

USING CONTACT ANGLE MEASUREMENTS FOR DETERMINATION OF THE SURFACE FREE ENERGY OF THE CERAMIC MEMBRANES

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ABSTRACT

The surface free energy is one of the factors that characterises the surfaces of materials. The sessile drop method is the most popular method for determining its value. A contact angle between the surface and the edge of liquid droplets is measured in this scenario. The substrate surface free energy was frequently determined using contact angle measurements for unique liquids. As shown in Table 1, contact angles were evaluated at room temperature with a model liquid (water) for all samples. It's important to note that a smaller contact angle indicates a solid's wettability (Ali, 2012) As a result, a higher contact angle indicates less model liquid absorption by the sample and consequently less interaction between the two. The largest contact angle was seen with the 200nm ceramic membrane sample, and the lowest contact angle was observed with the 15nm ceramic membrane sample. Apart from 200nm ceramic membrane sample, the DIM contact angles of the samples are quite near to each other. Scanning electron microscopy (SEM) examination was used to characterise the ceramic membrane. The ceramic membrane has a porous, rough morphological feature apart from 15nm pore size ceramic membrane appeared to have smooth on its surface. A close examination of the image reveals that the membrane was free of defects such as pinholes and cracks.

KEYWORDS : contact angle measurement, ceramic membrane, surface free energy, SEM analysis.

1 INTRODUCTION

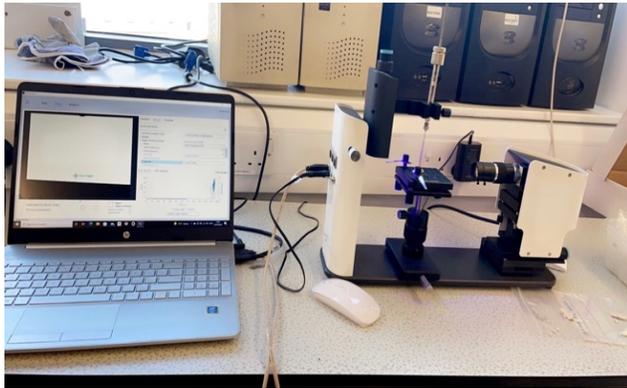
One of the most widely used techniques for solid surface characterization is contact angle measurement. Image analysis is used in contact angle measurements, and this method is a dependable method for ensuring the accuracy and repeatability of test results. The contact angle is generated when liquid encounters the surface of various solids, and it aids in understanding the solid's surface properties. Purposely, the "sessile drop method" is frequently employed to determine the contact angle. The contact angle is a measurement of a surface's wettability against a liquid. Depending on their surface free energy and shape. The contact angle concept may be explained using geometry because when a liquid drops in the form of a droplet on any surface, the droplet makes an angle with the solid surface, forming a three-phase boundary between the liquid, gas, and solid surface. The contact angle concept may be explained using geometry because when a liquid drops in the form of a droplet on any surface, the droplet makes an angle with the

solid surface, forming a three-phase boundary between liquid, gas, and solid surface. The contact angle measurement is a straightforward and extensively used method for determining surface properties in a wide range of applications, from special-wetting surfaces to inkjet and spray cooling technologies. (Doris et al. 2008). The contact angle is a macroscopic expression of the complex interaction between a liquid and a solid surface that can provide information about surface chemistry, topography, and capillary forces at the micro and nanoscale (Kwok and Neumann 1998). The ability to estimate solid surface tensions from contact angles is based on a relationship discovered in 1805 by Young. The mechanical equilibrium of the d surface (Young 1805). When the droplet is sitting on the surface and the three-phase boundary isn't moving, static (i.e., sessile drop) contact angles are recorded. The most widely measured wettability parameters are static contact angles. It's best used on surfaces that are quite smooth and uniform. The surface free energy (i.e., the surface tension of a solid) of the substrate is also defined by static

2 MATERIALS AND METHODS

Contact angle tests were carried out by dropping model liquids on the pelleted samples with an Attention Theta Lite contact angle measuring device. The wettability of the materials was determined using the sessile drop method. Static contact angles were measured using model liquid (water). Based on device measurements, the average droplet volumes of the model liquid at first contact with the solid surface was water, and DIM were approximately 5.5 μ l, for all the ceramic membranes with different of pore sizes of 15nm, 200nm, and 600nm. A software programme called "One Attention" on the computer attached to the device was used to study and record the contact angles (θ) formed by a single drop of model liquid. The image records were set to different seconds at a speed of different frames per second (FPS) for each of the samples. The image record for 6000nm ceramic membrane was 10 second at 50% FPS. The image record for 200nm ceramic membrane was 10 second at 2.5% FPS and the image record for 15nm ceramic membrane was 96 second at 2.5% FPS. The programme calculated the angle values produced between the established baseline and the model liquid droplet's right and left contact sites with the solid surface. The angle values of the right and left points are averaged in the software. Averaging all the mean results yielded the final average contact angle after different seconds

of testing. Each model liquid was measured for each sample separately, and the final contact angles were calculated using the method outlined above.



MODEL FOR DETERMINING SURFACE ENERGY

As previously indicated, there are numerous theoretical models for calculating surface free energy based on contact-angle observations. The Owens – Wendt – Rabel – Kaelble (OWRK) model [11], also known as the expanded Fowkes model [10] based on the Young – Dupree Equation, was utilised to determine surface free energies of samples in this investigation. The Attention Theta Lite contact angle device has given this model the name OWRK/Fowkes.

The Young's Equation is shown in Eq (1):

$$\frac{l}{\gamma_L \cdot \cos \phi} = \gamma_S - \gamma_{SL} \dots\dots\dots (1)$$

where, γ_S , γ_L and γ_{SL} are the surface free energies of solid, liquid, and solid liquid (mJ/m²); respectively and θ is the contact angle (°) between solid and liquid.

(γ_L in Eq (1)) is a well-known property of the model liquid. (θ in Eq (1)) is the liquid-solid contact angle, which can be measured. As a result, the work of adhesion (WA) equation is required to compute γ_S , and γ_L .

$$W_A = \gamma \quad \boxed{=} \quad \gamma_S + \gamma_L - \gamma_{SL} \quad (2)$$

When Eq. (2) computed with Eq. (2)

$$W_A \boxed{=} \gamma_L \cdot 1 + \cos \theta \quad (3)$$

Based on the Young–Dupree Equation, the Owens–Wendt–Rabel–Kaelble (OWRK) model, commonly known as the extended Fowke's model, leads to Eq (4): $\gamma_L \cdot 1 + \cos \theta$

$$\gamma_L \cdot 1 + \cos \theta = 2 \sqrt{\gamma_s^d \cdot \gamma_L^d} + \sqrt{\gamma_s^p \cdot \gamma_L^p} \quad (4)$$

Where, γ_L is the total surface free energy of liquid, γ_L^d is the dispersive surface free energy of liquid, γ_L^p is the component of solid surface free energy

STATE OF EQUATION.

Although there are other distinct Equation of state (EQS) formulations, the one described by Neumann [3] is the most well-known.

$$\overline{\cos \theta} = -1 + 2 \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}} e^{-\beta(\gamma_{lv} - \gamma_{sv})^2}} \quad (5)$$

The coefficient 0.0001247 is determined experimentally in this case. In theory, the equation of state requires just one liquid to be measured, and the surface free energy value should be the same regardless of which liquid is used.

ACID BASE

The polar component can be further separated into acid and base components using the acid-base approach, also known as the Van Oss- Chaudhury-Good method, and the equation can be written as:

$$\sqrt{\gamma_{sv}^d \gamma_{sv}^d} + \sqrt{\gamma_{sv}^{acid} \gamma_{lv}^{base}} + \sqrt{\gamma_{sv}^{base} + \gamma_{lv}^{acid}} = 0.5 \gamma_{lv} (1 + \overline{\cos \theta}) \quad (6)$$

CONTACT-ANGLE MEASUREMENT'S RESULTS

As reported in Table 1, contact angles were evaluated at room temperature using all model liquids for all samples.

Table 1. Contact angles measurement

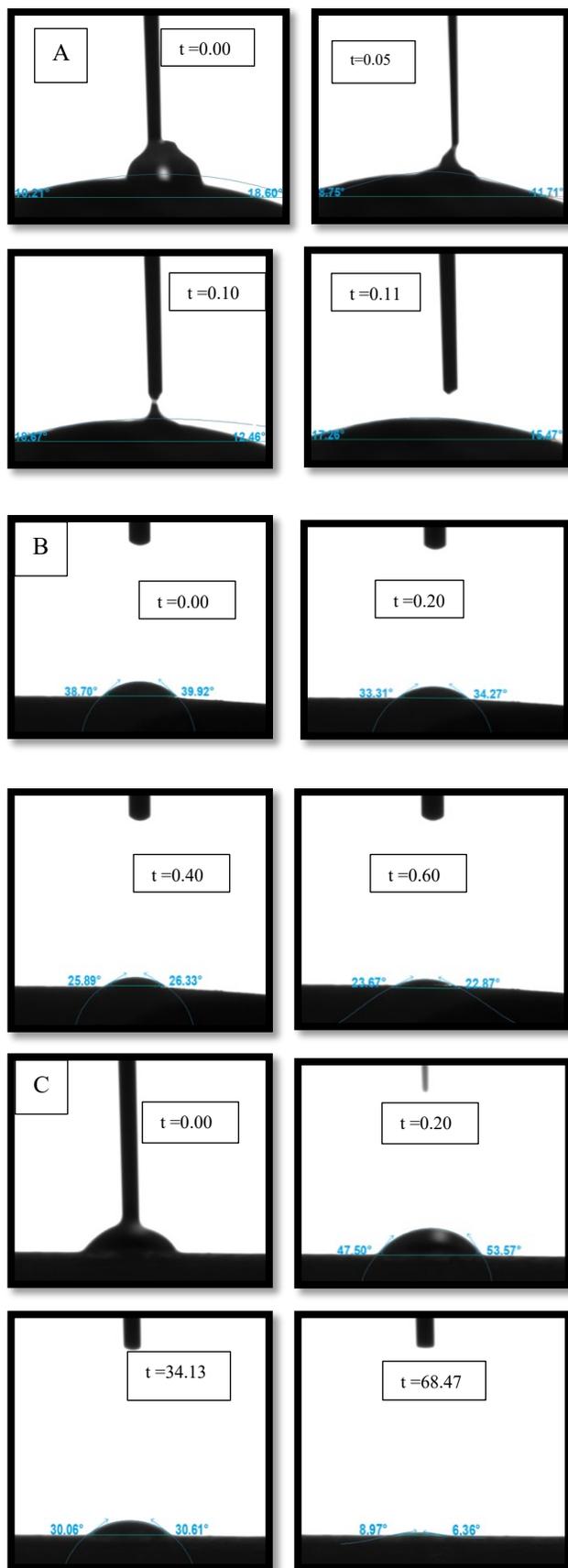
| Contact angle (θ) | |
|-------------------|-------|
| water | |
| 600nm sample | 15.77 |
| 200nm sample | 39.99 |
| 15nm sample | 12.54 |

As reported in Table 2, surface free energies were evaluated at room temperature using all model liquids for all samples and automatic mode was chosen for surface free energy formulation

Table 2 surface free energies for samples

| Samples | γ_{tot} [mN/m] | γ_d [mN/m] |
|---------|-----------------------|-------------------|
| 6000nm | 70.145 | 70.145 |
| 200nm | 63.662 | 63.662 |
| 15nm | 59.74 | 59.74 |

Figure 1 depicts images of contact angles with water for all samples. Images were obtained for three different scenarios: immediately after dropping (at around time $t = 0$), quickly after dropping (e.g., 0.20 s as seen in Fig. 1), and shortly after dropping (at a period when the droplet image in the sample did not change), respectively.



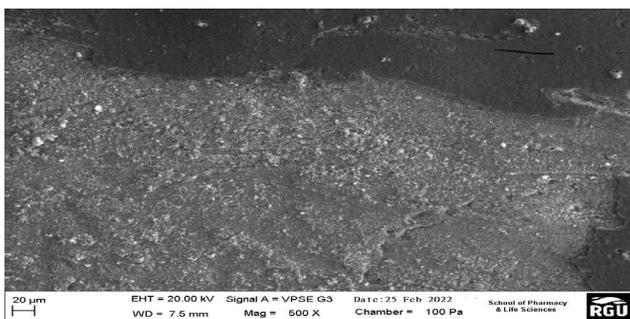
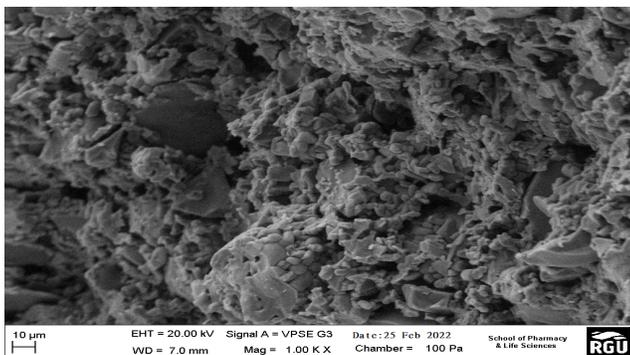
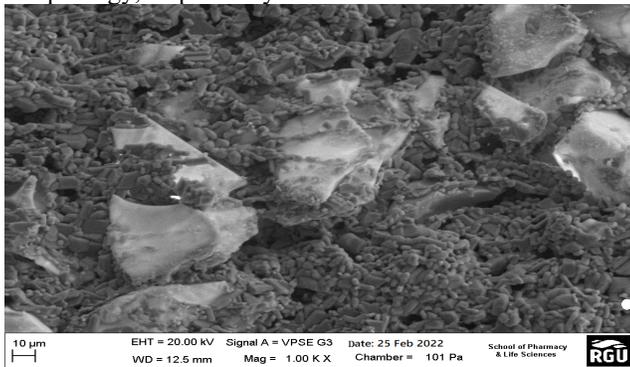
DISCUSSION OF RESULTS CONTACT-ANGLE MEASUREMENTS AND SURFACE FREE ENERGY

As shown in Table 1, contact angles were evaluated at room temperature with a model liquid (water) for all samples. It's important to note that a smaller contact angle indicates a solid's wettability (Ali, 2012). As a result, a higher contact angle indicates less model liquid absorption by the sample and consequently less interaction between the two. The largest contact angle was seen with the 200nm ceramic membrane sample, and the lowest contact angle was observed with the 15nm ceramic membrane sample. Apart from 200nm ceramic membrane sample, the DIM contact angles of the samples are quite near to each other. 6000nm ceramic membrane and 15nm ceramic membrane was shown to have the maximum interaction (lowest contact angle) with water. In this case we can say ceramic membranes are hygroscopic. As a result, 6000nm and 15nm pore sizes of ceramic membranes are likely to have a greater water adsorption impact than and 200nm pore size of ceramic membrane samples. The polar model liquids (water) have the lowest contact angles with 6000nm and 15nm pore sizes of ceramic membranes (Table 1). The polar model liquids (water) form lower contact angles on surfaces with more polar groups, according to several findings in the literature. Considering this, it's reasonable to conclude that 6000nm and 15nm pore sizes of ceramic membranes samples have more polar groups on their surfaces than 200nm pore size of ceramic membrane sample.

Furthermore, there is evidence in the literature that surface free energy increases as surface polarity increases (A salimi et al, 2010). The surface free energy of a sample with the highest surface polarity was found to be higher than the others in this analysis, confirming results in the literature (Salimi et al. 2010). (Table 2). Table 1 shows that 15nm pore size of ceramic membrane has the lowest contact angles for model liquid (water). As a result, 15nm pore size of ceramic membrane adsorbs DIM, water model liquid more effectively than 6000nm and 200nm pore sizes of ceramic membrane. As a result, it is expected that the surface free energy of 15nm pore size of ceramic membrane will be higher than that of the others. Table 3 shows that the surface free energy of 15nm pore size of ceramic membrane is larger than the others (72.20 γ_{tot} [mN/m] a). The fact that the surface free energy of the 15nm ceramic membrane is higher than the others is in accordance with Table 2's prediction. The contact angle measurement method has not been used to investigate 6000nm, 200nm, and 15nm pore sizes of ceramic membrane in the literature. This paper documents a considerable reduction in observed surface free energy in some circumstances. This lowering is usually explained by the creation of a liquid film on the mineral surface, and it was often observed when mineral surfaces were exposed to either hydrocarbons or water vapour. This observation rhymed with some similar observations in the literatures. As a result, the contact angles of the model liquid (water) on these samples could not be compared to a previous investigation.

SEM ANALYSIS

Scanning electron microscopy (SEM) examination was used to characterise the ceramic membrane. The SEM picture of the carbamic membranes is shown in Fig. 2. The ceramic membrane has a porous, rough morphological feature apart from 15nm pore size ceramic membrane appeared to have smooth on its surface. A close examination of the image reveals that the membrane was free of defects such as pinholes and cracks. The surface had a maximum pore size of roughly 10 μ m, 30 μ m, and 20 μ m for 6000nm, 200nm, and 15nm respectively. The surface of a porous membrane should have a uniform structure of small holes. SEM pictures of membrane samples, revealing the three membrane types have unique surface morphologies. The low (1 k) for 15nm sample and high (500k) for 6000nm and 200nm magnifications show the context and detail of surface morphology, respectively.



CONCLUSION

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ACKNOWLEDGEMENTS

The Authors express profound gratitude to the Petroleum Technology Funds (PTDF), TETFUND, NDDC for funding this research

REFERENCES

- (1) FOWKES, F.M., 1962. Determination of interfacial tensions, contact angles, and dispersion forces in surfaces by assuming additivity of intermolecular interactions in surfaces. *The Journal of physical chemistry*, 66(2), pp. 382-382
- (2) KWOK, D.Y. and NEUMANN, A.W., 1999. Contact angle measurement and contact angle interpretation. *Advances in Colloid and Interface Science*, 81(3), pp. 167-249
- (3) OWENS, D.K. and WENDT, R., 1969. Estimation of the surface free energy of polymers. *Journal of Applied Polymer Science*, 13(8), pp. 1741-1747
- (4) SALIMI, A., 2012. Characterization of nano scale adhesion at solid surface of oxidized PP wax/PP blends. *International Journal of Adhesion and Adhesives*, 33, pp. 61-66
- (5) SALIMI, A. et al., 2010. Studies of the Mechanical Properties and Practical Coating Adhesion on PP Modified by Oxidized Wax. *Journal of Adhesion Science and Technology*, 24(6), pp. 1113-1129
- (6) SPORI, D.M. et al., 2008. Beyond the lotus effect: roughness influences on wetting over a wide surface-energy range. *Langmuir*, 24(10), pp. 5411-5417
- (7) YOUNG, T., 1805. III. An essay on the cohesion of fluids. *Philosophical transactions of the royal society of London*, (95), pp. 65