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Droplet Impact Behaviour of Modified Alkali-Activated Material Solution on Urea Surface

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Abstract: Alkali-Activated Material (AAM) is a compound which undergo alkali silicate activation and formed into an aluminosilicate compound. In this research, AAM was proposed as the new Controlled Release Fertilizer (CRF) coating material as it exhibits specific properties to improve CRF coating, eco-friendly and manufactured through sustainable production process. Thus, the droplet impact behaviour of the modified AAM solution was studied to determine the wettability of the solution on the urea surface by identifying the surface tension and contact angle. Besides that, the maximum spreading factor of the modified AAM droplet was analyzed to observe the spreading behaviour of the droplet between within time intervals. The AAM solution was formulated by using 3:1 weight ratio of fly ash based powder and 10 M sodium hydroxide solution. Modified AAM solution was formed by adding up 1-4 wt.% nanoclay into the solution as a filler to improve the AAM microstructure. The droplet impact experiment of the modified AAM solution was observed by using high speed camera. In the experiment, the droplet impact behaviour of the AAM solution was analyzed by varying the wt.% nanoclay added. From the experiment, the AAM solution with 0 wt.% nanoclay was identified to have the highest wettability as indicated by its lowest surface tension and smallest contact angle but it has the lowest maximum spreading factor. On the other hand, the AAM solution with 4 wt.% nanoclay was found to have the lowest wettability as indicated by its highest surface tension and largest contact angle but it provides the largest maximum spreading factor as low penetration and low dissolution of AAM solution occurs at this amount.

Key words: Controlled release fertilizer, wettability, alkali-activated material, nanoclay, maximum spreading factor

INTRODUCTION

Controlled Release Fertilizer (CRF) is one of the studies to promote uniformity of nutrients release throughout the plant growth. Some of CRF advantages include inhibit nutrient loss, seed toxicity, hazardous emissions, leaf burning, dermal irritation and inhalation problems. Moreover, CRF also helps to improve soil quality, handling properties and germination rates (Azeem *et al*., 2014). The feasibility aspects of the coating include the wettability of the coating with the substrate surface, environmental aspect and economy aspect of synthesizing the coating. Urea is chosen in many CRF development studies because of its high nitrogen content, low cost and economical availability (Kent, 2007). The initial cause of the complications associated with nitrogen fertilizer is its water solubility (Chandrika and Goertz, 2010). The water solubility of nitrogenous compounds can be minimized by physical method which is subjected to coating or encapsulation of water soluble materials with outer layers of organic or inorganic materials characterized by diffusion controlled release of nutrients through the surface layer by using sulphur, polymer and mixed sulphur-polymer encapsulated materials (Chandrika and Goertz, 2010).

Some of the CRFs are coated using Polymer Based Materials (PBMs) (Mayer, 2010). PBMs coating are not environmental friendly as it will pollute the environment by releasing the chemical additives that are consumed during the manufacturing process (Erren *et al*., 2009). Agriculture films consisting of PBMs can also contain light-sensitive additives such as ferric and nickel dibutyldithio-carbamates and the blending mixture of the additives can be modified so that the film is usable during a specific growing season after which the product begins to photo-degrade (Klemchuk, 1990). The ultimate result in disintegration of the material so that it can be washed into the soil where they accumulate (Klemchuk, 1990). Furthermore, the thicker coating layers may reduce the soil quality if they are not degraded in parallel with

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nutrient release (Wu *et al*., 2012). Thus, due to higher expenditures and process complication along with issues of environmental pollution caused by polymers, research frontiers shifted towards developing low cost, easily manufactured and environmentally friendly materials (Niu and Li, 2012). In this research, Alkali-Activated Material (AAM) is proposed as a coating material on urea surface prior to its biodegradable property and it is considered as a green material which may not be one of the pollutants to the environment (Varela *et al*., 2007). Therefore, the droplet impact behaviour of the AAM solution with addition of nanoclay as filler will be investigated in this research to determine the wettability of the substance by observing the surface tension, contact angle and maximum spreading diameter.

AAMs are a novel cluster of inorganic polymetric materials produced by the alkali activation of a heat-treated aluminosilicate (Varela *et al*., 2007). The precursors of AAM consists of metakaolin and fly ash (Cilla *et al*., 2014). For the alkali activator, studies were reported that sodium hydroxide (NaOH) is extensively used for the synthesis of AAM compared to potassium hydroxide (KOH) due to ionic size where sodium ion, Na^+ is having smaller ionic size compares to potassium ion, K^+ (Rahim *et al*., 2014). AAMs behave similarly to zeolites which have the ability to immobilize hazardous elemental wastes within the compound matrix and seal hazardous materials into impermeable monolith which will prevent from direct contact of potential leachates for example ground water and percolating rain (Davidovits, 1994). Besides that, AAMs are green materials because it can be synthesized from natural resources and the chemistry is environmental friendly without producing any toxic residues or carbon dioxide emissions (Varela *et al*., 2007).

The effects of nanoclay as filler on composite material depends on its size, aspect ratio, hybrid morphology and dispersion quality (Nourbakhsh and Ashori, 2009). Nanoclays are nanoparticles of layered mineral silicates organized into several classes such as montmorillonite, bentonite, kaolinite, hectorite and halloysite depending on chemical composition and nanoparticle morphology (SACC, 2015). From a research conducted by Darie *et al*. (2014) according to the nanoclays hydrophilicity increasing order, it is identified that the mechanical strength and young's modulus increase, strain at the break decreases, impact strength and impact energy increase (Darie *et al*., 2014). A study done by Assaedi discovered that 2 wt.% usage of nanoclay in AAM composite enhances the density and decrease the porosity which subsequently exhibited higher flexural and compressive strength, hardness and flexural toughness (Assaedi *et al*., 2015). Nanofillers for example, layered

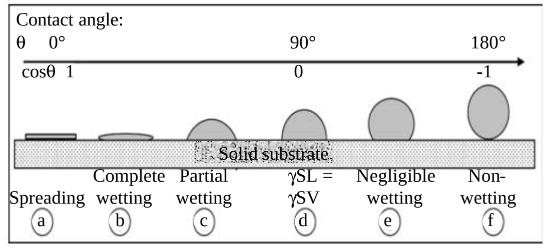


Fig. 1: Types of liquid drop on solid surface (Nourbakhsh and Ashori, 2009)

silicates have the ability to minimize the permeability of polymers. Studies found out that these nanoelements present a torturous path (Joshi *et al*., 2006). Besides that in polymer nanocomposites, uniform dispersion of these nanosized filler particles produces an ultra large interfacial/unit volume between the nanoparticle and the host polymer (Joshi *et al*., 2006).

High wettability and droplet spreading of the coating material is a paramount (Zulhaimi *et al*., 2011). Therefore, the droplet impact behaviour is characterized by observing the droplet's surface tension and contact angle. The surface tension is an essential factor that identifies the ability of the coating material to wet and adhere to a substrate (Zulhaimi *et al*., 2011).

The droplet's surface tension and contact angle are identified by using the digitized droplets where huge difference is observed between the low surface tension and high surface tension liquids, the wetting and spreading diameter is higher for lower surface tension (Zulhaimi *et al*., 2011). Based on Fig. 1, for droplet angle θ<90° defines that the solid is wet by the liquid, θ>90° defines non-wetting, θ = 0 and θ = 180° indicates complete wetting and complete non-wetting, respectively. The nature of the solid substrate has a significant role which will affect a single liquid to be non-wetting, partial wetting or complete wetting (Njobuenwu *et al*., 2007).

Nevertheless, the maximum spreading factor is one of the parameters need to be identified in order to determine the spreading behaviour of modified AAM solution on urea surface in addition of small amount of fillers or surfactants. Based on research, the maximum spreading behaviour indicates the spreading property of the liquid on the urea surface and the maximum spreading factor can be determined by D_t at certain time over the initial droplet diameter, D_0 (Yon Norasyikin *et al*., 2014).

MATERIALS AND METHODS

Preparation of urea surface: The urea surface was prepared in a form of pellet. The urea granules used

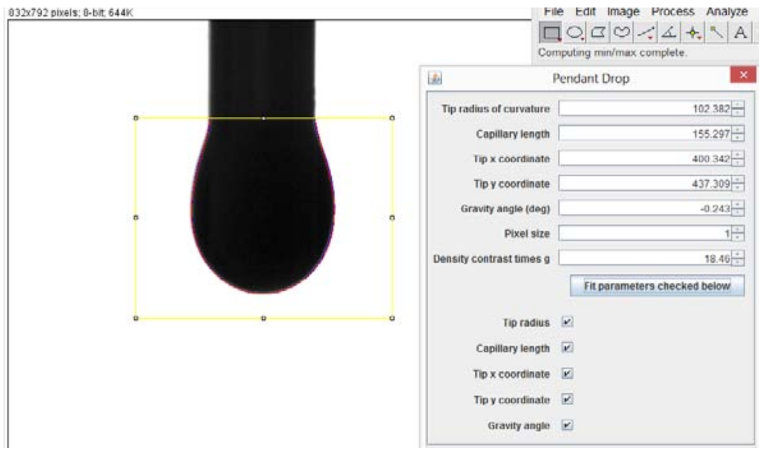


Fig. 2: Image with rectangular ROI selection

as particle cores for this experiment were commercial nitrogen fertilizer taken from Petronas Chemicals Fertilizer Kedah, Malaysia (PCFK). The urea granules were grinded into powder form. Then, the urea powder was sieved using 2 mm and 500 μm perforated plate sieves. The desired size of urea powder was inserted into a stainless steel mould and it was pelletized using hydraulic press machine at force between 5.9-6.1 kN for 2 min.

Preparation of coating solution: The AAM coating solution was prepared from the combination of fly ash-based powder, sodium hydroxide (NaOH) solution, deionized water and small additional amount of nanoclay as a filler. The preparation method and blending ratio for the coating solution was referred from experimental work conducted by Rahim *et al*. (2014) with a weight ratio of 3:1 of fly ash-based powder to NaOH solution (Rahim *et al*., 2014). About 30 g of fly ash-based powder was used along with 10g of 10 M NaOH solution. The deionized water of 5 mL was added into the mixture of fly ash-based powder and NaOH solution. Besides, additional of nanoclay with range of 1-4 wt.% of the fly ash-based powder and NaOH solution were proposed to be used in this project research. The mixture was stirred with electronic hand mixer for 5 min.

Droplet impact experiment: The sequences of drop generation and impact on solid surface were visualized through a canon vision research high speed camera. The droplet impacts were filmed at 1500 fps. The millimetre size drops were seen with a lens with 1216×552 resolution of pixel. The dispenser consists of a 1 mL of syringe with a blunt tip needle was mounted vertically above an impact surface at certain height depends on the impact velocity to be studied. In this experiment, the urea pellet was used as the impact surface and the droplet impact behaviour were studied at impact velocity of 1 m/sec. The height between the dispenser and the impact surface at respective impact velocity was determined using equation:

$$v = \sqrt{2gh} \tag{1}$$

Where:

v = Impact velocity
g = Gravitational acceleration at 9.81 m/sec^2
h = Height

The high speed camera images were supported by LED light source and the images were transmitted to Cine Software.

Surface tension: The surface tension was measured by the pendant drop method and analyzed using a software named ImageJ. By default, the pendent-drop plugin appears in the plugins menu of ImageJ in a folder termed drop analysis (Daerr *et al*., 2014). A rectangular Region Of Interest (ROI) was drew around the pendent drop before calling the Plugin, refer Fig. 2. The ROI should not include the blunt tip needle but only the free surface of the drop. The surface tension was calculated by using Eq. $\gamma = (\rho_{in}-\rho_{out})g = \Delta\rho g$ where the difference of the densities in/outside the drop multiplied by gravitational acceleration at 9.81/msec^2 and the surface tension was indicated in unit g/sec^2 or milli-Newton per metre (Daerr *et al*., 2014).

Contact angle: Sessile drop method was used to measure the contact angle of the droplet. The static contact angle was measured once the droplet has reached the equilibrium state which fit the Laplace-Young method while dynamic contact angle was measured in certain time intervals. In this experiment, dynamic contact angle was observed. ImageJ Software was

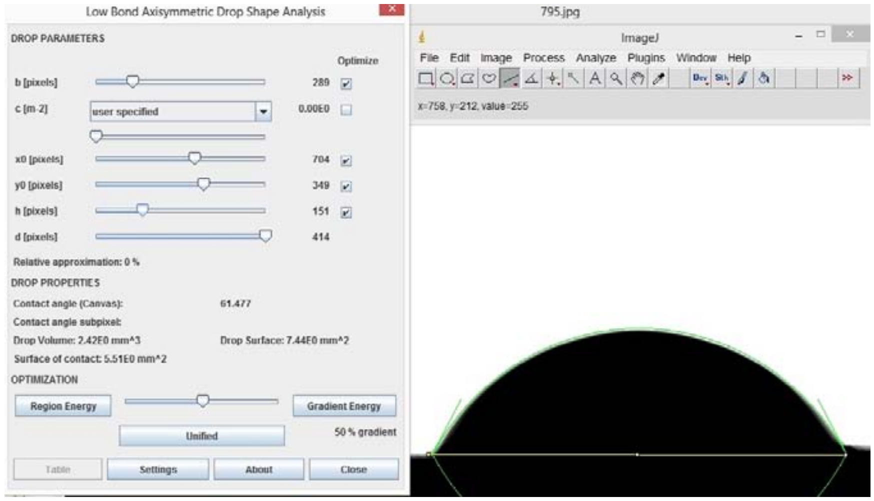


Fig. 3: Example of LBADSA plugin to determine contact angle in ImageJ

used to plot and measure the droplet contact angle using Low-Bond Axisymmetric Drop Shape Analysis (LBADSA) plugin (Fig. 3).

Maximum spreading factor: The initial droplet diameter, D_o and the diameter of the droplet after a certain period, D_t were measured using ImageJ where D_o was plotted when the droplet had not reached the urea surface while D_t can be plotted when the droplet reached its equilibrium state. The maximum spreading factor explained the spreading property of the liquid on the urea surface and it was calculated by D_t/D_o (Yon Norasyikin *et al*., 2012).

RESULTS AND DISCUSSION

Surface tension: The surface tension describes the intermolecular forces exerted within a fluid. If a liquid has small intermolecular forces, the wettability is high. Table 1 shows the images of the pendant drop for surface tension measurement captured by high speed camera.

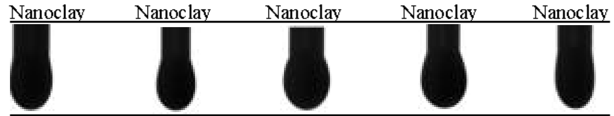
Figure 4 shows that surface tension of the solution increases as the amount of nanoclay added increases. The solution wettability decreases as the surface tension increases due to more intermolecular forces exerted within a liquid. Thus, AAM solution with 0 wt.% nanoclay has the lowest surface tension and highest wettability. Based on the modified AAM solution surface tension, the measurement do not shows a very large difference for an increment of only 1 wt.% nanoclay. Thus, for contact angle and maximum spreading factor measurement, only 0, 2 and 4 wt.% nanoclay are chosen to be analyzed for the trend of the graphs to obtain clearer observation on the droplet impact behaviour.

Contact angle: The study of the droplet contact angle measurement is to determine the wettability of the solution. As stated in the literature review, good wettability property is vital to provide uniform coating. Small contact angle represents high wettability and vice versa. Table 2 shows the images of droplet impact behaviour at 1 m/sec impact velocity. The measurement of the droplet's dynamic contact angle within time intervals are shown in Table 3.

From Fig. 5, as the amount of nanoclay increases, the contact angle of the droplet will increase. Increasing in contact angle indicates that the wettability of the AAM solution decreases as increasing amount of nanoclay. Thus, AAM solution with 4 wt.% nanoclay has the lowest wettability. The nanoclay provides hydrophobic property to the AAM solution as it inhibits the ability of the AAM to wet on the urea surface. Hence, the tendency of the AAM droplet to wet more on the urea surface is high with 0 wt.% nanoclay as indicated by the

Table 1: The images of the pendant drop for surface tension

0 wt.% Nanoclay	1 wt.% Nanoclay	2 wt.% Nanoclay	3 wt.% Nanoclay	4 wt.% Nanoclay



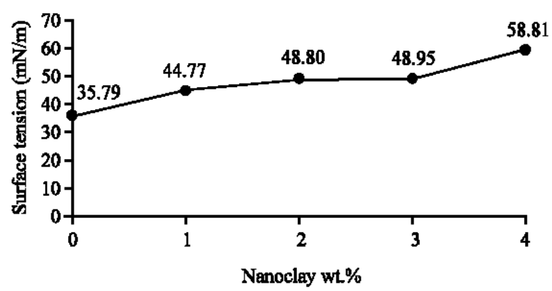


Fig. 4: Surface tension of modified AAM solution surface tension

Table 2: Droplet impact behaviour at 1 m/sec impact velocity

Nanoclay wt.%	t = 0 sec	t = 0.4 sec	t = 0.8 sec	t = 2.0 sec	t = 3.0 sec
0					
2					
4					

Table 3: Dynamic contact angle, θ at 1 m/sec

Nanoclay wt.%	t = 0.2 sec	t = 0.4 sec	t = 0.6 sec	t = 0.8 sec	t = 1.0 sec	t = 2.0 sec	t = 3.0 sec
0	75.75	71.37	69.56	67.35	65.62	64.30	62.77
2	85.55	83.17	82.03	80.18	79.63	78.64	78.11
4	97.66	95.03	91.86	90.44	88.97	88.64	88.25

Table 4: Droplet spreading diameter in mm

Nanoclay wt.%	t = 0 sec	t = 0.2 sec	t = 0.4 sec	t = 0.6 sec	t = 0.8 sec	t = 1.0 sec	t = 2.0 sec	t = 3.0 sec
0	2.95	4.80	4.91	5.01	5.08	5.13	5.22	5.30
2	2.43	4.52	4.64	4.73	4.77	4.77	4.80	4.87
4	1.69	3.98	4.05	4.15	4.16	4.19	4.19	4.19

Table 5: Maximum spreading factor, D_t/D_0

Nanoclay wt.%	t = 0 sec	t = 0.2 sec	t = 0.4 sec	t = 0.6 sec	t = 0.8 sec	t = 1.0 sec	t = 2.0 sec	t = 3.0 sec
0	1.0	1.62	1.65	1.67	1.70	1.72	1.75	1.77
2	1.0	1.86	1.91	1.95	1.96	1.96	1.98	2.00
4	1.0	2.36	2.39	2.40	2.46	2.48	2.48	2.48

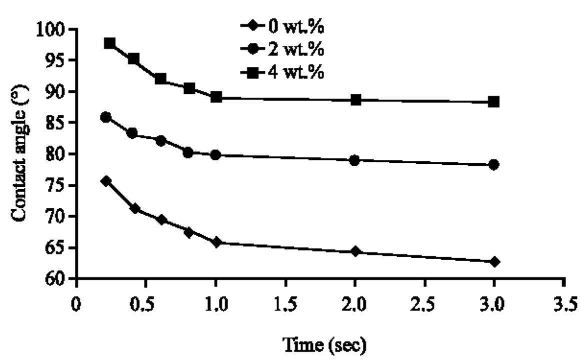


Fig. 5: Plot of dynamic contact angle contact angle (1 m/sec)

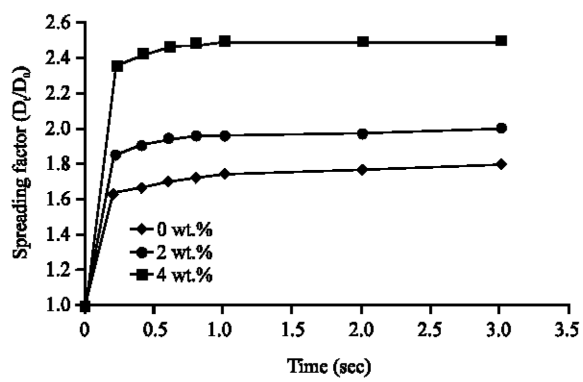


Fig. 6: Plot of maximum spreading factor maximaum spreading factor (1 m/sec)

smallest contact angle measurement. As time increase, the change in contact angle becomes minimal because the droplet has reached its equilibrium state. Hence, it is proven that the wettability of the AAM solution is the highest with 0 wt.% nanoclay. The result is further supported by the surface tension analysis earlier. Based on study, nanofiller produces an ultra large interfacial/unit volume between the nanoparticle and the host polymer which in this case affect the AAM wettability (Joshi *et al*., 2006).

Maximum spreading factor: The study of maximum spreading factor is to determine the spreading ability of modified AAM solution on urea surface at time intervals. Table 4 shows the measurement of droplet spreading diameter. The measurement of the droplet's maximum spreading factor within time intervals are shown in Table 5. Based on Fig. 6, 4 wt.% nanoclay gives the largest maximum spreading factor compared to other amount of nanoclay. The hydrophobicity of the AAM solution increases as the amount of nanoclay increases.

The nanoclay hinders the dissolution and penetration of the AAM solution on the urea surface causing the droplet to spread more between time intervals. Although, 4 w.t% nanoclay has the smallest initial diameter, D_0 but the factor of spreading between time intervals until reaching the equilibrium droplet diameter, D_t is the largest at this amount. This result can be further supported with a study done which points out that nanofillers have the ability to minimize the permeability of polymers (Joshi *et al*., 2006). This is an excellent property of nanoclay provides to the AAM solution. The characteristics of urea are porous and dissolutive. Thus, there are probability for the AAM solution to immediately penetrate into the urea.

CONCLUSION

From the experiment, it was determined that AAM solution has the highest wettability at 0 wt.% nanoclay as indicated by its lowest surface tension, 35.79 mN/m and smallest dynamic contact angle between time intervals while addition of 4 wt.% nanoclay has the lowest wettability as indicated by its highest surface tension, 58.81 mN/m and largest dynamic contact angle between time intervals. Thus, additional amount of nanoclay reduces the wettability of the AAM solution on urea surface. The surface tension of the AAM solution increases as the amount of nanoclay added increases, resulting the wettability to be decreased. However, nanoclay enhances the AAM solution maximum spreading factor as it helps to lower the penetration and dissolution of AAM solution into the urea surface. The AAM solution tends to spread more on the urea surface between time intervals with additional amount of nanoclay. From the experiment, 4 wt.% nanoclay gives the highest maximum spreading factor while 0 wt.% nanoclay gives the smallest maximum spreading factor.

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