Thermal runaway evaluation on batch polyvinyl acetate emulsion polymerization from calorimetric measurement

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Abstract

Emulsion polymerization is the most applied method in the vinyl acetate monomer (VAM)–polyvinyl acetate (PVAc) process. However, the flammable property and unexpected bulk polymerization for the reactant and product may occur in the batch reactor or storage tank. VAM is reactive enough to decompose readily into free radicals and then, initiate the polymerization, which may contribute to heat accumulation due to the monomer, initiator, and solvent mixtures. This study attempts to analyze the exothermic reaction and compare the thermal runaway potential for various VAM solutions during PVAc polymerizations. Summarily, 50%, 70%, and 100% of VAM solutions reacting with 2,2'–azobis(2-methylpropionitrile) readily increase the self-heating rate with their concentration from adiabatic calorimetric tests. Furthermore, kinetic parameters of 50, 70, and 100 mass% VAM solutions were evaluated to elucidate the self-heating model associated with thermal analysis and to determine heat production mechanisms that are practical to proactive safety protocol for the PVAc emulsion process.

Introduction

The heat production rate of a chemical reaction is affected by the quantity of reactants, catalysts, solvents, intermediates, and derivatives that may accompany the gas evolution. Many thermal runaway reactions initiate after an onset temperature and increase exponentially as pressure rises, which results from the vaporization or gasification of the components and products. The criteria for a thermal runaway include the failure of the cooling system, critical temperature threshold, successive temperature derivatives, and no detection in due time of the runaway initiation [1]. Thirty industrial incidents mainly caused by fine, intermediate, and heavy organic chemicals occurred in the United Kingdom between 1988 and 2013, with the incidents involving polymerization and decomposition processes resulting in ten failures (33.3%) and four failures (13.3%) of specialty chemical units, respectively [2]. Among the cases investigated, the possible causes of the incidents in chemical plants were related to technical, physical or human, and organizational factors. For example, on May 7, 2020, styrene monomer vapor leaked out of a storage tank on the premises of the LG Polymers unit located in India [3] due to the COVID-19 lockdown [4, 5].

Being a significant industrial demand, vinyl acetate monomer (VAM; $CH_3COOCH=CH_2$) is mainly used as a raw material in the manufacture of polyvinyl acetate (PVAc) and vinyl acetate copolymers [6]. It is used in various industrial products, such as ethylene–vinyl alcohol, polyvinyl butyral resin, and vinyl acetate–ethylene resin [7]. The VAM–PVAc process includes the solution, suspension, emulsion, and bulk polymerizations. Bulk polymerization is the most violent of all processes; hence, this method is not recommended in current industrial operations owing to the process safety. Additionally, some inhibitors are added during the delivery and storage to ensure the stability of VAM. The inhibitors, which can quickly homogeneously mix with the polymerizing materials, a basic safety treatment, e.g., hydroquinone (HQ; $C_6H_4(OH)_2$) and diphenylamine (DPA; $(C_6H_5)_2 NH$), could be fed to stop the propagation of free radicals [8].

Moreover, these products are widely applied in adhesives, chemical intermediates, coatings, food, plastics,

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textiles, and other applications. In the case of VAM–PVAc polymerizing with heat, bulk polymerization depends on the autocatalytic reaction. HQ is currently the most used inhibitor. Accordingly, due to its reaction activity, it is imperative to attach safety concerns to the VAM–PVAc process in storage, production, and transportation. In a polymerization reaction system, the polymerizing temperature is a key parameter for a thermal runaway reaction. Multiple polymerizing mechanisms, including auto-oxidation, degradation, and oxidative decomposition, were observed from the polymerization of acrylonitrile–butadiene–styrene (ABS) resin [9]. The exothermic phenomenon of thermal initiation and chain transfer schemes in a styrene polymerization was corroborated using calorimetric investigation, and the initiating onset temperature was 50 °C; the chemical kinetics of styrene in a thermal polymerization also obeyed an nth order reaction [10, 11]. The peroxidase would decompose into free radicals and initiate the self-sustaining polymerization in a sufficient concentration of monomers after induction. VAM is classified as a class C peroxidizable chemical—a chemical that may autopolymerize due to the decomposition of accumulated peroxide. The peroxidizable vinyl monomers may exothermically initiate bulk polymerization [12]. However, the incidence rate will rise along with the depletion of inhibitors. Therefore, monitoring inhibitor concentration and regular equipment maintenance are indispensable for safety management. For example, peroxidation occurs in the VAM storage vessel in the presence of atmospheric oxygen or light.

Calorimetric tests combined with thermal analysis methods that use a differential scanning calorimetry (DSC) and an adiabatic calorimeter—vent sizing package (VSP) have been applied to test the thermal decomposition and runaway potential of the energetic substances [13–16]. This study aims to evaluate the thermal runaway hazard of the self-sustaining process of VAM–PVAc emulsion polymerization using calorimetry methodology and establish an exothermic reaction model accompanying the n-order kinetic reaction rate. DSC was used to obtain the essential thermophysical properties for the thermal polymerization of VAM and PVAc, and the kinetic data were implemented by thermal reaction analytical equations. Thermally unstable monomers might undergo polymerization at specific temperatures accompanying the release of heat and flammable vapors/gasses. Therefore, the calorimetric experiments could be applied as a proactive safety protocol in manufacturing VAM–PVAc.
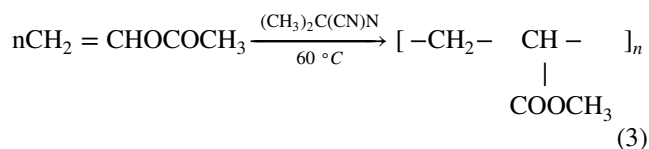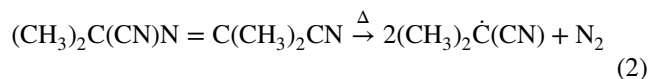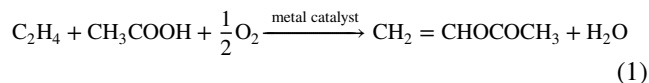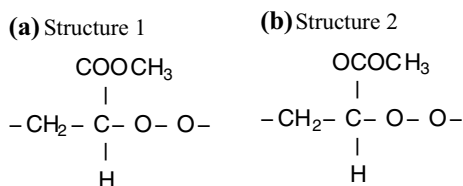
Experimental and methods

Materials

Emulsion and solution polymerizations are the most applied methods for manufacturing VAM–PVAc. The emulsion method under catalytic initiation adopted in this study and various concentration VAM/MeOH solutions of 50, 70, and 100 mass% by mass was examined for calorimetric tests. The various application of PVAc includes 15%–40% PVAc used in solvent-based coatings, inks, and adhesives or melt extrusion systems, 50%–60% PVAc designed for use in solvent-based general purpose or parquet adhesives, coatings and inks, and melt extrusion systems, and higher concentrations of PVAc used mainly in solvent-based coatings. 2,2'–Azobis(2-methylpropionitrile) (AIBN; $[(CH_3)_2C(CN)]_2N_2$) is an initiator and is used for VAM–PVAc polymerization. Samples involving VAM (a colorless liquid with a sweet but irritating odor), AIBN, HQ, and methanol were procured from a local chemical manufacturer. Three grades of VAM are offered for different storage times: 3–7 ppm HQ for two months, 12–17 ppm HQ stored for up to four months, and 200–300 ppm DPA applicable for an unlimited period [7]. VAM was stored in a refrigerator at 4 °C to prevent autopolymerization and vaporization. Undesired polymerization can be controlled by the feeding of inhibitors, which are radical scavengers and prevent the production of free radicals in the bulk liquid VAM.

VAM-PVAc polymerizing mechanism

The process units for the production of VAM–PVAc should consider the following two exothermic reactions that occur during operation because of their catalysts [17, 18]. VAM has a significant level of water-solubility solvent, which contributes to its wide polymerization application. Free-radical polymerization of VAM is illustrated as follows:

$$C_2H_4 + CH_3COOH + \frac{1}{2}O_2 \xrightarrow{\text{metal catalyst}} CH_2 = CHOCOCH_3 + H_2O \quad (1)$$

$$(CH_3)_2C(CN)N = C(CH_3)_2CN \xrightarrow{\Delta} 2(CH_3)_2\dot{C}(CN) + N_2 \quad (2)$$

$$nCH_2 = CHOCOCH_3 \xrightarrow[60\,°C]{(CH_3)_2C(CN)N} [-CH_2 - \underset{\underset{COOCH_3}{|}}{CH} -]_n \quad (3)$$

Free-radical-induced polymerization is the predominant reaction mechanism of VAM. The catalyzed initiation of VAM polymerization can be induced by peroxides, azo compounds, light, and high-energy radiation. To rapidly produce

(a) Structure 1

$$
\begin{array}{c}
COOCH_3 \\
| \\
-CH_2-C-O-O- \\
| \\
H
\end{array}
$$

(b) Structure 2

$$
\begin{array}{c}
OCOCH_3 \\
| \\
-CH_2-C-O-O- \\
| \\
H
\end{array}
$$

Fig. 1 Two structures of VAM peroxidation that occur in the presence of oxygen

the free radicals, initiators are usually poured into the reactor to supply a large amount of free radicals and reduce the activation energy needed for the initiation procedure. Peroxidation of VAM occurs in the presence of oxygen at ambient temperature, and two structures of VAM polyperoxide are shown in Fig. 1, with structure 2 being more unstable than structure 1.

The decomposition of the initiator can be induced by thermolysis or photolysis. Equation (3) shows that initiator (I) receives the external energy breaking into two radicals ($I\cdot$ and $I'\cdot$) and attracts the neighboring monomer (M) to form initiating radicals (I − M•). Naturally, the initiating radicals grow into propagating radicals (I − M − M•), combining with a new monomer. The polymer chain can grow interminably before the chain transfer or termination reaction occurs. Unstable VAM proceeds to thermally initiated polymerization on the effect of oxygen at 50 °C–120 °C [19]. An unpredictable bulk polymerization of VAM involving the monomer and solvent is dangerous because the exothermic reaction possibly occurred in the process vessels. VAM is recognized as an NFPA class IB flammable liquid due to a flash point of ca.−8 °C and boiling point of 72.7 °C (which is close to the process operation temperatures of 60 °C–70 °C). A higher vapor density of 2.97 (air is 1.0) allows the vaporizing VAM to form the vapor cloud in case of release or crack from the vessel or pipeline and then, to stay near the ground, which may ignite to cause a vapor cloud explosion (VCE). The workers should be aware of the flammable vapor mixed with air at ambient temperatures and take precautions against the ignition source in the processing or storing units [20]. The polymerization might be initiated under ambient temperatures, including a chemical acceleration trend related to the free-radical nature of the VAM chain reaction [21]. Both industrial accidents relating to VAM–PVAc processes occurred in a petrochemical plant in Taiwan [22, 23]. The first case caused severe fires in the plant because of failure management of change (MOC) in a residual vapors/gasses recycle system during a VAM polymerizing process in 2011. Due to the flammable VAM and methanol released during alkalization, both vaporizable reactants ran into heat sources from an alkaline machine, causing the unit to burst into flames. Another one resulted in an explosion of two refined vessels containing 76% PVAc and 24% methanol due to a

hot work error of maintenance in a feeding pipeline in 2012. The main reasons from the official investigation were tanks not completely empty and purged before using an electric welding machine in hot operations, as well as failures of MOC, preliminary hazard assessment (PHA), and contractors' management. Both accidents resulted in one death and eight injuries of the employees during two vessels rupture and severe blast effects. Figure 2 illustrates an overview of this accident.

Thermal analysis using differential scanning calorimetry

An exothermic behavior of VAM/PVAc polymerization can be evaluated by 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 by combining with STAR^e thermal analysis software to evaluate the behavior during thermal decomposition. The exothermic behaviors and thermokinetic data for a reactive system were obtained. In addition, dynamic temperature-programmed screening was used to determine the apparent onset temperature (T_0), apparent endset temperature (T_e), peak temperature (T_p), heat of decomposition (ΔH_d), and heat of polymerization (ΔH_p). DSC encompassed thermal analysis for measuring the exothermic properties of an energetic material.

Runaway test using adiabatic calorimetric method

Vent sizing package 2 (VSP2™; Fauske & Associates, Inc.), associated with XY-plot reduce software, is a reaction calorimeter system which is capably determined rates of temperature and pressure rise for an exothermic reaction. A VSP2 calorimeter is able to provide information on the runaway behavior of substance and reactions in closed or open mode. Both temperature and pressure equalization techniques are used to carry out the tests adiabatically. Its temperature detection range is from room temperature to 400 °C, with a maximum detectable sensitivity of 0.15 °C min⁻¹. The heat–wait–search mode of the VSP2 was applied for detecting the initial exothermic reaction and self-heating rate. A closed test vessel (116 mL and 37 g) ensured all of the released reaction heat and pressure elevation remained within the container. The sample in the vessel is heated until its self-heating is initiated, and the changes of temperature and pressure are determined by means of the thermocouples and pressure transducer, respectively. For
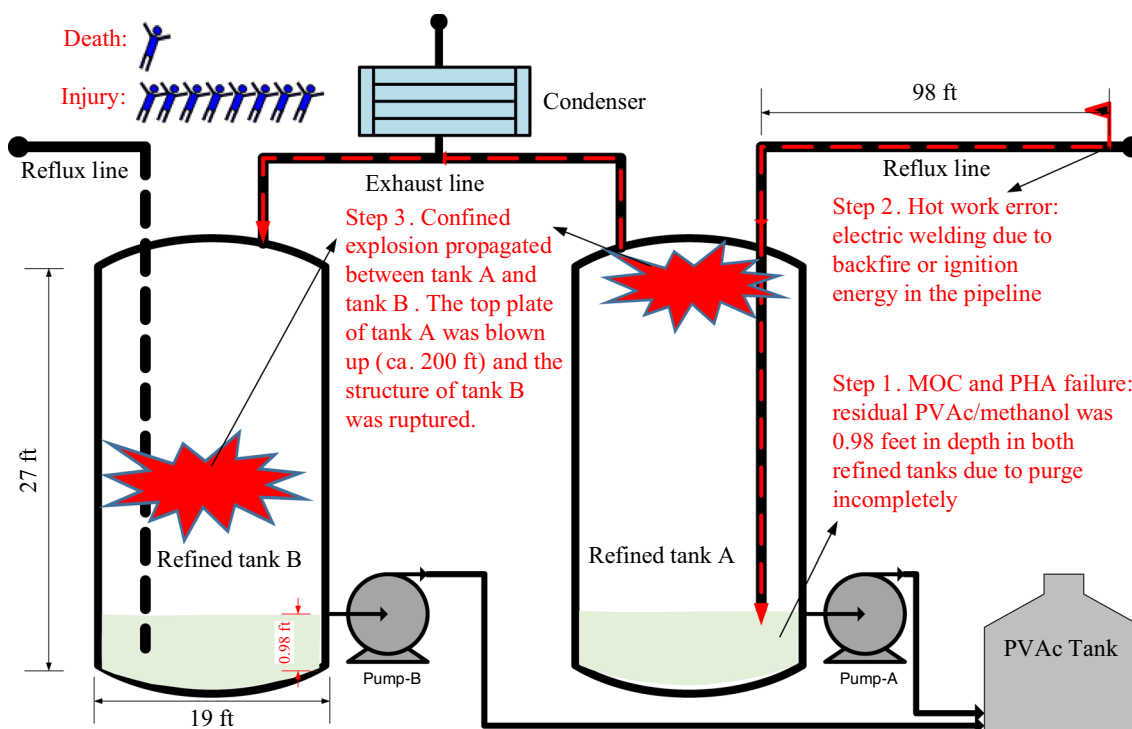
Fig. 2 Scheme of an explosion accident that occurred in two PVAc refined tanks due to a lack of proper hot work management

example, to ensure that the thermocouple junction measures the battery surface temperature, it was covered with thermal insulating tapes to prevent heat loss. The sample was inserted into a guard heater assembly with thermal insulating wool to maintain an adiabatic environment. The calibrations for both temperature and pressure connected to the measuring calorimeter were performed by the adjustable potentiometers in the present results. Furthermore, VSP2 was used to evaluate the thermal runaway reaction for the polymerizing process under an adiabatic condition to determine the profiles of temperature and pressure, which include exothermic onset temperature (T_0), maximum temperature (T_{max}), maximum pressure (P_{max}), self-heating rate (dT/dt), and pressure elevation rate (dP/dt), for fast exothermic reactions and to ascertain abnormal process conditions.
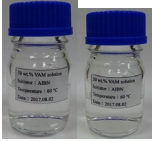
Results and discussion

Thermal analysis data using DSC1

We first used a Brookfield dial viscometer to measure the viscosity of 30%, 50%, 70%, and 100% VAM solutions after their polymerization initiated by AIBN in the oven isothermal tests. The apparent polymerizations of various VAM

solutions are displayed in Table 1, except for the 30% VAM solution.

To identify potential exotherms in the process units, it is necessary to understand the properties of energetic chemicals and reaction conditions. Thermal instability of the VAM/MeOH solution initiating AIBN for polymerizing was examined by DSC1 with a dynamic program scan. Table 2 and Fig. 3 display the exothermal properties of 50, 70, and 100 mass% VAM/MeOH solution containing 3 ppm HQ inhibitor, and their polymerizations were initiated by 300 ppm AIBN at elevated temperatures. AIBN 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, but it can release an abundance of heat during decomposition ($\Delta H_d = 2072.3$ J g^{-1}) due to its high thermal sensitivity and reactivity [24, 25]. Industrially, VAM should be distilled to remove the inhibitors increasing the conversion of VAM polymerization. In terms of reaction heat, VAM is more stable, with a substantially lower enthalpy change than polyvinyl acetate ($\Delta H_c = 1095.41–1156.64$ J g^{-1}) [26]. The earliest onset temperature for 100 mass% VAM was 93.5 °C, and its concentration increased thermal stability for the VAM solution. The highest heat of polymerization in the tests was 100 mass% VAM (747.2 J g^{-1}), initiated at the earliest temperature of 93.5 °C. From DSC1 thermal analysis, onset temperatures for thermal self-polymerizing of

Table 1 Viscosity and state of polymerization for 30, 50, 70, and 100 mass% VAM solutions in the oven isothermal tests

VAM/MeOH/ mass%	Mass/g	AIBN/mg	Oven Temperature/°C	Viscosity/Cp	State of polymerization	Images before and after polymerization
30%[*]	50	15	40	1	Colorless liquids	
			50	1		
			60	1		
50%	50	15	40	1	Colorless viscose	
			50	1		
			60	ca. 1.5		
70%	50	15	40	1	Colloids	
			50	1		
			60	10,000		
100	50	15	40	1	Solids	
			50	1		
			60	30,000		

*30% VAM has insignificant polymerization

50, 80, and 100 mass% VAM/MeOH solution were initiated at 93.5 °C–106.3 °C, and ΔH_p for the testing VAM solution ranged between 350.6 J g^{-1} and 747.2 J g^{-1} in thermal dynamic scanning tests. A variation occurs in the polymerization mechanism regarding the initiator or heat source. A material is considered hazardous if the heat of decomposition exceeds 200–300 kJ g^{-1} in terms of chemical and thermal stability [27]. Generally, VAM should be considered an energetic chemical because its ΔH_p exceeds 300 J g^{-1}. Polymerizing reactions of monomers occur in the presence of catalysts to form polymers or other large molecular structures by chaining and cross-linking. The polymerization is generally self-sustaining once initiated and accompanied by highly exothermic reactions. It should account for the thermal runaway reaction of VAM polymerization reacting with AIBN during processing. Furthermore, higher monomer concentration increases the reaction's conversion, raising the polymerization's enthalpy change.

## Thermal runaway evaluation of VAM polymerization using adiabatic calorimetry

The calorimetric experiments of 50, 70, and 100 mass% VAM solutions were tested using VSP2 to evaluate the reaction system, including exothermic nature polymerization, pressure evolution, and upset thermal runaway potential of polymerizing reagents. The calorimetric data are illustrated in Table 3.

The variance between temperature and pressure ascending curves in Fig. 4 showed that the VAM solution vaporized quickly at ambient temperature, resulting in high vapor pressure that increased with temperature. The rates of self-heating reaction and pressure elevation for VAM solutions at various concentrations are compared in Figs. 5 and 6. The gas evolution of the 50 mass% VAM solution was larger than that of the other two solutions, and its P_{max}, $(dT/dt)_{max}$, and $(dP/dt)_{max}$ were 334.8 psig, 44.86 °C min^{-1}, and 164.0 psi min^{-1}, respectively. However, the maximum $(dT/dt)_{max}$ and $(dP/dt)_{max}$

Table 2 Thermal analysis data of VAM solution for polymerization using DSC1

VAM/MeOH/ mass%	Mass/mg	Onset temperature T_0/ °C	Heat of polymerization[**] ΔH_p/ J•g^{-1}	Peak temperature/°C
50	6.0	106.3	350.6	114.3
70	5.8	104.7	597.1	113.1
100	6.0	93.5	747.2	107.1

Note:[*] VAM stabilized with 3 ppm of HQ and VAM solution was initiated using 0.1 g AIBN
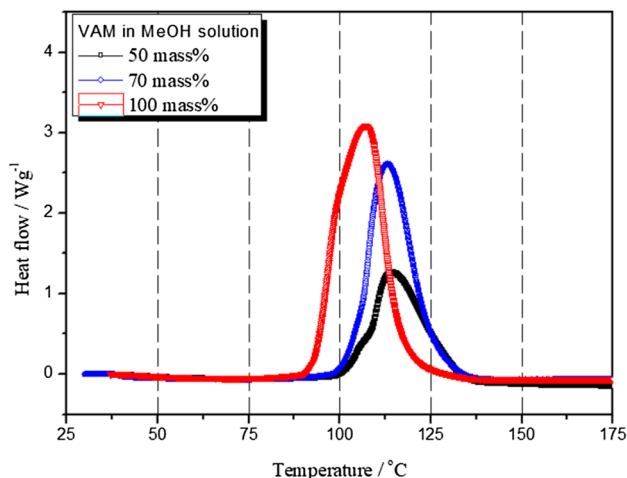
Fig. 3 Thermal curves of various polymerization of VAM solutions for initiating with AIBN

of 100 mass% VAM were approximately 105.3 °C min^{-1} and 310.1 psi min^{-1}, respectively. According to the VSP2 experimental data, the initial self-heating temperature of VAM solutions ranged between 80.5 °C and 90.5 °C, indicating that a spontaneous self-heating reaction might be induced near the operation temperature of 60.0 °C–70.0 °C during VAM–PVAc process. The substantial gas evolution with VAM solutions should raise safety concerns for processing and storage.

Furthermore, measuring the adiabatic temperature increase as a function of time can yield the apparent runaway model. Therefore, the initial temperature and maximum rate of pressure rise in a reaction system are crucial for process safety. Because an explosion would undergo an increasing rate of pressure elevation after initiating the runaway process, if overpressure in the reactor or tank with an inadequate relief system occurs during the runaway reaction, a severe accident, such as fire and explosion, will occur, potentially devastating the plant and surrounding areas for flammable and reactive VAM solution.

Self-heating model for VAM solutions polymerization

Calorimetric tests and thermal analysis methodologies were applied to estimate the reaction kinetics of VAM polymerization and verify the self-heating model of various concentrations of VAM solutions. The n-order reaction of VAM–PVAc without a catalyst is a homogeneous process that needs high energy to complete the polymerization [18]. Additionally, the 2nd reaction order gave the highest VAM–PVAc polymerization rate [28, 29]. Cheng et al. [26] proposed a self-heating model of VAM self-sustaining decomposition with a first-order reaction. The polymerization rate of VAM–PVAc obeyed an nth order reaction as follows:

$$\frac{d[C_{VAM}]}{dt} = -k[C_{VAM}]^n = -k_0\exp[\frac{-E_a}{RT}][C_{VAM}]^n \quad (4)$$

where k is a rate constant as an exponential function of temperature, k_0 is an Arrhenius rate constant, R is an ideal gas constant (8.314 J mol^{-1} °C^{-1}), E_a is the activation energy, and $[C_{VAM}]$ is the concentration of VAM.

To consider the self-heating rate of VAM–PVAc polymerization in thermal runaway reactions, the kinetic data relating to the temperature dependence can be evaluated from the adiabatic calorimetry method. Furthermore, the variations of the self-heating rate for various VAM solutions could be calculated by applying Arrhenius kinetic model, which is proposed by a simplified thermal analytic solution to describe the self-heating rate for VAM:

Table 3 VSP2 adiabatic experimental data for 50, 70 and 100 mass% VAM solutions

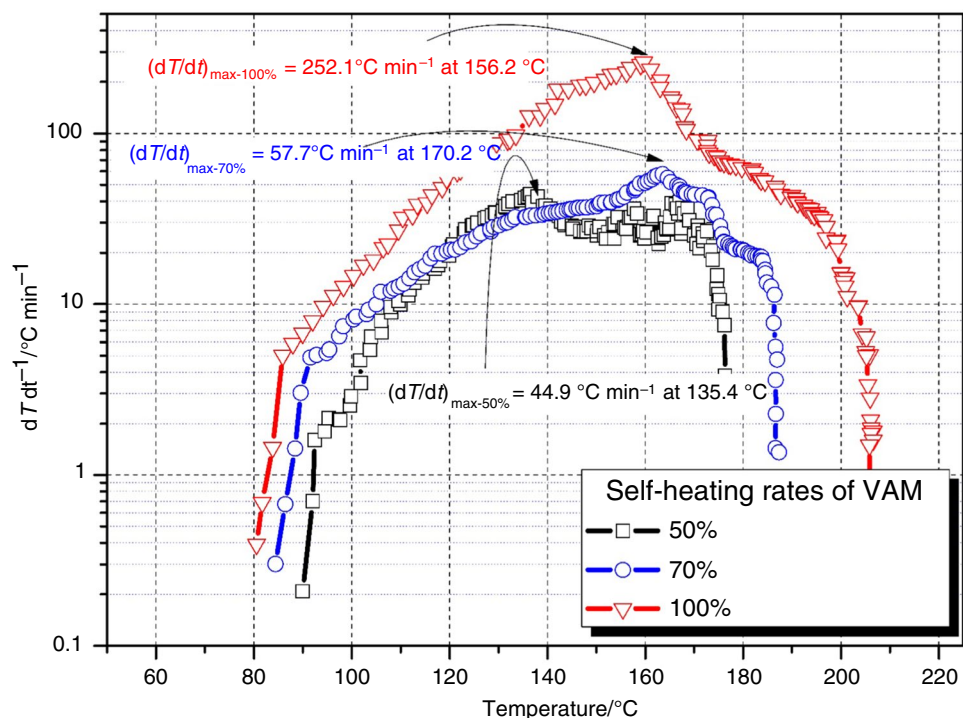| VAM/MeOH[a]/ mass%	50	70	100
Mass/g	50	50	50
T_0/°C	90.0	84.4	80.5
T_{max}/°C	176.5	187.9	208.0
ΔT_{ad} (°C)	86.5	103.5	127.5
$(dT\ dt^{-1})_{max}$ /°C min^{-1}	44.9	57.7	252.1
P_{max}/psig	334.8	318.9	272.4
$(dP\ dt^{-1})_{max}$/psi min^{-1}	164.0	153.3	310.1
$\varnothing$ [b]	1.15	1.16	1.17
Residual mass[c] /g	47.6	40.4	42.1

a Thermal runaway testings' of various VAM solutions were initiated using 300 ppm AIBN, respectively. [b] Thermal inertia (Φ) is defined as $\varnothing = (m_s c_{p-s} + m_v c_{p-v})/m_s c_{p-s}$ related to both the mass and heat capacity of the sample (m_s and c_{p-s}) and test vessel (m_v and c_{c-v}), where the heat capacity of VAM, MeOH, and the container is 1.97, 2.53, and 0.5 J g^{-1} K^{-1}, respectively; the heat capacity of solution involving VAM (m_{VAM}; c_{p-VAM}) and MeOH (m_{MeOH}; c_{p-MeOH}) is $m_s = m_{VAM}•c_{p-VAM} + m_{MeOH}•c_{p-MeOH}$ [16]. [c] mass of the residual sample after a VSP2 test

Fig. 4 Temperature versus pressure curves for 50, 70, and 100 mass% VAM in VSP2 trials
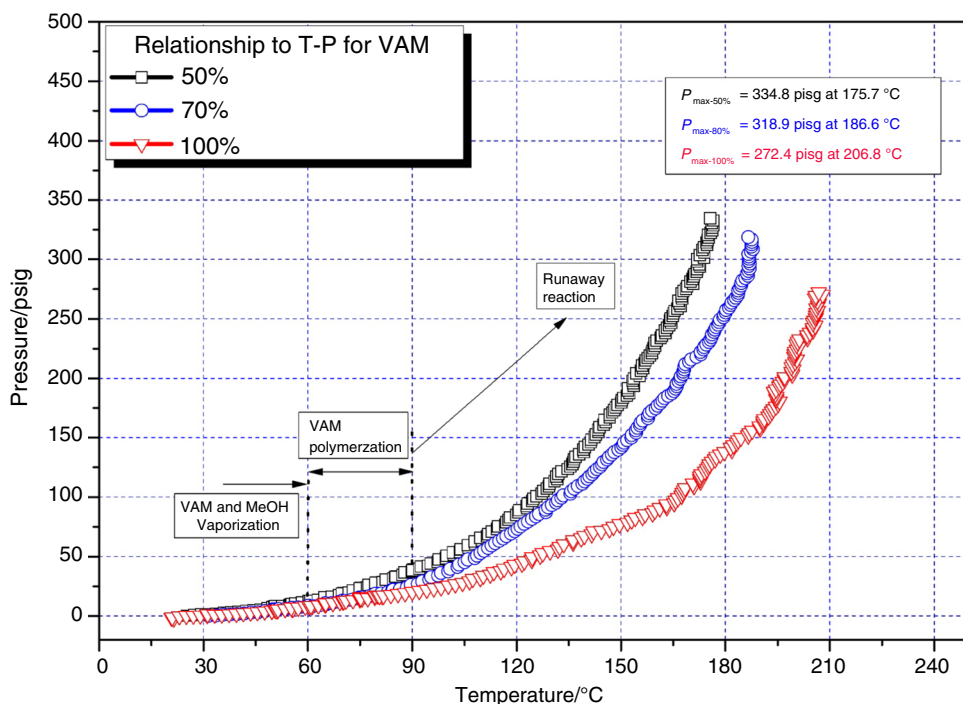
Fig. 5 Self-heating rate versus temperature for 50, 70, and 100 mass% VAM solutions in VSP2 trials


$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{VAM}} = \Delta T_{\mathrm{ad}} \cdot k_0 \cdot \exp\left[\frac{-E_{\mathrm{a}}}{\mathrm{RT}}\right]\left[1 - \frac{(T_{\max} - T)}{\Delta T_{\mathrm{ad}}}\right]^n \quad (5)$$

$$\ln\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{VAM}} \cong \ln\left(\Delta T_{\mathrm{ad}} \cdot k_0\right) - \left(\frac{E_{\mathrm{a}}}{R}\right)\left(\frac{1}{T}\right) \quad (6)$$

The plots from the VSP2 adiabatic experiments can be used to evaluate the kinetic reaction data. It can also examine the fundamentals of heat generation in a VAM polymerizing system and develop a kinetic reaction model in agreement with the Arrhenius kinetic equation under adiabatic conditions. The kinetic parameters for various Cu-etching solutions (Fig. 2) can be calculated

Fig. 6 Pressure elevation rate versus temperature for 50, 70, and 100 mass% VAM solutions in VSP2 trials
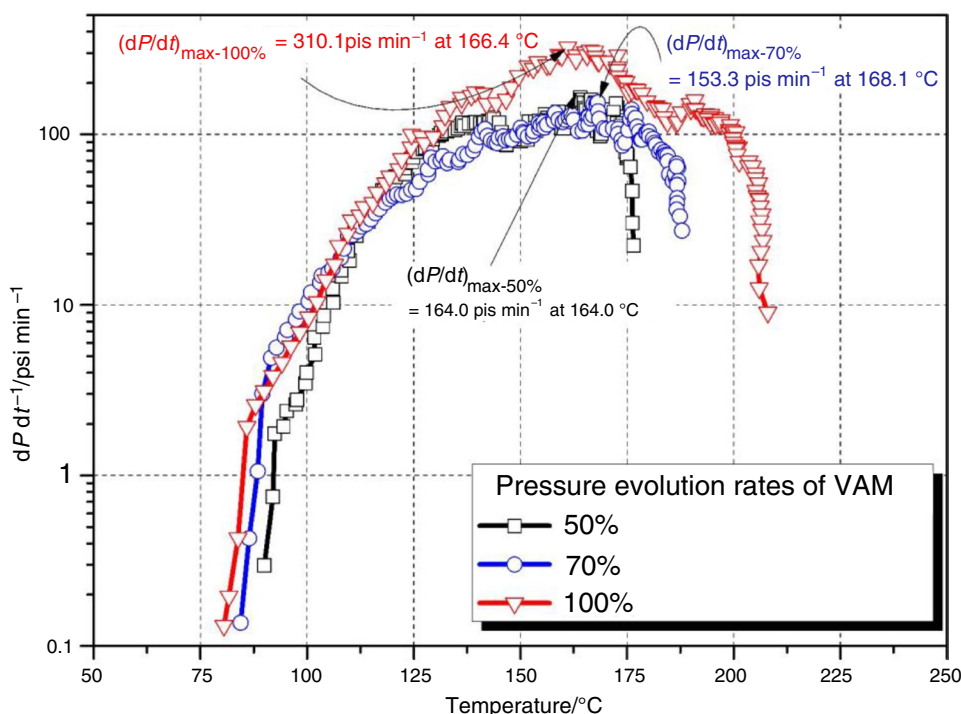
Table 4 Kinetic parameters evaluations of 50, 70, and 100 mass% VAM solutions from VSP2 adiabatic tests

VAM	$-E/R$	E_a/KJ mol^{-1}	$\ln/k_0 \cdot \Delta T_{ad}$	ΔT_{ad}	k_0
50 mass%	-12.512	104.0	34.795	86.5	1.49×10^{13}
70 mass%	-5.7584	47.9	17.55	103.5	4.05×10^{5}
100 mass%	-8.4193	70.0	25.264	127.5	7.35×10^{8}

from the VSP2 experimentally measured self-heating rate. According to Eq. (6), the plot of ln (dT/dt) versus (1/T), in which the product of ($\Delta T_{ad} \cdot k_0$), is the intercept and E_a is calculated from its slope (E_a/R). The particular kinetic data can be commonly characterized using the empirical Arrhenius relationship. The activation energy (E_a) and reaction rate constant (k_0) for various concentrations of VAM solutions are listed in Table 4, which were evaluated from Fig. 7.

The self-heating model ((dT dt^{-1})$_{sim}$) for various VAM emulsion polymerization can be obeyed by an n-order reaction and applying the Arrhenius kinetic equation. The adiabatic calorimetry data in this study are used to estimate the nth order reaction kinetic data for the thermal runaway of VAM solutions. The self-heating model of VAM can be evaluated from the thermokinetic method using the adiabatic calorimetry test from Eqs. (5) and (6). Figure 8 illustrates the self-heating reaction rates involving VSP2 adiabatic experiments and C++ program simulations for the VAM solutions in the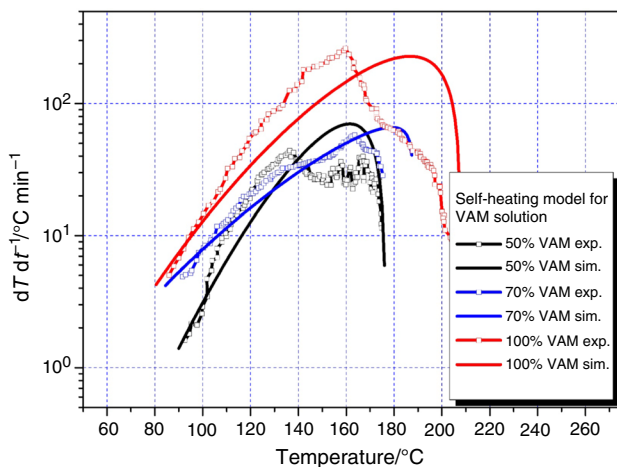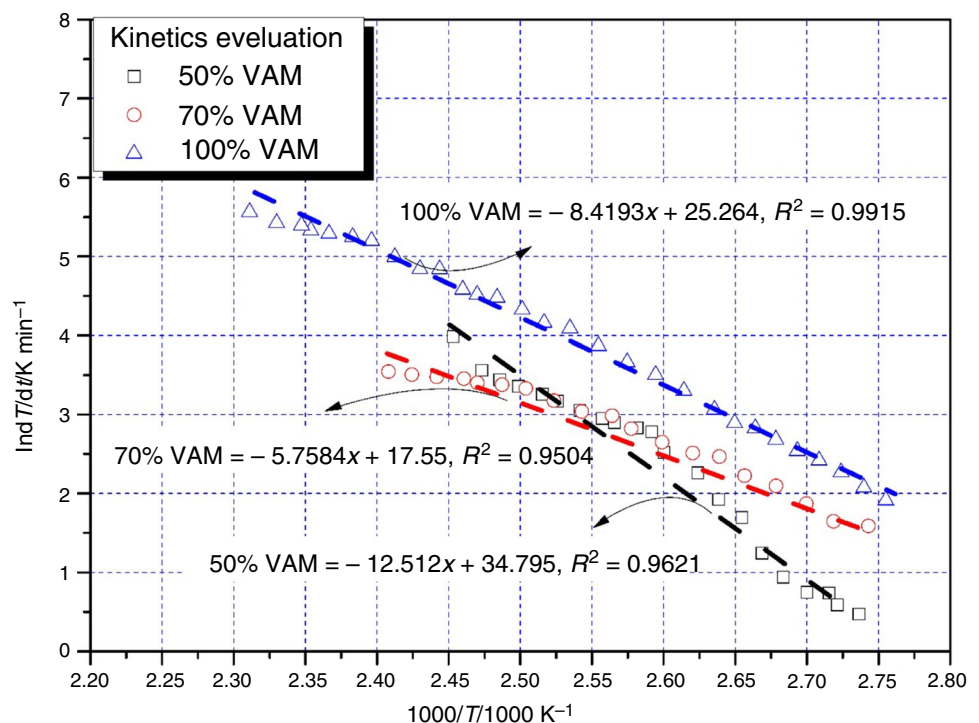 case of emulsion polymerization. Under adiabatic conditions, the VAM solutions underwent a thermal runaway. The self-heating rates were fitted to VSP2 experimental data respecting various VAM solutions. The n values for the 50%, 70%, and 100% VAM solutions were 1, 0.25, and 0.85, respectively.

Conclusions

VAM–PVAc emulsion polymerization is an exothermic reaction, and its thermal unstable potential might induce a runaway risk at abnormal conditions or elevated temperatures. The polymerization of VAM forms a large of molecules accompanied by significant quantities of heat release and pressure elevation. Thus, VAM might not proceed with a significant polymerizing reaction from catalyst initiation at elevated temperatures. Moreover, an initiator catalyzing a reaction with the monomers should take thermal runaway into account. The heat of VAM–PVAc emulsion polymerization increased with their concentrations. The measurement of the temperature–pressure–time profile of VAM–PVAc emulsion polymerizations using adiabatic calorimetry can particularly outline the runaway procedure for process safety precautions. The normal operation temperatures of VAM–PVAc emulsion polymerization range between 60 °C and 90 °C; if temperatures exceed this scheme, a thermal runaway will occur. Furthermore, higher concentrations of the VAM/MeOH polymerizing process need to control the operation temperature below 80 °C to prevent a self-heating reaction.

Fig. 7 Kinetic plots for various VAM solutions using VSP2 adiabatic tests

$$100\%\ VAM = -8.4193x + 25.264,\ R^2 = 0.9915$$

$$70\%\ VAM = -5.7584x + 17.55,\ R^2 = 0.9504$$

$$50\%\ VAM = -12.512x + 34.795,\ R^2 = 0.9621$$

Fig. 8 Self-heating models for 50%, 70%, and 100% VAM are simulated to compare the calorimetric experiment

The worst case might result in a runaway reaction if the VAM–PVAc polymerization process is out of control because of wrong feeding, high process temperatures, and containments, etc. The flammable and reactive deviations from VAM–PVAc could damage workers or destroy the facilities in the plant. Therefore, emergency response to uncontrolled reactions involving monomers should be planned carefully for feeding inhibitors to prevent the onset or cut off of a polymerization. The results of this study illustrated that the self-heating rate of VAM–PVAc polymerization increased with its concentration. Adiabatic calorimetric tests and thermal analysis combined with a self-heating model can effectively understand exothermic behaviors and provide an emergency relief design for VAM–PVAc emulsion polymerization.

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