosθ versus Υ_L. In fact, it was observed that the plot approach may not be valid for asphalt binders.

1. Introduction

Recently, researchers have reported use of surface free energy (SFE) to evaluate compatibility of asphalt binder-aggregate system [1–3]. According to the acid-base theory [4], SFE (Υ) is divided into three components: Lifshitz-van der Waals or Dispersive (Υ^{LW}), Lewis acid (Υ^{+}) and Lewis base components (Υ^{-}), where, Υ^{+} and Υ^{-} together forms the polar components (Υ^{AB}) (Eqs. (1) and (2)).

$$\Upsilon = \Upsilon^{LW} + \Upsilon^{AB} \tag{1}$$

$$\Upsilon^{AB} = 2\sqrt{\Upsilon^{+}\Upsilon^{-}} \tag{2}$$

The SFE components of asphalt binders and aggregates are used to estimate adhesion (in dry and wet condition). Work of adhesion in absence of moisture is called dry adhesion energy (W_{AB}^{dry}) (Eq. (3)), while it is called as wet adhesion energy (W_{AB}^{wet}) in presence of water (Eq. (4)) [1].

$$W_{AB}^{dry} = 2\sqrt{\Upsilon_A^{LW}\Upsilon_B^{LW}} + 2\sqrt{\Upsilon_A^{+}\Upsilon_B^{-}} + 2\sqrt{\Upsilon_A^{-}\Upsilon_B^{+}} \tag{3}$$

$$W_{AB}^{wet} = \Upsilon_{AW} + \Upsilon_{BW} - \Upsilon_{AB} \tag{4}$$

where Υ_A^{+}, Υ_A^{-} and Υ_A^{LW} are acid, base and Lifshitz-van der Waals SFE components of aggregate, respectively. Similarly, Υ_B^{+}, Υ_B^{-} and Υ_B^{LW} are acid, base and Lifshitz-van der Waals SFE components of asphalt

* Corresponding author.
E-mail address: dvsingh@civil.iitb.ac.in (D. Singh).

https://doi.org/10.1016/j.conbuildmat.2018.04.199
0950-0618/

binder, respectively. Cohesion energy (W_{BB}) of asphalt binder can be calculated as twice of its total SFE (Υ_B) (Eq. (5)) [5].

$$W_{BB} = 2\Upsilon_B \tag{5}$$

Based on $W_{AB}^{dry}, W_{AB}^{wet}$ and W_{BB} parameters, compatibility ratio (CR) of aggregate-binder system is calculated using Eq. (6). CR is the ratio of wettability ($W_{AB}^{dry} - W_{BB}$) to the wet adhesion energy (W_{AB}^{wet}). Researchers have recommended using CR parameter to rank the bonding potential of aggregates and asphalt binders [6,7]. Higher value of CR is desirable to ensure better bond between aggregate-asphalt binder interfaces.

$$CR = \left| \frac{W_{AB}^{dry} - W_{BB}}{W_{AB}^{wet}} \right| \tag{6}$$

1.1. Motivation of the work

As shown from (Eqs. (3)–(6)), estimation of adhesion energy (dry or wet conditions) and CR require SFE of aggregate and asphalt binder. There is no direct method to measure SFE of these materials. The SFE of asphalt binder and aggregate can be estimated based on Young-Dupree Eq. and acid-base theory proposed by Van Oss et al. [4] (Eq. (7)). It can be seen that to solve Eq. (7), it needs contact angle measurement of aggregate and asphalt binder with at least three probe liquids. However, selection of reliable probe liquid triplet is important to estimate realistic SFE components of asphalt binder. Hence, knowledge of appropriate methods for selecting reliable probe liquid triplets is imperative.

$$\Upsilon(1 + \mathrm{Cos}\theta) = 2\sqrt{\Upsilon_s^{LW}\Upsilon_L^{LW}} + 2\sqrt{\Upsilon_s^{+}\Upsilon_L^{-}} + 2\sqrt{\Upsilon_s^{-}\Upsilon_L^{+}} \tag{7}$$

Little and Bhasin [6] suggested that probe liquids (i) should be chemically homogeneous and pure, (ii) should have higher SFE than the anticipated SFE of asphalt binder, (iii) should be chemically inert to the solid surface, (iv) should have known SFE components. Based on these assumptions, Hefer et al. [7] recommended five probe liquids namely, water (W), ethylene glycol (E), diiodomethane or methylene iodide (D), formamide (F) and glycerol (G) for measuring SFE of asphalt binder. Any three probe liquids out of five can be used to measure contact angle and to estimate SFE of asphalt binders. Although random selection of three probe liquids may theoretically be correct, however, improper choice of probe liquids followed by a small experimental error can drastically affect estimated SFE of materials [7]. Any error in SFE of asphalt binder may affect work of adhesion and cohesion energies (Eqs. (4) and (5)), and CR (Eq. (6)). Therefore, it may lead to an inappropriate combination of aggregate-asphalt binder system. Hence, identification of appropriate method for selection of reliable probe liquids is of utmost importance.

2. Relevant literature study

Little and Bhasin [6] determined SFE of nine different types of unmodified and twelve modified asphalt binders using W, F, D, E and G probe liquids. The liquids were selected on the basis of their known SFE components and immiscibility with the asphalt binder. They suggested the concept of condition number (CN) for selection of probe liquids. CN of any linear system of equations can be understood as the rate at which output variable will change with respect to change in input variable. Thus, it implies that if CN is high, then the slightest error in input variable may cause a large error in the output. For example, in Eq. (7), a small error in measured contact angle (i.e. input variable) for a probe liquid combination with high CN can drastically change the evaluated SFE (i.e. output variable). Improper choice of probe liquids increases ill-conditioning of the system of equations thereby increases CN and yield falsified results [8]. Generally, a combination of three probe liquids with CN more than 10 are sensitive to errors in the measurement of SFE [6]. Thus, triplet probe liquids with lowest CN was preferred. Kakar et al. [9] selected W-D-E for the determination of SFE of PG-64 and PG-76 binders with 0–0.4% warm mix additive (WMA). The selection was made considering the low CN value (4.47) of this triplet. However, sometimes probe liquids with high CN may estimate reasonable SFE values for some asphalt binders, thus it is important to study how CN approach works for selection of probe liquids for different types of binders.

Another approach for selection of probe liquids is to generate the plots of Υ_L Cosθ versus Υ_L [10]. A smooth linear plot between Υ_L Cosθ and Υ_L is desired for selected polar liquids. Hefer et al. [7] selected four probe liquids namely W, E, D, and G based on the plot of Υ_L Cosθ versus Υ_L to determine SFE of several asphalt binders. Similarly, Feng et al. [11] selected W, G, and F based on the plot of Υ_L Cosθ versus Υ_L to measure the SFE of base and modified binders. However, probe liquids giving smooth linear plot may sometimes produce unrealistic values of SFE, and vice versa.

Furthermore, many studies [12–14] have been conducted considering the properties of probe liquids proposed by Little and Bhasin [6]. Numerous researchers have selected W, G, and F to determine the SFE of asphalt binder [3,5,15,16]. Hossain et al. [17] incorporated W, F, and E to evaluate the moisture sensitivity of ground tire rubber (GTR) modified asphalt binder using SFE approach. Azarhoosh et al. [13] and Koc and Bulut [14] selected W, D, and E to estimate SFE of asphalt binder. Combination of W, D, and E includes a non-polar probe liquid (D), bi-polar probe liquid (W) and polar probe liquid (E) and is recommended for estimating SFE of binder [13]. The summary of probe liquids used by researchers and range of SFE are reported in Table 1. Υ_B value of asphalt binders was found to be in range of 9.23–36.53 mJ/m^2 (Table 1).

3. Objectives and scope of study

The authors observed that although the concepts of CN and plot of Υ_L Cosθ versus Υ_L for selection of probe liquids are reported in the open literature, however, they are not frequently used by many researchers. In addition, it was observed that combination of W-G-F with high CN (18.66) and Bi-polar, Polar and Polar nature is the most frequently used probe liquid triplets [15,18–22] (Table 1) rather than W-G-D, W-F-D and W-D-E with Non-polar (D), Bi-polar (W), and Polar (G, F, or E) natures which are known to estimate reliable SFE of asphalt binder. Also, the combination of W-F-E [17] with Bi-polar, Polar and Polar nature was used to estimate SFE of binders. Moreover, no specific criterion was mentioned by the researchers to identify appropriateness of selected probe liquids combination (i.e. W-G-F and W-F-E). Hence, it was observed that selection of probe liquids using CN and plot between Υ_L Cosθ and Υ_L approach were not given much importance. The value of CN for selected probe liquids can be calculated prior to testing, while Υ_L Cosθ versus Υ_L plot is possible after measurement of contact angle. Thus, CN can be time saving and efficient. Both the approaches (CN and Υ_L Cosθ versus Υ_L plot) may give a different combination of probe liquids. Therefore, a sense of uncertainty exists in adopting a precise approach for selection of appropriate probe liquid to be used for measurement of SFE, which might result in varying magnitude.

The present study addresses this ambiguity by determining the SFE of three asphalt binders (unmodified and modified binders) with five commonly used probe liquids (W, F, E, D, and G) mentioned in the literature [7]. According to acid-base theory, minimum three probe liquids are required for the evaluation of