

## **ROUGHNESS AS AN IMPORTANT PARAMETER IN ADHESION CONSIDERATIONS**

**D.Q. van Lent, M.F.C. van de Ven and A.A.A. Molenaar**

Delft University of Technology  
P.O. Box 5048  
2600 GA Delft, the Netherlands  
d.q.vanlent@tudelft.nl

### **Abstract**

The adhesion between bitumen and aggregate is very important for the durability of asphalt concrete. This adhesive bond is affected by the presence of water. In this paper the water-repellent behaviour of a standard and therefore flat bitumen surface is compared to a specially roughened bitumen surface. It is shown that standard bitumen shows a hydrophobic and that a specially roughened bitumen surface shows a super-hydrophobic behaviour.

1. INTRODUCTION

The adhesion between bitumen and aggregate is very important for the durability of asphalt concrete. Four major models exist for theoretically explaining the adhesion between bitumen and aggregates. These theoretical models are mechanistic approach, molecular orientation, chemical reaction and thermodynamic approach. (Bagampadde et al, 2001) The main assumption for the mechanistic approach is that, during coating the aggregate, bitumen enters present pores, holes, cracks and unevenness in the aggregate surface texture. After hardening of the bitumen, the adhesive bond is caused by the surface friction between bitumen and aggregate surface. The theory may provide an explanation for the stronger adhesive bonds of rougher aggregate surface textures. First of all, more irregularities provide more interlock for the bitumen. Secondly, a rougher aggregate surface has a larger physical area of contact and so provides a larger surface friction between bitumen and aggregate surface. Due to the roughness of the aggregate surface the stresses in the bitumen coating are better redistributed as well. This results in less peak stress concentrations and so a decrease in the chance of rupture. However the theory also states that with an increasing roughness of the aggregate surface the wetting with bitumen becomes more difficult and the wetting could become incomplete. This may result in a less strong adhesive bond.

The molecular orientation theory the functional groups from both the bitumen and aggregate cause an adhesive bond. The bitumen functional groups migrate and aim towards the aggregate surface, resulting from the electric field caused by the dipole charges of the functional groups on the aggregate surface. The bitumen functional groups align in accordance with the electrical field around the aggregate. The level of adsorption and desorption of bitumen functional groups is influenced by the distance from the particle and the magnitude of the dipole charges. At close distances of the aggregate surface the bitumen functional group with the highest potential will form a layer. The potential of the aggregate surface decreases over a growing distance of this surface causing lower charged bitumen functional groups to form a less firmly attached layer around the first layer of bitumen functional groups. The layer with the stronger bond is called the stern layer and the secondary layer is called the Gouy-Chapman layer.

The chemical reaction theory is based on the supposition that the adhesion between bitumen and aggregate is caused by chemical reactions. After coating the aggregate with bitumen, adsorption of the bitumen chemical active components on the surface of the aggregate takes place. The chemical active components from both the bitumen and the aggregate interact, resulting in electron transfers between active components in the bitumen and the aggregate and between active components in the bitumen itself. The electron transfers are caused by the difference in potentials. When different active components interact, some components will have the tendency to donate electrons and others will receive them. Bitumen consist of both type active components, so of components, which will have the tendency to donate electrons quickly and components, which receive electrons quickly. Also carbonate aggregates consist of both easy donor and acceptor active components. Quartz aggregates on the other hand, predominately consist of components, which will mainly act as electron receivers. The theory continues by pointing out that stronger adhesive bonds develop in interface layers in which a proper balance between donating and receiving active components from both the bitumen and the aggregate surface exist.

The thermodynamic approach for the adhesive bond strength between bitumen and aggregate is based on the change of surface energy of the bitumen after coating the aggregate. This

## 10<sup>th</sup> CONFERENCE ON ASPHALT PAVEMENTS FOR SOUTHERN AFRICA

approach combines elements from the chemical reaction and the molecular orientation theory. After wetting the aggregate with bitumen, intermolecular forces at the aggregate surface and the bitumen interact, resulting in a released bonding energy. The total initial and final energy state of a system is called Gibbs energy and the release of the bonding energy results in a change of Gibbs energy. To break the bond between the aggregate surface and the bitumen energy is needed. This needed work to be applied equals the change in Gibbs energy before and after coating the aggregate with bitumen. This work needed to break the bond is a measure for adhesion of the bitumen on the aggregate surface.

### 1.1 Thermodynamic adhesion approach

The adhesive bond between bitumen and aggregate, also under influence of water, has been characterized with thermodynamics by many researchers. (Lytton et al, 2005; Groenendijk, 1998; Taylor and Airey, 2009) The fundamental work of adhesion between aggregates and bitumen can be calculated with the Young-Dupré equation.

$$W^a = -\Delta G_{12}^a = \gamma_{lv} \cdot (1 + \cos \theta_{sl}) \quad (\text{Eq.1})$$

where  $W^a$  = fundamental work of adhesion

$\Delta G_{12}^a$  = change of Gibbs free energy per unit area

$\gamma_{lv}$  = interfacial energy between liquid and vapour

$\gamma_l$  = surface energy of liquid

$\theta_{sl}$  = contact angle between solid and liquid

The fundamental work of adhesion represents the minimum required energy to separate the bitumen from the aggregate. (Hefer and Little, 2005) This thermodynamic characterization of adhesion is based on Young's equation (Young, 1805):

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \theta_{sl} \quad (\text{Eq.2})$$

where  $\gamma_{sv}$  = interfacial energy between solid and vapour,

$\gamma_{sl}$  = interfacial energy between solid and liquid,

$\gamma_{lv}$  = interfacial energy between liquid and vapour and

$\theta_{sl}$  = contact angle between solid and liquid

Young's equation shows the relationship between the interfacial energies on the three-phase boundary and the contact angle of a liquid on an ideal flat solid in a vapour atmosphere. However solid surfaces are not ideal flat. The influence of the roughness on the contact angle in the liquid-solid system was first studied by Wenzel. He introduced a roughness factor, which accounts for the fact that the actual surface of any real solid will be greater than the geometric surface because of surface roughness (Wenzel, 1936):

$$r = \text{roughness factor} = \frac{\text{actual surface}}{\text{geometric surface}} \quad (\text{Eq.3})$$

Wenzel's relation for the contact angle on an ideal flat surface and the contact angle on a rough surface is:

$$\cos \theta_{sl}^* = r \cdot \cos \theta_{sl} \quad (\text{Eq.4})$$

where  $\theta_{sl}^*$  = contact angle found on a rough surface,

**10<sup>th</sup> CONFERENCE ON ASPHALT PAVEMENTS FOR SOUTHERN AFRICA**

$\theta_{sl}$  = Young's contact angle on an ideal flat surface and

$r$  = roughness factor

Cassie and Baxter developed another model as an extension of Wenzel's model to porous materials. (Cassie and Baxter, 1944)

$$\cos \theta_{sl}^* = f_1 \cdot \cos \theta_{sl} - f_2 \quad (\text{Eq.4})$$

where  $\theta_{sl}^*$  = contact angle found on a rough surface,

$\theta_{sl}$  = Young's contact angle on an ideal flat surface,

$f_1$  = total area of solid liquid interface and

$f_2$  = the total area of liquid-air interface in a plane geometrical area of unity parallel to the rough surface

Wenzel's relation shows that a contact angle of a wetting liquid ( $\theta < 90^\circ$ ) will become smaller when the solid is roughened and that a contact angle of a non-wetting liquid ( $\theta > 90^\circ$ ) will become larger when the roughness of the solid increases. However it is found that this is only valid for limited roughness. At a specific surface roughness a liquid is unable to contact the whole area of the solid surface. At some points in the surface roughness air is trapped between the liquid and the rough surface. This results in extra high contact angles between the surface and the liquid. The liquid forms almost spherical droplets with contact angles larger than  $150^\circ$ . Surfaces that initiate such liquid droplets are called super-hydrophobic. (Quéré, 2005) The maximum contact angle that can be reached at flat surfaces is about  $120^\circ$ . (Wong and Ho, 2009) A high contact angle of water means that cohesion forces of the water droplet are more preferable than the wetting forces of the substrate. Very high apparent contact angle surfaces are therefore classified as water-repellent. (Nosonovsky and Bhushan, 2008)

**1.2 Aggregate surface roughness**

In a previous paper it was shown that contact angles of wetting liquids are well related to the roughness of mineral aggregate surfaces by Wenzel's relation (van Lent et al, 2009). With an increasing roughness the contact angles of the wetting liquids decreased. This is because the contact angles of the used wetting liquids are smaller than  $90^\circ$  (Table 1).

**Table 1: Average contact angles of wetting liquids on aggregate surface. (van Lent et al, 2009)**

Aggregate	Average contact angle diiodo-methane [°]	Work of adhesion diiodo-methane $\gamma_{lv} \cdot (1 + \cos \theta_{sl})$ [mJ/m <sup>2</sup> ]	Average contact angle water [°]	Work of adhesion water $\gamma_{lv} \cdot (1 + \cos \theta_{sl})$ [mJ/m <sup>2</sup> ]	Average contact angle glycerol [°]	Work of adhesion glycerol $\gamma_{lv} \cdot (1 + \cos \theta_{sl})$ [mJ/m <sup>2</sup> ]
Bestone sawn (lower roughness)	25.15	96.78	22.70	139.96	35.98	115.79
Bestone sandblasted (higher roughness)	17.46	99.26	12.99	143.74	26.70	121.18

The contact angles vary because of the roughness of the aggregates. The aggregates are found to have a certain roughness by laser scanning confocal microscopy (Figure 1). This roughness is described in micrometers.

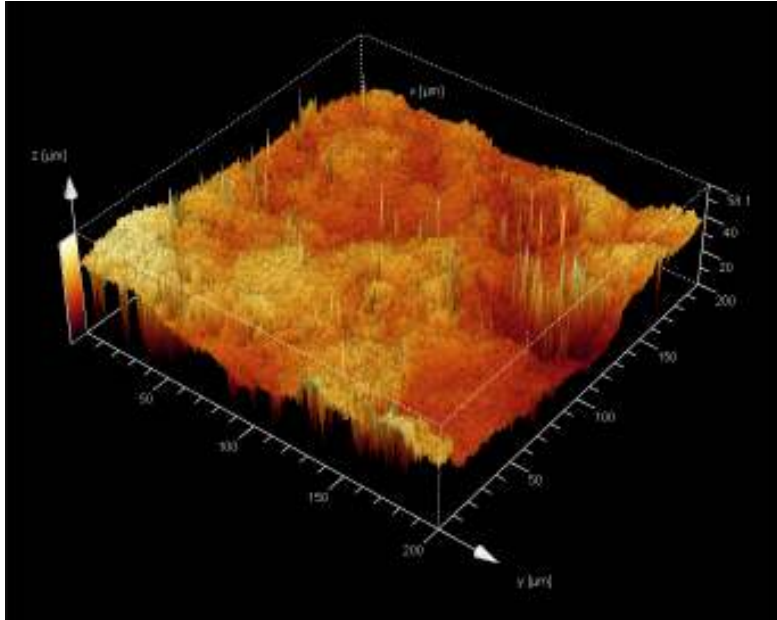


Figure 1: Microscopic picture of Bestone aggregate roughness

### 1.3 Roughness of bitumen

In this paper we show that water contact angles on bitumen with a similar roughness scale as the aggregates has a different behaviour. We will show that the contact angle of water on pure flat bitumen is more than 90° and that bitumen with the special roughness shows super-hydrophobic behaviour.

## 2. EXPERIMENTAL PROGRAM

Contact angles of water droplets are measured on bitumen surfaces using the sessile drop method (Little and Bashin, 2006) at  $20^{\circ}\text{C} \pm 1$ . At first the bitumen is tested with a flat surface. After that the surface of the same bitumen is tested with a forced roughness. The roughness is forced by pressurizing the bitumen through an aluminium filter with 50 µm sized holes (Figure 2) at ambient temperature.

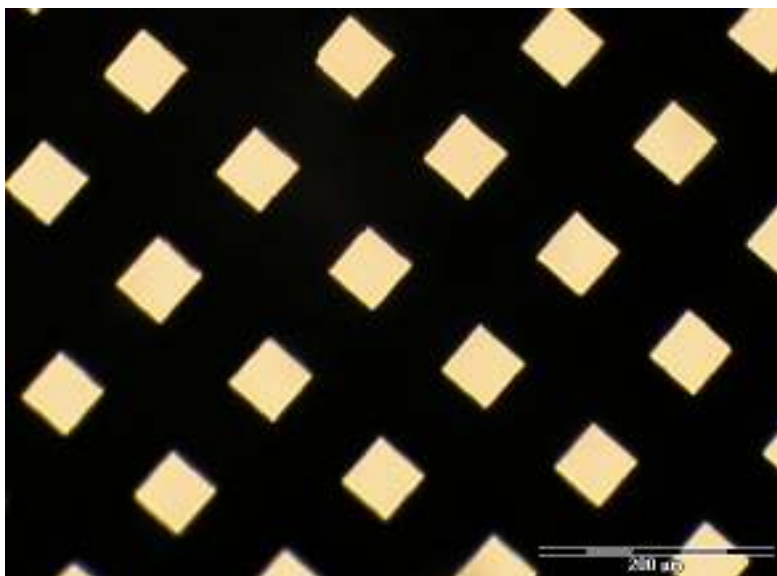


Figure 2: Microscopic picture of holes in aluminium filter

### 3. MATERIALS

The bitumen used is, is a Kuwait (Q8) bitumen with a pen. grade of 70/100. The bitumen is not aged and not modified.

### 4. EXPERIMENTAL RESULTS

Five bitumen samples with normal flat surfaces are tested with the sessile drop method. The average measured contact angle of water on the flat bitumen samples is 101.53°, as shown in Table 2.

**Table 2: Sessile drop method results on bitumen with a flat surface**

Material	Average measured contact angle of water
Q8 bitumen 70/100 (flat surface)	101.53°

The aluminium filter was also tested with the sessile drop method to rule out its influence on the water contact angle of the roughened bitumen samples. The average measured contact angle of water on the aluminium filter is 97.48°, as shown in Table 3.

**Table 3: Sessile drop method results on the aluminium filter**

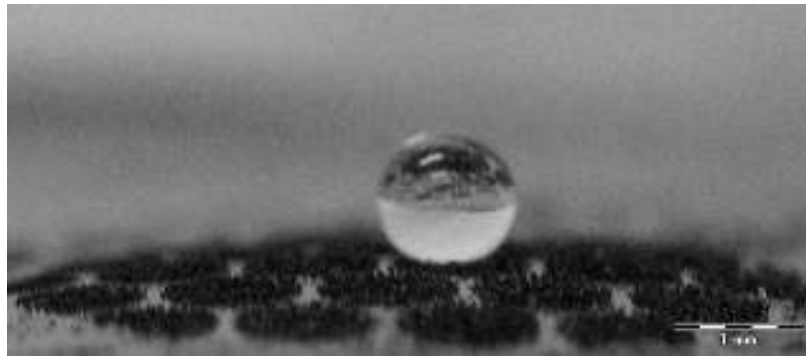
Material	Average measured contact angle of water
Aluminium filter	97.48°

Now bitumen is pressurized through the mesh of the aluminium filter. The bitumen through the filter forms a surface consisting of vertical bitumen hairs. The average measured contact angle of water on these bitumen surfaces is 155.05°, as shown in Table 4. However, it should be noted that because the rough bitumen surface is so difficultly wetted by water, the water droplets have to be pushed more on the rough surface in contrast to the other surfaces tested. This results in lower observed contact angles. So the contact angles of the water droplets on the roughened bitumen surface may even be much higher.

**Table 4: Sessile drop method results on bitumen with a roughened surface**

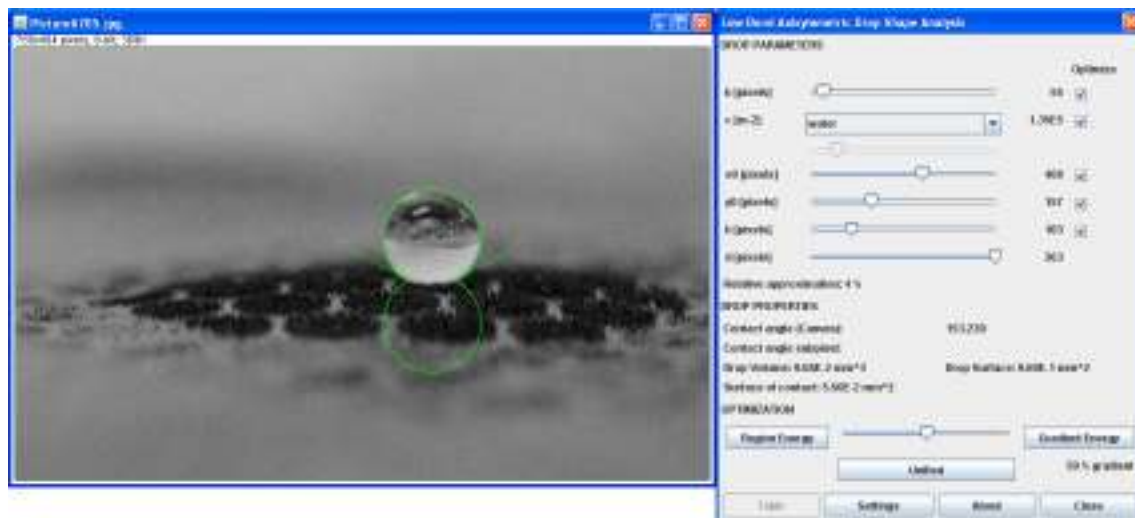
Material	Average measured contact angle of water
Q8 bitumen 70/100 (roughened surface)	155.05°

In Figure 3 the bitumen with roughened surface is shown with a water droplet on it.



**Figure 3: Water droplet on roughened bitumen surface**

As additional illustration the contact angle of the water droplet in Figure 3 is evaluated with the program Low Bond Axisymmetric Drop Shape Analysis. (Stalder et al, 2010) In the program a circle is made following the contours of the droplet. At the bottom the water droplet deviates from the perfect circle, so we know that this is the baseline of the droplet. Putting the contact point on this base line gives a contact angle of 153.23° (Figure 4).



**Figure 4: Water droplet on roughened bitumen surface in the Low Bond Axisymmetric Drop Shape Analysis program**

## 5. CONCLUSIONS AND FURTHER RESEARCH

In this paper it is demonstrated that a standard bitumen with a special roughness behaves super-hydrophobic. The average contact angle of water droplets on the roughened bitumen surface is about 155°. It is however expected that the observed contact angles can be larger when the water droplet do not have to be pushed as much on the roughened bitumen surface, when a smaller needle is used.

Further research will focus on the question whether super-hydrophobicity of the bitumen film may also play a role in stripping of the bitumen from the aggregate surface in bitumen-aggregate systems in actual road and highway constructions.

REFERENCES

Bagampadde U., Isacson U. and Kiggundu B.M., 2001. **Fundamentals of stripping in bituminous pavements. State-of-the-Art.** Research Report ISSN 1650-867X. Division of Highway Engineering, Royal Institute of Technology, Stockholm, Sweden.

Cassie A.B.D. and Baxter S., 1994. **Wettability of porous surfaces.** Trans. Faraday Soc. vol. 40. pp. 546–551

Groenendijk J., 1998. **Accelerated testing and surface cracking of asphaltic concrete pavements.** Ph.D. dissertation. Delft University of Technology, Delft, the Netherlands

Hefer A. and Little D., 2005. **Adhesion in bitumen-aggregate systems and quantification of the effects of water on the adhesive bond.** report ICAR/505-1, 2005. Texas Transportation Institute, Texas A&M University System, College Station, Texas, USA.

Little D. and Bashin A., 2006. **Using surface energy measurements to select materials for asphalt pavement.** Final report for NCHRP project 9-37. Texas Transportation Institute, Texas A&M University System, College Station, Texas, USA.

Lytton R.L., Masad E.A., Zollinger C., Bulut R. and Little, D., 2005. **Measurements of surface energy and its relationship to moisture damage.** Report 0-4524-2. Texas Transportation Institute, Texas A&M University System, College Station, Texas, USA

Nosonovsky M., and Bhushan B., 2008. **Multiscale dissipative mechanisms and hierarchical surfaces.** Springer Berlin Heidelberg New York. ISBN 978-3-540-78424-1

Quéré D., 2005. **Non-sticking drops.** Reports on Progress in Physics. vol. 68. pp. 2495–2532

Stalder A.F., Melchior T., Müller M., Sage D., Blu T., Unser M., 2010. **Low-bond axisymmetric drop shape analysis for surface tension and contact angle measurements of sessile drops.** Colloids and Surfaces A: Physicochemical and Engineering Aspects. vol. 364. no. 1-3. pp. 72-81

Taylor R. and Airey G.D., 2009. **Influence of surface interactions between bitumen and mineral fillers on the rheology of bitumen-filler mastics.** In: Efficient Transportation and Pavement Systems – Al-Qadi, Sayed, Alnuaimi & Masad (eds). Taylor & Francis Group, London. ISBN 978-0-415-48979-9

Young T., 1805. **An essay on the cohesion of fluids.** Phil. Trans. R. Soc. Lond. vol. 95, 1805, pp. 65–87

van Lent D.Q., Molenaar A.A.A. and van de Ven M.F.C., 2009. **Influence treatment in laboratory of stone surface on the surface roughness.** Journal of Testing and Evaluation, ASTM International, Vol. 37, No. 5, pp. 417-423

Wenzel R.N., 1936. **Resistance of solid surfaces to wetting by water.** Industrial and Engineering Chemistry. vol. 28, no. 8, pp. 988-994

Wong T.S. and Ho C.M., 2009. **Dependence of macroscopic wetting on nanoscopic surface textures.** Langmuir. vol. 25(22), pp. 12851–12854

**KEY WORDS**

bitumen, hydrophobicity, super-hydrophobicity, water-repellent