Thermal Runaway of Self-Sustaining Polymerizing for Vinyl Acetate Monomer using Calorimetry Methodology

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ABSTRACT

Polyvinyl acetate (PVAc) and vinyl acetate copolymers are the products in vinyl acetate monomer (VAM) polymerization process that are widely used as adhesives, intermediates, coatings, food, plastics, textiles and other industrial applications. Generally, solution and emulsion polymerizations are most applied in the VAM chemical process. During the PVAc process, VAM solution is a polymerizing monomer to decompose readily into free radicals and to induce the polymerization. This study attempts to analyze and compare the exothermal hazards during the polymerization for VAM reacting with various initiators under catalytic conditions. 50 and 70 wt.% VAM/methanol solution reacting with various initiators: 2,2'–azobis (2-methylpropionitrile) (AIBN), benzoyl peroxide (BPO) and potassium persulfate $(K_2S_2O_8)$ for determining the reaction enthalpy changes by dynamic thermal scan and to ascertain kinetic data. Furthermore, two inhibitors–hydroquinone (HQ) and diphenylamine (DPA)–were the inhibition candidates for stopping the exothermic behaviors and also to terminate the polymerizing during operation failure. Understanding the thermal runaway hazards and elucidating the self-heating rates associated with kinetic model are beneficial to proactive safety protocol for the VAM polymerization process.

KEYWORDS: Vinyl acetate monomer, VAM, initiator, inhibitor, self-heating rate.

INTRODUCTION

In the industrially chemical process, the quantity of the reactant, catalyst, solvent and side products could affect the reaction rate. Likewise, accompanying the heat and gas evolution might lead to uncontrolled thermal runaway in case of operating failures. Saada et al. [1] summarized the main causes and consequences of the industrial incidents which occurred in the UK from 1988 to 2013. Among these cases investigation, the inherently hazards for plastics, rubbers and resins manufacturing were merely lower than the fine, intermediate and heavy organics chemicals in the current industries. However, the polymerization process brings 10 failures in statistic 30 incidents of specific unit processes and it followed by the decomposition process. As a significant industrial demands, vinyl acetate monomer (VAM; CHCOOCH=CH) is mainly used as a raw material in the manufacture of polyvinyl acetate (PVAc) and vinyl acetate copolymers. Moreover, these products are widely applied in adhesives, chemical intermediates, coatings, food, plastics, textiles and other applications [2, 3].

The VAM processes included the solution, suspension, emulsion and bulk polymerizations, for which, some industrial accidents have been reported. The polymerization initiator dissolved in VAM that could induce its unwanted exothermic reactions in a reactor or a storage vessel [4]. Accordingly, it is imperative to evaluate the safety of VAM in the storage, production and transportation due to its self-polymerization activity. Both industrial accidents relating to VAM and

PVAc processes occurred in a petrochemical plant in Taiwan [5, 6]. The first case resulted in severe fires because of the flammable VAM and methanol released during the *process* of *alkalization. Both vaporizable chemicals ran into heat sources from an alkaline machine and the unit was in flames*; another one caused an explosion of two storage tanks containing PVAc and methanol due to the feeding pipeline's hot work error and to cause a flareback in 2012. In case of VAM/PVAc reacting with oxidizing agents and free radicals, it may be exhibit an uncontrolled heating. VAM is considered as a NFPA Class IB flammable liquid with a flash point of −8°C and boiling point of 72.7 °C; the high vapor density of 2.97 (air is 1.0) allows the vaporizing VAM easily to form the vapor cloud in the case of release. It is usually used in a variety of industrial production, such as ethylene-vinyl alcohol, poly(vinyl butyl) and vinyl acetate-ethylene resins [7, 8]. The operator should be aware of the flammable VAM vapor mixed with air at ambient temperature and take precautions against the ignition source in the operating or storage units. Free-radical induced polymerization is the main chemical reaction of VAM. The process units for the production of VAM-PVAc could consider the following two catalytic reactions that exothermic reactions occur during operation [8, 9]:

Vinyl acetate process,

$$C_2H_4 + CH_3COOH + \frac{1}{2}O_2 \xrightarrow{metal\ catalyst} CH_2 = CHOCOCH_3 + H_2O \tag{1}$$
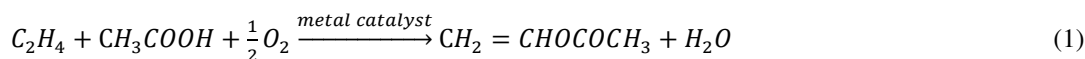
Free-radical polymerization of VAM,

$$\tag{2}$$
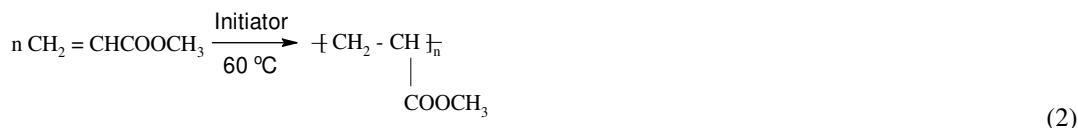
The catalytic initiation of VAM polymerization can be induced by peroxides, azo compounds, light, and high energy radiation. The operation inhibitors include aromatic hydroxyl, nitro or amine compounds, oxygen, copper salts, sulfur, and so on [4]. In order to produce the free radical rapidly, initiators are usually pour in the reactor to supply large amount of free radical and to reduce the activation energy in initiation procedure [10]. In the terms of chemical reactivity, VAM is a self-reactive polymerizing material, which is thermal unstable to arise a runaway risk at elevated temperatures. The polymerization of VAM is an exothermic reaction to form large polymers accompanied with the significant quantities of off-gas evolution and heat release. The deviations of undesired runaway reaction could damage workers or destroy the facilities in the plant due to the risk of conflagration and explosion [11]. For example, in the presence of atmospheric oxygen or light, peroxidation takes place in the VAM storage vessel. The peroxides would decompose into free radicals and to initiate the self-sustaining polymerization in a sufficient concentration of monomers after induction time. VAM is classified as a Class C peroxidizable chemical, a chemical which may auto-polymerize as a result decomposition of accumulated peroxide. The peroxidizable vinyl monomers may exothermically to initiate bulk polymerization [12].

Undesired polymerization can be controlled by the addition of inhibitors which could prevent the production of free radicals in the bulk liquid monomer. In general, some inhibitors are added during delivery and storage to ensure the stability of VAM. The amount of inhibitors determines the shelf life of the monomer and the induction time before the reaction begin. Hydroquinone (HQ) is the most used inhibitor nowadays. Three grades of VAM are offered for different storage time as follow: 3–7 ppm HQ for two months; 12–17 ppm HQ stored up to four months; 200–300 ppm diphenylamine (DPA) applicable for unlimited period [7]. However, the incidence rate will arise along with the depletion of inhibitor. The monitoring of inhibitor concentration and regular maintenance of equipment are indispensable for safety management. The decomposition of the

initiator can be induced by the thermolysis or photolysis. Naturally, the initiating radicals grow into a propagating radicals combining with new monomer. The polymer chain can grow interminably before the chain transfer or termination reaction occurs. Inhibitor decomposes into free radicals as well. The ionizing inhibitor can capture the radical chain and stop the propagation to form a stable substance. This property is further capitalized on the inhibitor injection system design of the process.

Calorimetric measurements and thermal analysis methods using differential scanning calorimetry (DSC) have been applied to test the thermal decomposition and runaway reaction of the energetic chemicals [13-16]. This study aims to evaluate thermal hazard of the self-sustaining polymerization of VAM/PVAc processes using calorimetry methodology and exothermic reaction model accompanies n-order kinetic equation. Three initiators: 2,2'–Azobis (2-methylpropionitrile) (AIBN; $[(CH_3)_2C(CN)]_2N_2$), Benzoyl peroxide (BPO; $[C_6H_5C(O)O]_2$), and Potassium Persulfate ($K_2S_2O_8$) were used for processing dynamic thermal scanning to evaluate various VAM polymerization conditions; the inhibiting effect was selected two inhibitors, hydroquinone (HQ; $C_6H_6O_2$) and diphenylamine (DPA; $(C_6H_5)_2NH$), to add in the PVAc polymerization when runaway reaction was underwent. Monomers that are thermally unstable might undergo polymerization at specific temperatures accompanying release of heats and consequent runaway reactions. Emergency response to uncontrolled reactions involving polymerizable chemicals needs planned carefully for adding inhibitors to prevent the onset or cut off of a polymerization. DSC was used to obtain the essential thermophysical properties for thermal polymerization of VAM/PVAc, and the kinetic data is implemented by the thermally analytical equations for proactive safety protocol in VAM/PVAc process units.

EXPERIMENTAL

Materials

VAM (99.9+ mass%) including 1.5 ppm inhibitor HQ was procured from local chemical corporation and methanol (99.9+ mass%) was as its solvent. VAM was stored in a refrigerator at 4 °C to prevent from auto-polymerization. Three of initiators of AIBN (99.9+ mass%), BPO (97 mass%) and $K_2S_2O_8$ (99 mass%) were obtained from local chemical corporation, Alfa Aesar and J.T. Baker, respectively. Inhibitors, HQ (99.9+ mass%) and DPA (98+ mass%), were purchased from local chemical corporation and Alfa Aesar. Initiators and inhibitors were placed in a damp-proof case at 40% relative humidity.

Differential scanning calorimetry (DSC)

An exothermic polymerizing behavior of VAM/PVAc was evaluated using a Mettler Toledo DSC1 between the temperature ranges of 30–300 °C at a heating rate of 4 °C min^{-1}. A sample was loaded in a gold-plated high pressure crucible (Mettler ME-26732) that could withstand pressure of up to 15 MPa to prevent apparatus damage. Approximately 4–5 mg of sample was added to the crucible before hermetic sealing followed by manual sealing with special equipment. Thermal curves were obtained combining with STAR^e thermal analysis software to evaluate the behavior during thermal decomposition. In addition, dynamic temperature-programmed screening was used to determine the apparent onset temperature (T_0), apparent maximum temperature (T_{max}), temperatures rise (ΔT_r), heat of decomposition (ΔH_d) and heat of polymerization (ΔH_p). The industrial polymerization of VAM includes bulk, solution, suspension, and emulsion method. Gustin indicates bulk polymerization is the most violent of all process, hence, this method is not recommended in the present industrial operations owing to the process safety [4]. In general, solution and emulsion polymerizations are most applied in vinyl acetate manufacturing. Solution method is adopted in the

study. Various concentration VAM solutions, 30, 50, and 70 wt.% VAM solutions were examined for DSC dynamic and isothermal programs.

RESULTS AND DISCUSSION

Thermal analysis data using DSC methods

To identify potentially exothermic hazard in the unit processes, first of all, it is necessary to understand the properties of chemicals and reaction conditions. Thermal instability of VAM reacting with various initiators for chemical process and reacting with various inhibitors for emergency chain-breaker candidates were examined by DSC with a dynamic thermal scanning. Table 1 and Fig. 1 present the exothermal properties of 100 wt.% VAM, two inhibitors (HQ and DPA) and three catalysts (AIBN, BPO and $K_2S_2O_8$). Pure VAM is thermally stable with catalyst to initialize the polymerization, but it could be self-polymerizing at approximately 215.0 °C; ΔH_d was only 25.7 J/g after thermal scanning that if enthalpy greater than 130 J/g can be recognizing as an energetic material [17]. Three initiators and two inhibitors were sealed in an aluminum crucible and examined the thermal stability by DSC. The T_0 of AIBN, BPO, $K_2S_2O_8$ were 104.2°C, 108.5°C and 188.2°C, respectively. An endothermal peak that is a melting phase change of solid to liquid occurred firstly for both AIBN and BPO were shown in Fig. 1. AIBN, which is a common and effective initiator applied in polymerization for vinyl monomers, blowing agents for the production of vinyl foaming, and some organic reaction processes, released abundance of heat when it went through decomposition (ΔH_d = 2072.3 J/g) due to its high thermal sensitivity and decent amounts of decomposition heat [18, 19]. The onset temperature of AIBN and BPO were really similar, however, the enthalpy change of AIBN was greater than BPO (ΔH_d = 879.8 J/g). The decomposition of $K_2S_2O_8$ took place at a higher temperature liberating the lowest energy of 221.3 J/g. To compare with the DSC thermal scanning trails, the values of heat of decomposition for both AIBN and BPO initiators were agreed with the previous study [20]. In the event of polymerizing termination, feeding of the inhibitor is an effective way to play a radical scavenger and to prevent the following polymerization, namely, VAM is stable under well inhibited and proper storage. Industrially, VAM should be distilled to remove the inhibitors increasing the conversion of VAM polymerization. In terms of heat of reaction, VAM is more stable that enthalpy changed is lower than polyvinyl acetate (ΔH_d = 1022.2 J/g) [21]. The thermograms of two inhibitors both had endothermic curves. The T_0 of DPA (T_0 = 53.0 °C) is much earlier than HQ (T_0 = 169.3 °C), whereas, the endothermic value of HQ (ΔH_d = −246.3 J/g) is higher than DPA. The inhibiting effect is largely affected by the nature and reactivity of stable radicals [22].

Table 1. Data of thermal analysis for pure VAM, three catalysts (AIBN, BPO and $K_2S_2O_8$) and two inhibitors (HQ and DPA) evaluated from STAR[e] system

Sample	Mass/mg	T_0 [a], °C	ΔH [b], J/g	T_P [c], °C
100 wt.% VAM	3.5	215.0	25.7	223.3
AIBN	4.1	104.2	2072.3	112.2
BPO	4.6	108.5	879.8	109.4
$K_2S_2O_8$	4.7	188.2	221.3	204.9
HQ	3.9	169.3	−246.3	172.6
DPA	4.3	53.0	−105.9	54.0

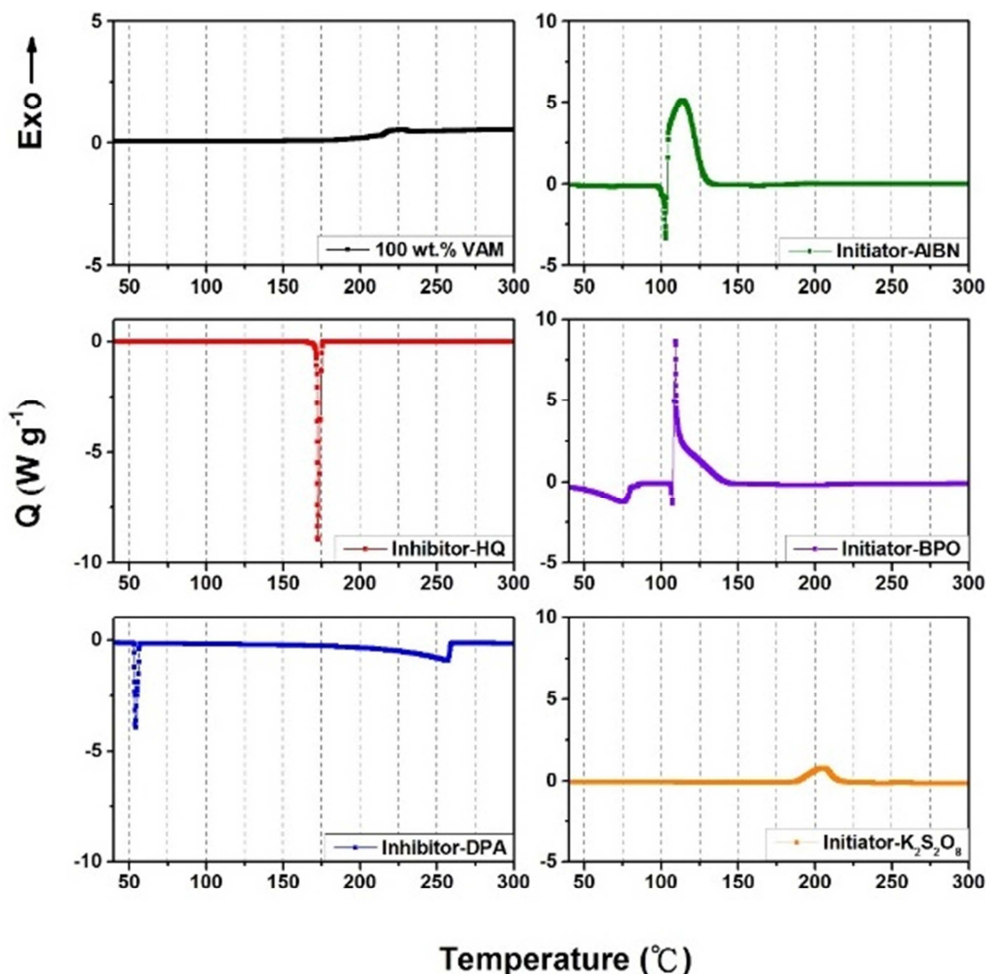[a] Onset Temperature. [b] Heat of Decomposition. [c] Peak Temperature.

Fig. 1. Thermal curves of 100 wt.% VAM, both inhibitors of HQ and DPA and three catalysts of AIBN, BPO and $K_2S_2O_8$ using DSC1 thermally dynamic scanning from 30–300 °C at 4 °C/min.

Dynamic scanning test for initiating VAM polymerization

Polymerizing reaction of monomers are catalyzed to form polymer or other large molecules by chaining and crosslinking. The polymerization is generally self-sustaining once initiated and accompanied exothermic potential. The industrial recipe of emulsion polymerization contains 30–70 % VAM with the catalyst. Therefore, 30, 50 and 70 wt.% VAM in methanol solution were tested under various catalytic conditions. VAM solution contained the 5 wt.% catalyst were mixed well and proceeded DSC thermally dynamic program. The thermal analysis data of VAM polymerization initialized by AIBN, BPO and $K_2S_2O_8$ were summarized in Table 2. According to DSC testing results, the VAM/PVAc process initiating by AIBN had the lowest onset temperature ($T_0 = 76.6$ °C for 50 wt.% VAM/AIBN) and the highest enthalpy change ($\Delta H_p = 524.1$ J/g for 70 wt.% VAM/AIBN). The polymerization which was initiated by BPO also had significant exothermic behaviors. Otherwise, only for a 70 wt% VAM polymerization catalysing of $K_2S_2O_8$ had exothermic reaction. Both 30 and 50 wt.% VAM/$K_2S_2O_8$ polymerization were insignificant of the heat of polymerization. Figure 2 illustrated the thermal curves which were compared with various initiators to affect the exothermic trends during VAM polymerization. It should take into account of thermal

runaway reaction of VAM reacting with both initiators of AIBN and BPO in processing. Furthermore, higher monomer concentration increases the conversion of reaction, namely, raising the enthalpy change of polymerization [23].

Table 2. Data of DSC1 thermal analysis for various concentration of VAM solution which initiated by AIBN, BPO and K2S2O8 from STARe system

Sample	Initiator	Mass/mg	T_0, °C	ΔH, J/g	T_P, °C
30 wt.% VAM	—	2.9	203.2	6.7	209.1
	AIBN	5.4	79.7	158.1	114.5
	BPO	4.4	87.4	90.2	119.0
	$K_2S_2O_8$	4.8	223.0	14.1	226.2
50 wt.% VAM	—	4.5	218.9	4.1	219.8
	AIBN	4.4	76.6	326.9	107.3
	BPO	4.4	88.8	156.3	113.5
	$K_2S_2O_8$	4.3	207.1	5.7	220.2
70 wt.% VAM	—	4.5	213.1	8.1	214.4
	AIBN	4.9	82.6	524.1	103.4
	BPO	3.4	104.2	225.5	114.1
	$K_2S_2O_8$	4.4	171.6	149.7	184.2

Isothermal testing for polymerization stopping effect of the inhibitors

A chemical is considered to be energetic when the enthalpy exceeds 50–70 cal/g (0.2–0.3 kJ/g) in the view of thermal stability [11]. In Section 3.2, higher enthalpy were evaluated for 70 wt.% VAM initiated by AIBN (ΔH_p = 524.1 J/g) and BPO (ΔH_p = 225.5 J/g) during VAM/PVAc polymerization processes. DSC also can be carried out isothermal scanning for determining the amount of conversion and enthalpy at a constant temperature. An isothermal DSC test to measure the inhibition during uncontrolled polymerization reactions is a rather well-established emergency response. When an inhibitor being a negative catalyst that will reduce the polymerization or side reactions to a sufficiently low level for continuing the reaction. It is used to stabilize VAM during processing or storage stage, quench the reaction out of control, and regulate polymerization when a desired conversion reached [23]. Isothermal testing was applied to detect the enthalpy reduce in the catalyzing process restrained by inhibitors of HQ and DPA. The programming isothermal temperature of both processes were set at 80°C, which at this temperature the exothermic reaction has been induced the VAM polymerization, for 8 hours to evaluate enthalpy and the effect of inhibition. The effects of two inhibitors compared with heat decreasing for VAM-AIBN polymerization process that scanned isothermally at 80°C by DSC1 have displayed in Table 3 and Fig. 3. Obviously, the onset time (t_0) of polymerization reaction was delayed along with both 1000 ppm HQ and DPA. Furthermore, the heat decreasing of the polymerization inhibited by 1000 ppm DPA (ΔH_p = 167.3 J/g) was more effective. In other words, applying a killer system used DPA as an inhibitor is more useful than HQ in a VAM-AIBN polymerization process.
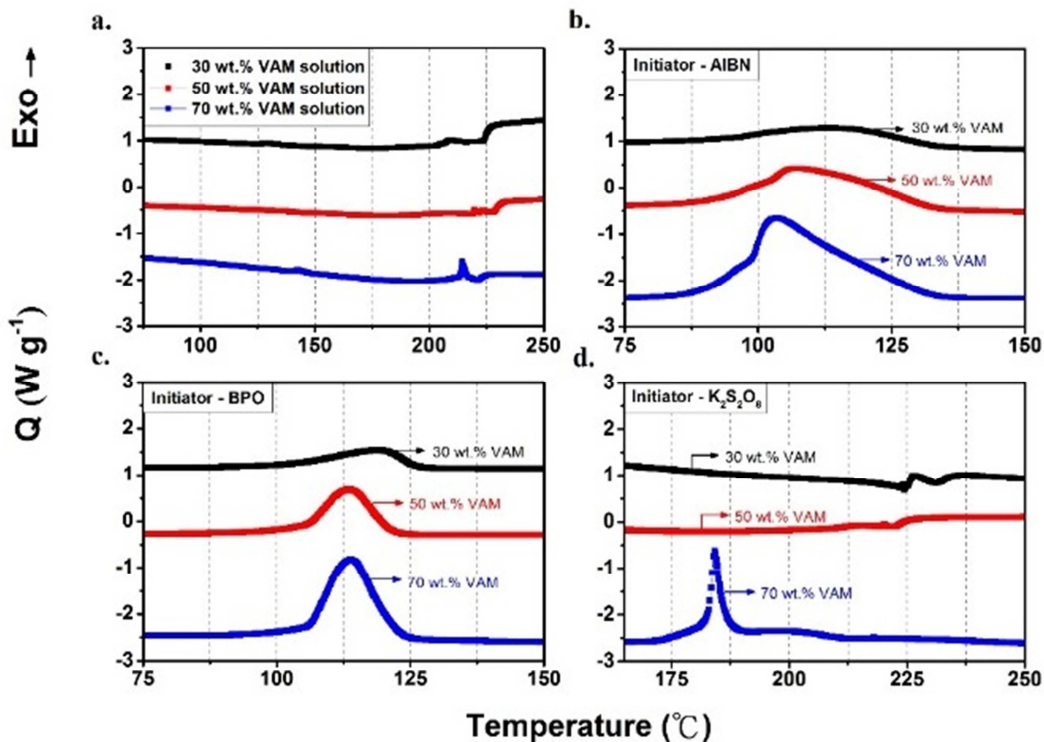
Fig. 2. DSC thermal curves of (a) various concentration of VAM solution and (b)−(d) reacting with various initiators (AIBN, BPO and $K_2S_2O_8$).

Table 3. Data of the effects inhibition on VAM-AIBN polymerization process that isothermal scanned at 80°C in 8 hours

Sample	Initiator	Inhibitor	Mass, mg	t_0 [a], min	ΔH, J/g
		100 ppm HQ	3.9	14	348.8
		500 ppm HQ	3.9	42.4	362.9
70 wt.% VAM	AIBN	1000 ppm HQ	3.6	80	316.9
		100 ppm DPA	3.4	16.2	345.6
		500 ppm HQ	4.6	20.6	355.8
		1000 ppm DPA	4.9	39	167.3

[a] Onset time to begins an exothermic polymerization reaction.

DPA was being an anti-oxidant to form free radicals of diphenylnitric oxide $((C_6H_5)_2NO\cdot)$ and to terminate the VAM polymerization because of the oxidation of $(C_6H_5)_2NOR)$. The inhibition mechanisms were described as follows [24]:

$$2(C_6H_5)_2NH + O_2 \rightarrow 2(C_6H_5)_2NO\cdot + H_2O \tag{3}$$

$$(C_6H_5)_2NO\cdot + R\cdot \rightarrow (C_6H_5)_2NOR \tag{4}$$

AIBN decomposed to the free radicals during polymerization at atmosphere, and then it reacted with an inhibitor of diphenylnitric oxide to generate a stable product (X).
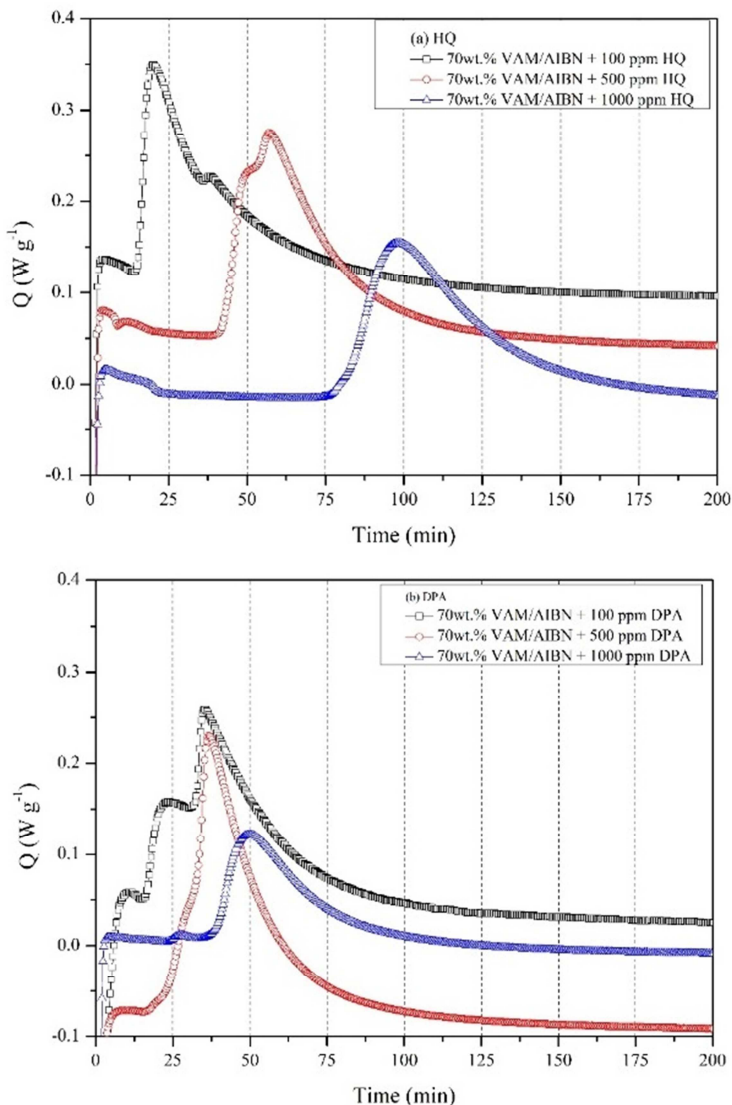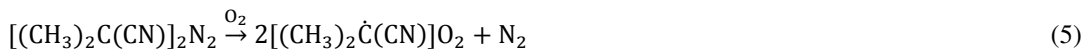
$$[(CH_3)_2C(CN)]_2N_2 \overset{O_2}{\rightarrow} 2[(CH_3)_2\dot{C}(CN)]O_2 + N_2 \tag{5}$$

$$[(CH_3)_2\dot{C}(CN)]O_2 + (C_6H_5)_2NO\cdot \rightarrow X \tag{6}$$

Fig. 3. Comparison of effects on two inhibitors (a) HQ and (b) DPA during 70 wt% VAM-PVAc polymerization.

A model of self-heating rate for VAM polymerization

Thermal safety software (TSS) was developed by CISP [24] and the computing program language was used to estimate the kinetics of VAM polymerization. Flory pointed that the n-order of chain initiation reaction of vinyl polymerization without catalytic and homogeneous processes might be

either second or third process due to the high energy requirement [10]. In another studies, AIBN was considered as the most active initiator for the polymerization of VAM in methanol. The reaction was of second order and gave the highest polymerization rate [25, 26]. The rate of the reduction of concentration of VAM is in the following equation obeyed n-th order reaction:

$$\frac{d[VAM]}{dt} = -k[VAM]^n \qquad (7)$$

where k is a reaction rate and [VAM] is the concentration of VAM.

For an exothermic reaction, the enthalpy from the reaction will result in temperatures rise, which, in turn, represented the rate of reaction and pressure elevation [24, 27]. The conversion of reaction (x) could be approximately related to the variation of the concentration, enthalpy or temperature in a VAM/PVAc polymerizing system.

$$x = \frac{[VAM]}{[VAM]_0} = \frac{[\Delta H]}{\Delta H_p} = \frac{mc_p(T-T_0)}{mc_p \Delta T_r} = \frac{(T-T_0)}{\Delta T_r}, 0 \le x \le 1 \qquad (8)$$

where $[VAM]_0$ is the initial concentration of VAM, T_0 is an initial temperature, and ΔT_r is the temperatures rise during polymerization.

For a normal chemical reaction rate of VAM,

$$k = k_0 \exp[\frac{-E_a}{RT}][VAM]^n \qquad (9)$$

where k_0 is the Arrhenius rate constant, R is the ideal gas constant, 8.314 J/(mol·K), and E_a is the activation energy.

Heat of polymerization reaction (ΔH_p) evaluated from the DSC thermal curve can therefore be determined form the proposed as follows:

$$\Delta H_p = mc_p \Delta T_r , \qquad (10)$$

where m is the reactant mass and c_p is the specific heat of the reactant.

The variations relating to the VAM concentration and degree of conversion for an nth-order reaction can be described by Eqs. (11):

$$\frac{d[VAM]}{dt} \cong \frac{dx}{dt} = k[1-x]^n . \qquad (11)$$

TSS was used to analyze and simulate the raw data examined from DSC testing data [28,29]. The kinetic evaluating approach under simplified enthalpy change assumptions, which the heat flux (Q, W) can be considered as the independent variable taken from DSC dynamic thermal scanning.

$$\Delta H = \int_{t_0}^{t_f} Qdt . \qquad (12)$$

In Eq. (12), t_0 and t_f were time at initially exothermic onset temperature and maximum temperature, respectively, in DSC testing. Figure 4 illustrates the fitting from DSC thermal curves using TSS simulation results of heat flux (Q) vs. time for various concentration of VAM and its initiators (AIBN and BPO). The self-heating rate was calculated by DSC data of physical properties and TSS kinetic simulation. The kinetics of reaction estimated (in Table 4) substitute to calculate the self-heating rate (dT dt^{-1}) in C++ computing program. The method for kinetic parameters estimation is according to conversion degrees as enthalpy variables [25]. For the variations of self-heating rate for VAM polymerization could be calculated by applying Arrhenius kinetic model, which was proposed by a simplified thermal analytic solution to describe self-heating rate for VAM:

$$(\frac{dT}{dt})_{VAM} = \frac{\Delta H_p}{mc_p}\frac{dx}{dt} \cong \Delta T_r k[1-x]^n = \Delta T_r k_0 \exp[\frac{-E_a}{RT}][1 - \frac{(T_{max}-T)}{\Delta T_r}]^n . \qquad (11)$$
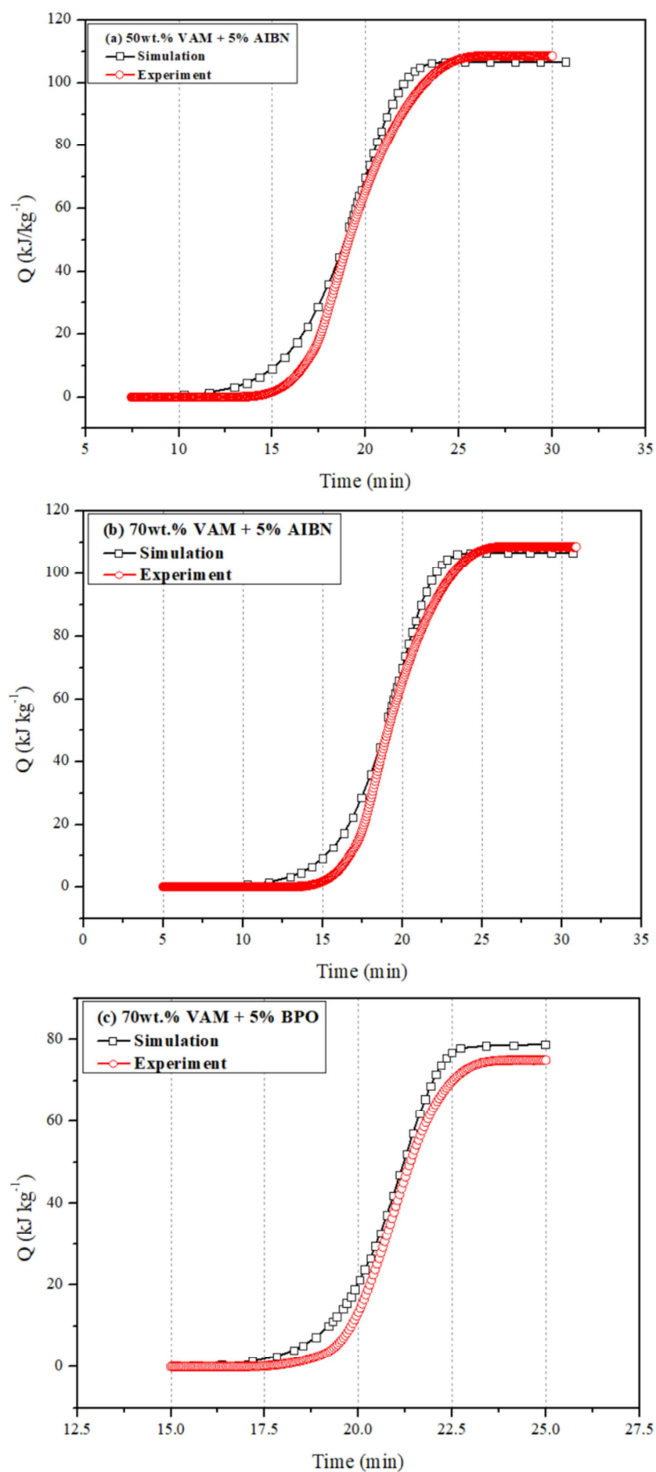
Fig. 4. TSS simulation results of heat flux vs time for (a) 50 wt%VAM-AIBN, (b) 70 wt%VAM-AIBN and (c) 70 wt%VAM-BPO from DSC experiments.

The trend of self-heating rates for VAM polymerization was displayed in Fig. 5 using Eqs. (8)−(11) and kinetic data of thermal analysis. The various nth-order reactions with the VAM initiation reactions were used for verification of the exothermic hazards for the PVAc polymerizing reactions. 70 wt.% VAM initiated by BPO could cause more extreme self-heating rates at elevated temperatures. However, AIBN could result in a thermal runaway at temperatures close to operation temperature. During BPO and AIBN initiating for a VAM polymerization process, the initiators feeding and temperature control should take into account.

Table 4. Kinetic data evaluated for VAM polymerization, which initiated by AIBN and BPO, using TSS analytic solutions

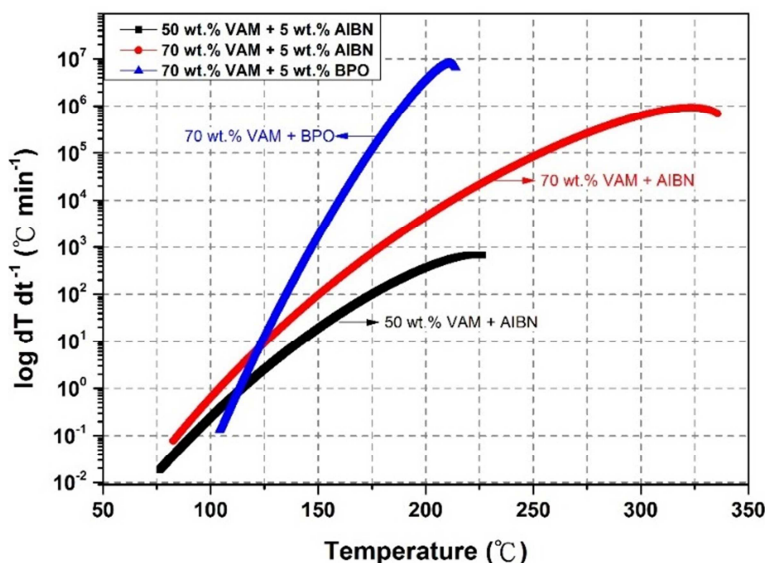| Sample	Initiator	T_0, °C	ΔH, kJ/kg	$\ln(k_0)/s^{-1}$	E_a, kJ/mol	n
50 wt.%VAM	AIBN	76.6	326.9	34.2	125.9	1
70 wt.%VAM	AIBN	82.6	524.1	38.8	137.8	1
	BPO	104.2	225.5	86.4	292.1	0.89

Fig. 5. The self-heating models of the VAM polymerization processes initiated both AIBN and BPO initiators.

CONCLUSIONS

VAM might not undergo a significant self-polymerizing reaction in the absence of initiators at ambient temperatures. However, understanding the formation of free radicals and regular inspection of inhibitor sampling concentration are necessary during a long term of bulk storage and transport because adding the inhibitors beyond the polymerization limits could be taken as a safety operation. Otherwise, in case of a catalyzing reaction of the initiators reacting with the monomers should consider a risk of the exothermic reaction due to the flammable reactants and solvents. In the polymerizing process, using of initiators makes the reaction exothermic and needs to control the operation temperature to avoid self-heating reaction and gas eruption. The worst case might result in a runaway reaction if the VAM polymerization process is out of control, such as initiators over feeding, process temperature out of control, containments, etc. The results of our study showed that

VAM reacting with higher concentration of AIBN or BPO during polymerization may induce a dramatic self-heating rate. Feeding ratio of monomers and catalysts must be monitored. Calorimetric thermal analysis with a self-heating model can be used to study the exothermic behavior of thermal instable chemicals. The first order self-heating is possible with strongly exothermic reactions. In addition, DPA is proposed as an effective inhibitor to terminate a VAM runaway reaction. A killer system of above 0.1% DPA solution should be used in a process emergency response in the event of a runaway case.

ACKNOWLEDGEMENTS

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