UNDERSTANDING VINYL ACETATE POLYMERIZATION ACCIDENTS

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Vinyl acetate is processed to produce polymers and copolymers used in water based paints, adhesives, paper coatings or non-woven binders and various applications at moderate temperatures. The polymerization processes used include solution, suspension and emulsion processes. Many incidents involving the runaway polymerization of Vinyl Acetate Monomers (VAM) are known. The incidents happened either in batch or semi-batch polymerization processes in connection with wrong catalyst introduction.

In processes where the polymerization catalyst is dissolved in the monomers, the catalyst premix has polymerized violently in the premix vessel. In polymerization processes where the vinyl acetate monomer conversion ratio is not 100 %, storages of recycled monomers containing no polymerization inhibitor and possibly some traces of polymerization catalyst have exploded due to the VAM violent bulk polymerization.

In this paper, a review of polymerization incidents is given. Radical chain polymerization kinetics are used to explain some accident features such as polymerization isothermal induction periods. Experimental results on bulk VAM polymerization obtained in DSC, Dewar flask and VSP are given. The accidental polymerization of VAM in a vessel is simulated using the WIN SIM software. The simulation is based on radical chain polymerization kinetics and thermochemical data on VAM and polymers and on specified initial and boundary conditions. Simulation of accidental polymerisations is useful to validate accident scenarios and evaluate various cause hypotheses.

Introduction

Vinyl acetate (VAM) is processed to produce polymers and copolymers used in water based paints adhesives, paper coatings or non-woven binders and various applications at moderate temperatures.

The polymerization processes used include semi-batch or continuous, solution, suspension and emulsion processes. The bulk polymerization of vinyl acetate is not used in industrial operations due to the violent reaction obtained. However the unwanted bulk polymerization of vinyl acetate is involved in many industrial accidents where the polymerization occurred in storage vessels containing fresh or recycled monomers or in premix vessels where a polymerization initiator was dissolved in vinyl acetate monomer, previous to its use in the polymerization process.

Therefore, the study of vinyl acetate bulk polymerization is of great interest from a process safety point of view, even if it is not a commercial wide-spread process.

The bulk polymerization of vinyl acetate in storage vessels occurs spontaneously under constant temperature conditions, due to a chemical acceleration phenomenon related to the free radical nature of vinyl acetate chain polymerization.

The incidents in polymerization processes happen either in semi-batch or continuous polymerization processes due to wrong catalyst introduction, absence of agitation or inadequate priming operation.

The consequences of the unwanted or uncontrolled vinyl acetate polymerization depend on the various process conditions. The bulk polymerization of vinyl acetate is extremely violent and may generate a pressure surge to above 40 bar, a pressure exceeding most storage vessels pressure resistance.

The uncontrolled polymerization of vinyl acetate in the presence of light solvents in polymerization reactors may also result in a high pressure surge due to the solvent high vapour pressure under the runaway reaction final temperature. If the runaway polymerization causes the vessel rupture, this may occur with severe mechanical and blast effects.

The vessel inventory consisting of polymers would be released in the neighbourhood. In most incidents involving the bulk polymerization of vinyl acetate, the release did not ignite. This is probably due to the high conversion ratio reached. The presence of a flammable solvent or a lower conversion ratio of the monomers may allow the release ignition.

Therefore vinyl acetate runaway polymerization incidents are very serious and they occur with a high frequency. The polymerization of vinyl acetate is probably the second most frequent cause of runaway reaction accidents in the chemical industry, after the phenol + formaldehyde runaway reaction.

Therefore it is of interest to describe the circumstances where a runaway polymerization can occur and to explain the causes of accidents and the factors influencing their occurrence. As an example, the bulk polymerization of vinyl acetate initiated by a peroxide was studied on an experimental and theoretical point of view based on radical chain polymerization kinetics and on simulation using the Win Sim software.

Thermal stability of vinyl acetate monomer. Runaway reaction hazard in storage vessels

Thermal stability of commercial monomers

Vinyl acetate is a reactive monomer which may undergo a free radical chain polymerization phenomenon under constant temperature conditions. The chain polymerization of monomers may be initiated by radical initiators i.e. inorganic or organic peroxides, azobisisobutyronitrile (AIBN), others ...

In monomer storage vessels, there is no such initiator in normal process conditions. However, there is a slow thermal production of free radicals in the bulk liquid monomer even under ambient temperature. The thermally produced radicals may *accumulate and further initiate the free radical chain polymerization of the monomers* in the storage vessel. To provide enough thermal stability, some polymerization inhibitor is added to the commercial product, which is a radical scavenger.

The polymerization inhibitor used for the stabilization of vinyl acetate monomers is hydroquinone (H.Q.). Rhône-Poulenc is a leading supplier for hydroquinone and other polymerization inhibitors.

Two grades of vinyl acetate monomers are currently supplied :

- the low hydroquinone grade containing 3 - 7 ppm H.Q. to be used within two months of delivery
- the high hydroquinone grade containing 12 - 17 ppm H.Q. for storage up to four months before use.

Compared to other vinylic or acrylic monomers i.e. acrylic acid (AA), methacrylic acid (MAA) or methyl methacrylate (MMA), the polymerization inhibitor concentration in VAM is very low owing to the low thermal activity of VAM in storage conditions.

Influence of oxygen

Many questions arise concerning the recommended storage conditions of vinyl acetate.

It is sometimes recommended to store vinyl acetate monomer under ambient air atmosphere to enhance the polymerization inhibitor efficiency as it is known that phenolic inhibitors need oxygen to be active. For example, air is bubbled in acrylic acid storage vessels to allow the polymerization inhibitor, hydroquinone mono methyl ether (MeHQ) to be active (1).

However, contrary to acrylic acid which is stored at a temperature below 25°C and has a flash point of 49°C (2), above the storage temperature, vinyl acetate monomer is a highly flammable liquid with a flash point of -7°C (2). Under ambient temperature conditions, the storage vessel gas phase under air atmosphere would be flammable for VAM. Therefore, storage of VAM under air atmosphere should be avoided.

It was further pointed out by A. Nicholson (3) that the optimum stability of methacrylic acid in the presence of HQ or MeHQ as polymerization inhibitor was obtained at much lower equilibrium oxygen concentration than that provided by an air atmosphere.

The most favourable oxygen concentration was shown to depend on the inhibitor considered and on its concentration in the monomer. A higher oxygen concentration than the optimum value was shown to decrease the monomer thermal stability due to unstable peroxide formation. Therefore, any monomer/inhibitor couple is specific and requires a special consideration for the choice of storage conditions.

In the case of vinyl acetate containing hydroquinone as an inhibitor, it was later pointed out byLeon B. Levy (4) (5) that the optimum thermal stability was obtained under dry nitrogen atmosphere without any oxygen present in the storage vessel gas phase.

It was shown that between 30°C and 120°C, the length of vinyl acetate polymerization isothermal induction period is about - 0.4 order in oxygen partial pressure. The detrimental effect of the presence of oxygen in the monomer gas phase, on the thermal stability of vinyl acetate containing hydroquinone as an inhibitor, is explained by the low thermal stability of the peroxides formed when VAM is stored in the presence of dissolved oxygen. The decomposition of accumulated peroxides near ambient temperature can induce an increased inhibitor consumption.

Therefore, for flammability and thermal stability reasons, it is recommended to store vinyl acetate under dry nitrogen blanket. The above conclusion holds for high temperature (100°C) and ambient temperature conditions. However, when stabilized with 3 - 5 ppm H.Q., both air saturated and oxygen-free VAM exhibit adequate thermal stability at normal transport and storage temperature (25°C - 50°C).

Influence of impurities

It was shown by Leon B. Levy that acetaldehyde impurity does not cause oxygen induced destabilization of vinyl acetate (5).
The presence of humidity in vinyl acetate would produce some degree of hydrolysis and alter the monomer quality.

Influence of the storage vessel wall material

As for other reactive monomers and especially in the case of polymerization accident inquiries (6) the influence of the storage vessels and transport containers wall material has been investigated.
The influence of carbon steel on the thermal stability of VAM containing 5 ppm HQ, at 48.9°C, blanketed with 10 % oxygen, was investigated by Leon B. Levy (5). It was found that untreated carbon steel covered with rust has a strong destabilizing influence on VAM compared to a glass vessel, whereas clean carbon steel would increase thermal stability.
The influence of carbon steel on vinyl acetate thermal stability can also be measured by monitoring of the inhibitor concentration as a function of time.

Two 2 litre samples of vinyl acetate containing approximately 20 ppm hydroquinone were submitted to aging at 20°C, one in a coloured glass vessel, the other in a 2 litre oxidized carbon steel vessel. Both vessels where closed under air atmosphere.

The following depletion of H.Q. concentration was observed by UV spectrometric determinations.

Table 1 : Vinyl acetate in 2 litre coloured glass vessel

Time (days)	H.Q. concentration (mg/kg)
0	20.1
5	19
18	18.4
41	17.8
55	18
67	17.6

Table 2 : Vinyl acetate in 2 litre oxidized carbon steel Vessel

Time (days)	H.Q. concentration (mg/kg)
0	21.7
1	20.8
7	19.2
12	19.1
22	17.6
48	16.5
61	16.5
76	15.9

In these experiments the hydroquinone consumption in carbon steel vessel was twice the H.Q. consumption in coloured glass vessel. Also enough inhibitor concentration would be present under ambient temperature, to prevent polymerization over a very long period of time in both containers.
However, considering the lower thermal stability of VAM in oxidized carbon steel vessels, it is recommended to design stainless steel storage vessels for VAM and to prevent existing carbon steel storage vessels from rust. This should be easier under dry nitrogen blanket.

Accidental polymerization of recovered vinyl acetate

The data found in the literature and additional data provided, show that commercial vinyl acetate should never polymerize in normal storage conditions. However polymerization accidents in storage vessels are known concerning VAM which is not exactly the commercial product. This is the case for vinyl acetate recovered from polymerization processes where the conversion ratio is not 100 %. An example of such a process is the manufacture of polyvinyl alcohol by polymerization of vinyl acetate in the presence of methanol initiated by azobisisobutyronitrile (AIBN), followed by alkaline hydrolysis of the polyvinyl ester.

The unreacted vinyl acetate is separated from the polymer and recycled to the polymerization step. The recovered vinyl acetate is free of polymerization inhibitor and may possibly contain some traces of polymerization initiator. A 35 m^3 storage of recovered VAM happened to polymerize during the summer vacations in a southern country.
The long residence time and the warm temperature, possibly one month and 50°C, allowed the polymerization to occur. The polymerization was violent. The storage vessel roof was ejected to 100 m distance and polymers were spread in the neighbourhood.

The conditions where this accident occurred are fairly compatible with the stability data of Leon B. Levy for VAM with no H.Q., 10-20 % vol. O_2 and the presence of carbon steel wire.
Also it was shown that oxidized iron lowered the product thermal stability measured in DTA stainless steel closed cell under 5°C/min. temperature scan.
The polymerization exotherm onset temperature was shifted from 300°C to 230°C in the presence of oxidized carbon steel. The product polymerization exotherm was 1221 j/g close to the literature data of 1036 j/g (7).
A sample of recovered VAM showed polymerization isothermal induction periods at high temperature in DTA but such data cannot be extrapolated to ambient temperature where induction periods are too long to be measured using DTA machines.
Our comment on this incident is that one should take care of the thermal stability of non commercial or recovered vinyl acetate in particular if high storage temperature and long residence time are possible. The storage of uninhibited monomer should be avoided.

Polymerization incidents in premix vessels

It is a surprizing practice, from a process safety point of view, that concentrated solutions of polymerization initiators are used in premix to be injected in a continuous or semi-batch polymerization process. Premix vessel polymerization accidents are known for many reactive monomers. This type of incident has occurred also in vinyl acetate polymerization processes.

1.8 % wt dilauroylperoxide was dissolved in vinyl acetate in a premix to be injected in a VAM polymerization process. The premix was prepared in advance, to be used 8 hours later. Due to the hot summer temperature, the premix happened to polymerize. The reaction was extremely violent. A two phase flow of polymer and vapour was ejected in the vessel vent header. The release did not ignite. This incident has been investigated on an experimental and theoretical point of view to assess the conditions of occurrence and to evaluate the venting requirement of this scenario.

The relevant experimental study and simulation using Win Sim are given in the experimental and simulation sections of this paper.

Our conclusion on this issue is that the practice of dissolving the polymerization initiator in the reactive monomer in a premix, should be eliminated from polymerization processes for process safety reasons.

Incidents, accidents in polymerization processes

Runaway reaction incidents in polymerization processes are related to the reactive monomer accumulation in the polymerization reactor and the subsequent runaway polymerization of the accumulated quantity of unreacted monomer.

The monomer accumulation may have several causes.

- The polymerization initiator was not injected and could reach later the reaction vessel.

  In a semi-batch solution polymerization process where VAM was polymerized in acetone as a solvent, a valve was closed on the polymerization initiator feed pipe. A large quantity of vinyl acetate was charged to the reactor when the polymerization catalyst could reach the reaction vessel through the vent line. A runaway polymerization occurred with a severe pressure surge which may have been caused by the use of a light solvent.

  Other frequent causes of monomer accumulation are :
- Too low a process temperature which does not allow the monomer charged to react.
- No agitation. This process deviation allows the monomer and the polymerization catalyst to be in two separate liquid phases. The accumulated monomer may react violently if the agitation is restarted.
- The process is a batch process with respect to the reactive monomer and the polymerization initiator.

  In a series of incidents on various VAM polymerization processes, the common factor seems to be the fact that the processes are batch processes with respect to the reactive monomer and the polymerization initiator. This made the reaction mixture temperature control more difficult and the process sensitive to loss of cooling. In a batch process the heat of reaction is released over a short period of time, producing a high heat flux and making the reaction mixture temperature control critical. Batch processes are better replaced by semi-batch operations where the controlling reactant and the initiator are introduced over a period of time long enough to adjust the heat flux produced to the reactor available cooling capacity. This advantage is well explained for vinyl acetate polymerization by H.U. Moritz (8).

- Incidents in priming procedures

  The initiation of polymerization in semi-batch or continuous processes is frequently made using a priming procedure where a limited charge of controlling reactant is introduced in the reaction vessel to check the reaction initiation through the detection of the reaction exotherm.

  On detection of the reaction exotherm, a continuous feed of controlling reactant to the reaction vessel is established. If the continuous feed of reactant is established too early or too late with respect to the priming charge reaction, an "unexpected" faster reaction is obtained due to a larger amount of unreacted monomer in the reaction mixture, if the continuous feed is established too early or due to the priming reaction extinction and monomer accumulation, if the continuous feed is established too late. See also ref. (8).

Experimental investigation of the bulk polymerization of vinyl acetate initiated by a peroxide.

Cause of the isothermal induction period phenomenon

As pointed out earlier, this bulk polymerization of VAM occurs during the storage of a premix where the polymerization initiator has been dissolved in the monomer. The very violent polymerization occurs after an isothermal induction period caused by the chemical acceleration of the radical chain polymerization. This phenomenon can be accounted for as follows.

The kinetic behaviour of radical chain polymerisations has been presented by Flory (9) And will be described in the simulation section of this paper.

In this theory, the rate of monomer consumption is referred as the rate of polymerization.

$$R_P = -\frac{d\,[M]}{dt} = k_P[M][P]$$

where [M] is the monomer concentration, [P] is the polymer radical concentration

kP is the propagation rate constant.

According to the theory of Flory, the rate of polymerization is controlled by the initiator concentration (9) (10).

$$R_P = -\frac{d\,[M]}{dt} = k_P[M]\left(k_d\, f[I]/k_t\right)^{1/2}$$

Where k_d is the initiator decomposition rate constant, k_t the termination rate constant, [I] the initiator concentration, f the fraction of initiator radicals successfully reacting with the monomer.

Consequently, the rate of polymerization is an Arrhenius function with first order with respect to the monomer concentration and half order with respect to the initiator concentration which controls the population of polymer radicals.

Considering the maximum rate of polymerization, the higher the initiator concentration, the faster the maximum rate of polymerization. This explains the very violent polymerization observed in premix vessel polymerization accidents, where very high initiator concentration are present.

In storage vessels of monomer where some polymerization inhibitor is present, the polymerization induction period is the time necessary for the thermally - generated radicals $R^\bullet$ or $M^\bullet$ to consume the polymerization inhibitor and produce enough radical concentration to initiate the chain polymerization reaction.

Radicals are produced by the polymerization initiator if any, or by the monomers themselves. Consequently, the isothermal induction period is influenced by the inhibitor and polymerization catalyst concentrations in the monomer.

In the case of commercial monomer storage, there should be no polymerization catalyst present, and the induction period is the time necessary for the monomer thermally generated radicals to consume the inhibitor concentration (11).

$$\tau = \frac{[Z]}{k_0\, e^{-E/RT} \cdot [M]} \qquad \tau = \frac{m\,[Z]}{k_0\, e^{-E/RT} \cdot [M]}$$

depending on whether one or more monomer radicals react with each molecule of inhibitor Z. Consequently, the induction period is an Arrhenius function of the inhibitor concentration with an activation energy characteristic of the monomers.

$$\tau = K[Z]e^{E/RT}$$

For storage vessels of commercial monomer, the slope of the Arrhenius plot of the isothermal induction period is a characteristic of the monomer.

This may not be the case if a polymerization catalyst is present and if the inhibitor is eliminated first.

Then the isothermal induction period is :

$$\tau = \frac{m[Z]}{k_0 \cdot e^{-E/RT} \cdot [M] + k_{d0}\, e^{-Ed/RT}[I]}$$

In this case, the polymerization inhibitor is consumed by the monomer thermal generation of radicals and by the decomposition of the polymerization initiator.

Under moderate temperature where the polymerization initiator is active and the thermal generation of monomer radicals negligible compared to that of the initiator, the above equation reduces to :

$$\tau = \frac{m[Z]}{k_{d0} \cdot e^{-Ed/RT}[I]}$$

In this case, the polymerization isothermal induction period is an Arrhenius function of the inhibitor and polymerization initiator concentrations with an activation energy Ed characteristic of the polymerization initiator

$$\tau = K\,[Z][I]^{-1} e^{\,Ed/RT}$$

The slope of the Arrhenius plot of the induction period is a characteristic of the polymerization radical initiator. The Arrhenius plot of the polymerization induction period is a key piece of information to prevent runaway polymerization accidents. Also interesting is the experimental data on the polymerization exotherm, rate of reaction, pressure effect. This experimental information is presented in the following for the bulk polymerization of VAM containing 1.8 % wt dilauroylperoxide, concerning a premix vessel polymerization accident.

DTA determinations

VAM samples containing 1.4 % wt, 1.8 % wt, 2.2 % wt dilauroylperoxide were submitted to DTA test under 5°C/min. temperature scan conditions in stainless steel closed cell.

The samples exhibit two separate exotherms :

- the first asymmetric exotherm, $\Delta Q1 = 639 - 676$ J/g is due to the monomer initiated radical polymerization,
- the second exotherm of $\Delta Q = 296 - 469$ J/g is due to the monomer high temperature thermal polymerization.

This is proved by the uncatalysed thermal polymerization of VAM giving up an exotherm of 1221 J/g above 290°C. The polymerization overall exotherm of 970 - 1221 J/g is of the order of magnitude of VAM heat of polymerization known in the literature (7). $\Delta H = -1036$ J/g.

Polymerization induction period of vinyl acetate in the presence of 1.8 % wt dilauroylperoxide

The bulk polymerization of vinyl acetate containing 1.8 % *wt of radical initiator* dilauroylperoxide can be initiated by constant temperature exposure under different temperatures.

The polymerization induction period was measured using various experimental techniques : (12)

- DTA for high temperature short induction periods
- closed Dewar experiments and VSP experiments for low temperature long induction periods.

The isothermal induction periods are given for the exotherm onset detection since in some VSP experiments the test cell exploded due to the very fast pressure surge. Consequently, the maximum rate of reaction could not be observed. The Arrhenius plot of the polymerization induction periods obtained is given on Fig. 1.

VSP closed cell experiments

The runaway polymerization of vinyl acetate containing 1.8 % wt dilauroylperoxide was initiated on a 80 g sample under isothermal exposure conditions in a 116 cm^3 Hastelloy C VSP closed cell. The isothermal exposure temperatures were 37°C and 45°C. In one experiment at 37°C the test cell did not rupture. The maximum heat-rate was 4967°C/min. The maximum rate of pressure rise was 2544 bar/min. i.e. 42.4 bar/s. The maximum rates were obtained for a temperature of 144-174°C. The final temperature was 268°C and the final pressure 44.5 bar. The heat-rates obtained are given on Fig. 2. The pressure corrected for the nitrogen pad as a function of the reciprocal temperature is given on Fig. 3 for the three experiments. The VAM vapour pressure is also represented (13).

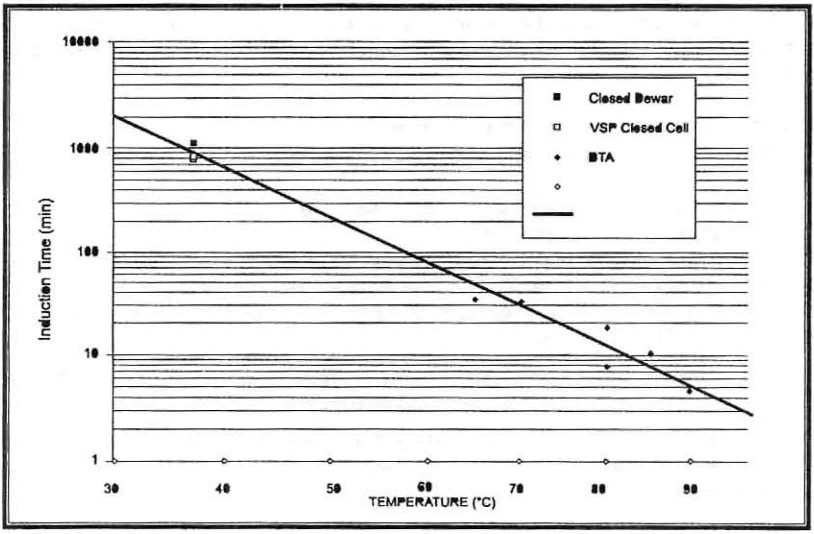

Figure 1: Polymerization of vinyl acetate monomers containing 1.8% w/w peroxide. Induction time vs Temperature.

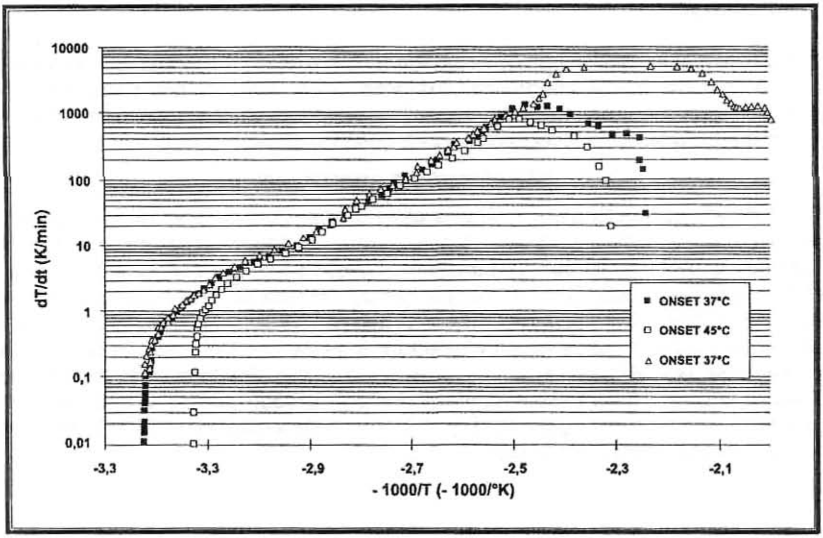

Figure 2: VSP closed cell experiment. Polymerization of vinyl acetate monomers with 1.8% w/w dilauroyl peroxide initiated by constant temperature exposures at 37°C and 45°C. Heat rate curves.

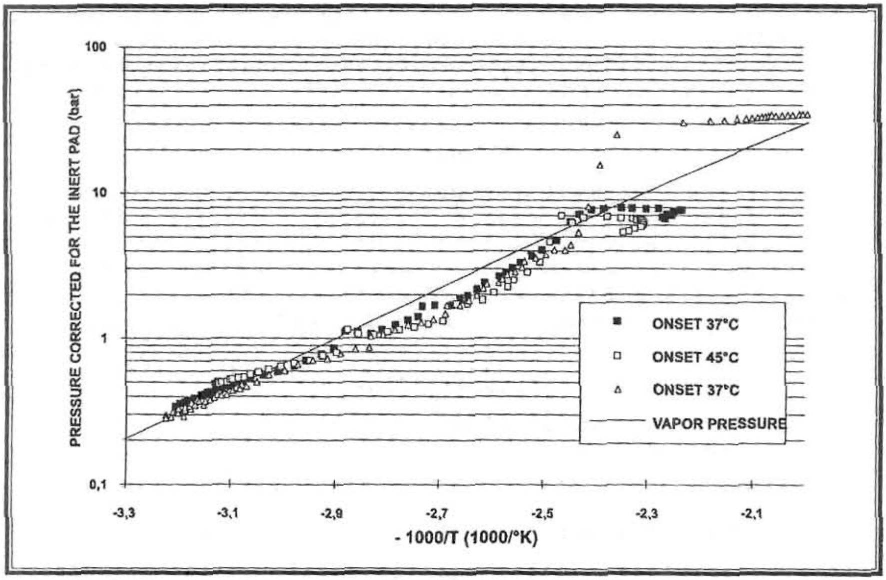

Figure 3 : VSP closed cell experiments. Polymerization of vinyl acetate monomers with 1.8 % w/w dilauroyl peroxide initiated under constant temperature exposures at 37°C and 45°C - P vs T data - Curve represents vapour pressure of monomers.

Simulation of vinyl acetate runaway polymerization using Win Sim

In this section, a kinetic model is proposed to represent the radical chain polymerization of vinyl acetate. The relevant kinetic data are obtained from the literature and discussed. The software used for the simulation is described. The use of this software is exemplified by the prediction of the runaway polymerization of vinyl acetate in the presence of dilauroylperoxide as an initiator i.e. to represent a premix vessel polymerization incident.

Kinetic model

A reaction mixture containing the following stable components is considered : Polymerization initiator (I), Monomer (M), Polymer (D), Solvent (S). The following radical components are also present : Monomer radical ($R^\bullet$), Polymer radical (P).
The kinetic model includes the following reaction steps : Initiation, Propagation, Termination together with the relevant kinetic equations. The kinetic model chosen is the model used in the "Polymer Plus" software of Aspen Tech using Arrhenius type rate equations.

Reaction mechanism

The model reaction steps and rate equations are the following :

Initiator decomposition	$I \longrightarrow nR^\bullet$	$R_d = k_d\,[\,I\,]$
Chain initiation	$R^\bullet + M \longrightarrow P_1$	$R_i = k_i\,[R^\bullet][M]$
Thermal generation of radicals	$M \longrightarrow P_1$	$R_{th} = k_{th}\,[M]$
Chain propagation	$M + P_n \longrightarrow P_{n+1}$	$R_p = k_p\,[M][P]$
Transfer to monomer	$M + P_n \longrightarrow D_n + P_1$	$R_{trm} = k_{trm}\,[M][P]$
Chain termination by disproportionation	$P_n + P_m \longrightarrow D_n + D_m$	$R_{td} = k_{td}\,[P]^2$
Chain termination by combination	$P_n + P_m \longrightarrow D_{n+m}$	$R_{tc} = k_{tc}\,[P]^2$

The following constituent balances must be satisfied :

Initiator $\frac{d[\,I\,]}{dt} = -R_d$ Monomer radicals $\frac{d[R]}{dt} = n\,.\,f\,.\,R_d - R_i$

Monomers $\frac{d[M]}{dt} = -R_i - R_{th} - R_p - R_{trm}$ Polymer radicals $\frac{d[P]}{dt} = R_i + R_{th} - 2R_{td} - 2R_{tc}$

Polymers $\frac{d[D]}{dt} = -R_{trm} + 2R_{td} + R_{tc}$

The quasi stationary state hypotheses is assumed and is written as follows :

$$\frac{d[R]}{dt} = 0 = f\,n\,R_d - R_i \qquad \frac{dP}{dt} = 0 = Ri + Rth - 2R_{td} - 2R_{tc}$$

$$[P] = \sqrt{\frac{R_i + R_{th}}{2(k_{tc} + k_{td})}}$$

Hence : $R_i = f\,.\,n\,.\,R_d$

Gel effect

The Gel effect or Trommsdorff effect is related to the reaction mixture increase of viscosity with increasing polymerization conversion ratio. The Gel effect may induce an increase in the rate of polymerization due to slower termination reaction caused by increased viscosity.

The kinetic interpretation of the Gel effect is that given in the "Polymer Plus" software where the termination reaction rate constants are multiplied by a fraction X_p depending on the polymer mass fraction in the reaction mixture.

$$k_t = GF \,.\, k_{t^\circ} \qquad \text{where} \qquad GF = \exp(-gf_1\, X_P - gf_2\, X^2_P - gf_3\, X^3_P)$$

Dynamic model

The reaction mixture is assumed to be enclosed in a vessel under constant volume conditions.

The initial mass, composition, temperature, must be specified by the user.

In step one the model determines the reaction mixture thermodynamic state : vapour fraction, composition of liquid and vapour phases, vessel pressure, vessel filling ratio.

In step two, the boundary conditions are specified : vessel wall under constant temperature, reaction mixture and vessel under constant temperature, specified heat exchange through the vessel walls.

The model determines the reaction mixture temperature, pressure, composition in the vessel, as a function of time.

The following system of differential equations is integrated using a variable step Runge Kutta method :

- Enthalpy change = heat exchanged through the wall + heat of reaction released.
- Enthalpy change of the vessel wall = heat exchange with the reaction mixture + heat flux specified by the user.
- Change in constituents mole number = contribution of every reaction.

The polymer molecular weight is calculated assuming a constant total mass of the reaction mixture.

The following simplifying hypotheses are assumed : the liquid volume is constant during the polymerization reaction, the reaction mixture specific heat is constant during the polymerization reaction.

We know that both hypotheses are not true since the polymerization conversion ratio can be determined by measuring the reaction mixture volume and the liquid specific heat changes during the reaction. However the relevant experimental data is not available and no model to account for these properties change was introduced. The liquid volume and liquid specific heat are calculated for the initial conditions together with the reaction mixture thermodynamic properties.

Kinetic data obtained in the literature

Polymerization initiator decomposition

The reaction is : $I \longrightarrow nR^\bullet$

The initiator decomposition rate is : $-\frac{d[I]}{dt} = k_d\,[\,I\,]^{nd} = k_d \exp(-E_d/RT)\,.\,[\,I\,]^{nd}$

The initiator considered is dilauroylperoxide (LPO). The following decomposition kinetics are available for dilauroylperoxide.

1 - Paper of Korbar and Malavasic (14)

Order n_d	E_d (kJ/mol)	T = 65°C		T = 75°C		T = 85°C	
		K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)
1.1	135.7	$0.22.10^{-4}$	8.8	$0.88.10^{-4}$	2.20	$3.27.10^{-4}$	0.60

2 - Data of manufacturer mentioned by Korbar and Malavasic (14)

Order n_d	E_d (kJ/mol)	T = 65°C		T = 75°C		T = 85°C	
		K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)
-	127.3	$0.28.10^{-4}$	6.8	$1.04.10^{-4}$	1.90	$3.56.10^{-4}$	0.50

3 - Data of Warson (15) used in Polymer Plus

Order n_d	E_d (kJ/mol)	$K_d°$ (s^{-1})	Half-life = 60 s		Half-life = 1 h		Half-life = 10 h	
			T (°C)	$T_{1/2}$ (h)	T (°C)	$T_{1/2}$ (h)	T (°C)	$T_{1/2}$ (h)
1	127.4	$1.44.10^{15}$	116		80		62	

4 - Other data

Half life periods are given in various works. A half-life period of 10 hours at 62°C is mentioned in (16). A half-life of 1 min. at 115°C is mentioned by SRI. The following data was measured :

$T_{1/2}$ (h)	42	12	3.2	1
T (°C)	50	60	70	80

Thermal generation of radicals by the monomer

The reaction is : $M \longrightarrow M^{\bullet}$

The monomer radical generation rate is : $R_{th} = k_{th}\,[M] = k_{th}^{\circ}\,\exp(-E_{th}/RT)\,[M]$

No kinetic data is available on this reaction rate in the literature, due to the many factors influencing the thermal generation of radicals by the monomer.

Chain propagation

The reaction is : $M + P_n \longrightarrow P_{n+1}$

The heat of polymerization is basically the heat of propagation reaction.

The data available on this reaction is :

1 - The data of Flory (17)

ΔHr (kJ/mol)	kp° (mol-l-s)	Ep (kJ/mol)
-	24.10^7	30.5

2 - The data of the Encyclopedia of Polymer Science and Engineering

ΔHr (kJ/mol)	kp° (mol-l-s)	Ep (kJ/mol)
87.5 à 89.1	$3.2.10^7$	26.2

Termination reaction

The chain termination can occur following two reactions :
by combination $P_n + P_m \longrightarrow D_{n+m}$ by disproportionation $P_n + P_m \longrightarrow D_n + D_m$
The data from the literature suggests that the combination reaction is negligible compared to the disproportionation reaction. The data on the disproportionation reaction are :

1 - The data of Flory (17)

K_{td} at 60°C	K_{td}° (mol-l-s)	E_{td} (kJ/mol)
$7.4.10^7$	$2.1.10^{11}$	21.8

2 - The data of the Encyclopedia of Polymer Science and Engineering

K_{td} at 60°C	K_{td}° (mol-l-s)	E_{td} (kJ/mol)
$2.9.10^7$	$3.7.10^9$	13.3

Transfer to monomer

There is a scarcity of data on the transfer to monomer reaction. Encyclopedia of Polymer Science and Engineering gives data on the ratio $C_m = kt_m / k_p$:

$C_m = 1.10^4$ at T = 0°C $C_m = 3.10^4$ at T = 70°C

C_m may influence only the polymer mean molecular weight.

Gel effect

Limited data is available concerning the gel effect of vinyl Acetate polymerization. The factor values of Polymer Plus are assumed :

gf1	0.44
gf2	6.36
gf3	0.17

Use of the model

The model described above is used for the simulation of vinyl acetate bulk polymerization but could be used also for any other polymerization with or without a solvent provided that the thermodynamic properties are available through UNIPHY.
The program run provides various information displays.
Main screen : pressure, temperature, temperature gradient and liquid/gas phase compositions as a function of time.
Secondary displays : kinetic descriptions, initial conditions, vessel characteristics, alarm conditions.

Application to the simulation of the bulk polymerization of vinyl acetate

The Software is used to simulate the bulk polymerization of vinyl acetate in the presence of 1.8 % dilauroylperoxide under isothermal temperatures of 37°C and 47°C in a VSP test cell.

The test conditions are the following :

Test cell volume :	115 cm³
Charge :	81.7 g
Dilauroylperoxide :	1.8 % w/w

Initial pressure : 1 bar abs.

The following kinetic parameters are used :

	k°	E (kJ/mole)
Initiator decomposition	$1.44.10^{15}$	127.4
Thermal generation of radicals	0	0
Propagation	$3.2.10^{7}$	26.2
Transfer to monomer	0	0
Termination by combination	0	0
Disproportionation	$3.7.10^{9}$	13.3

Initiator efficiency factor : $f = 0.6$
Enthalpy of polymerization $\Delta hr = 88$ kJ/mole.

A first simulation was made without gel effect.
A progressive polymerization was obtained which did not represent the runaway polymerization obtained in the VSP, because the rate of polymerization decreased as a function of time. If a gel effect is introduced using the Polymer Plus parameters an induction period phenomenon is obtained. For an isothermal exposure at 47°C, an isothermal induction period of 90 min. is obtained. The gel effect is found to occur for a conversion ratio of approximately 50 %. By tuning the kinetic parameters and the heat losses from the test cell, the simulation can be adjusted to represent the experimental data.

Conclusion

The prediction of the runaway polymerization of vinyl acetate based on simulation using a kinetic model and kinetic data from the literature provides an estimate of the polymerization isothermal induction period.
In the model used, the only cause of chemical acceleration is the gel effect obtained for a conversion ratio of 50 %. The radical chain reaction is not found to speed up the reaction under isothermal conditions and the presence of a polymerization inhibitor is not taken into account. Much effort will be devoted to better define the initial and boundary conditions to represent experimental conditions.
The simulation is specific for a premix vessel containing a high concentration of polymerization initiator.
For storage vessels containing monomer, the polymerization induction period near ambient temperature is controlled by the inhibitor consumption as explained in this paper.
The authors hope that this work will be useful to Process Safety in polymerization processes. We thank our colleagues from the Process Safety Laboratory for the experimental work and the Rhône-Poulenc Company for allowing this research to be done.

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