Characterization and Preparation of Polyvinyl Alcohol (PVA) as Inhibitor in Formation of Hydrates

Najihah JAMIL[1,a*], Hazlina HUSIN[1,b], Ahmad Waseem ALFIDA[1,c], Zachary AMAN[2,d] and Zulkafli HASSAN[3,d]

[1]Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Malaysia
[2]School of Mechanical and Chemical Engineering, University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia
[3]Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang, Gambang Kuantan, Malaysia

[a]najihah_jamil90@yahoo.com, [b]hazlina858@salam.uitm.edu.my, [c]waseemalfida55@gmail.com, [d]zachary.aman@uwa.edu.au, [e]zulkafli@ump.edu.my

ABSTRACT. The thermal properties of PVA with different degree of hydrolysis (DH) was studied by preparation of aqueous polymer solution, followed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The DSC result showed the typical partially crystalline materials, showing some phases of separation are characterized by a glass transition (T_g = 25-26 °C) related to the amorphous part of the material, followed by two endothermic peaks related to the melting point (T_m = 185-225) of the crystallites. Due to the same material (PVA) used, the main composition temperatures are close to each other (for peak I between 320 K and 350 K, and for peak II between 429 K and 430 K). Finally, FTIR confirmed that between the three materials P 100, P 87 and P 85, there were distinctness in the band absorbed between fully hydrolysed PVA, P 100 and partially hydrolysed PVA, P 85 and P 87.

1. INTRODUCTION

Gas hydrate is an ice-like crystal composed of light gases such as methane, nitrogen and carbon dioxide, and it can be formed at a specific temperature and pressure condition. The formation of these hydrates can cause serious plugging inside the oil and gas pipeline [1]. Conventional method of removing hydrates is called thermodynamic hydrate inhibitor (THI) and this method uses a large dosage of chemical to shift the hydrate equilibrium curve to lower the temperature. Meanwhile, the alternative method for THI is the low dosage hydrate inhibitor (LHDI), whereby it is developed and the dosage intake is below 1 wt.%. There are two types of LHDI, which are kinetic hydrate inhibitor (KHI) and anti-agglomerant (AA). KHIs function is to inhibit and delay the nucleation of hydrate formation, whereas AAs keep the hydrate particles agglomerated in small particles. Previously tested KHIs polymers in several other researches are polyvinylcaprolactam (PVCap), polyvinylpyrrolidone (PVP), polyacrylamide (PAM) and more. Despite the abundance of research done on KHIs, the mechanisms of hydrate inhibition are not fully understood. Only several mechanisms [2-4] have been proposed. It is necessary to fully understand the properties of the polymer first in terms of molecular

organisation and composition to predict the interaction between the hydrate and inhibitor. In this way, the significant knowledge gap can be filled [5], where the general ideas of hydrate inhibition is known to be by the KHI's polymers absorbing onto the hydrate surface crystals to prevent the complete formation of hydrate. Poly(vinyl alcohol) (PVA) is extensively used in industries in diverse applications such as biopolymer film, coating industry, food processing, medical industries, and it has also been used as hydrate inhibitor in oil and gas industries. PVA is a synthetic water-soluble polymer. Its backbones are composed only of carbon atoms, which are biodegradable [6-9] under both aerobic and anaerobic conditions. In order to study the KHIs polymer adsorption process, it is important to look on the pendant group existing on the polymer itself. For example, some of the previous studied KHIs such as PVP and PVCap show a strong KHI performance associated with the amide pendant group, whereby it is prone to adhere because of its hydrophilic properties [10,11]. Similar process goes with PVA. PVA is prepared via hydrolysis of polyvinyl acetate. There are two types of PVA, fully hydrolysed and partially hydrolysed. Different degree of hydrolysis (DH) of PVA is the result of incomplete hydrolysis reaction of PVA. Through several methods of characterisation, the behaviour of KHIs polymer adsorption can be predicted. For these reasons, PVA was chosen as inhibitor to study the effect of different degree of hydrolysis (DH) of PVA and what it may contribute through the polymer-water interaction. Therefore, in this research paper, characterization methods such thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) were used to predict the structural behaviour and interaction of the PVA inhibitor.

2.   MATERIALS AND METHODS

Polyvinyl alcohol, fully hydrolysed (degree hydrolysis of 99%, molecular weight MW = 145,000 g/mol), polyvinyl alcohol, partially hydrolysed (degree hydrolysis of 87%, molecular weight MW = 70,000 g/mol), polyvinyl alcohol, partially hydrolysed was acquired from Merck Millipore Singapore. Distilled water was used to prepare the aqueous solution. The solution concentration is in weight per hundred (%). A total of 10 samples of varying concentration (wt.%) were prepared from 0.1-1.1%.

Table 1 Sample composition and molecular weight (Mw)

Samples class	Degree of hydrolysis (%)	Molecular weight (Mw)
P 85	85	70,000
P 87	87	70,000
P 100	100	145,000

2.1 Fourier transforms infrared spectroscopy (FTIR). A Perkin Elmer Spectrum One FTIR spectrometer equipped with Spectrum software was used to perform the FTIR analysis. The samples were scanned over the range 14000 to 2100 cm^{-1} with the best resolution of 0.5 cm^{-1}.

2.2 Thermogravimetric analysis (TGA). Thermal stability analysis was run on a Perkin-Elmer Thermoanalyser in a nitrogen atmosphere. The temperature ranges used were between 0 to 530 °C. The heating rate applied throughout the process was 10 °C/min.

2.3 Differential scanning calorimetry (DSC). The thermal properties of polyvinyl alcohol were performed by the Metler Toledo instrument model DSC1/700. The heating scans were carried out at a heating rate of 10 °C/min from 0 to 530 °C.

3.   RESULTS AND DISCUSSION

3.1 Differential scanning calorimetry (DSC).

The DSC thermograms obtained showed 3 peaks. The first peak was not very significant, it presented dehydration of water that were used as solvent. It also showed a glass transition (Tg) occurring between 20 to 27 °C (Table 2), related to the amorphous part of the material. The second peak refers to the melting of the crystalline phase which is in relation to the melting temperature (Tm) of the crystals. The last peak referred to the decomposition of residual acetate group. Fig. 1 shows the DSC results of pure PVA at different degree of hydrolysis (DH). The melting temperature of P100, P87 and P85 were found to be 225 °C, 192.41 °C and 185.08 °C, respectively. Other studies showed that Tm of pure PVA occurred around 191 °C [12]. The melting temperatures of PVA at different DH are found to have increased with an increasing in DH number. At P100, the melting temperature is higher compare to P85 and P87, this is due to more orderly structure of P100 as fully hydrolysed PVA have a symmetrical structure. Whereas, for PVA with lower DH, the lower melting point is due to the less orderly structure of PVA that allow the bond to break easily. From the result, it showed that the same polymer with different DH can produce a different melting temperature range. These different behaviors of PVA from the same group of polymer bring the conjecture that the sample of PVA with different DH are constituted of several fractions of different pendant groups such as acetyl and hydroxyl [13]. These can be proved through FTIR studies, which will be shown in next section.

Table 2 DSC data for PVA with different degree of hydrolysis at P85, P87 and P100

Code	Melting temperature, Tm (°C)	Glass transition, Tg (°C)
P85	185.08	25.86
P87	192.41	28.75
P100	225.00	26.02
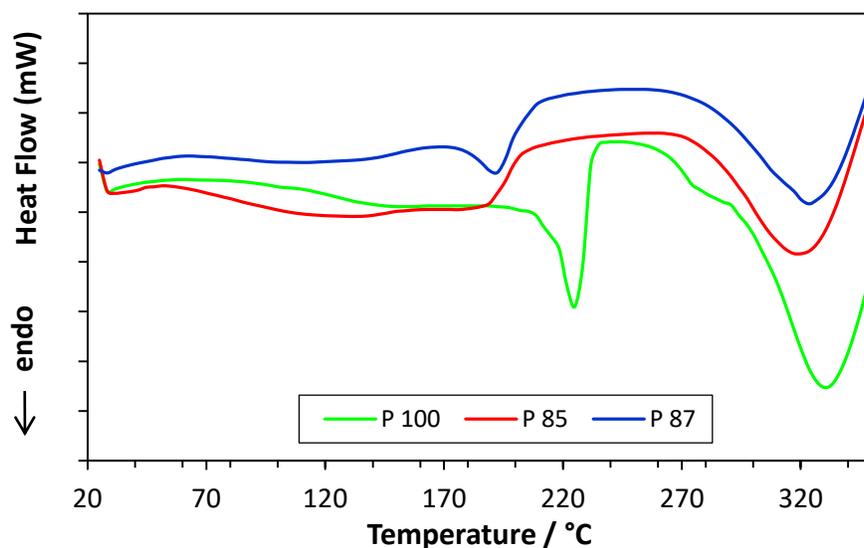
Fig.1 DSC curves of P100, P87 and P85

3.2   *Thermogravimetric analysis (TGA).*

The results from TGA are presented in Fig. 2. The deflection temperatures are shown in Table 3. All three results of PVA, P100, P87 and P85 had a slight weight loss in the early stage of thermal analysis, which could be in regards to the loss of moisture and the trapped and adsorbed water by PVA [14]. All samples of PVA with different DH also show the same trend of roughly 2 step of degradation in the whole range of testing temperature. For P 85, the two peaks were observed with a maximum temperatures at 328.56 °C and 429.38

°C. Whereas at P 87, the two peak of maximum temperature were at 328.56 °C and 432.28 °C meanwhile, for P100 are at 356.62 °C and 429.94 °C. The first temperature can be assigned to the side chain of the PVA while the second temperature can be related to a decomposition of the main chain of PVA. The first degradation is corresponding to the dehydration of PVA chains and formation of polyene structure, and the other step was relative to the degradation of the polyene chain [15]. The result showed that higher DH of PVA shows a slightly better thermal stability. It is expected from PVA with a DH higher than 88%. They hardly dissolves in water without added heat compared to the one with a lower degree of hydrolysis [16]. The decrease in number of hydrophobic acetate groups (decrease of DH) increases inter and intra chain hydrogen bonding. Hence, it increases degree of hydrogen bonding between the PVA chains and water molecules that contributed to higher thermal stability with increasing DH.

Table 3 Degradation temperature of P100, P87 and P85 at peak I and II

Samples	Tpeak I (°C)	Tpeak II (°C)
P 85	328.56	429.38
P 87	333.49	432.28
P 100	356.62	429.94
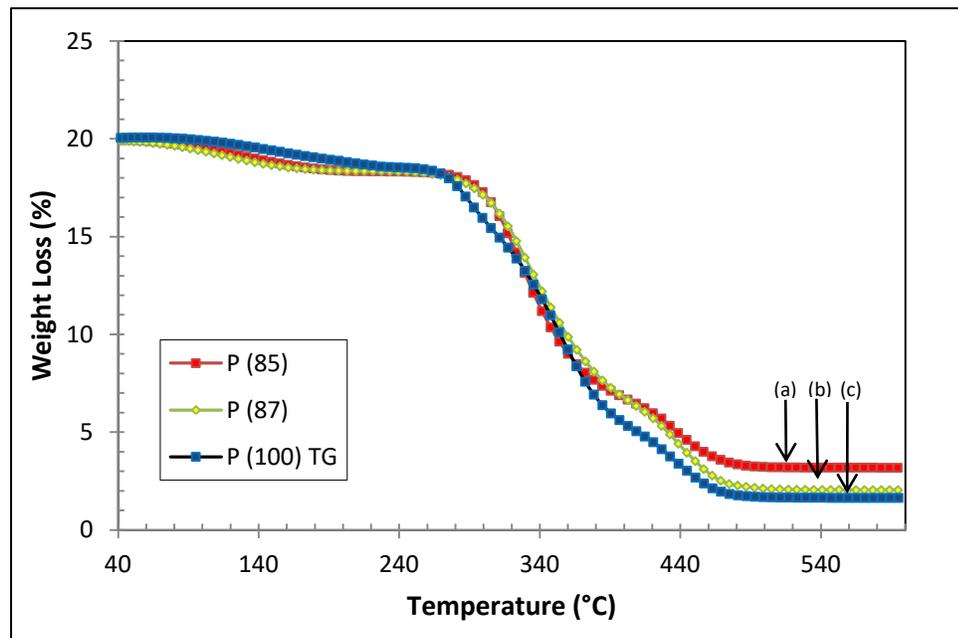
Fig. 2 Thermal stability analysis (TGA) curves of (a) P85, (b) P87 and (c) P100

3.3   *Fourier transforms infrared spectroscopy (FTIR).*

Table 4 shows the most evident characteristic band of PVA and their respective assignment. Fig. 3 shows the FTIR spectrum of P100, P87 and P85. All major peaks related to hydroxyl and acetate group were observed. The large bands observed between 3550 and 3200 cm^{-1} are linked to the stretching O-H from the intermolecular and intramolecular hydrogen bonds (region (a) in Fig. 3). The vibrational band observed between 2840-3000 cm^{-1} refers to the stretching C-H from alkyl groups (region (b) in Fig. 3) and the peaks between 1720 - 1705 cm^{-1} (region (c) in Fig. 3) are due to the stretching of carbonyl, C=O from acetate group remaining from PVA. Also in Fig. 3, the FTIR spectrum is only shown for P85 and P87. The intensity of the

                   Najihah Jamil et al., 2018

1720 - 1705 cm^{-1} is weak for PVAs with high DH, indicating that only a few acetate groups are present in the polymer chain and, whereas the intensity is very strong for PVAs with low DH. For P100, there is no signal in the region of 1720 - 1705 cm^{-1}. This might be due to P100 is a highly hydrolysed grades PVA and have a symmetrical PVA molecular structure. These resulted in no change in dipole moment when the carbon-carbon double bond stretches. Meanwhile, the peaks observed between 1260 - 1000 cm^{-1} (region (e) in Fig. 3) belong to the C-O in the carboxylic group. The peak for P85 appears to be increased by twofold compared to P87 due to hydrogen bonding [17]. The C-H group in phenyl ring of P100 is 828.11 cm^{-1}, and for P85 and P87, the band shifted towards higher value, suggesting that this is due to asymmetric stretching in CH$_3$ [18].
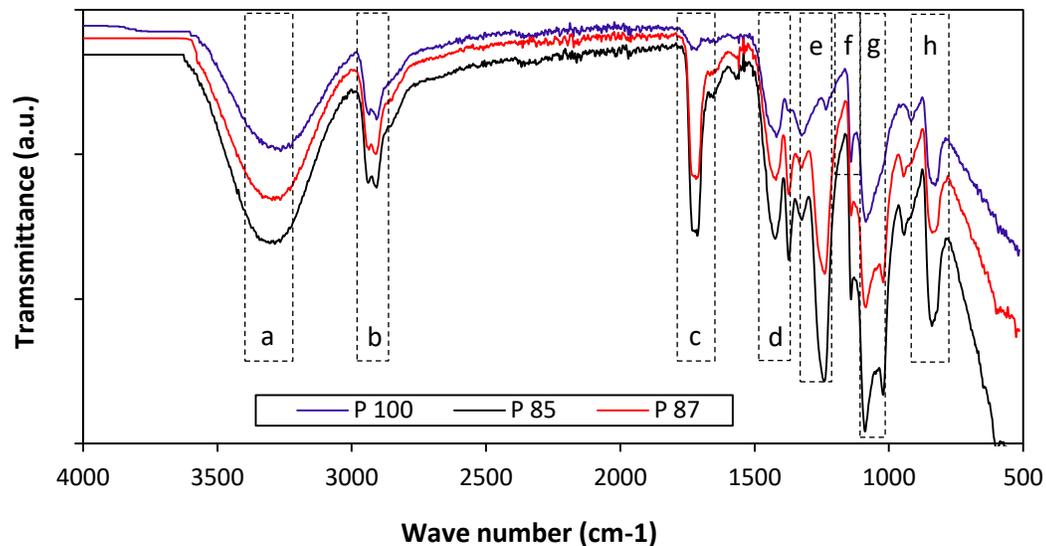
Fig. 3 FTIR spectra of P 100, P 87 and P 85

Table 4 Chemical group present through analysis

No	PVA spectrum	Wave number cm^{-1}			
		References	P100	P87	P85
1	PVA – OH from inter and intra hydrogen bonds	V 3550 – 3200	3265.09	3286.16	3296.95
2	PVA from alkyl groups C – H	V 2840 – 3000	2907.80	2908.01	2910.25
3	PVA, C = O (H bonded) carbonyl	V 1720 – 1705	-	1713.58	1718.49
4	PVA C – O asymmetric stretch	V 1260 - 1000	-	1239.74	1241.08
5	PVA C – O – C ether	V 1150 – 1085	1086.77	1087	1089.38
6	PVA CH$_2$	V 1461 – 1417	1419.10	1420.54	1423.97
7	PVA C-H phenyl ring	V 870 – 675	828.11	839.11	840.20

4.   SUMMARY

In this study, the thermal properties of PVA was investigated with different degree of hydrolysis (DH) (P100, P87 and P85) at different concentrations (0.1-1.1 wt.%). The DSC measurement showed that the melting temperatures of PVA at different DH were found to have increased with an increasing in DH and increasing concentration. The melting temperature range of PVA at different DH did not show much distinction because the result came from the same polymer, although it was with different DH. As for TGA measurement, it showed the same trend where the lower DH of PVA showed a slightly better thermal

stability. Degree of hydrolysis is associated with different number of acetate groups within the PVA itself. The increase in number of hydrophobic acetate groups reduced the interchain and intrachain hydrogen bonding, which explained the higher stability of PVA with decreasing DH. FTIR analysis showed in the region between 1720 - 1705 cm^{-1}, belongs to carbonyl group (C=O) stretched from the acetate group in PVA. For P87 sample (with high DH), the intensity of carbonyl stretching was weak, whereas for P 85 (with low DH) the intensity was strong. This proved that the number of acetate group in PVA had affected their interaction. Thus, it can be concluded that different of DH can affect the thermal properties of PVA.

ACKNOWLEDGEMENT

REFERENCES

[1] E.D. Sloan, Clathrate Hydrates of Natural Gases, second ed., Colarado School of Mines Golden, Colarado, (1998).

[2] C.A. Koh, Towards a fundamental understanding of natural gas hydrates, Chem. Soc. Rev. 31 (2002) 157-167.

[3] M.T. Storr, P.C. Taylor, J.P. Monfort, P.M. Rodger, Kinetic inhibitor of hydrate crystallization, J. Am. Chem. Soc., 126 (2004) 1569-1576.

[4] T.J. Carver, M.G.B. Drew, P.M. Rodger, Molecular dynamics calculations of N-methylpyrrolidone in liquid water, Phys. Chem. Chem. Phys., 1 (1999) 1807-1816.

[5] J. Yang, B. Tohidi, Characterization of inhibition mechanisms of kinetic hydrate inhibitors using ultrasonic test technique, Chem. Eng. Sci., 66 (2011) 278-283.

[6] E. Chiellini, A. Corti, S.D. Antone, R. Solaro, Biodegradation of poly (vinyl alcohol) based materials, Prog. Polym. Sci., 28 (2003) 963-1014.

[7] C.K. Riew, E.H. Rowe, A.R. Siebert, Toughness and brittleness of plastics, Advances in Chemistry Series, 154 (1976) 326.

[8] A. Aina, A. Morris, M. Gupta, N. Billa, N. Madhvani, R. Sharma, S. Doughty, V. Shah, Y. Boukari, Dissolution behavior of poly vinyl alcohol in water and its effect on the physical morphologies of PLGA scaffolds, UK JPB, 2 (2014) 1-6.

[9] N. Ben Halima, Poly(vinyl alcohol): review of its promising applications and insights into biodegradation, RSC Adv., 6 (2016) 39823-39832.

[10] A. Perrin, O.M. Musa, J.W. Steed, The chemistry of low dosage clathrate hydrate inhibitors, Chem. Soc. Rev., 42 (2013) 1996-2015.

[11] M.F. Mady, M.A. Kelland, N,N-dimethylhydrazidoacrylamides. Part 1: Copolymers with N-isopropylacrylamide as novel high-cloud-point kinetic hydrate inhibitors, Energy and Fuels, 28 (2014) 5714-5720.

[12] E. Chiellini, P. Cinelli, E.G. Fernandes, E.R.S. Kenawy, A. Lazzeri, Gelatin-based blends and composites, morphological and thermal mechanical characterization, Biomacromolecules, 2 (2001) 806-811.

[13] P.J. do A. Sobral, R.A. de Carvalho, I.C.F. Moraes, A.M.Q.B. Bittante, E.S. Monterrey-Quintero, Phase transitions in biodegradable films based on blends of gelatin and poly (vinyl alcohol) , Food Science and Technology, 31 (2011) 372-379.

[14] O. Demchenko, T. Zheltonozhskaya, A. Turov, M. Tsapko, V. Syromyatnikov, Poly(vinyl alcohol)-graft-polyacrylamide with different grafts number and length as studied by 1H NMR spectroscopy, Mol. Cryst. Liq. Cryst., 427 (2005) 225-233.

[15] K. Maruyama, K. Takeuchi, Y. Tanizaki, Activation parameters for degradation of polyenes produced in heated poly(vinyl alcohol) film, Polymer, 30 (1989) 476-479.

[16] B. Briscoe, P. Luckham, S. Zhu, The effects of hydrogen bonding upon the viscosity of aqueous poly(vinyl alcohol) solutions, Polymer, 41 (2000) 3851-3860.

[17] I. Ahmed, A. Idris, M.Y. Noordin, R. Rajput, High Performance ultrafiltration membranes prepared by the application of modified microwave irradiation technique, Ind. Eng. Chem. Res., 50 (2011) 2272-2283.

[18] J.C. Morris, InfraRed and raman spectra of polyatomic molecules XIX. Acetaldehyde and Acetaldehyded, J. Chem. Phys.,11 (1943) 230-235.