



Thermal hazard evaluation of runaway polymerization of acrylic acid

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ABSTRACT

To clarify the thermal hazards of acrylic acid runaway polymerization, the amount of energy release and the products in each event of the polymerization sequence were investigated. The thermal hazard was analyzed using accelerating rate calorimetry (ARC), Karl-Fisher titration, and thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS). The present study revealed that acrylic acid generates water, which increases the impact of tank destruction when the tank filling level is more than 15%. In addition, the Michael addition reaction of acrylic acid induces the monomer to polymerize due to its exotherm and produce Michael adducts, which generate larger amounts of gases and water than does the monomer. Therefore, the accumulation of Michael adducts increases the frequency of crack initiation in the tank, as well as the potential for tank destruction, due to the presence of monomer and water in the tank at a lower filling level than in the case of monomer alone. The present study determined that the accumulation of Michael adducts is the worst case scenario for accidents caused by acrylic acid.

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1. Introduction

In 2012, an explosion and subsequent fire occurred in a chemical plant in Japan, killing one person and injuring 36. The investigation report (Nippon shokubai Co., Ltd., 2013) stated that the runaway polymerization of acrylic acid occurred in its intermediate storage tank.

Acrylic acid is one of the most common feedstocks for acrylic resins and water absorptive polymers. It is prone to free radical polymerization, which releases a large amount of heat. Once the runaway polymerization of substances is initiated, it is difficult to restore the normal condition because of the gel effect, which auto-accelerates the reaction due to the viscous medium and massive rates of heat production (O'Shaughnessy and Yu, 1994; O'Neil et al., 1996; Verros and Achillas, 2009). Acrylic acid runaway polymerization has caused many accidents in chemical industries (Center for Chemical Process Safety, CCPS, 1995; Levy and Penrod, 1989; Kao and Hu, 2002; Kalfas et al., 2009; Gromacki, 2000; Kurland and Bryant, 1987; Gustin, 2002; Ogiso and Uehara, 1986; Pfeifer et al., 2016). King (1990) described that when a runaway polymerization occurs in a storage tank of liquid monomers, the temperature of the unpolymerized material will increase until it reaches its

boiling point, and then boil vigorously as the rest of it polymerizes. With large storage tanks and pressurized spheres, the flow of escaping vapor may be so large that it is impossible to contain or dispose of safely. In more severe cases, the unpolymerized monomers cause a boiling liquid expanding vapor explosion (BLEVE). BLEVE causes severe damage due to the overpressure wave and ejected fragments. BLEVE originates as follows (Prugh, 1991; Center for Chemical Process Safety, CCPS, 1994; Bosch and Weterings, 1997): when a vessel containing a pressure-liquefied gas ruptures, the vapor that was hitherto in equilibrium with its liquid, begins to blow off. As a result, the liquid pressure drops rapidly, equilibrium is lost, and the liquid is suddenly rendered "superheated" as its temperature is now way above its boiling point at the accidentally reduced pressure (Abbasi and Abbasi, 2007).

For accident prevention and damage control, safety countermeasures are essential. These safety countermeasures must correspond to the impact of the explosion phenomena, which depends on the materials in the tanks just before crack generation. Thus, it is necessary to characterize the materials and the products by tracing every event in the runaway polymerization. The aim of the present study is to gain a better understanding of the thermal hazard of acrylic acid runaway polymerization. To that end, we constructed an acrylic acid tank explosion scenario that would explain the progress of runaway polymerization of acrylic acid.

There are many reports in the literature of reactions related to acrylic acid. It is known that radical inhibitors such as hydroquinone

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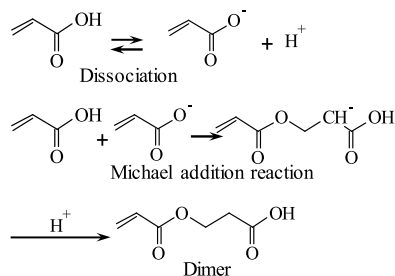


Fig. 1. Acrylic acid dimer formation by Michael addition reaction.

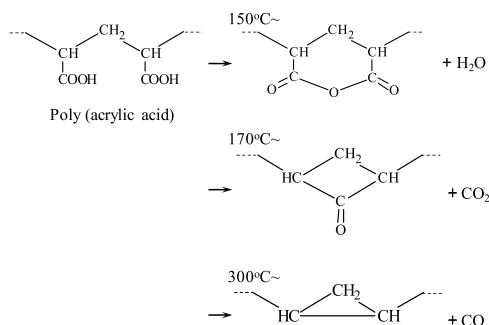


Fig. 2. Thermal decomposition mechanism of acrylic acid polymer, poly-(acrylic acid) (Maurer et al., 1987).

and *p*-methoxyphenol cannot inhibit radical initiation when the concentrations of the inhibitors and oxygen are insufficient (Krause et al., 2014). A differential scanning calorimetry study at 10 K min^{-1} heating rate (Kao and Hu, 2002) determined that the onset temperature of acrylic acid containing 0.02 wt% inhibitor was 145°C and the heat value was 1064 J g^{-1} , which agrees with the theoretical value of acrylic acid polymerization of 1076 J g^{-1} .

Acrylic acid undergoes a mild and slow reaction called a Michael addition reaction (MAR). This reaction proceeds exothermically via an ionic mechanism as shown in Fig. 1 and no inhibitors are known to be effective for retarding or preventing it (Basic Acrylic Monomer Manufacturers, Inc., BMM, 2013). The rate of dimer formation is temperature dependent. For example, after one month at 30°C , about 1.2 wt% dimer is formed. MAR is one of the causes of the increasing temperature in acrylic acid (Levy and Penrod, 1989; Krause et al., 2014). The heat generation is small (heat of dimer formation: $130\text{--}150 \text{ J g}^{-1}$ (Levy and Penrod, 1989)) and the reaction rate is slow (rate of dimer formation: $0.02 \text{ wt\% day}^{-1}$ at 25°C (Basic Acrylic Monomer Manufacturers, Inc., BMM, 2013)). The Michael addition dimer formation is important to consider for quality control (Rohm and Haas Co., Ltd., 1987; Hartwig et al., 2011). Furthermore, in an adiabatic test of acrylic acid (Nippon shokubai Co., Ltd., 2013), the temperature rose to more than 180°C from 90°C despite an excess amount of radical inhibitor. After the test, there were Michael addition dimers, trimers and radical polymers in the test vessel. Therefore, MAR can be a cause of polymerization initiation and complicate the composition in the tank.

The thermal decomposition mechanism of the acrylic acid polymer has been reported (Dubinsky et al., 2004; Maurer et al., 1987). The polymer decomposes and evolves water and carbon dioxide via side chain desorption over 150°C as shown in Fig. 2. The existence of water intensifies the impact of BLEVE as determined experimentally (Prugh, 1991; Salla et al., 2006; Hemmatian et al., 2019). The energy released from a water BLEVE will be significantly stronger than that originating from the same amount of other substances (Hemmatian et al., 2019). Therefore, the impact of BLEVE increases if water induced by thermal decomposition of the acrylic acid polymer exists in the tank.

We constructed a model of the contents in the tank at the moment of rupture caused by runaway polymerization, shown in Fig. 3. Our model included two scenarios: first, thermal decomposition of polymer and, second, accumulation of Michael adducts. In the thermal decomposition scenario, the polymer produced by unintended radical initiation of acrylic acid decomposes to water, which may increase the impact of the explosion phenomena including BLEVE. On the other hand, in the accumulation scenario, Michael adducts and the reaction products of runaway polymerization can exist in the tank and potentially increase the risk of tank explosion.

The present study verified our model based on experimental studies. We performed accelerating rate calorimetry (ARC) to understand the events occurring in an adiabatic system, such as a storage tank during a runaway polymerization. To assess the effect of the filling level, which affects the adiabaticity in the sample bomb, we tested various filling levels. We investigated not only thermal characteristics but also the products of the runaway reaction to understand the liquid materials in the tank just before rupture. To clarify the products of the acrylic acid polymer thermal decomposition after self-polymerization, we used thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS). A closed vessel heating test, which demonstrated the successive reactions from thermal polymerization to polymer thermal decomposition, was conducted to analyze the products after the reactions using Karl-Fisher titration. To examine the accumulation of Michael adducts scenario, we prepared the acrylic acid Michael dimer as well as the monomer in the closed vessel heating test.

2. Experimental

2.1. Materials

Acrylic acid (99.6%) and *p*-methoxyphenol (hydroquinone monomethyl ether: MQ) as a radical inhibitor were obtained from Kanto Chemical. In the present study, to examine the accumulation of Michael adducts scenario, we prepared samples containing 0.1 wt% MQ, which is a concentration five times higher than that of an industrially suitable concentration (Center for Chemical Process Safety, CCPS, 1995). These samples begin polymerizing at a higher temperature with MAR proceeding for a prolonged time. The Michael addition dimer of acrylic acid was obtained from Sigma-Aldrich as 2-carboxyethyl acrylate containing 0.1 wt% MQ.

2.2. Accelerating rate calorimetry (ARC)

ARC has been used worldwide (dos Santos et al., 2014; Babasak et al., 2015; Ma et al., 2016; Bhattacharya, 2005) to evaluate the runaway hazards of chemical reaction processes. A schematic diagram of the ARC is shown in Fig. 4. ARC can measure self-heat rate, pressure, and pressure rate in the pseudo-adiabatic condition to analyze and assess thermal hazards. In the present study, a TIA ARC was used to compare the runaway polymerization hazards of acrylic acid monomer (AA) and its Michael addition dimer (DAA). The sample amounts were 2 g and 4 g to measure the difference in self-acceleration due to a difference in the filling level. The bomb material for ARC was Titanium 9 mL. The volume of the pipeline to a pressure transducer was 5 mL. Hence, the total volume of the bomb and pipeline was 14 mL. The experimental atmosphere was air to activate the MQ. ARC was run in heat-wait-search (HWS) mode. The heating step was 5°C . The exothermic detection threshold was $0.02^\circ\text{C min}^{-1}$. The time searching exothermic was 15 min, and the starting temperature was 50°C .

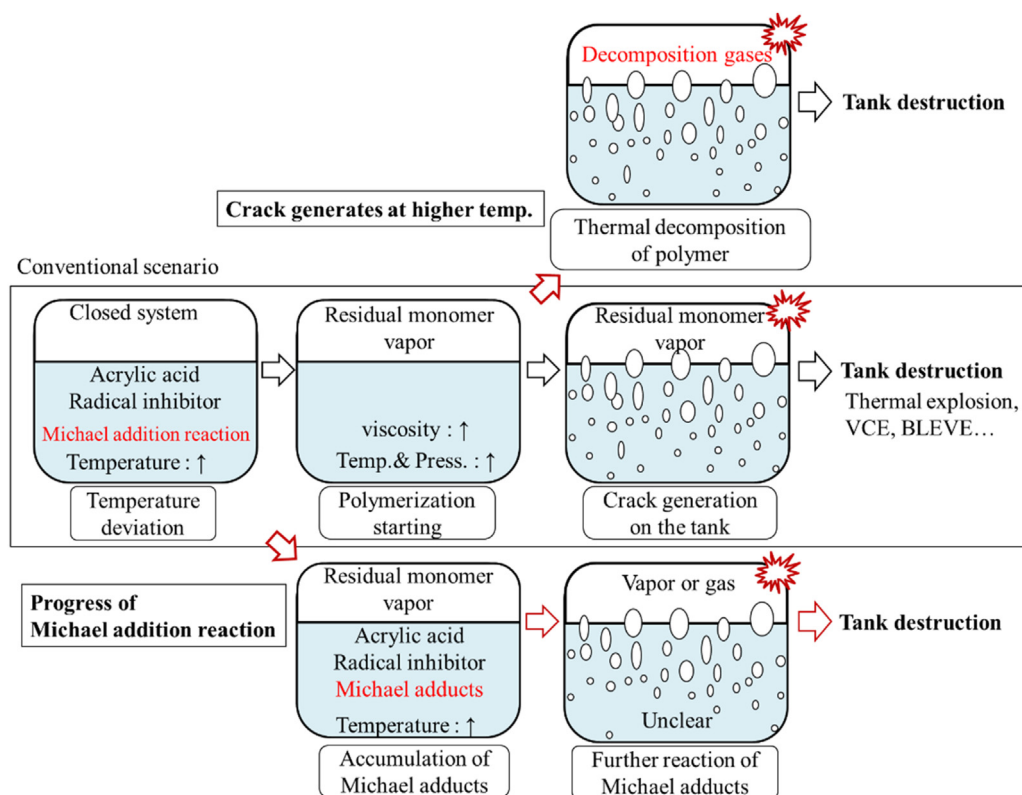


Fig. 3. Model of the acrylic acid tank explosion scenario.

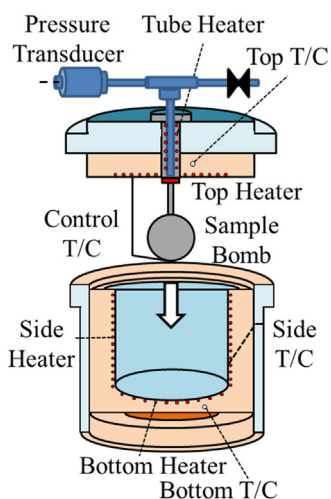


Fig. 4. Schematic of adiabatic rate calorimeter (ARC).

2.3. Evolved gas analysis of acrylic acid polymer using TG-DTA-MS

The sample polymer was prepared by self-polymerization of acrylic acid tempered at 130 °C for 3 h. The TG-DTA-MS apparatus consisted of a Rigaku TG8120 and Shimadzu GCMS-QP2010 connected as shown in Fig. 5, which is employed for thermal analysis of polymers (Parra et al., 2002) and energetic salts (Izato and Miyake, 2015). The connecting line and transfer tube were tempered at 200 °C. The 2 mg sample was placed in an Al pinhole pan. The blank Al pinhole pan was used as a reference. The experimental temperature range was 50–500 °C at a heating rate of 5 K min⁻¹. The helium carrier gas was flowed at 50 mL min⁻¹.

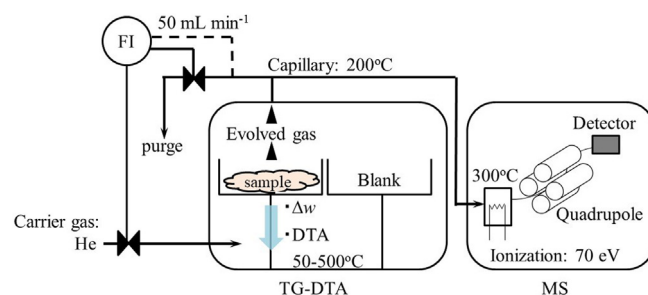


Fig. 5. Schematic of TG-DTA-MS apparatus.

2.4. Closed vessel heating test for demonstration of superheated water generation

A closed vessel heating test was conducted using a ceramic electrical furnace as shown in Fig. 6. We defined the filling level criterion (C_{FL}) as an original value for hazard evaluation. C_{FL} is the filling level at which superheated water can be present as a liquid in the tank after the runaway polymerization of acrylic acid. The water is generated by sequential phenomena, which include polymerization and self-accelerating polymer thermal decomposition. Theoretically, condensable gases can be liquefied in a tank when the vapor pressure (P_v) equal to inner gas pressure (P_g). Therefore, C_{FL} is the ratio of sample volume (V_s) to container volume (V_c), V_s/V_c , when P_v equals P_g at maximum temperature during runaway polymerization due to self-acceleration. P_v can be calculated based on the liquid composition and Antoine coefficients of water and acrylic acid (Yaws and Yang, 1989). In this calculation, any liquid other than water is assumed to be acrylic acid monomer. Given that the liquid components are only water and acrylic acid, the vapor pressure can

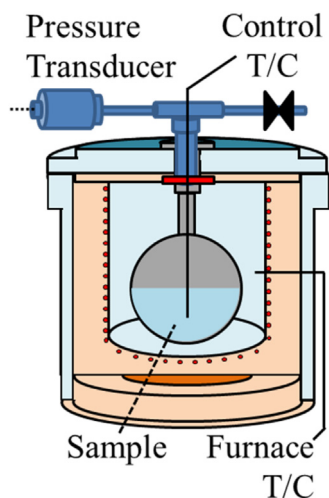


Fig. 6. Overview of the closed vessel heating test apparatus.

be calculated as below by Raoult's law,

$$P_v(T) = \left\{ \frac{r_w \times M_s}{MW_w} \times p_w(T) + x_{AA} \times \frac{1}{MW_{AA}} \times p_{AA}(T) \right\} \times \left\{ \frac{r_w \times M_s}{MW_w} + x_{AA} \times \frac{1}{MW_{AA}} \right\}^{-1} \quad (1)$$

where r_w : water generation ratio [g/g], M_s : weight of sample [g]; p_w, p_{AA} : partial vapor pressure estimated using Antoine coefficient of each material [MPaG]; x_{AA} : residual (unreacted) ratio of liquid acrylic acid [-]; MW_w, MW_{AA} : molecular weight of water and acrylic acid [g mol⁻¹]; p_w, p_{AA} : partial pressure of water and acrylic acid [MPaG]; T : Temperature [K]. The water generation ratio (r_w) is a ratio between the weight of water generated and that of the original acrylic acid.

P_g can be described as below according to the gas state equation,

$$P_g(T) = \frac{n_s \times r_g \times RT}{V_c - V_s} \quad (2)$$

When P_g equals P_v , V_s/V_c is C_{FL} . Hence,

$$C_{FL} = \left(1 + \frac{n_s \times r_g \times RT_{max}}{P_v(T_{max}) \times V} \right)^{-1} \quad (3)$$

where C_{FL} : the criterion of filling level [-]; r_g : gasification ratio [-]; n_s : moles of sample [mol]; R : gas constant [J mol⁻¹ K⁻¹]; T_{max} : maximum temperature due to self-acceleration measured by ARC [K]; P_v : saturated vapor pressure [MPaG]; V : gas volume in the test vessel ($V = V_c - V_s$) [mL].

The water generation ratio increases as polymerization progresses. The water generation ratio must be estimated when the polymerization is at its maximum. Therefore, we estimated the residual liquid ratio, x_{AA} in Eq. (1), based on the mass of liquid in the vessel after the test and after cooling the sample to ambient temperature. x_{AA} becomes smaller upon the conversion of acrylic acid to a solid. When the residual liquid ratio is small, the conversion to solid is viewed as high. The saturated vapor pressure was calculated at the maximum conversion to solid. The water composition in the liquid can be determined from the water generation ratio. The maximum pressure in the container is then estimated based on the gasification ratio, temperature, material mass and gas volume.

Samples were acrylic acid monomer and Michael addition dimer, both containing 0.1 wt% MQ. The sample weights were 2 g and 4 g. The sample bomb for the ARC test was used as the sample container. The total volume of the bomb and pipeline to the pressure transducer was 25 mL. First, the sample was tempered above

the polymerization starting temperature determined by the ARC test to obtain the thermal polymer. The sample was then heated and tempered at T_{max} obtained by the ARC test to yield the decomposition products of the polymer. After the heating test, the liquid products were analyzed using a Karl-Fisher titration instrument to determine the water abundance ratio from the runaway polymerization of acrylic acid. The liquid products were recovered in the vacuum trap by condensation in liquid nitrogen. In the Karl-Fisher titration, we used Hiranuma AQV-2100 as the automatic titration machine and Sigma-Aldrich HYDRANAL water-in-methanol 5.0 as the Karl-Fisher reagent. The tests were conducted more than 5 times with each sample weight and confirmed that the results of r_w and r_g were reproducible as long as x_{AA} was about the same.

3. Results and discussion

3.1. Accelerating rate calorimetry of acrylic acid

Fig. 7 shows the results of the ARC tests, with sample weights of 2 g and 4 g. The plots show the actual measured values without phi correction. The area highlighted in Fig. 7 indicates where the pressure rate is highest in the tests. For the 2 g sample, self-heat generation derived from auto-acceleration caused by the gel effect (O'Shaughnessy and Yu, 1994; O'Neil et al., 1996; Verros and Achilias, 2009) was detected from 156 °C to 202 °C, but the pressure rate did not increase during this adiabatic temperature rise. Therefore, an exothermic reaction without pressure generation occurred. Polymerization changes the volatile monomer to a low volatile and high molecular weight polymer. Hence, the exothermic reaction was polymerization. In the region around 265 °C, the pressure rate reached the maximum value. The polymer can decompose to low molecular weight material in this temperature range. In the 2 g sample test, self-heating did not reach the pressure generating temperature of around 265 °C. Therefore, the probability of tank destruction is low at this filling level. In the test, it was impossible to reproduce the adiabatic condition perfectly because the heat generated by the reactions was lost to the sample container and as the heat of vaporization. The heat loss to the sample container was corrected by the phi factor; $1 + M_b C_{p,b} / M_s C_{p,s}$, using the following equation.

$$\Delta T_{AB} = \left(1 + \frac{M_b C_{p,b}}{M_s C_{p,s}} \right) \times \Delta T = \left(1 + \frac{10.1 \text{ g} \times 0.54 \text{ J/g} \cdot \text{°C}}{2.1 \text{ g} \times 2.1 \text{ J/g} \cdot \text{°C}} \right) \times 46 \text{ °C} = 103 \text{ °C} \quad (4)$$

Therefore, the corrected value of the maximum temperature under the adiabatic condition with phi correction was 259 °C (= 156 °C + 103 °C). If the adiabaticity increases, it is possible that the self-heat of polymerization will lead to polymer thermal decomposition with the pressure increasing seamlessly.

For the 4 g sample, self-heat generation at 115–280 °C was observed. The increase in the filling level resulted in the detection of the small heat generation at 115–141 °C. This heat generation behavior could be due to that of the Michael addition reaction. This result indicates that the Michael addition reaction, which occurs even at 25 °C, leads to a transition to undesired polymerization. The detection temperature decreased with the increased filling level of the sample. In the study by Krause et al. (2014), an adiabatic hot storage test demonstrated that Michael addition of acrylic acid caused a gradual rise in temperature from 20 °C. If the filling level of the sample is larger than that in the 4 g-test, this undesired temperature rise can start at less than 115 °C. The ARC test showed the maximum temperature was 280 °C. Hence, the closed vessel heating test of AA discussed later, was conducted at 280 °C.

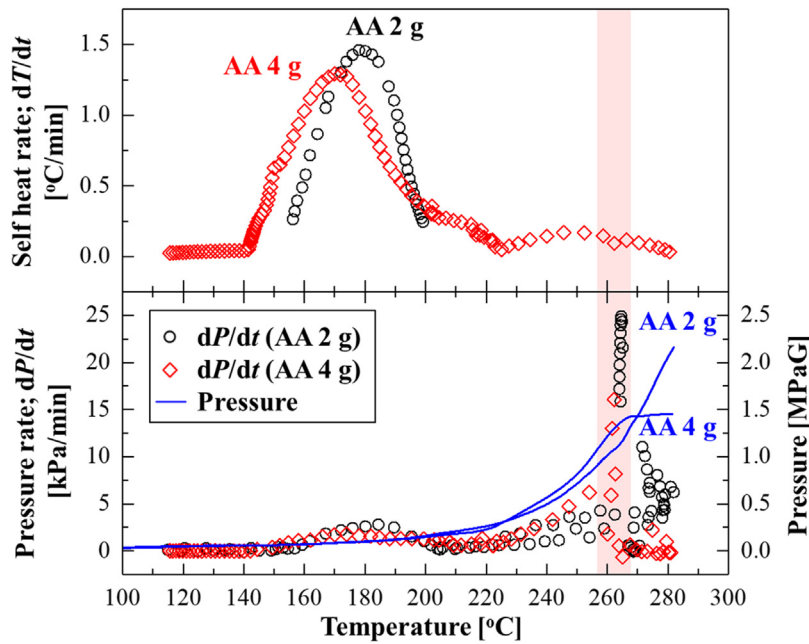


Fig. 7. ARC result of acrylic acid monomer.

Table 1

Gasification ratio in the ARC test of acrylic acid monomer.

Filling level [vol%]	16	32
Initial pressure value [MPa]	0.103	0.110
Pressure value after the ARC test [MPa]	2.85	N/A
Gasification ratio [mol/mol %]	43	–

In the ARC test, the gasification ratio, r_g , was obtained from the difference in pressure between the values at the start of the test and at the end of cooling at the same temperature as follows,

$$r_g [\text{mol/mol}\%] = \frac{n_g}{n_s} \times 100 = \frac{\left(\frac{\Delta PV}{RT}\right)}{\left(\frac{M_s}{MW_{AA}}\right)} \times 100$$

$$= \frac{\left(\frac{(P_{i,T} - P_{f,T}) \times (V_c - M_s/\rho)}{RT}\right)}{\left(\frac{M_s}{MW_{AA}}\right)} \times 100 \quad (5)$$

where n_g : amount of gasified material [mol]; n_s : amount of sample material [mol]; ΔP : pressure difference before and after the test [MPa]; V : gas volume in the sample container [mL]; R : gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]; T : temperature [K]; M_s : sample weight [g]; MW_{AA} : molecular weight of sample [g mol^{-1}]; $P_{i,T}$: pressure after the test at T [MPa]; $P_{f,T}$: pressure before the test at T [MPa]; V_c : volume of sample container [mL]; ρ : density of sample [g cm^{-3}].

Table 1 shows the calculation results of the gasification ratio. For the 2 g sample, the gasification ratio was 42.7%. The gasification ratio for the 4 g sample could not be obtained because the maximum pressure could not be measured as a result of blockage by a solid polymer produced in the line to the pressure transducer. In Fig. 7, the pressure profile of the 4 g-test was almost a constant 1.5 MPa G at more than 265 °C. It was considered that the blockage occurred at this temperature. The filling level increased the risk of blockage as well as adiabaticity in the tank. The blockage due to solid polymer in a tank would make venting and the injection of shortstopping agents physically impossible.

We succeeded in observing the heat generation of the Michael addition reaction in the 4 g sample test. The concentration of Michael adducts was estimated based on the adiabatic tempera-

ture rise calculated by the heat of the Michael addition reaction and the measured value in the ARC test. The adiabatic temperature rise is calculated as follows.

$$\Delta T_{\text{MAD}} = \frac{\Delta H}{C_{p,s}} \quad (6)$$

$$\Delta T_{\text{MAD}} = \frac{131}{2.09} = 63.6 \text{ K} \quad (7)$$

$$\Delta T = 141 - 115 = 26 \text{ K} \quad (8)$$

$$C_{\text{MAD}} = \frac{\Delta T_{\text{AB}}}{\Delta T_{\text{ad}}} \times 100 = \frac{26}{64} \times 100 = 41 \text{ wt}\% \quad (9)$$

where ΔT_{MAD} : adiabatic temperature rise due to Michael addition reaction [K]; ΔH : the heat of Michael addition reaction obtained in our previous study, 131 J g^{-1} (Fujita et al., 2017); C_{MAD} : concentration of Michael adducts [wt%]; ΔT : the measured temperature rise [K].

Therefore, 41 wt% of acrylic acid was converted to Michael adducts when the polymerization was initiated due to the heat accumulated from the Michael addition reaction at 141 °C. Run-away polymerization can start as a mixture of monomer and Michael adducts. To understand the self-accelerated heat generation of the Michael adducts, the ARC test of Michael addition dimers was conducted.

Fig. 8 shows the comparison between the monomer (AA) 2 g sample test and dimer (DAA) 2 g sample test. For DAA, a small self-heat generation was detected at 150 °C, while the self-heat generation of polymerization was detected at 260 °C. After that, the self-heat rate peaked at 283 °C and the pressure rate peaked at 290 °C. It was considered that a gasification reaction accompanied by a small heat generation occurred. The maximum pressure and polymerization initiation temperature of DAA were higher than those of AA. In the accumulation of Michael adducts scenario, the risk of tank destruction due to gasification increases.

Table 2 shows the gasification ratios calculated based on Eq. (5). The gasification ratio of DAA was 2.5 times larger than that of AA. Michael adducts gasify and generate a large amount of pressure. Therefore, we concluded that the risk of the tank destruction

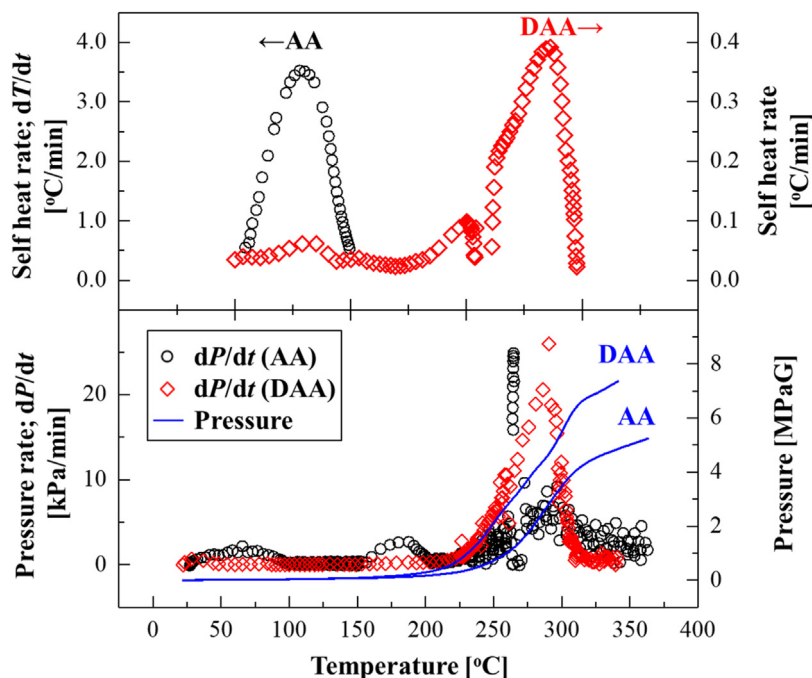


Fig. 8. ARC results of acrylic acid monomer and Michael addition dimer.

Table 2

Comparison of gasification ratios of AA and DAA.

	Gasification ratio[mol/mol %]
DAA	103
AA	43

increases as the Michael addition reaction progresses. The maximum temperature, T_{\max} , of DAA was 290 °C.

3.2. Evolved gas analysis of acrylic acid polymer

Fig. 9 shows the TG-DTA-MS results. The MS intensity curves showed that unreacted acrylic acid monomer and water were detected at 180 °C, carbon dioxide was detected at 200 °C and carbon monoxide was detected at 300 °C. The detection of unreacted acrylic acid monomer agreed with the literature (Nippon shokubai Co., Ltd., 2013). The vapor evolved from the polymer was caused by the glass transition of the polymer over 128 °C. The other evolved gases were in accordance with the previous study (Maurer et al., 1987).

The gas composition was calculated by the MS intensity of each gas. From Fig. 9, carbon dioxide was the main gaseous species. According to the decomposition mechanism of the acrylic acid polymer (Maurer et al., 1987), the ratio of carbon dioxide and water generation is 1:1. Fig. 9 shows that the amount of carbon dioxide generation was larger than that of water, indicating that the dehydrogenation had already started, and water was generated in the sample preparation at 130 °C.

Consequently, the final products of the acrylic acid runaway polymerization were unreacted acrylic acid, polymer, polymer thermal decomposition residue, water, carbon dioxide, and carbon monoxide. The water generated by the polymer thermal decomposition has the potential to amplify the impact of tank destruction if the water exists in the liquid phase in the tanks. The amount of water generated by thermal decomposition and the possibility of superheated water generation are discussed in the next section based on the results of the closed vessel heating test.

Table 3

Results of x_{AA} in the closed vessel heating test.

Sample (T_{\max})	AA (280 °C)	DAA (290 °C)
Sample weight [g](filling level [%])	4.1(16%)	2.2(7%)
Residual liquid ratio x_{AA} [-]	0.16	0.12

Table 4

Results of the criterion of filling level in the closed vessel heating test ($x_{AA} = 0.20$).

Sample (T_{\max})	AA (280 °C)	DAA (290 °C)
Sample weight [g] (filling level [%])	4.1(15%)	2.2(7%)
Water generation ratio r_w [g-water/g-sample]	0.012	0.091
Saturated vapor pressure P_v [MPaG]	2.9	4.4
Gasification ratio r_g [mol/mol %]	13%	74%
Criterion of filling level generating superheated water C_{FL} [vol%]	25%	15%

3.3. Closed vessel heating test for demonstration of superheated water generation

We determined the residual liquid ratio, x_{AA} , after the runaway polymerization in order to estimate the water generation ratio when the polymerization reached its maximum. x_{AA} becomes smaller with conversion to solid. Table 3 shows the results of x_{AA} in the closed vessel heating test. From these results, we determined that the x_{AA} is 0.20, meaning that the conversion ratio to solid polymer was more than 80% of the sample in the test. The tests were conducted more than 5 times with each sample weight and confirmed that the results of r_w and r_g were reproducible as long as x_{AA} was about the same.

Table 4 shows the results of the closed vessel heating test at T_{\max} . In the test, at less than 16% of the filling level, the pressure generation was smaller than the saturated vapor pressure in the sample container. These results mean that water generated by polymer thermal decomposition exists as a vapor in the gas phase. The calculated value is shown as the criterion of filling level generating

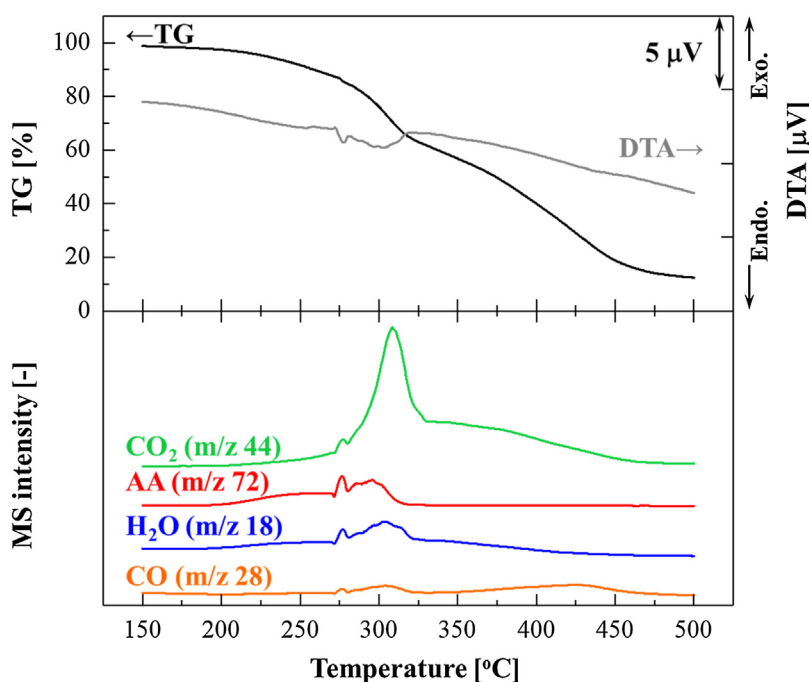


Fig. 9. TG-DTA-MS results of acrylic acid radical polymer.

superheated water in Table 4. In the case of acrylic acid monomer, superheated water will exist as a liquid in a container at more than 25% of the filling level. In the case of the Michael addition dimer, superheated water will exist as a liquid in a container at more than 15% of the filling level. Therefore, superheated water generated from DAA exists as a liquid at a lower filling level than AA. DAA may undergo vinyl polymerization, whereupon the polymer is then decomposed and gasified with more violent gas generation than AA. Therefore, the impact and frequency of tank destruction increase with the accumulation of the Michael adducts.

3.4. Accident scenarios of the acrylic acid runaway polymerization

We identified two accident scenarios caused by melting operations of acrylic acid based on the investigations in this study. Manufacturers of acrylic acid perform melting operations to improve its flowability of acrylic acid whose melting point is 13.5 °C. The scenarios were described on the assumption that liquid or partly solidified acrylic acid is heated to improve the flowability in tanks, pipes, or drums.

Scenario i. In the case of overheating acrylic acid to 150 °C with an electromagnetic induction heating coil:

Consequential events depend on the filling level of the tank. If the filling level is larger than 44%, the heat accumulation of polymerization leads to polymer thermal decomposition. The risk of tank destruction is high. In addition, if the filling level is larger than 25%, water generated due to the polymer thermal decomposition will exist as a liquid and increase the impact of tank destruction after crack initiation in the tank.

Scenario ii. In the case of overheating acrylic acid to 100 °C with steam:

The Michael addition reaction gradually raises the temperature to 150 °C and initiates undesired polymerization. The Michael adducts will be polymerized and react exothermically, after which polymer thermal decomposition occurs. This generates a larger amount of pressure and destroys the tank at a lower filling level (15%) than in Scenario i. The water generated by the polymer ther-

mal decomposition increases the impact of the tank destruction, as with Scenario i.

Based on the present experimental studies, we modified the explosion scenario runaway polymerization of acrylic acid, as shown in Fig. 10. Depending on the filling level in a tank, undesired polymerization starts and leads to polymer thermal decomposition. The worst-case scenario in our model is the BLEVE due to superheated water generated by the polymer thermal decomposition after the polymerization of Michael adducts.

We constructed safety countermeasures corresponding to the scenario progress in Event Tree form (Alileche et al., 2017) as shown in Fig. 11. There are three clear domains describing the extent of the impact labeled as “Quality control”, “Safety control” and “Out of control”. The reliability of temperature monitoring must always be ensured. If the temperature monitoring is non-operational, all of the scenarios in the tank fall under the domain of “Out of control”. In this case, the only countermeasure is to evacuate and maintain a suitable distance from the tank. The scenario begins when the control temperature deviates from the adequate temperature, 25 °C. The concentration control of Michael adducts is in the domain of “Quality control”. In this scenario, to prevent the acceleration of the Michael addition reaction, a shortstopping water/inhibitor injection is necessary. This operation makes it impossible for manufacturers to maintain the quality of products and results in economic losses. On the other hand, if the tank temperature exceeds 150 °C, the external injection of coolant or diluent becomes impossible. At this point, the external cooling and venting system will become non-functional due to the decreasing heat conductivity and blockage of the line caused by a solid polymer. Even if the venting system works successfully, the discharge of harmful vapors and gases creates an environmental impact. Unfortunately, if there are ignition sources around the tank, an explosion will occur. After the failure of venting, the BLEVE can also occur. The operators can only evacuate and maintain an adequate distance from the tank.

Basic Acrylic Monomer Manufacturers (BAMM) (Basic Acrylic Monomer Manufacturers, Inc., BAMM, 2013) caution that if the temperature of acrylic acid reaches 60 °C, an explosion is likely.

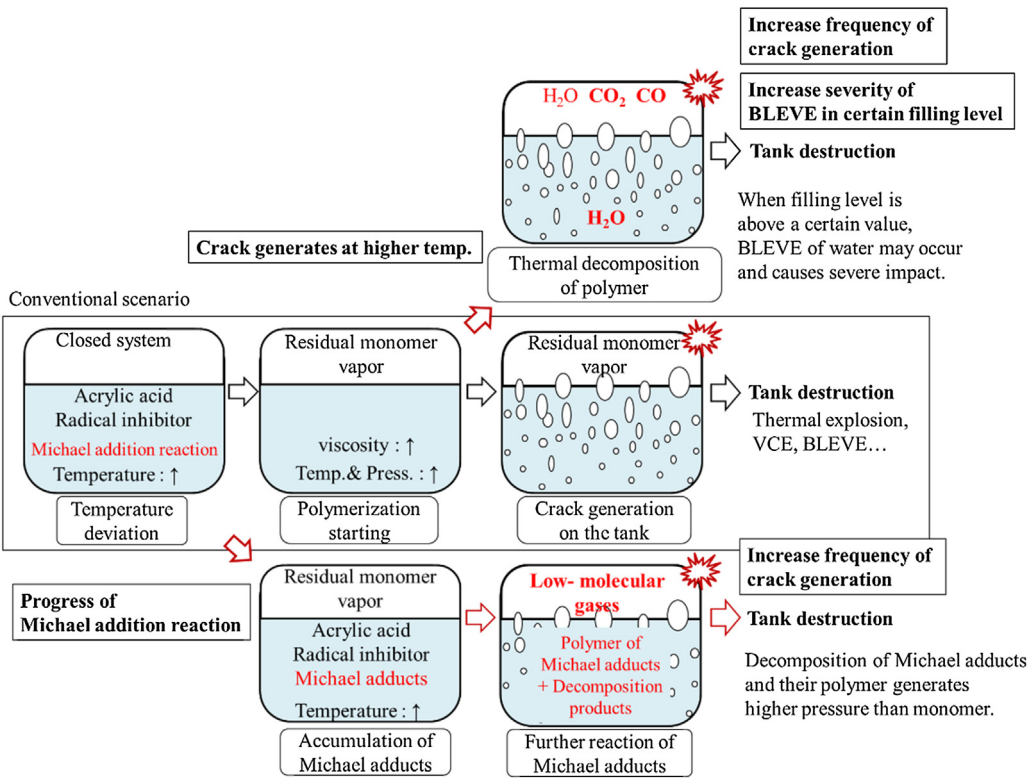


Fig. 10. Modified model of the acrylic acid tank explosion scenario.

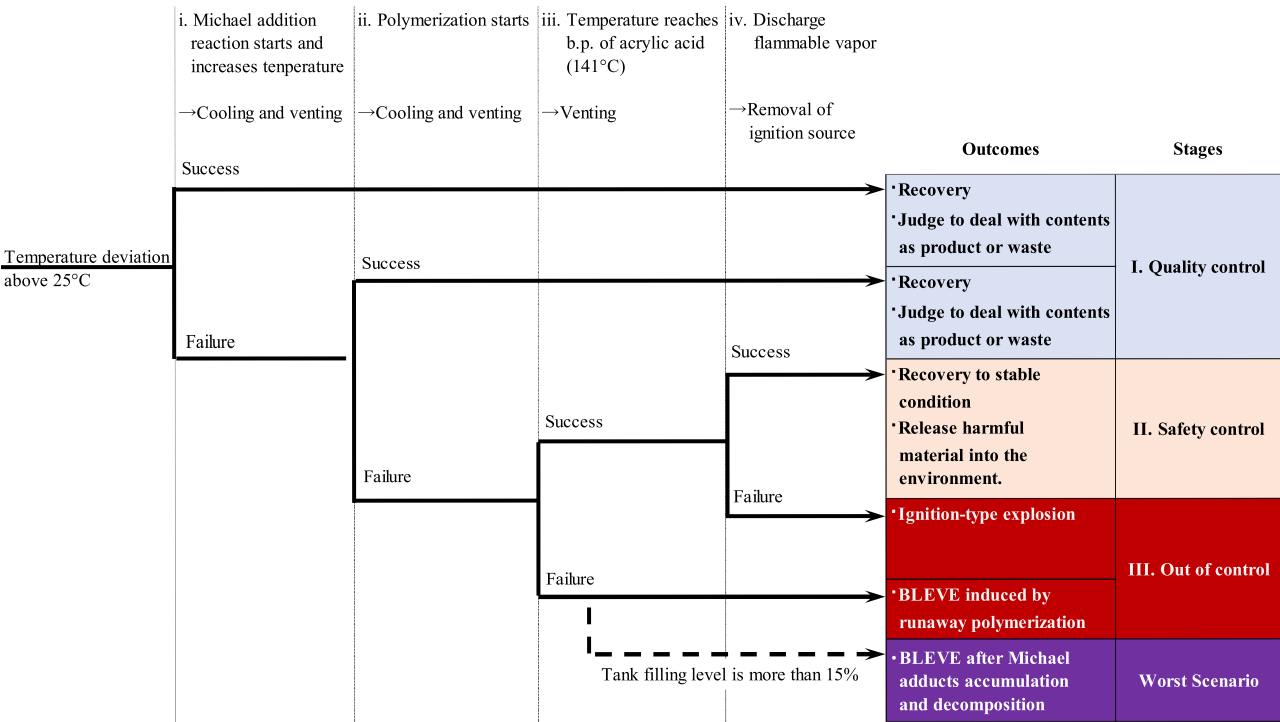


Fig. 11. Safety countermeasures corresponding to scenario progression as Event Tree form.

In this case, operators should evacuate to at least a half mile (approximately 800m) area surrounding the storage container, tank, and trailer. In addition, the European Basic Acrylic Monomer group (EBAM) (European Basic Acrylic Monomer group, EBAM, 2012), cautions that if the temperature of acrylic acid reaches 50°C, to not approach its road tankers. These guidelines may

assume the worst-case scenario and that acrylic acid is stored at a high filling level and in high adiabaticity containers. Their evacuation criteria, 60°C or 50°C, are lower than the onset temperature in the ARC test of the present study, 115°C. An adiabatic hot storage test (Krause et al., 2014) demonstrated that Michael addition of acrylic acid can increase the tempera-

ture gradually from 20 °C and lead to self-initiation of radical polymerization.

4. Conclusions

The amount of energy release and the chemical species of the acrylic acid runaway polymerization were analyzed through various samples and techniques.

The results of ARC tests and closed vessel heating tests showed that not only monomer but also Michael addition dimer produce water through runaway polymerization. Moreover, the dimer generates a larger amount of heat and pressure than the monomer. Consequently, the dimer has the potential to superheat water and cause BLEVE at a lower tank filling level than the monomer.

We devised an acrylic acid tank explosion scenario accompanied by runaway reactions. We demonstrated two scenarios, which created a more severe case to prevent relapse than the conventional scenario. From our experimental results, the filling level of the tank and the concentration of Michael adducts were both associated with a transition to more severe scenarios. We suggested safety countermeasures in Event Tree form corresponding to the sequence of events in the tank.

To understand runaway polymerization, preparation of the sample, to reproduce contents in accidental tanks or reactors, is essential. Through runaway polymerization, the contents can change their state. Gas, liquid and solid can all exist intricately in the tank or reactor at uncertain levels. The key to process hazard analysis on a runaway reaction is the investigation of the energy release and the identification of chemical species through segmenting the reaction progress into each reaction stage in an accident scenario.

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