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Rheological Properties of Urea-CaLS Mixture for Urea Fertilizer Granulation

Jariah Mohamad Juoi[1,a], Farahani Irna Nazari [2,b], Nona Merry Merpati Mitan[3,c] and Azizah Shaaban [4, d]

[1]Department of Manufacturing Process, Faculty of Manufacturing Engineering, University Teknikal Malaysia Melaka, Hang Tuah Jaya,76100 Durian Tunggal, Melaka, Malaysia

[a] jariah@utem.edu.my, [b] m051120010@student.utem.edu.my, [c] nona.merry@utem.edu.my, [d]azizahs@utem.edu.my

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Abstract. The rheological properties of feedstock for granulation process are important in controlling the parameters throughout the process. This study identifies the type of fluid that mixtures of Urea and Calcium Lignosulfonates (CaLS) possessed through the viscosity profiles using a parallel plate rheometer. The viscosity behavior of mixtures with varied weight percentages (wt %) of CaLS in urea solution were analysed. Results identified that the mixtures show shear thickening behavior of non-Newtonian fluid. It is also observed that the increases of CaLS content increase the viscosity of the mixtures. Moreover, the mixture with 50 % CaLS addition is found not suitable for further investigation as its viscosity is too high (3.450-6.773 Pa.s at zero shear rate) compared to molten urea (0.002 Pa.s).

Introduction

Urea fertilizer is widely known as one of the nitrogen fertilizer with the highest nitrogen content (~46%) and available in the market in many forms, usually preferred in the form of granules compared to prills. Currently, formaldehyde is widely used in urea fertilizer granulation process as anti-caking agent; 0.3-0.5% of formaldehyde in the form of 37% formaldehyde solution is added before or during granulation [1]. However, formaldehyde has been officially declared *(by National Toxicology Program, Department of Health and Human Services, 2011)* as a known human carcinogen or cancer-causing substance [2]. Lignins are complex natural polymers, derived mostly from trees, plants and agriculture crops and have no exact chemical structures [3]. Calcium Lignosulfonate (with low reducing sugar content) possesses nitrification and urease inhibition properties [4], and also has been used as binder for granules and seed coatings [5].Thus, in our work, CaLS is studied as biodegradable binder for replacing formaldehyde in urea granulation.

Granulation process is one of the methods used to form the final product of urea fertilizer. Rheological properties for example viscosity will help to determine the suitable process parameters to be used for smooth feed flow for the granulation process. Melt granulation for example, requires the melt to have very low viscosity (<0.005 Pa.s) [6]. Generally, the factors affecting viscosity include shear rates, temperature, pressure, etc [7]. In this paper, the rheological properties of urea-CaLS mixtures are investigated to understand its flow behaviour. The flow behavior is analyzed by determining the viscosity profile at a certain ranges of shear rates. However, in this experiment, the shear rates of 10^3-10^4 s-1 were used in consideration of spraying process during granulation [8]. The effect of different CaLS weight % on the flow behavior of the urea-CaLS mixtures are also investigated in finding the appropriate amount to proceeds with granulation and properties analyses.

Materials and methods

The materials used in this experiment were mixtures of 70% Urea solution and CaLS with varied content (in wt %). Urea in powdered form was supplied by Sigma-Aldrich while the CaLS was supplied by Gremont Agrochem (M) Sdn. Bhd.

Before mixing those two, urea solution was prepared at 70% by weight and heated up to ~70ºC in order for urea to fully dissolve in water [9]. 70% urea solution was achieved by 7g urea and 3g distilled water (thus 10g of urea solution). Then, the amount of CaLS required was weighed based on different wt% (1%, 5%, 10%, 20%, 35% and 50%). For example, 10g of CaLS was required for 50% CaLS in 10g of 70% urea solution. The specifications of the raw materials are as listed in Table 1.

Table 1. Raw material specifications

Materials	Melting Point (ºC)	Boiling Temperature (ºC)
Urea	135	na
Calcium Lignosulfonates (CaLS)	>130	104

For this rheological experiment, the temperature of the urea-CaLS mixtures had to be maintained throughout the experiment to avoid the mixture from hardening at lower temperature. Zero-shear rate viscosity profiles and viscosity vs. shear rates profiles are observed in this experiment. The experiment was conducted at a constant heating rate and temperature of ~140ºC for 1 hour for each sample.

Results and discussion

Influence of shear rate on viscosity. Fig. 1 shows that for all CaLS weight% addition, the increase in shear rates would increase the viscosity of the mixture.

This suggests that the mixtures have shear-thickening fluid behavior. Shear-thickening fluid behavior is observed when its viscosity increases as shear rates increases [10]. This result also identified that the mixtures are non-Newtonian Fluids.

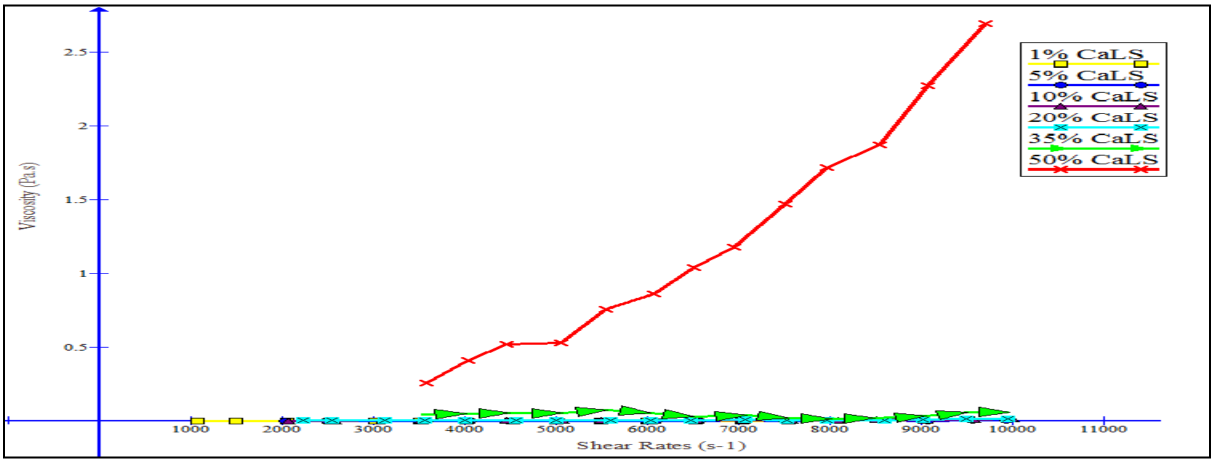

Fig. 1. Viscosity vs. Shear Rates for all different CaLS content

Influence of CaLS weight % viscosity. The effect of CaLS addition to the viscosity of the mixture at a constant shear rate (for example $2500s^{-1}$) is shown in Fig.2. It was observed at 1% CaLS addition, the viscosity of the mixture is 0.002 Pa.s and slightly increased to 0.003 Pa.s for 5% CaLS addition. However, a drastic change in viscosity is observed with 50% CaLS addition where the viscosity increased up to 1.279 Pa.s.

Thus, this suggests that 50% CaLS addition is not suitable for the granulation process as the viscosity value is too far compared to the zero shear viscosity of pure molten urea and might cause difficulty in the granulation process.

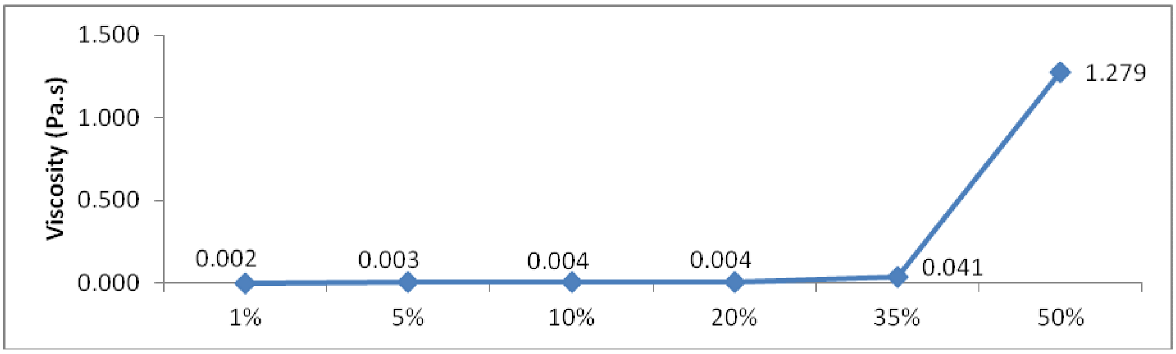

Fig. 2. Viscosity vs. CaLS content at 2500s⁻¹ shear rate value

Influence of CaLS weight % on zero-shear viscosity. In general, it was observed that the addition of CaLS increased the viscosity of the urea solution compared to pure molten urea. For example, with only 1% CaLS addition, the zero shear viscosity of urea solution became 0.01-0.02 Pa.s which is higher than the zero shear viscosity of pure molten urea at 140ºC; 0.002 Pa.s [11].

The zero shear viscosity of the urea solution is observed to be increasing with the increase of CaLS content, as shown in Fig.3. This suggests that the addition of CaLS affects the non-Newtonian behaviour of the urea solution. The same behaviour is also observed in previous research where concentration of a polymer in a solution affects the non-Newtonian behaviour of the solution [12]. Based on this result, it is also confirmed that the 50% CaLS addition is not suitable for further investigation due to the high viscosity observed (3.450-6.773 Pa.s) even at zero shear rate.

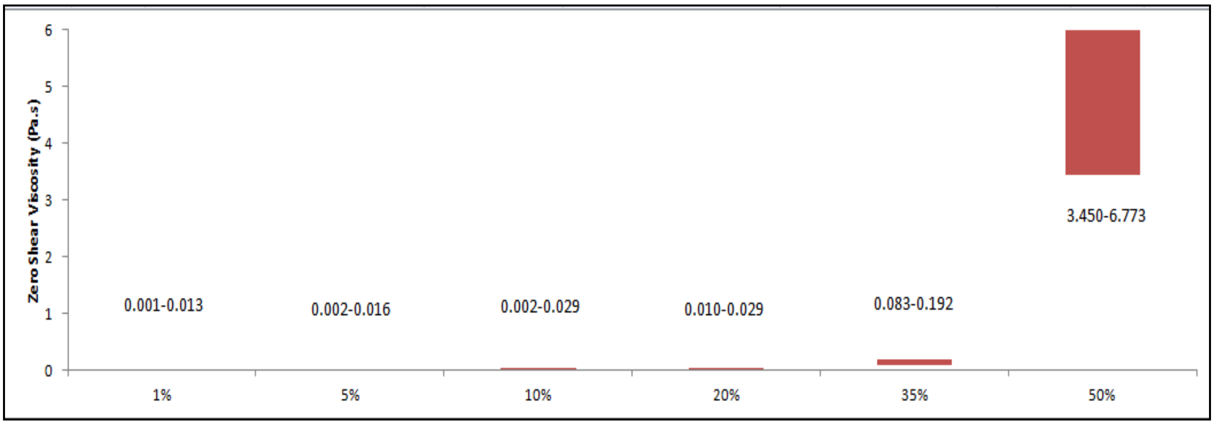

Fig. 3. Zero Shear Viscosity vs. CaLS content

Conclusions

Rheological analyses were conducted to determine the flow behaviour of the urea-CaLS mixtures for granulation. The mixtures showed shear-thickening behaviour of non-Newtonian fluid (increased in viscosity is observed with increase in shear rates). The viscosity of the urea-CaLS mixtures increased with higher CaLS (wt. %) content. Viscosity of urea-CaLS mixture with 50 wt. % CaLS is too high to be adopted for spraying process in urea granulation. Thus, further investigation on the granulation process and properties analyses will only be conducted on urea-CaLS mixture with up to 35 wt. % CaLS content.

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References

[1] V. Gowariker, V.N. Krishnamurthy, S. Gowariker, M. Dhanorkar, and K. Paranjape: *The Fertilizer Encyclopedia* (J.Willey and Sons Inc., New Jersey 2009).

[2] Information on http://www.cancer.gov/cancertopics/factsheet/Risk/formaldehyde

[3] Information on http://purelignin.com/lignin

[4] Information on http://www.nj.gov/dep/watersupply/pdf/append-b-section-i.pdf

[5] Information on http://www.lignotech.com/Industries/Agriculture/Agricultural-Chemicals

[6] Information on http://www.wiley-vch.de/books/sample/3527316043_c01.pdf

[7] Information on http://www.viscometers.org/PDF/Downloads/More%20Solutions.pdf

[8] H.A. Barnes, J.F. Hutton and K. Walters: *An Introduction to Rheology,* (Elsevier Science Publishers, Amsterdam, 1989).

[9] Information on http://www.scribd.com/doc/30134331/Urea

[10] Information on http://web2.clarkson.edu/projects/subramanian/ch330/notes/Non-Newtonian%20Flows.pdf

[11] S. Kohnke, U. Ladwig and J. Maaz, U.S. Patent 7,998,235. (2011)

[12] A.Y. Malkin and A.I. Isayev: *Rheology Concepts, Methods, and Applications* (ChemTec Publishing, Toronto 2012)