

# Studies on the runaway reaction of ABS polymerization process

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Received 1 July 2007; accepted 16 September 2007

Available online 16 October 2007

## Abstract

Taiwan has the largest acrylonitrile–butadiene–styrene (ABS) copolymer production in the world. Preventing on unexpected exothermic reactions and related emergency relief hazard is essential in the safety control of ABS emulsion polymerization. A VSP2 (Vent Sizing Package 2) apparatus is capable of studying both normal and abnormal conditions (e.g., cooling failure, mischarge, etc.) of industrial process. In this study, the scenarios were verified from the following abnormal conditions: loss of cooling, double charge of initiator, overcharge of monomer, without charge of solvent, and external fire. An external fire with constant heating will promote higher self-heat rate and this is recommended as the worst case scenario of emulsion polymerization on butadiene. Cooling failure coupled with bulk system of reactant was determined to be the credible worst case in ABS emulsion polymerization. Finally, the emergency vent sizing based on thermokinetics from VSP associated with DIERS methodology were used for evaluating the vent sizing and compared to that of the industrial plants.

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**Keywords:** ABS copolymer; Emulsion polymerization; Runway reaction; Vent sizing; Calorimetry

## 1. Introduction

Acrylonitrile–butadiene–styrene (ABS) copolymer is one of the most common used engineering plastics containing rubber. ABS resin is almost the most important product at polymer industry in Taiwan. Taiwan has the largest acrylonitrile–butadiene–styrene copolymer resin production in the world. It has been characterized to be a two-phase system with a glassy SAN (poly(styrene–acrylonitrile)) copolymer and a rubbery polybutadiene (PB) domain [1,2]. The PB latex is usually produced from emulsion polymerization of 1,3-butadiene. The rubbery segment of polybutadiene constitutes a rubber phase and exists as a spherical particle dispersed in the glassy matrix of poly(styrene-co-acrylonitrile) (SAN, or AS). Styrene and Acrylonitrile are grafted onto the PB latex (PBL) by the second emulsion polymerization in order to enhance the steric stability and impact resistance. Chains of poly(acrylonitrile-co-styrene) are grafted onto the rubber particles by adding across the resid-

ual double bonds of the PBL or abstraction of hydrogen from the polybutadiene, to initiate a radical which react with the monomer to form a grafted branch. The glassy copolymer can be varied in composition and become tougher as the acrylonitrile (AN) or styrene content is increased.

Since the early pioneering works of Harkins and then Smith and Ewart, the advanced knowledge of the kinetics of emulsion polymerization was established and summarized as the classical description of the three intervals [3,4]. Emulsion polymerization process is used for the commercial production of ABS resin plastics. Emulsion polymerization of 1,3-butadiene or polybutadiene latex is a basic ingredient of ABS resin. Various studies on the aspects of kinetics, stirring conditions, monomer/water ratio, initiator concentration, emulsifier concentration, and effect of thiols on the emulsion polymerization of butadiene has been intensively conducted [5–8]. Rapid expansion of ABS resin production has resulted in a great demand for proper hazard review of PBL reactions. In spite of the enormous industrial application of polybutadiene-containing copolymers prepared by emulsion polymerization (e.g., polybutadiene rubber, ABS, styrene–butadiene rubber), very little effort was focused to the adiabatic runaway of emulsion polymerization containing butadiene or polybutadiene. Similar study on the

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thermal stability and runaway behavior of styrene–acrylonitrile copolymerization has been performed by Mannan and coworkers [9]. Recent evaluation on the dimerization and secondary reaction of 1,3-butadiene has been conducted by the adiabatic calorimetry [10].

Process engineers of the ABS plants have paid much more attention to the safe operations of the PBL, SAN and ABS polymerization process in Taiwan. Both runaway and venting behaviors are required for venting sizing and flare load sizing for whole ABS plant. Verification on various credible scenarios provides the essential data for process safety management and emergency relief system design. Owing to the high monomer ratio (larger than 50% of volume), large batch sizes (reactor volume from 16 to 50 m<sup>3</sup>) and higher operation temperature/pressure, the ERS design such as vent sizing, knock-out drum, relief piping systems, and flare capacity, etc. are important for the ABS plants in the blowdown of overpressure caused by runaway reaction. In 1982, a severe explosion killed 6 persons and injured 198 people occurred and was originated by runaway reaction of AS (poly(styrene–acrylonitrile), SAN) in Japan. Volatile acrylonitrile and styrene released from the stack of the emergency relief system were ignited by the spark of the electrical set-up and resulted in the explosion [11]. Besides, some near-miss events were occurred in the flare system while the emergency relief activated by the PBL reactors in the petrochemical industry in Taiwan. Polymerization temperatures are controlled by heating/cooling system at about 60–80 °C. The related set pressure of blowdown is set at about 10–18 bar dependent upon the various ABS process or products. Both the transient runaway and relief behaviors in reactor are required for vent sizing and flare load assessed by using DIERS methodology in an ABS plant.

The aim of this work is to apply the various calorimeters to determine the thermal hazard and runaway behaviors of emulsion polymerization. Moreover, direct measurement on the runaway behaviors of 1,3-butadiene and ABS emulsion polymerization for commercial/non-commercial emulsion recipes and on identifying operation parameters that may lead to worst case scenario. Huge heat of polymerization and heat generation rate tell that the ABS polymerization reactor will possess potential hazards. Verification of worst credible scenarios is essential for process safety design, risk assessment and control of loss.

## 2. Experiment

### 2.1. Sample

CHP80%, PB latex solution, styrene, 1,3-butadiene and acrylonitrile were freshly supplied from local petrochemical company prior to use. 1,3-Butadiene of commercial grade with inhibitor TCB removed by caustic wash was used. Potassium persulfate, a kind of inorganic peroxide with commercial grade, was used as initiator. The emulsifier was a mixture of rosin soap, fatty acid and sulfonate. *tert*-Dodecyl-mercaptan of commercial grade is used for the modifier. The purity of these chemicals was better than 99%.

### 2.2. DSC (Differential Scanning Calorimeter)

The temperature programmed screenings were performed on a Mettler TA4000 system coupled with a DSC25 measuring cell [12]. The system was connected to an IBM compatible PC where the data were stored and analyzed. Disposal high pressure crucible (ME-26732) was used for acquiring data. Standard aluminum crucible (ME-27331) was used for heat capacity measurement which was utilized to calculate adiabatic temperature rise and thermal inertia in adiabatic runaway tests. The programmed scanning rate was chosen to be 4 K/min. The exothermic onset temperature here was chosen to be a signal-to-noise ratio around 5.

### 2.3. RSST (Reactive System Screening Tool)

A computer controlled reactive screening tool manufactured by FAI was used for advanced thermal analysis [13]. The system consisted of an insulated 10 ml spherical glass test cell of low thermal inertia open to a safe stainless steel containment vessel fitted with a bursting disc. A Ni–Cr heater was used to compensate for heat loss and to add heat to initiate the reaction to runaway.

### 2.4. VSP2 (Vent Sizing Package 2)

A PC controlled adiabatic calorimeter system, the Vent Sizing Package 2 manufactured by FAI [14], was used to measure the thermokinetic and thermal hazard data such as temperature and pressure trace in relation to time and also for worst case identification. The low heat capacity of the cell assures that essentially all the reaction heat released remains within the test sample. Thermokinetics and pressure behaviors in the small test cell (112 ml) can therefore be extrapolated directly to process scale due to the low thermal inertia of about 1.05–1.12. Three types of cells containing 1 in. stir bar for closed testing, top venting or bottom dumping are available. Thermal runaway behaviors can be acquired by using the cell of closed type. The two-phase flow pattern such as churn-turbulent or homogeneous equilibrium flow can be determined directly from top venting experiments. Detailed information on the performance of the VSP calorimeter can be found in the literature. Both the emulsion polymerization of butadiene and polymerization of ABS were carried out in a test cell with volume of 112 ml in the VSP2 calorimeter. The aqueous mixture consisted of emulsifier and initiator was first filled by vacuum suction and the monomers (butadiene, styrene, and acrylonitrile) were charged sequentially by vacuum filling, gravity or nitrogen padding. Data of thermal runaway reactions were collected by heat-wait-search or constant heating-power modes. The volume ratios of the reactants to that of the test vessel were from 60 to 93%.

### 2.5. Runaway reactions of credible worst case

For engineering design purposes, these adiabatic runaway scenarios were tested for verifying the credible worst cases which may be occurred in the process area. Operation devi-

ations that may lead to the credible worst case scenarios were verified by adiabatic runaway experiments. These possible deviations were chosen through delicate discussions with process engineers in the process site which may be encountered. The worst cases determined and assigned by the process engineers might be selected for the further blowdown experiment using VSP2 or bench apparatus. The following scenarios were chosen for PBL emulsion polymerization:

- (1) Normal recipe for simulating the cooling failure.
- (2) Normal recipe and no stirring for simulating the stirrer failure.
- (3) Normal recipe with half emulsifier for simulating the mischarge.
- (4) Normal recipe with air or oxygen in vapor phase for simulating the oxygen effect.
- (5) Double charge of initiator for simulating the mischarge.
- (6) Normal recipe with constant electric heat power for simulating the external fire.

The following scenarios were chosen for ABS emulsion polymerization:

- (1) Normal recipe for simulating the cooling failure.
- (2) Normal recipe with double charge of initiator for simulating the mischarge.
- (3) Normal recipe with double charge of styrene for simulating the mischarge.
- (4) Normal recipe with double charge of acrylonitrile for simulating the mischarge.
- (5) Normal recipe without charge of solvent (bulk polymerization) for simulating the mischarge.

### 3. Process description

An ABS plant is basically composed of process area of polymerization of butadiene (PBL plant), process area of copolymerization of styrene and acrylonitrile (SAN plant), process area of copolymerization of ABS (ABS plant), process area of ABS basic powder (ABS plant), and ABS/SAN compounding region (ABS plant). Most of the emergency relief systems constructed were based on the guides of API520 and API521. The volume of reactor for both PBL and ABS are about 45 m<sup>3</sup>. The normal recipe, operation conditions and design data are listed in Table 1.

### 4. Results and discussions

#### 4.1. Thermal analysis

The onset temperatures and heat of reactions of ABS copolymerization or SAN copolymerization in process recipes can be easily acquired by using programmed scanning in DSC calorimetry. Individual reactants or monomers, such as styrene, cumene hydroperoxide and acrylonitrile, were screened for potential heat sources investigation. These thermograms of reactive monomers for thermal analysis are depicted in Fig. 1. For styrene, the exothermic onset temperature is at about 100 °C and

Table 1

Operation conditions and design data for existing (a) PBL emulsion polymerization reactor and (b) ABR emulsion polymerization reactor

(a) PBL reactor	
Temperature control	Cooling coil with NH <sub>3</sub> (l)
Dosing	Batch
Recipe	
BD (kg)	19,200
Emulsifier (kg)	11,300
Initiator (kg)	1365
TDDM (kg)	38
Operation pressure (kgw cm <sup>-2</sup> G)	6–12
Reaction temperature (°C)	62–75
Initial volume fraction of reactant (%)	88
Final volume fraction of product (%)	72
Thermal inertia ( $\phi$ )	1.18
Heat of polymerization of BD (kcal/kg)	346
Existing PSV	3L4
Relief setting pressure (kgw cm <sup>-2</sup> G)	15
PSV overpressure setting (%)	10
ERS design base	Cooling failure
(b) ABS reactor	
Temperature control (°C)	60–70
Volume of reactor (m <sup>3</sup> )	45
Recipe	
H <sub>2</sub> O (solvent) (l)	17,070
Emulsifier (l)	3558
PBL latex (l)	6384
TDDM (l)	70
FeSO <sub>4(aq)</sub> (4%) (l)	1610
Styrene (l)	8565
Acrylonitrile (l)	4236
CHP (80%) (l)	53
Thermal inertia ( $\phi$ )	1.2
Existing PSV	4M6
Relief setting pressure (kgw cm <sup>-2</sup> G)	2
PSV overpressure setting (%)	20
ERS design base	Cooling failure

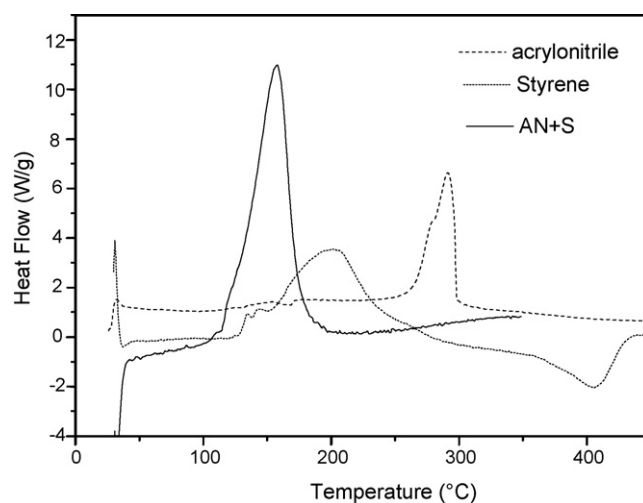


Fig. 1. (---) Thermogram of acrylonitrile detected by DSC. (···) Thermogram of styrene detected by DSC. (—) Thermogram of acrylonitrile mixed with styrene detected by DSC.

Table 2  
DSC data for thermal analysis

Sample	Weight (mg)	Onset temperature (°C)	Peak temperature (°C)	$\Delta H$ (J g <sup>-1</sup> )	Scanning rate (4 K/min)
S	6.50	100	202	647	4
AN	5.00	260	323	2290	4
CHP 80%	5.05	90	159	1510	4
S(1) + AN(1)	5.78	125	181	892	4
S(1) + AN(2)	5.51	125	166	904	4
S(2) + AN(1)	6.45	125	180	802	4
S(1) + AN(1) + CHP(1)	6.28	110	157	883	4
S(1) + AN(2) + CHP(1)	6.79	110	161	969	4
S(2) + AN(1) + CHP(1)	8.10	105	154	782	4
S(1) + AN(1) + CHP(2)	7.25	105	156	902	4

Weight ratio—S(1):AN(1):CHP(1) = 1 g:2.272 g:15.94 mg. S: Styrene; AN: Acrylonitrile; CHP: Cumene hydroperoxide.

the heat of polymerization is about 647 J g<sup>-1</sup>. Onset temperature and heat of polymerization of acrylonitrile are measured to be 260 °C and 2290 J g<sup>-1</sup>, respectively. However, the mixed reactant of styrene and acrylonitrile has a lower onset temperature at about 125 °C. Cumene hydroperoxide decomposed at the lowest temperature of 90 °C that provided the needed free radicals for the initiation of polymerization of ABS. The onset temperatures and heat of reactions of these reactive materials were determined and listed in Table 2. The heat of copolymerization of ABS by combined the styrene, acrylonitrile and PB latex was determined to be (890 ± 20) J g<sup>-1</sup> of monomer. Heat of polymerization and heat source for initiation to runaway in case of process deviation thus can be attributed to be the copolymerization of SM and AN. Enthalpies change of SAN copolymerization were listed in Table 2 for illustrating process deviation of mischarge of reactants. For the copolymerization of styrene and acrylonitrile, the credible worst case from thermal analysis is the double charge of acrylonitrile in comparison to normal recipe due to the largest heat of polymerization released.

#### 4.2. RSST screening

RSST calorimeter was a fast and inexpensive approach for screening or assessing thermal runaway behaviors. The normal recipe of ABS emulsion process was first conducted in RSST. However, an apparent thermal runaway phenomenon was observed in this case. This is because the highly volatile property of acrylonitrile and the bubbly feature of polymerizing styrene. Without the water for heat sink, the runaway characteristics were easily assessed by RSST with acquiring temperature and pressure traces shown in Fig. 2. Data of runaway reaction of ABS emulsion polymerization in process recipe without solvent detected by RSST were listed in Table 3.

Table 3  
Runaway data by RSST tests

Sample	Weight (g)	Final temperature (°C)	Maximum pressure (psi)	Exothermic heat rate (°C/min)	N <sub>2</sub> backing pressure (psi)
S	8.55	320	117	3.3	100
S + AN + PBL + CHP (process recipe, bulk (without solvent))	9.7	170	111	2.0	100

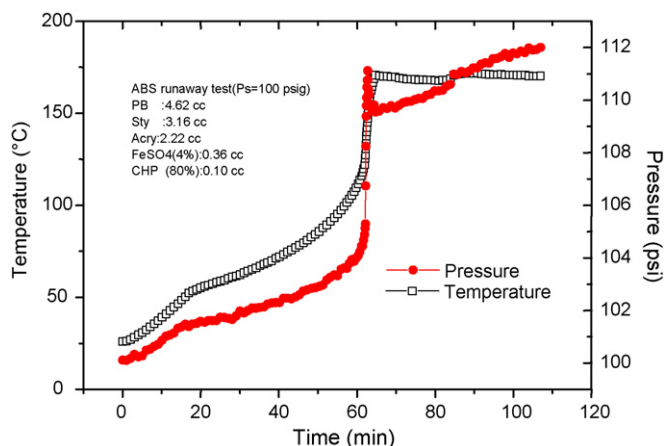


Fig. 2. Runaway behavior on emulsion polymerization of ABS detected by RSST.

#### 4.2.1. Adiabatic runaway behaviors on emulsion polymerization of butadiene

Two stages of runaway reaction are observed for the emulsion recipe. The second stage reaction may or may not be observed depending the influence of mixing or the transport polymerizing micelle. Mixing has a strong effect on the rate of emulsion polymerization. The concentration of initiator does not mainly affect the runaway behavior. Increased emulsifier concentration will result in an increased self-heat rate. The pressure behavior of PBL system contributed from the vapor of butadiene is a tempered system. The presence of oxygen will inhibit polymerization of butadiene. An external fire with constant wall heating will promote higher self-heat rate and this is recommended as the worst case scenario of emulsion polymerization on butadiene.

The data which characterize the runaway behaviors of the emulsion polymerization are listed in Table 4. Figs. 3 and 4 show

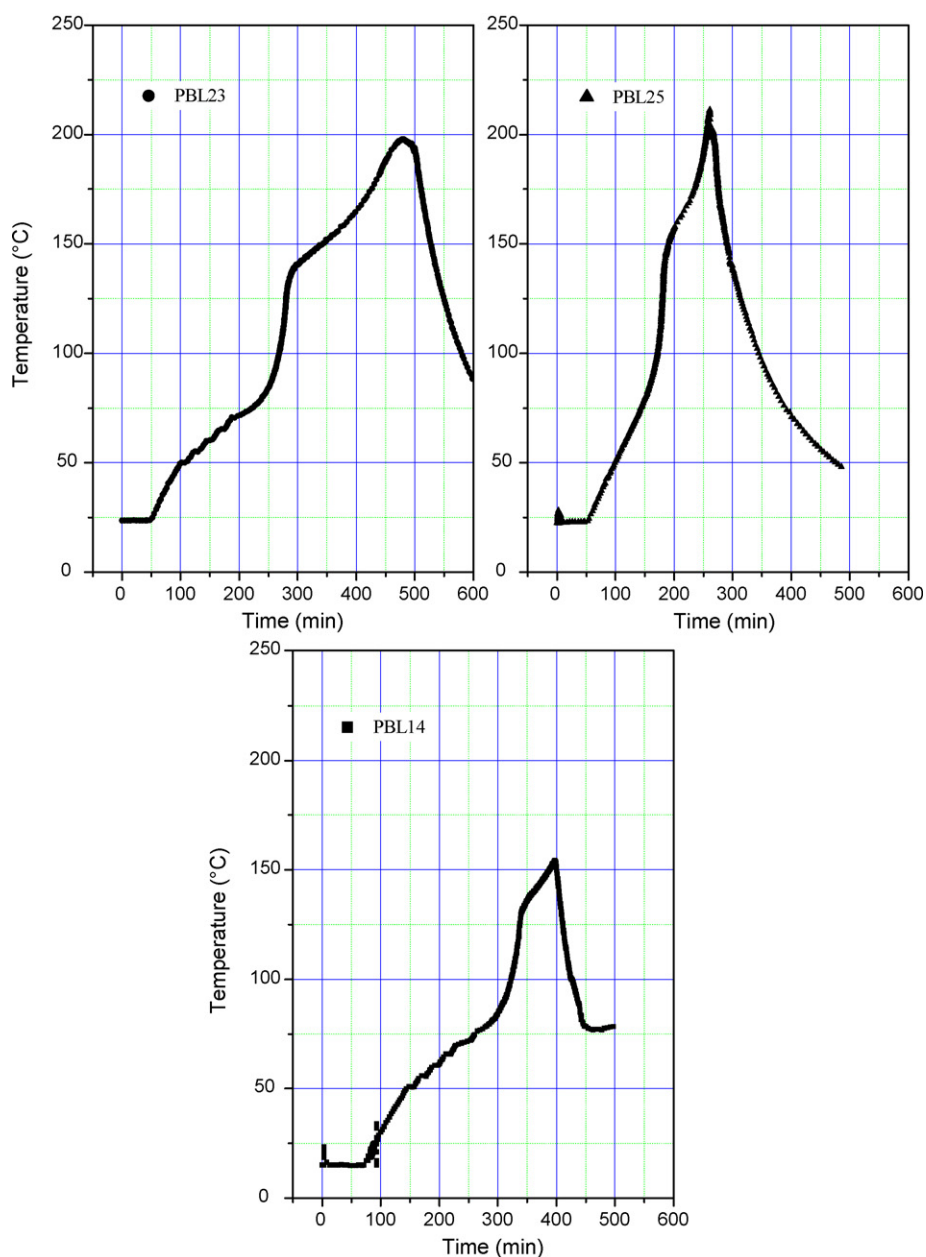


Fig. 3. Temperature runaway curves on emulsion polymerization of butadiene detected by VSP2. (■) PBL14; (●) PBL23 (▲) PBL25.

the characteristics of temperature runaway curve and adiabatic self-heat rate. Deviations of process or reaction conditions are selected and compared for determining the credible worst cases. We assume that:

- (1) The final temperature and adiabatic temperature rise depend on the conversion of butadiene in emulsion polymerization.
- (2) Self-heat rate is proportional to the rate of propagation rate of polymerization or the effective particle number per unit time.
- (3) Pressure of the emulsion system is a function of recipe and the fraction of free oil phase containing butadiene.
- (4) Pressure rising rate is a function of vapor–liquid equilibrium and energy transfer within the mixed reactant.

The heat of polymerization of butadiene is  $346 \text{ cal g}^{-1}$ , which is very close to the heat of polymerization of 1-butene ( $87 \text{ kJ/mol}$ ) [15] or styrene ( $73 \text{ kJ/mol}$ ) [16].

In a fully mixing condition, the temperature runaway curve possesses two amazing regions detected in an adiabatic reactor. An Arrhenius type or parabola was observed in the temperature range of  $62\text{--}135^\circ\text{C}$ . However, a linear curve was then detected between  $135$  and  $195^\circ\text{C}$ . These results were summarized in the following:

- (1) PBL1 (low BD ratio): a linear exothermic curve with the self-heat rate about  $0.2^\circ\text{C/min}$  from  $62$  to  $100^\circ\text{C}$ .
- (2) PBL2 (low stirring rate): a parabola curve was detected from  $62$  to  $125^\circ\text{C}$ .

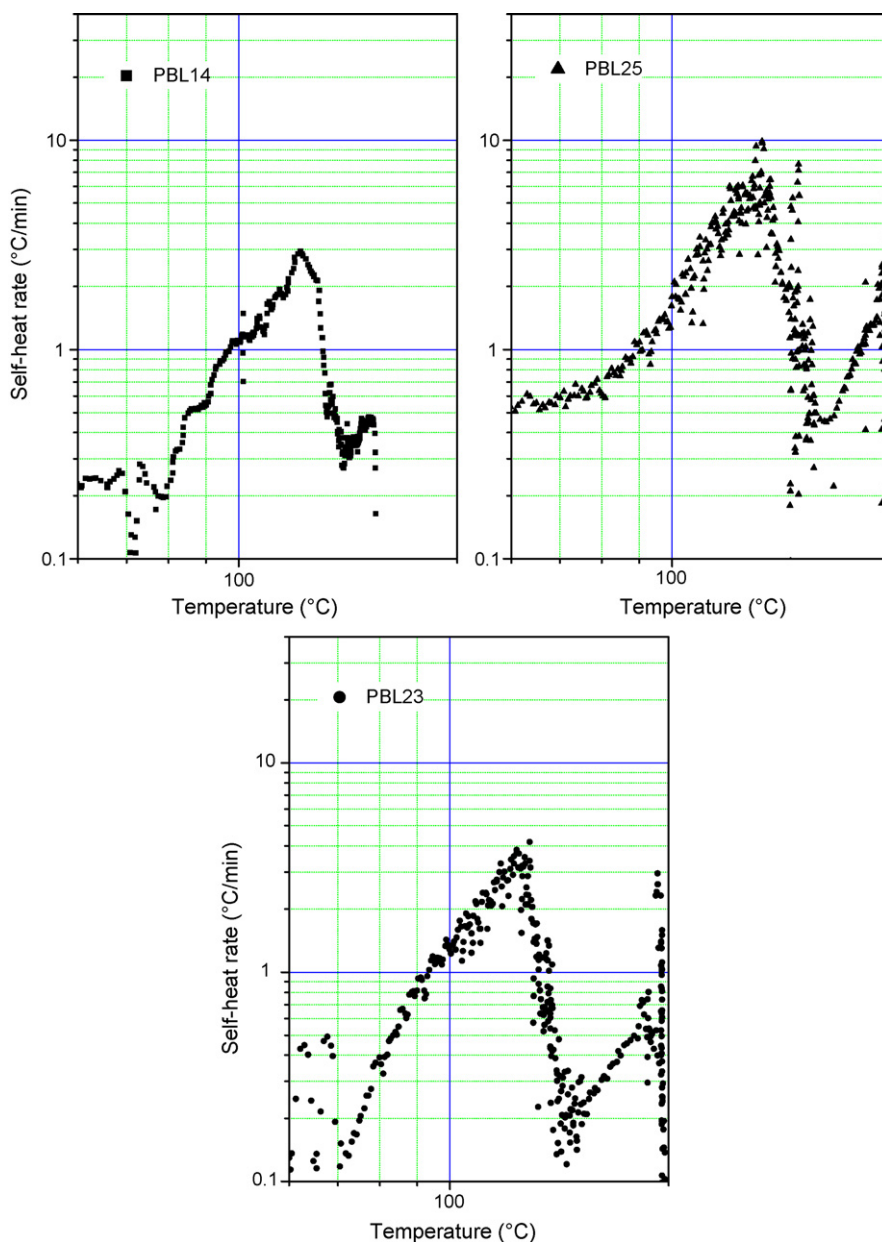


Fig. 4. Self-heat rate of runaway reaction on emulsion polymerization of butadiene. (■) PBL14; (●) PBL23; (▲) PBL25.

- (3) PBL3 (no stirring): a parabola curve was detected from 62 to 125 °C.
- (4) PBL4 (double initiator and low stirring rate): a parabola curve was detected from 62 to 130 °C.
- (5) PBL8 (half emulsifier and low stirring rate): a linear exothermic curve with the self-heat rate about 0.7 °C/min from 90 to 115 °C.
- (6) PBL17 (one-third emulsifier more and high stirring): a parabola curve from 62 to 135 °C and a linear exothermic curve with the self-heat rate about 0.2 °C/min from 135 to 195 °C were detected.
- (7) PBL21 (1 atm oxygen in vapor phase): a parabola curve was detected from 62 to 130 °C.
- (8) PBL22 (high stirring rate): a parabola curve from 62 to 135 °C and a linear exothermic curve with the self-heat rate about 0.2 °C/min from 135 to 170 °C were detected.
- (9) PBL23 (1 atm in vapor phase): a parabola curve from 62 to 135 °C and a linear exothermic curve with the self-heat rate between 0.2 and 0.5 °C/min from 135 to 198 °C were detected.
- (10) PBL25 (constant heat power): a parabola curve from 62 to 135 °C and a linear exothermic curve with the self-heat rate between 0.3 and 2.0 °C/min from 135 to 210 °C were detected.

These novel findings can be explained by the bond energy, Harkins' model [3] and rate of emulsion polymerization. Thermodynamic conversion  $\alpha$  of butadiene is defined as

$$\alpha = \left( \frac{T - T_0}{T_f - T_0} \right)$$

Table 4  
Data of runaway reaction on emulsion polymerization

Test name	PBL14	PBL23	PBL25
Scenario	High stirring speed	1 atm air	Constant heat power (17.5%)
Modifier (g)	0.0901	0.0923	0.0902
Initiator (g)	3.19	3.197	3.190
EME (g)	26.32	26.332	26.32
Butadiene (g)	45.6	43.2	44.2
Total amount	75.2011	72.8213	73.8002
Method of BD charging	Gravity	Gravity	Gravity
$V_{\text{reactant}}/V_{\text{cell}}$ (%)	91.8	88.4	89.8
$\phi$	1.072	1.074	1.073
Magnetic stirring rate	High 3.5	Low 8	Low 8
$T_{\text{on set}}$ (°C)	75	70	–
$T_{\text{max}}$ (°C)	154.5	197.9	210
$P_{\text{max}}$ (psig)	592.3	619.9	989
$(dT/dt)_{\text{max}}$ (°C/min)	3.6	3.2	6.2
$(dP/dt)_{\text{max}}$ (psi/min)	10	23	65
Remarks	Halted manually		

The development of the kinetics of an emulsion is traditionally proposed and divided into three distinct intervals [3,4]. Interval 1 is the particle nucleation stage early in the batch reaction with a typical conversion less than 10% of monomers. Most of the particles are formed in interval 1. The reaction proceeds by polymerization with the micelle particles. The monomer concentration in the polymer particle is thermodynamic limited because of the free energy required to expand the surface area of the colloidal particle. Interval 2 is characterized by a constant number of particles, while the reaction in the particle continue in the presence of a separate monomer phase. The starting of interval 2 is considered as the conversion that the emulsifier concentration drops below the critical micelle concentration (CMC) [3–8], thus the lower exothermic self-heat rate or polymerization rate can be probed. The emulsion mixtures consist of three phases: monomer droplets, monomer-swollen latex particles, and aqueous solution. The number of particles is also remained constant in interval 3. When the conversion has proceeded at about 60%, the monomer droplets disappear sharply, and the emulsion system becomes a two-phase of aqueous phase and the monomer-swollen latex particles. Continuing polymerization reduces the monomer concentration and causes the decrease in pressure. We therefore concluded that, from the temperature runaway data, the transition point from interval 1 to interval 2 is determined at about 135 °C. By the conversion of bond energy of butadiene, the initial point of interval occurs at the conversion of mole fraction in the vicinity of 30%. However, the distinguishable features between interval 2 and interval 3 can be determined by corresponding temperature when pressure starts to drop off sharply. Consequently, interval 3 is found at about 195 °C in an adiabatic condition.

During the particle nucleation and growth stages (interval 1), the overall polymerization reaction rate law is proposed [4–8] and as followed:

$$R_p = k_p C_M \left( \frac{n}{N_0} \right) N$$

or

$$R_p = R_p(k_p, T, S, R, A_s, d_p)$$

The overall self-heat rate can be given as:

$$\frac{dT}{dt} = k \Delta H R_p$$

where  $k$  is a temperature function related to  $k_p$ ,  $T$ ,  $S$ ,  $R$ ,  $A_s$ ,  $d_p$ , thermal inertia, micelle concentrations and effective particles.

If the micelle concentration is lower than the critical micelle concentration, the particle nucleation stage is terminated. The adiabatic temperature curve versus time in interval 1 is determined to be a parabolic curve which correlates to the nucleation and growth of the particles. However, the temperature trace is intrinsic linear at interval 2. The self-heat rates are proposed to be the diffusion-controlled and mass-transported types in these two intervals, respectively.

**4.2.1.1. Effect of external fire.** Relief capacity and runaway behaviors for the polymerization vessel are evaluated on the basis of the wetted area exposed to external fire. PBL 25 in Table 4 represents the runaway situation under fire case. The heat power input from fire exposure is calculated by using the equation recommended by API 520. The definition of  $Q$  is

$$Q = 21,000A^{0.82}$$

External heat power of 3.73 W (73 g times 50.5 W/kg) transferred to test cell was generated by electric heating, which corresponded to the fire exposure of 800,500 W to the industrial reactor containing the reactant of 15,851 kg.

#### 4.2.2. Adiabatic runaway behaviors on ABS emulsion polymerization

Only one stage of runaway reaction is observed for the emulsion recipe. Mixing has a strong effect on the rate of emulsion polymerization. The pressure behavior of ABS emulsion polymerization system is also a tempered system, which is attributed to the combined vapor pressures of monomers. An external fire with constant wall heating will enhance higher self-heat rate.

The data detected by VSP2 which characterize the runaway behaviors of the emulsion polymerizations are listed in Tables 5a and 5b. Figs. 5 and 6 show the characteristics of temperature and pressure runaway curves. Deviations of process or reaction conditions are selected and compared for determining the credible worst cases. We assume that:

Table 5a  
Test recipes in VSP2 of credible cases

Credible cases	PBL (g)	S (g)	AN (g)	H <sub>2</sub> O (g)	CHP (mg)
Process ratio	12.00	14.89	6.52	43.91	106.5
AN double	12.61	14.85	13.06	44.25	108.08
S double	11.81	29.69	6.69	43.43	104.53
CHP double	11.90	14.83	6.55	43.32	207.92
Bulk (without solvent)	33.50	21.48	13.41	–	210.0

Table 5b  
Credible cases in VSP2 tests

Credible cases	Onset temperature (°C)	$\Delta T_{ad}$ (°C)	$T_f$ (°C)	$P_{max}$ (psi)	$(dT/dt)_{max}$ (°C/min)	$(dP/dt)_{max}$ (psi/min)
Process ratio	56	52	108	13.33	0.33	0.08
AN double	85	83	168	250.0	90.34	245.4
S double	81	42	123	40.0	1.745	7.594
CHP double	50	61	111	13.30	0.433	0.157
Bulk (without solvent)	39	252	291	311	2301.0	1677.0

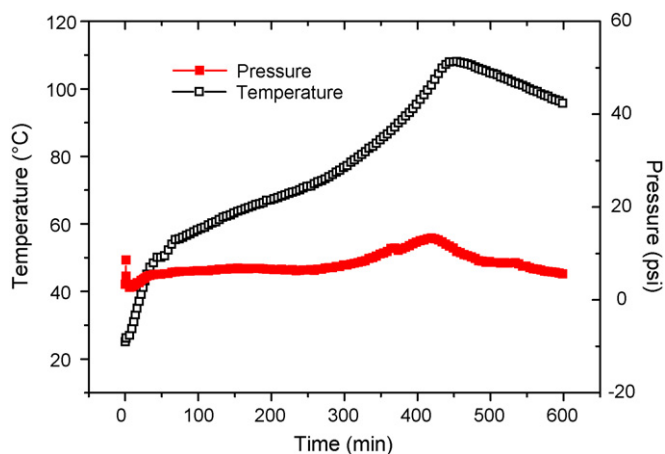


Fig. 5. Runaway behavior on emulsion polymerization of ABS in process recipe detected by VSP2.

- (1) The final temperature and adiabatic temperature rise depend on the conversion of styrene and acrylonitrile in emulsion polymerization.
- (2) Self-heat rate is proportional to the rate of propagation rate of polymerization or the effective particle number per unit time.
- (3) Pressure of the emulsion system is a function of recipe and the fraction of free oil phase containing monomer.
- (4) Pressure rising rate is a function of vapor–liquid equilibrium and energy transfer within the mixed reactant.

Runaway reaction corresponding to the rate constant belong to the Arrhenius type was observed in the whole temperature range. These results of adiabatic runaway of ABS emulsion polymerization were summarized in the following:

- (1) Recipe of process ratio: this can be assigned to be an inherent safer condition, associated with an adiabatic temperature rise of 52 °C and the maximum pressure does not exceed the setting pressure of safety relief valve.
- (2) Recipe of process ratio with the double charge of acrylonitrile: this is a more hazardous process deviation, associated with an adiabatic temperature rise of 83 °C a maximum self-heat rate of 90 °C/min, however the maximum pressure exceeds the setting pressure of safety relief valve. Double charge of acrylonitrile is recognized to be the credible and acceptable worst case which can be controlled by emergency relief system in case of runaway reaction occurred. This is recommended to be the design base for emergency relief system for ABS emulsion polymerization.
- (3) Recipe of process ratio with the double charge of styrene: this is a more hazardous process deviation than the normal recipe, associated with an adiabatic temperature rise of 42 °C, however the maximum pressure exceeds the setting pressure of safety relief valve.
- (4) Recipe of process ratio with the double charge of initiator (cumene hydroperoxide 80%): this is also a safer process deviation than the normal recipe, associated with an adiabatic temperature rise of 61 °C, however the maximum pressure does not exceeds the setting pressure of safety relief valve.
- (5) Recipe of process ratio without the charge of solvent: this is a most hazardous process deviation, associated with an adiabatic temperature rise of 252 °C and a maximum self-heat rate of 2300 °C/min. This scenario of runaway cannot be eliminated by emergency relief system, which is a worst condition with unacceptable risk and have to be avoided by process control.

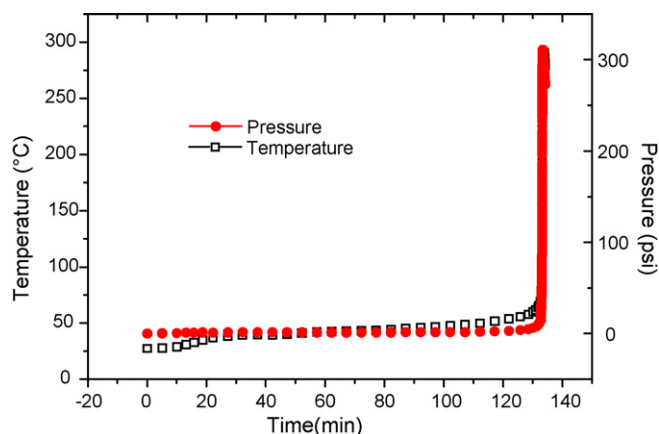


Fig. 6. Runaway behavior on emulsion polymerization of ABS without adding solvent detected by VSP2.

These experimental findings in adiabatic calorimeter can be explained by the bond energy, kinetic model of emulsion polymerization and rate of emulsion polymerization. Various recipes for acquiring credible worst cases experiments in VSP2 were summarized in Tables 5a and 5b. The chosen upset conditions were cooling failure, bulk polymerization without solvent (water) for emulsion polymerization in suspending condition, and double charge of monomers or initiators. From adiabatic



Table 6  
Data for calculating vent sizing of an ABS reactor

$m_o$ (kg)	18.240
$P_s$ (psig)	20
%Overpressure (%)	20
$V$ (m <sup>3</sup> )	45
$C_p$ (J/kg K)	2470
$(dT/dt)_s$ (°C/min)	0.7
$(dT/dt)_m$ (°C/min)	1.0
$T_s$ (°C)	58
$T_m$ (°C)	61

runaway data such as final temperature, adiabatic temperature rise, maximum pressure, and self-heat rate, the worst case was determined to be the bulk polymerization in ABS reactor. The importance of sequence for reactant charging is enhanced in process safety control. Fig. 5 displayed the temperature and pressure trajectories through ABS polymerization of normal recipe under runaway situation. Double charge of monomers or initiator is also possible in an ill process operation. Another worse credible situation was the double input by quantity of AN. Fig. 6 displayed the temperature and pressure trajectories through ABS bulk polymerization without solvent under runaway situation. Tables 5a and 5b displayed the severity of runaway of these credible examples. From these calorimetric data, it is obviously that the worst case may be encountered in the process is the bulk ABS polymerization without dosing of solvent.

#### 4.3. Emergency relief vent sizing

Under abnormal process operation in ABS emulsion polymerization, the maximum pressure of the double charge of styrene, the double charge of acrylonitrile and the bulk polymerization would exceed the relief setting pressure (2 kgw cm<sup>-2</sup> G). However, the building pressure of bulk polymerization and double charge of monomer in case of runaway will trigger the opening of SRV. While the maximum pressures of the credible cases studied by the VSP2 exceed the setting pressure of safety relief valve. The DIERS methodology is recommended for constructing emergency relief systems in emergency blowdown of two-phase flow for the runaway system. The experimental vapor pressure and self-heat rate data were used for calculating the venting size of PBL and ABS reactor by Leung's  $\omega$  method [17–19]. The design data were given in Table 6. The overpressure of the reactor was selected to be 20%, then the calculated vent diameter was 5 cm (2 in.) for the ABS reactor. For safety reason in ABS reactor, the SRV changed from 4M6 ( $d = 2.14$  in.) to 4N6 ( $d = 2.35$  in.) or 4P6 ( $d = 2.85$  in.) was strongly recommended [20]. By the same methodology and procedures, the calculated vent diameter was 8 cm for the PBL reactor. For safety reason in PBL reactor, the SRV changed from 3L4 to 6Q8 was strongly recommended.

## 5. Conclusions

Systematic investigations of thermal and pressure hazard of the PBL and ABS emulsion polymerizations were performed

by thermal analysis and adiabatic calorimetry. Runaway hazard resulted from PBL emulsion polymerization and ABS copolymerization was verified to be the bond energy released from polymerization of butadiene, styrene and acrylonitrile. In a normal operation condition or an acceptable upset condition, it can be controlled safely under the appropriate function of emergency relief system with limited risk. A venting diameter of 2.35 or 2.85 in. was suggested for an existing ABS copolymerization reactor in case of double charge of monomers which might lead to thermal runaway. For an existing PBL emulsion polymerization reactor, the design base is the acceptable worst case of normal recipe with an external fire, the calculated venting diameter of 8 cm was suggested for safe relief homogeneous two-phase flow of PBL emulsion polymerization reactor.

## Acknowledgments

The authors wish to thank National Science Council, ROC, for financial support of this study under contract No. NSC-92-2216-E-407-001 and Mr. Shi-Xin Wei of Grand Pacific Petrochemical Co., Kaohsiung, ROC, for providing uninhibited monomers and the necessary chemicals.

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