

The reactivity of 1,3-butadiene with butadiene-derived popcorn polymer

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Abstract

Adiabatic calorimetry performed on butadiene-derived popcorn polymer samples from industrial facilities has revealed exothermic behavior accompanied by non-condensable gas production, indicative of possible decomposition, at elevated temperatures. In the presence of low concentrations of 1,3-butadiene, reactivity is observed at temperatures of 60–70 °C; that is, 20–30 °C below those usually seen for butadiene alone. Once the butadiene is consumed, the reaction behavior reverts to that of the popcorn polymer alone. At higher butadiene concentrations, the low temperature reaction persists, eventually merging with typical butadiene behavior.

The butadiene reactivity with popcorn polymer is attributed to polymerization reaction at free radical sites in the popcorn polymer. Different popcorn polymer samples exhibit distinct extents of reactivity, presumably depending on the nature and concentration of the free radical sites and the structure of the material. Uninhibited butadiene exposed to 100 psia air, which may act to generate peroxide species, shows a small, additional exotherm around 50–80 °C. Contact of butadiene with lauroyl peroxide, providing free radicals upon decomposition, generates an exotherm at temperatures as low as 60 °C.

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1. Introduction

1.1. Background

1,3-Butadiene constitutes a major product from petrochemical ethylene plants. It is also an important starting material for building larger species, such as polymers. Butadiene can participate with a wide array of compounds in a variety of reactions. Its reactivity has been the subject of numerous open literature studies identifying free radical, ionic, and thermal pathways for reaction [1–6]. The conjugated double bond of 1,3-butadiene predisposes it to react with other species containing a double bond (including itself) to form an agglomerate [7,8]. This Diels–Alder condensation is unaffected by the presence of inhibitors, such as *tert*-butyl catechol, intended to scavenge oxygen and inhibit polymerization. The

reaction path, though, can proceed with formation of dimer (of which 4-vinylcyclohexene is the primary species) continuing onward with formation of oligomer, and ultimately resulting in high-temperature decomposition of the oligomer [9,10]. All of these steps, including oligomer decomposition, are exothermic. A simplistic diagram illustrating some butadiene reaction pathways is provided in Fig. 1.

Butadiene can also react with oxygen (such as would be available from air intrusion into a process) to form a shock-sensitive polyperoxide, which, upon continued exposure to butadiene, can produce a species commonly referred to as “popcorn polymer” [11,12]. This material grows through a free radical-catalyzed polymerization-like pathway, but forms in a manner that accumulates considerable molecular strain. Eventually, the rupture of bonds takes place, generating free radicals and catalyzing further exothermic, butadiene addition. The reactivity of the polymer generally increases rapidly with successive polymer generations. This material is often produced in butadiene-processing facilities where air

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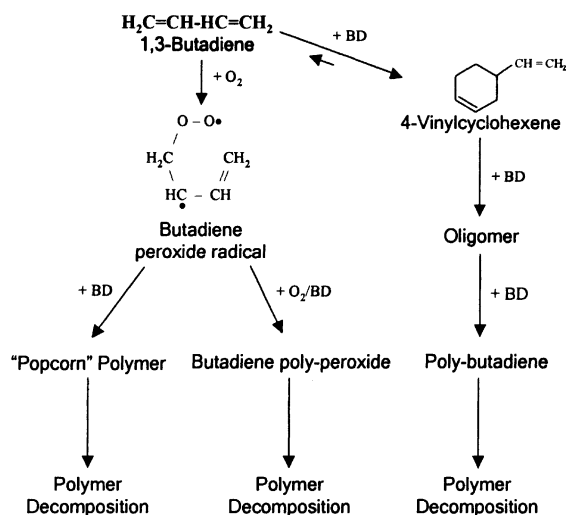


Fig. 1. Reaction scheme for 1,3-butadiene.

intrusion occurs. When sufficient popcorn polymer has accumulated in a section of equipment, the release of the molecular strain and accompanying expansion can lead to damage of the equipment, hence the association with the name "popcorn". The material, in some cases, also has a popcorn-like white and fluffy appearance.

Because the popcorn polymer can continue to react with butadiene, the potential exists for particular popcorn polymer combinations with butadiene to pose a significant reactive hazard in manufacturing equipment. In particular, reactivity can potentially occur for combinations of butadiene with popcorn polymer at lower temperatures than for either component alone.

1.2. Approach

In this study, the reactive behavior of butadiene-derived popcorn polymer alone and in combinations with butadiene has been examined through use of adiabatic calorimetry. Through measurement of heat release and pressure generation, this approach provides the opportunity to observe and characterize in a laboratory setting the accelerating reaction environment that might be experienced in an industrial-scale event.

2. Experimental

2.1. Equipment

Testing for this study was carried out in the Automatic Pressure Tracking Adiabatic Calorimeter (APTACTM) available from TIAX, LLC, described in previous studies [10,13,14]. The instrument operates on the principle of minimizing the heat loss from the sample plus 2–1/2 in., 0.02 in.-wall titanium sample cell by heating the gas space surrounding the cell to match the sample temperature, as measured by

an internal thermocouple. This allows a sample undergoing an exothermic reaction to self-heat at a rate and extent comparable to that in a large-scale, adiabatic environment. The APTAC heaters and containment vessel pressurization control can match temperature and pressure rise rates of up to 400 °C/min and 10,000 psi/min, respectively. Stirring is accomplished via a Teflon[®]-coated magnetic stir bar inserted in the sample cell.

The relative thermal capacitance of the cell plus sample to the sample alone is expressed by the thermal inertia factor, ϕ ,

$$\phi = 1 + \frac{m_c C_p c}{m_s C_p s}$$

where m denotes the mass, C_p the heat capacity, subscript c the cell + stir bar, and s the sample. The ϕ factor of commercial equipment approaches a value of unity; a value of 1.15–1.30 is typical of APTAC tests.

Operation is typically in the heat-wait-search mode. That is, the sample is heated to a pre-selected temperature and upon reaching this temperature, the instrument waits for a period of time (usually 25 min) for the cell and containment vessel temperatures to stabilize. After the wait period, the instrument "searches" at that temperature (for another 25 min) for any exothermic activity. During this time, the temperature of the containment vessel gas space is adjusted to match that of the sample thermocouple. If no heat-up activity exceeding a pre-set self-heating rate threshold is observed, it is concluded that there is no exotherm. The sample is then heated to the next temperature and the process repeated. If an exotherm is detected, the APTAC tracks the sample conditions and adjusts the temperature and pressure of the containment vessel accordingly (adiabatic or exotherm mode).

APTAC exotherm thresholds of 0.05–0.06 °C/min are employed to reduce the likelihood of the occurrence of "drift" (in which a slight thermocouple calibration imbalance yields a slow temperature rise rate and is interpreted as an exotherm).

2.2. Samples

2.2.1. 1,3-Butadiene

In previous studies, 1,3-butadiene was acquired from Matheson, Sigma-Aldrich, and Shell Chemical Company. Two sources provided 1,3-butadiene for this current study. Butadiene inhibited with *tert*-butyl catechol (TBC) was purchased from Sigma-Aldrich (#29, 503–5). Uninhibited 1,3-butadiene was obtained from a polymerization laboratory that obtains inhibited butadiene and removes the inhibitor by passing the material through an alumina bed. The laboratory's success in making polymer depends heavily on their effectiveness in removing inhibitor.

2.2.2. Polybutadiene

One sample of polybutadiene from Sigma-Aldrich (#43, 477–9) was obtained for this study.

2.2.3. Popcorn polymer

Several samples of 1,3-butadiene-derived popcorn polymer were obtained from butadiene extraction facilities at Shell Chemical Company manufacturing plants. These samples were generally harvested from piping and/or equipment damaged by the popcorn polymer. Typically, once the damaged hardware was removed from the butadiene unit, it was sealed and sent to the laboratory. Upon removing the seal, the popcorn polymer was removed (while exposed to air), but quickly transferred to a nitrogen-purged dry box. The sample labeled as “BD popcorn polymer #4” was stored in a glass jar outside of a dry box for an extended period of time. While the popcorn polymer in the dry box retained a white color, “BD popcorn polymer #4” was visibly yellow in appearance, reflecting exposure to and reaction with oxygen.

2.2.4. Lauroyl peroxide

Lauroyl peroxide at 97 wt.% concentration was procured from Sigma–Aldrich (#29, 078–5) and stored in a refrigerator when not in use.

2.3. Procedures

The following procedures were invoked to enable charging of specified amounts of butadiene to the sample cell while limiting exposure of the popcorn polymer and butadiene to air.

2.3.1. Popcorn polymer addition

For each test involving popcorn polymer, a new, clean titanium cell was fitted with a septum, purged with nitrogen, and placed in the nitrogen-purged glove box containing the jars of popcorn polymer. Once the septum was removed, the target amount of popcorn polymer was then added to the cell, and the septum then replaced on the cell. In experiments with both butadiene and popcorn polymer, the popcorn polymer was first added by this procedure before butadiene was transferred into the cell.

2.3.2. Butadiene addition

To charge 1,3-butadiene to the titanium sample cell, the targeted amount of butadiene was first collected in a nitrogen-purged, dry ice/acetone-cooled, graduated glass condensation apparatus. With the sealed titanium sample cell immersed in a separate dry ice/acetone bath, one end of a cannula was inserted through a septum in the condensation apparatus and purged with nitrogen. The other end of the cannula was then inserted (along with a syringe needle as vent) through the sample cell septum. The butadiene was then slowly transferred by submerging the cannula in the butadiene liquid with a slightly elevated pressure of nitrogen in the condensation apparatus. Once the liquid was transferred, the cannula was removed from the sample cell, the sample cell removed from the dry ice/acetone bath, and the sample cell wiped to remove acetone and condensate on the outside. The sample cell (with

septum and syringe needle) was then quickly weighed to determine the amount of butadiene transferred. The sample cell (with septum and syringe needle) was then re-immersed in the dry ice/acetone bath and the needle removed. The process was repeated if additional butadiene needed to be added.

For tests involving lauroyl peroxide, addition was performed in two tests by solubilizing the initiator in chlorobenzene and then adding to the APTAC cell prior to charging with butadiene. In the final two tests with lauroyl peroxide, the initiator was added as dry powder directly into the cell without solvent. In all cases, the cell was fitted with a septum and purged with nitrogen before butadiene was introduced.

2.3.3. APTAC mounting

To attach the titanium sample cell to the APTAC containment vessel head while limiting exposure to air, the sample cell (with septum), along with the dry ice/acetone bath in which it was immersed, were placed inside a glove bag. The glove bag was then secured to the containment vessel head and the interior purged five times successively with nitrogen followed by evacuation via house vacuum. The septum was then removed from the titanium sample cell, the cell was mounted onto the containment vessel head, and the cell nut was then tightened. Once the cell was firmly attached, the glove bag was removed, the nut tightness checked, and the containment vessel closed.

Total sample weights ranged from 22.6 g to 53.6 g, while the total weight of titanium cell and stir bar ranged between 34.0 g and 40.8 g.

No gas samples for compositional analysis were taken at the end of any of the tests. A summary of test characteristics may be found in Tables 1–4.

3. Results and discussion

The tests are categorized into several groupings. The first examines the behavior of several butadiene-based popcorn polymer alone (i.e., with no 1,3-butadiene), along with a polybutadiene sample. This behavior is contrasted with that of neat 1,3-butadiene. The second grouping focuses on selected mixtures of 1,3-butadiene with popcorn polymer. The third grouping reports results for selected mixtures of 1,3-butadiene with a different popcorn polymer. The final grouping studies the effect of lauroyl peroxide as a free radical source on the behavior of 1,3-butadiene as well as the effect of air as a peroxide source with 1,3-butadiene as a peroxide source.

3.1. Butadiene-based popcorn polymer

To establish reference points for the behavior of mixtures of 1,3-butadiene with popcorn polymer, calorimetry for 1,3-butadiene alone and for several samples of butadiene-derived popcorn polymer alone were examined. The temperature versus time results are shown in Fig. 2. As demonstrated

Table 1

Summary of APTAC and VSP test conditions and results for 1,3-butadiene and butadiene-based polymers. Experiments typically set to search from 40 °C to 400 °C, with an upper temperature limit of 420–430 °C for exotherms. Experiments shutdown parameters typically set to 450–460 °C, 1800 psia, 1000–2000 °C/min, and 10,000 psi/min.

Run ID	FAIA044-29	A00287	AOO375	A00117	A00285a	A00522	A00281	AOO282
Date	FAI1995	May 11, 2000	January 11, 2001	January 12, 1999	May 8, 2000	Feb. 19,2002	April 27, 1999	May 1, 2000
LR	A044-29	LR24555-149	LR24922-91	LR24139-125	LR24555-147	LR25132-157	LR24555-142	LR24555-143
Material	1,3-Butadiene (uninhibited)	1,3-Butadiene (uninhibited)	1,3-Butadiene	Polybutadiene	BD popcorn polymer #1	BD popcorn polymer #2	BD popcorn polymer #3	BD popcorn polymer #4
Source	Matheson CP	Shell chemical	Sigma–Aldrich	Sigma–Aldrich	BD plant, May 2000	BD plant, May 2001	BD plant, April 2000	“Aged” BD plant, June 1998
ID		LR23143-1802	#29, 503–5	#43, 477–9	LR23143-52-27	LR23143-83-07	LR23143-52-24	LR23143-30-12
Sample mass [g]	53.6	34.86	38.94	40.08	30.35	34.74	30.30	30.20
Sample cell mass (Titanium) [g]	40.76 (SS)	31.01	31.10	35.03	31.16	32.34	31.07	31.10
Stirring bar mass (Teflon) [g]	–	3.47	3.41	3.49	3.46	3.42	3.48	3.42
Stirring rate (magnetic) [rpm]	–	300	550	200	300	300	300	300
Heat-wait-search increment [°C]	10	10	5	20	100	10	10	10
Exotherm threshold [°C/min]	0.05	0.05	0.05	0.06	0.05	0.06	0.06	0.05
Number of exotherms	1+	1+	1+	1	1	1	1	2
Initial observed exotherm temperature [°C]	99	85	105	244	120	156	172	72
Maximum observed temperature [°C]	474	894	533	522	422	453	468	420
Maximum observed pressure [psia]	1965	2089	2159	1630	200	341	438	1550
Maximum observed self-heat rate [°C/min]	2500 ^a	6100 ^a	10,300 ^a	890	9.3	29.5	90	0.57
Maximum observed pressure rate [psi/min]	6440	19800 ^a	29,640 ^a	2990	15.6	95.9	212	6.2
Temperature at maximum self-heat rate [°C]	336	893	533	487	409	410	435	374
Temperature at maximum pressure rate [°C]	304	367	486	519	418	448	467	419
Residual pressure at 50 °C [psia]	–	1208	–	395	45	107	130	46
Thermal inertia ^b , ϕ	1.14	1.20	1.16	1.12	1.20	1.16	1.17	1.23
Experiment duration (before S/D) [min]	410	734	899	543	1713	1979	1850	1006
Experiment shutdown cause	Pressure limit	Pressure limit	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit
Comments	VSP test 2.5 wt.% Hexane VSP can failed	pressure rate	Includes 0.4 g of 4.2 wt.% TBC/cyclohexane mixture; cell dislodged and containment vessel RD burst				Popcorn polymer “Neutralized” with DEHA	“Yellowed” popcorn polymer

^a Self-heat and pressurization rates sufficiently high to cause possible temperature, pressure reading lags.

^b Assuming a heat capacity of 0.5 cal/g K for the popcorn polymer nitrogen pad gas.

Table 2

Summary of APTAC test conditions and results for 1,3-butadiene + BD popcorn polymer sample #1 (LR#23143-52-27). Experiments typically set to search from 40 °C to 400 °C, with an upper temperature limit of 420 °C for exotherms. Experiment shutdown parameters typically set to 460 °C, 1800 psia, 2000 °C/min, and 10,000 psi/min.

Run ID	A00288	A00300	A00353a	A00354	A00361
Date	May 12, 2000	June 6, 2000	October 31, 2000	November 2, 2000	November 14, 2000
LR	LR24555-150	LR24555-166	LR24922-52	LR24922-54	LR24922-62
Butadiene concentration [wt.%]	5.8	74.9	67.4	53.5	79.8
Butadiene source	Polymer lab	Polymer lab	Polymer lab	Polymer lab	Polymer lab
Butadiene inhibited	No	No	No	No	No
Butadiene mass [g]	1.90	29.94	29.18	20.79	17.99
BD popcorn polymer mass [g]	30.61	10.02	14.13	18.07	4.56
Sample cell mass (Titanium) [g]	31.56	30.90	32.05	31.19	30.58
Stirring bar mass (Teflon) [g]	3.46	3.52	3.43	3.35	3.45
Heat-wait-search increment [°C]	10	10	5	5	5
Exotherm threshold [°C/min]	0.05	0.05	0.05	0.05	0.05
Number of exotherms	2	2+	2+	2+	2+
Initial observed exotherm temperature [°C]	62	92	71	71	87
Maximum observed temperature [°C]	420	696	803	556	627
Maximum observed pressure [psia]	216	1380	2120	1627	2084
Maximum observed self-heat rate [°C/min]	2.6	13,600 ^a	15,190 ^a	3602 ^a	7690 ^a
Maximum observed pressure rate [psi/min]	15.8	11,090 ^a	18,900 ^a	6770	30,480 ^a
Temperature at maximum self-heat rate [°C]	408	668	685	492	618
Temperature at maximum pressure rate [°C]	417	413	276	406	609
Residual pressure at 50 °C [psia]	< 49	932	1052	435	776
Thermal inertia ^b , ϕ	1.23	1.17	1.17	1.18	1.30
Experiment duration (before S/D) [min]	1884	578	815	729	775
Experiment shutdown cause	Exotherm limit	Exotherm limit pressure rate	Pressure limit pressure rate	Exotherm limit	Exotherm limit
Comments	Test shutdown at 148 °C due to blown heater fuse; test restarted				

^a Self-heat and pressurization rates sufficiently high to cause possible temperature, pressure reading lags.

^b Assuming a heat capacity of 0.5 cal/g K for the popcorn polymer nitrogen pad gas stirring rate in all tests set at 300 rpm.

Table 3

Summary of APTAC test conditions and results for 1,3-butadiene + BD popcorn polymer sample #2 (LR23143-83-07). Experiments typically set to search from 40 °C to 400 °C, with an upper temperature limit of 420 °C for exotherms. Experiment shutdown parameters typically set to 460 °C, 1800 psia, 2000 °C/min, and 10,000 psi/min.

Run ID	A00514	A00515	A00516	A00517	A00518	A00519	A00520	A00521
Date	December 18, 2001	December 19, 2001	February 11, 2002	February 12, 2002	February 13, 2002	February 14, 2002	February 15, 2002	February 18, 2002
LR	LR25132-123	LR25132-124	LR25132-151	LR25132-152	LR25132-153	LR25132-154	LR25132-155	LR25132-156
Butadiene concentration [wt.%]	50.1	75.6	25.7	62.7	20.2	50.4	14.0	50.0
Butadiene source	Polymer lab	Polymer lab	Polymer lab	Polymer lab	Polymer lab	Polymer lab	Polymer lab	Sigma–Aldrich #29, 503–5
Butadiene inhibited	No	No	No	No	No	No	No	Yes
Butadiene mass [g]	22.47	34.19	11.69	28.41	8.81	23.52	5.67	23.17
BD popcorn polymer mass [g]	22.40	11.01	33.74	16.87	34.75	23.12	34.71	23.12
Sample cell mass (Titanium) [g]	32.38	31.71	32.65	32.31	32.25	32.20	31.27	32.08
Stirring bar mass (Teflon) [g]	3.39	3.40	3.37	3.40	3.36	3.36	3.33	3.35
Stirring rate (magnetic) [rpm]	500	500	500	500	500	500	500	500
Heat-wait-search increment [°C]	5	5	5	5	5	5	5	5
Exotherm threshold PC/mini	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Number of exotherms	2+	2+	2+	2+	2+	2+	2+	2+
Initial observed exotherm temperature [°C]	86	86	82	86	84	81	72	77
Maximum observed temperature [°C]	429	505	462	540	468	513	425	441
Maximum observed pressure [psia]	1570	2018	464	2142	578	1435	325	2008
Maximum observed self-heat rate [°C/min]	4447 ^a	4990 ^a	42.3	11,510 ^a	58.2	9177 ^a	6.2	9800 ^a
Maximum observed pressure rate ^b [psi/min]	4292	14,380 ^a	171	32,810 ^a	277	4748	32.5	10,640 ^a
Temperature at maximum self-heat rate [°C]	329	440	420	436	438	513	388	374
Temperature at maximum pressure rate [°C]	626	456	458	536	466	425	420	431
Residual pressure at 50 °C [psia]	359	1805	142	1140	166	263	105	1356
Thermal inertia ^b , ϕ	1.16	1.15	1.16	1.16	1.16	1.15	1.18	1.16
Experiment duration (before S/D) [min]	872	917	985	848	8%	835	1856	705
Experiment shutdown cause	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit	Exotherm limit
Comments				temperature rate	temperature rate	temperature rate		

^a Self-heat and pressurization rates sufficiently high to cause possible temperature, pressure reading lags.

^b Assuming a heat capacity of 0.5 cal/g K for the popcorn polymer nitrogen pad gas stirring rate in all tests set at 500 rpm.

Table 4

Summary of APTAC test conditions and results for 1,3-butadiene + lauroyl peroxide (Sigma–Aldrich #29, 078–5). Experiments typically set to search from 25–30 °C to 400 °C, with an upper temperature limit of 300 °C for exotherms (420 °C for A00317). Experiment shutdown parameters typically set to 200–460 °C, 1800 psia, 1000–2000 °C/min, and 5000–10,000 psi/min.

Run ID	A00592	A00593	A00594	A00595	A00317
Date	March 26, 2003	April 1, 2003	April 7, 2003	April 10, 2003	July 3, 2000
LR	LR25703-O63	LR25703-066	LR25703-O71	LR25703-O74	LR24555-184
Butadiene concentration [wt.%]	98.3	92.2	98.5	92.4	100
Butadiene source	Sigma–Aldrich #29, 503–5	Sigma–Aldrich #29, 503–5	Sigma–Aldrich #29, 503–5	Sigma–Aldrich #29, 503–5	Polymer lab
Butadiene inhibited	Yes	Yes	Yes	Yes	No
Butadiene mass [g]	37.40	37.72	39.49	39.70	28.80
Lauroyl peroxide/chlorobenzene mass [g]	0.03/0.60	0.19/3.00	0.59/0.00	3.28/0.00	–
Lauroyl peroxide content [wt.%]	0.08	0.46	1.46	7.6	–
Pressure of air [psia]	–	–	–	–	100
Sample cell mass (Titanium) [g]	32.33	32.27	32.20	32.46	30.98
Stirring bar mass (Teflon) [g]	3.46	3.38	3.42	3.39	3.44
Stirring rate (magnetic) [rpm]	500	500	500	500	300
Heat-wait-search increment [°C]	5	5	5	5	5
Exotherm threshold [°C/min]	0.05	0.05	0.05	0.05	0.06
Number of exotherms	1+	2+	2+	2+	2+
Initial observed exotherm temperature [°C]	106	66	61	61	51
Maximum observed temperature [°C]	906	906	802	427	721
Maximum observed pressure [psia]	2375	1950	1711	1432	1890
Maximum observed self-heat rate [°C/min]	27,440 ^a	25,710 ^a	22,480 ^a	1263	10,035 ^a
Maximum observed pressure rate [psi/min]	36,690 ^a	25,080 ^a	21,230 ^a	16,640 ^a	36,560 ^a
Temperature at maximum self-heat rate [°C]	808	906	745	388	531
Temperature at maximum pressure rate [°C]	615	859	711	388	289
Residual pressure at 50 °C [psia]	731	–	1109	992	1038
Thermal inertia ^b , ϕ	1.18	1.18	1.19	1.18	1.26
Experiment duration (before S/D) [min]	1223	1121	1019	581	834
Experiment shutdown cause	Exotherm limit	Exotherm limit	Temperature limit	Temperature limit	Pressure rate
Comments					

^a Self-heat and pressurization rates sufficiently high to cause possible temperature, pressure reading lags.

^b Assuming a heat capacity of 0.5 cal/g K for the popcorn polymer nitrogen pad gas stirring rate in tests set at 500 rpm (300 rpm for A00317).

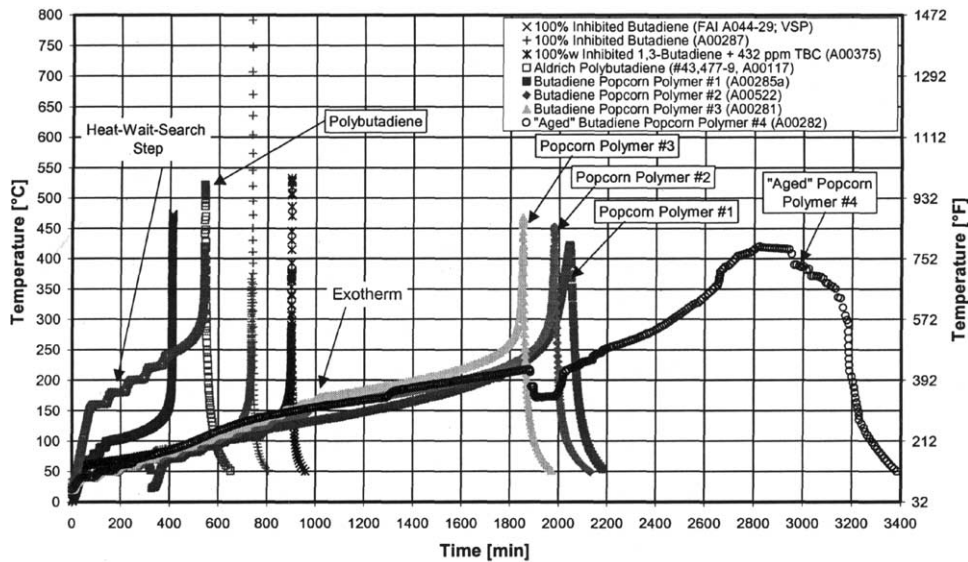


Fig. 2. Temperature–time history of butadiene and butadiene popcorn polymer; APTAC experiments, in nitrogen.

previously in the literature [6,13–15] butadiene exhibits exothermic reactivity (at 0.02–0.1 °C/min detection limit) when heated to temperatures of 90–105 °C. Note that temperatures exceeding 800 °C can be achieved if the test is allowed to continue without shutdown. For several different samples of popcorn polymer, exothermic behavior is observed above about 120 °C and continues to the point of instrument shutdown, i.e., around 420 °C. An exotherm for the commercially-available polybutadiene sample first appears around 241 °C. It is intriguing that the “aged” popcorn polymer sample in test A00282 displays exothermic reactivity beginning at a temperature as low as 70 °C accompanied by a more gradual increase in temperature with time. This could arise from an oxidation reaction utilizing oxygen already incorporated into the popcorn polymer.

The corresponding pressure profiles with time are given in Fig. 3. In the case of neat butadiene, pressures in excess of 1800 psia can develop prior to instrument shutdown. The polybutadiene sample also surpassed 1600 psia before the test was ended. For three of the four popcorn polymer samples, the final pressures prior to shutdown were more modest, ranging from 200 psia to 450 psia. On the other hand, the “aged” popcorn polymer sample clearly shows behavior different than the other popcorn polymer samples and nearly reached 1600 psia in the test.

The qualitative kinetic behavior of the sample is more directly illustrated in the self-heat rate plot in Fig. 4. This graph displays temperature rise rate versus negative reciprocal temperature (with the corresponding temperatures in °C shown).

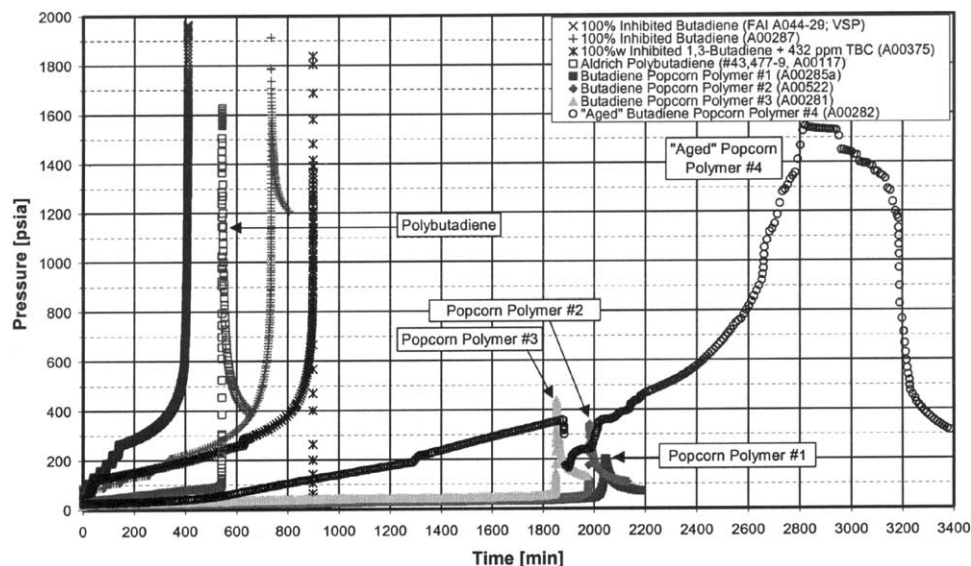


Fig. 3. Pressure–time history of butadiene and butadiene popcorn polymer; APTAC experiments, in nitrogen.

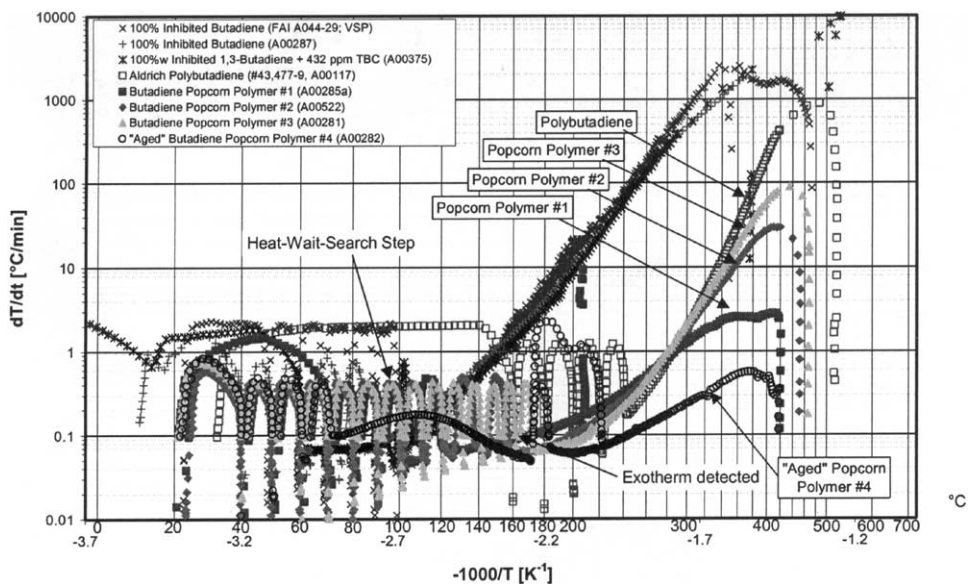


Fig. 4. Self-heat rate versus temperature behavior of butadiene and butadiene popcorn polymer; APTAC experiments, in nitrogen.

The direct link to an Arrhenius-plot can be obtained by multiplying the self-heat rate by the sample heat capacity and dividing by the heat of reaction to yield the observed reaction rate. The cycling of heat rates in the initial portion of the graph simply reflects the phases of the heat-wait-search steps. Beyond this cycling behavior, the slopes of the curves reflect the activation energy of the reaction. Fig. 5 displays the same information as Fig. 4, except that the initial heat-wait-search steps have been removed for clarity.

The characteristic exotherm of butadiene beginning approximately around 100 °C and continuing with a more-or-less linearly increasing rate on this log versus reciprocal tem-

perature plot is evident in Fig. 5. This behavior reflects the Diels–Alder dimerization of the diolefin in an environment without a significant concentration free radicals. The three butadiene plots clearly indicate the repeatability of the tests, even across different instruments (APTAC versus Vent Sizing Package (VSP)), butadiene charging techniques (cryogenic pre-loading versus manual syringe pump injection for the VSP test), and experimentalists. The plots also demonstrate that additional inhibitor does not affect the reactivity of the butadiene.

The polybutadiene and popcorn polymer samples all exhibit exotherms at higher temperatures than butadiene, start-

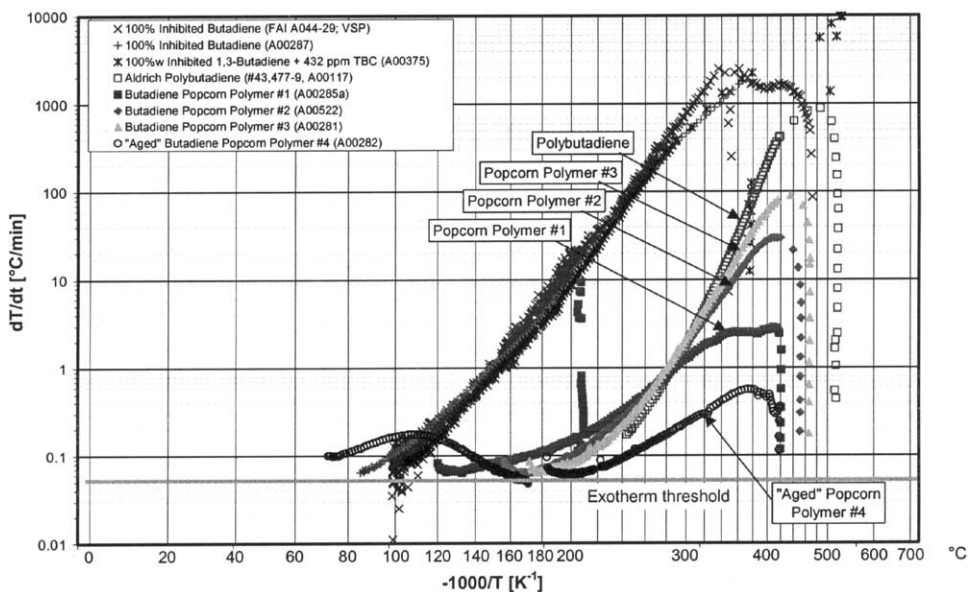


Fig. 5. Self-heat rate versus temperature behavior of butadiene and butadiene popcorn polymer; APTAC experiments, in nitrogen; heat-wait-search steps removed.

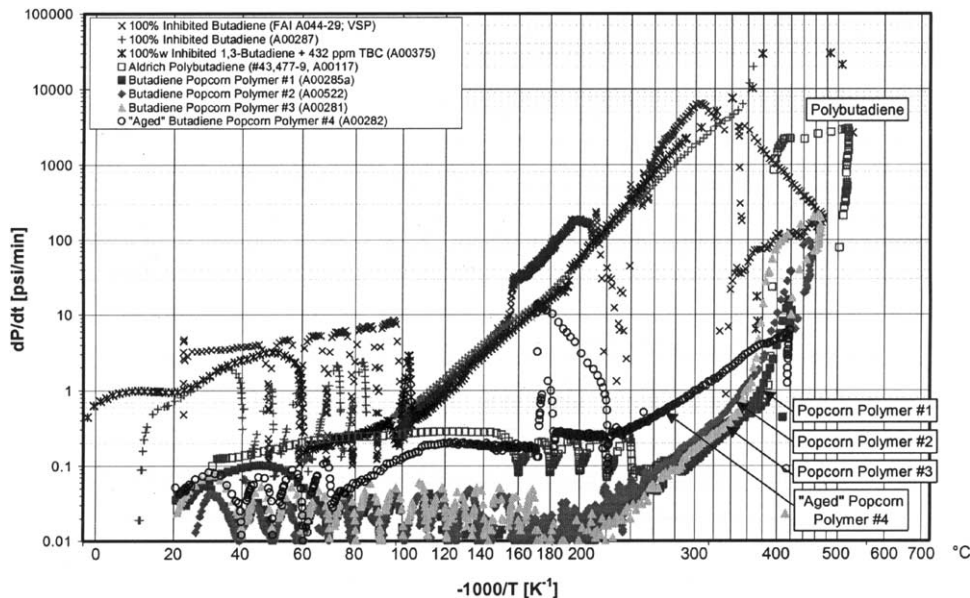


Fig. 6. Pressure rate versus temperature behavior of butadiene and butadiene popcorn polymer; APTAC experiments, in nitrogen.

ing at 180 °C and proceeding upward in rates until the point of instrument shutdown around 420 °C. The self-heat rate for popcorn polymer sample #1 reaches its maximum value prior to instrument shutdown. The “aged” popcorn polymer displays a similar behavior. Again, in addition to this exotherm, the “aged” popcorn polymer sample also shows an additional peak initiating at about 70 °C and reaching a maximum around 110 °C. This behavior suggests that contact of the popcorn polymer with oxygen (albeit, over a long period of time) can generate reactive species.

Two separate slopes are exhibited for the popcorn polymer at high temperature. One slope appears comparable to that of the polybutadiene sample. The other is significantly

less. This suggests that there may be two separate decomposition paths for the popcorn polymer or that other effects, such as mass transfer, are affecting the decomposition behavior. Exothermic behavior around 400 °C in polybutadiene has been attributed to cyclization [16].

The pressurization rate versus temperature behavior is illustrated in Fig. 6. The linear behavior (on the logarithmic versus reciprocal temperature scales) of butadiene up to 300 °C parallels that seen for the self-heat rates. At higher temperatures, the pressurization rate climbs more rapidly, exceeding 10,000 psi/min, suggesting the presence of oligomer decomposition. In the case of test A044-29, a very rapid drop in pressure at 350 °C indicates that the test can may have

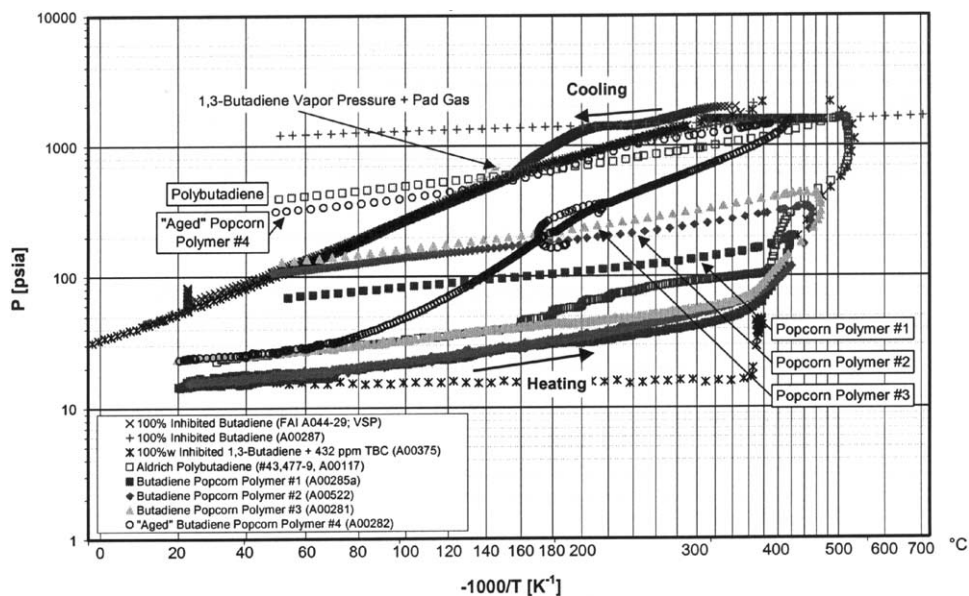


Fig. 7. Pressure versus temperature behavior of butadiene and butadiene popcorn polymer; APTAC experiments, in nitrogen.

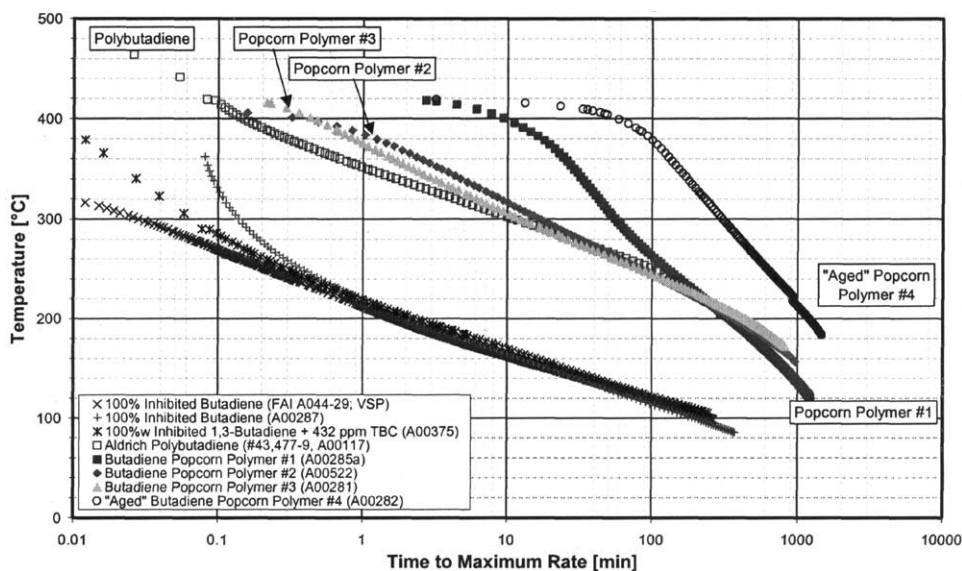


Fig. 8. Time to maximum rate for butadiene and butadiene popcorn polymer; APTAC experiments, in nitrogen.

failed leading to the inability to continue tracking the pressurization rate.

Not surprisingly, the polybutadiene and popcorn polymer exhibit pressurization rates that are much lower than for the butadiene. In the 350–380 °C temperature range, the pressurization rates for the polybutadiene and popcorn polymer increase abruptly with temperature, signaling the occurrence of decomposition. The “aged” popcorn polymer sample is an exception to this trend. The increase in its pressurization rate reaches an apparent maximum and is eventually orders of magnitude less than those for the other popcorn polymers.

The pressurization rate trends in Fig. 6 are reflected in the pressure versus temperature behavior of Fig. 7. At temperatures of 360 °C and above, sharper increases in the pressure

are found, most notably, for the polybutadiene and popcorn polymer and to a lesser extent for the butadiene.

The time-to-maximum rate for each sample as a function of temperature is found in Fig. 8. Again, the curves for the three butadiene tests coincide for much of the range. The polybutadiene and two of the popcorn polymer samples show similar behavior to the butadiene except for being shifted upward 120–140 °C. Popcorn polymer sample #1 displays very different behavior with a much greater slope. The “aged” popcorn polymer sample behaves quite similarly to popcorn polymer sample #1, but is shifted to higher temperatures. The effect of the initial exotherm on the time-to-maximum-rate in the “aged” sample is not captured due to the occurrence of the heat-wait-search step between the exotherms in the test.

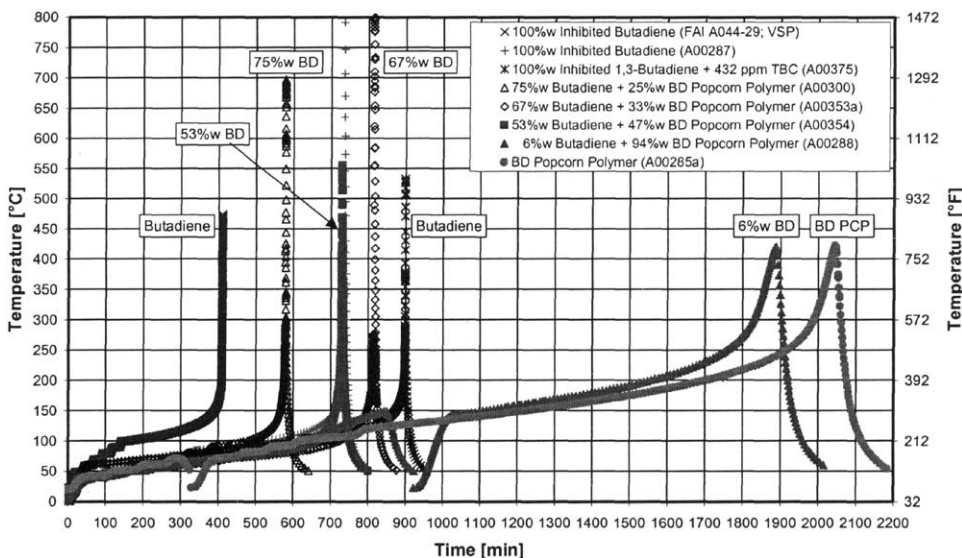


Fig. 9. Temperature–time history of combinations of butadiene and butadiene popcorn polymer #1; APTAC experiments, in nitrogen.

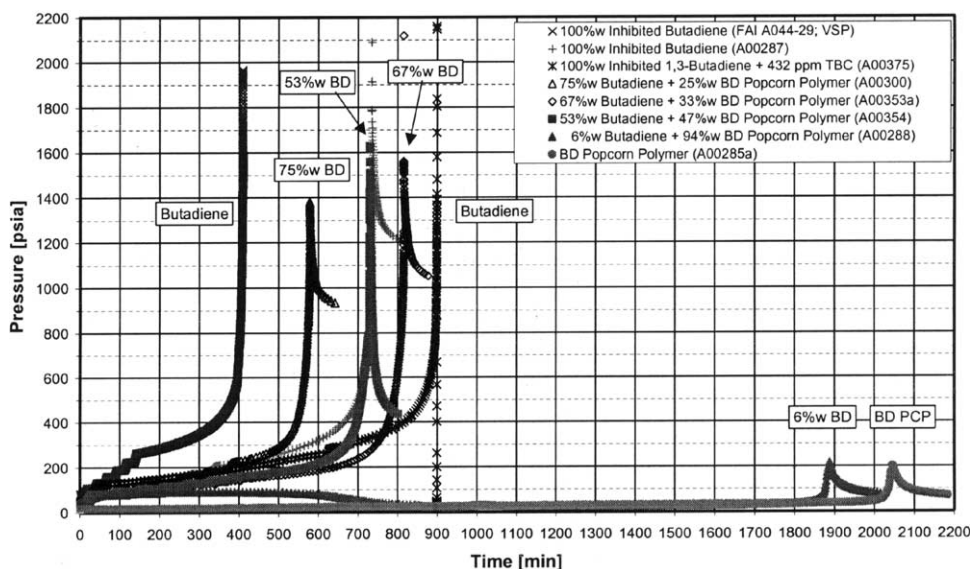


Fig. 10. Pressure–time history of combinations of butadiene and butadiene popcorn polymer #1; APTAC experiments, in nitrogen.

3.2. Mixtures of butadiene with popcorn polymer #1

Several mixtures of butadiene-based popcorn polymer #1 combined with butadiene were tested in the APTAC. The butadiene content of the mixtures ranged from 75 wt.% down to 6 wt.%. The temperature histories of these tests, along with the traces for 100% butadiene and for popcorn polymer #1 alone from the previous section, are shown in Fig. 9. For butadiene concentrations at 53 wt.% or higher (the balance being popcorn polymer), the temperature profiles are similar to those of neat 1,3-butadiene, with maximum temperatures of at least 550 °C. In the case of the 6 wt.% butadiene, there is a slight shift in temperature above that of the neat popcorn

polymer that is observable at temperatures above 120 °C. This particular experiment was marred by a blown heater fuse causing a premature shutdown. The test was subsequently restarted and allowed to continue, albeit, with a significant loss of temperature between 845 min and 1045 min run time. At higher times and temperatures, the 6 wt.% test results more closely resemble the profile for the neat popcorn polymer.

Similar observations arise from comparison of the pressure profiles of the butadiene + popcorn polymer mixtures compared with butadiene alone and popcorn polymer alone (Fig. 10). The samples with elevated butadiene levels behave more similarly to neat butadiene, exhibiting pressures ultimately of around 1400 psi and higher. On the other hand, the

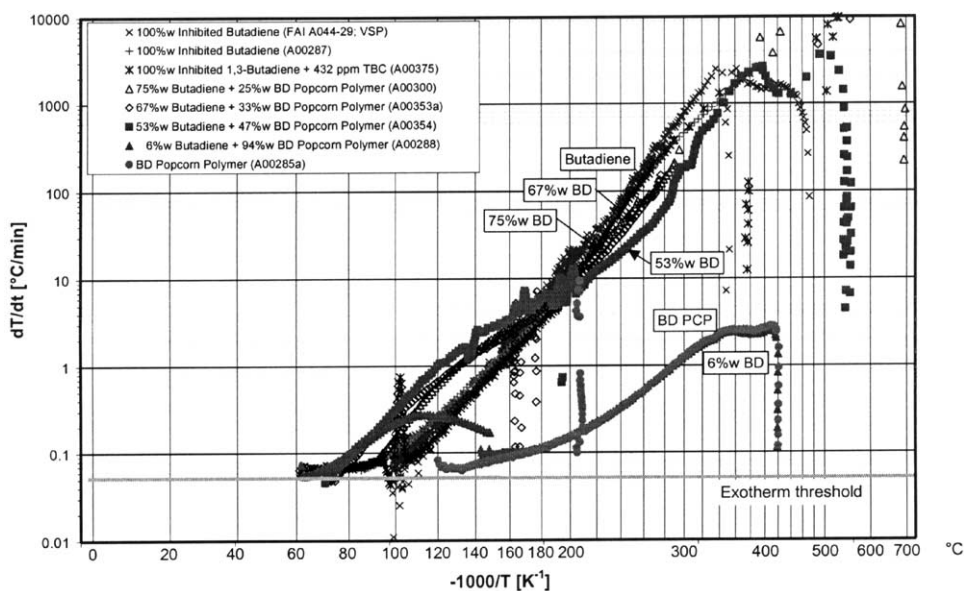


Fig. 11. Self-heat rate versus temperature behavior of combinations of butadiene and butadiene popcorn polymer #1; APTAC experiments, in nitrogen, heat-wait-search steps removed.

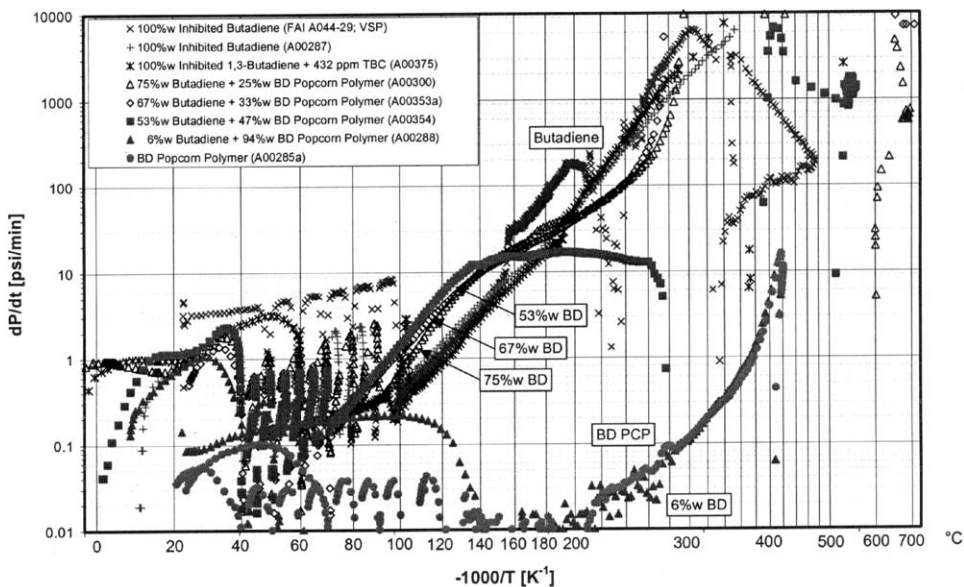


Fig. 12. Pressurization rate versus temperature behavior of combinations of butadiene and butadiene popcorn polymer #1 APTAC experiments; in nitrogen.

6 wt.% butadiene sample showed a modest increase in pressure early in the test and then later dissipated. Thereafter, the pressure profile was more like that of the neat popcorn polymer.

The associated self-heat rate plots without the heat-wait-search steps are found in Fig. 11. In these graphs, it is apparent that the presence of popcorn polymer leads to reaction at lower temperatures than with 1,3-butadiene alone. Reactivity is found as much as 25 °C lower when popcorn polymer is present compared to butadiene alone. Even for the 6 wt.% butadiene mixture, an exotherm beginning around 70 °C is found. However, that exotherm reaches a maximum above

110 °C and diminishes thereafter. This can be attributed to the conversion of the butadiene present. From 160 °C onward, the 6 wt.% butadiene test replicates the neat popcorn polymer test, including the apparent 380 °C “dimple” near the region of maximum rate in the test. For the 53–75 wt.% samples, the early exotherm has the appearance of a “shoulder” on the normal butadiene self-heat rate. Once the reactivity of the “shoulder” disappears, the self-heat rate actually dips below that of butadiene—again possibly because of the depletion of butadiene from the system.

The dependence of pressurization rate with temperature, as appears in Fig. 12, qualitatively shows similar trends as

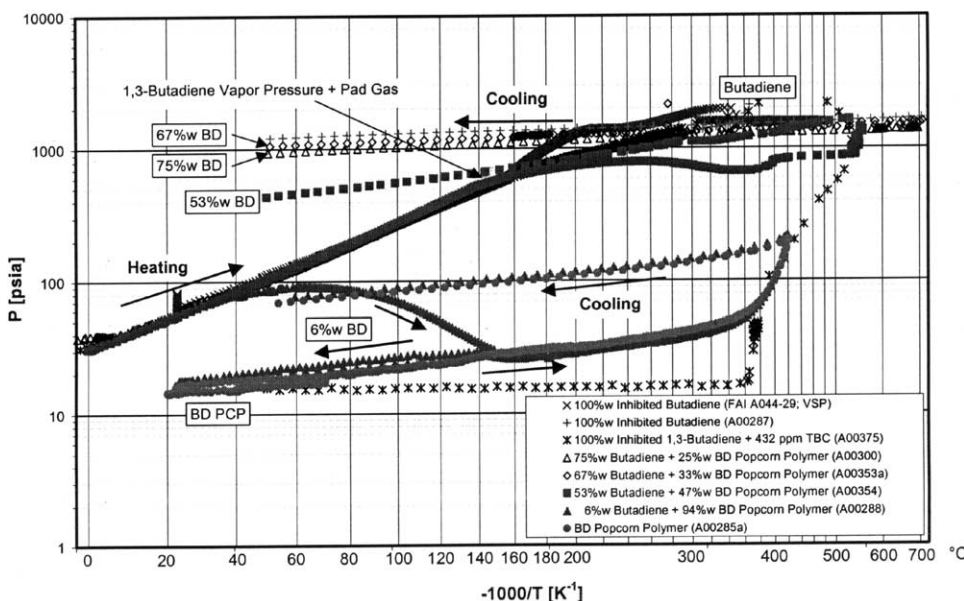


Fig. 13. Pressure versus temperature behavior of combinations of butadiene and butadiene popcorn polymer #1; APTAC experiments, in nitrogen.

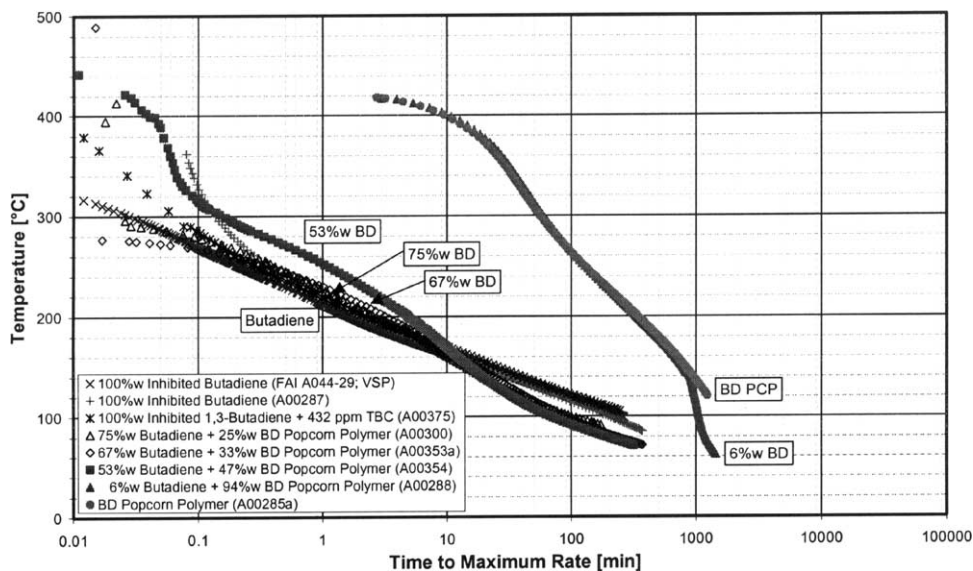


Fig. 14. Time to maximum rate of combinations of butadiene and butadiene popcorn polymer #1; APTAC experiments, in nitrogen.

the self-heat rates. The 6 wt.% butadiene sample essentially retraces the behavior for the popcorn polymer (the pressurization rate of 0.1–0.2 psi/min between 25 °C and roughly 145 °C arises from reheating of the sample after the inadvertent shutdown). The 53–75 wt.% butadiene samples showed pressurization rates above that of butadiene alone at low temperatures while dipping below butadiene at higher temperatures. At higher temperatures, the 67 wt.% and 75 wt.% samples show a dramatic upswing in pressurization rate in the range of 260–280 °C. On the other hand, the pressurization rate of the 53 wt.% sample reaches a maximum, then decreases, becoming negative, before resuming at very high rate.

Generation of non-condensable species for the 53–75 wt.% samples is evident in Fig. 13 by the residual high pressures at the end of the test. The profile for the 6 wt.% butadiene sample shows more complexity due to the 148 °C shutdown and subsequent sample cooling. However, upon reheating and resuming the test, its pressure–temperature behavior coincides with that of the neat popcorn polymer.

In the time-to-maximum rate plot of Fig. 14, it is apparent that, for the butadiene–popcorn polymer mixtures with 53–75 wt.% butadiene and below 150 °C, the presence of the popcorn polymer reduces the available time to respond to reaction compared with butadiene alone. This is consistent with the lower temperature reactivity in the presence of pop-

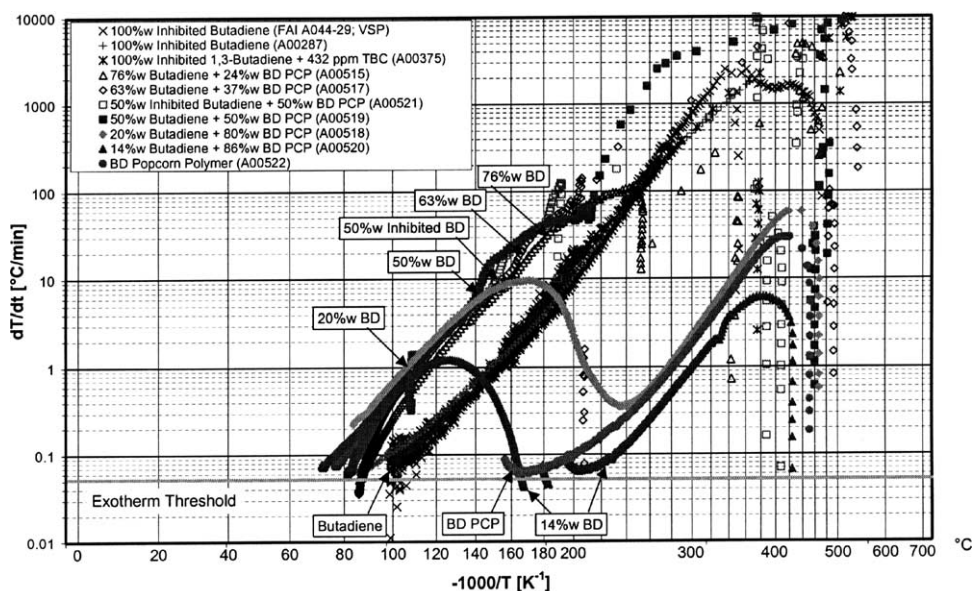


Fig. 15. Self-Heat rate versus temperature behavior of combinations of butadiene and butadiene popcorn polymer #2; APTAC experiments, in nitrogen; heat-wait-search steps removed.

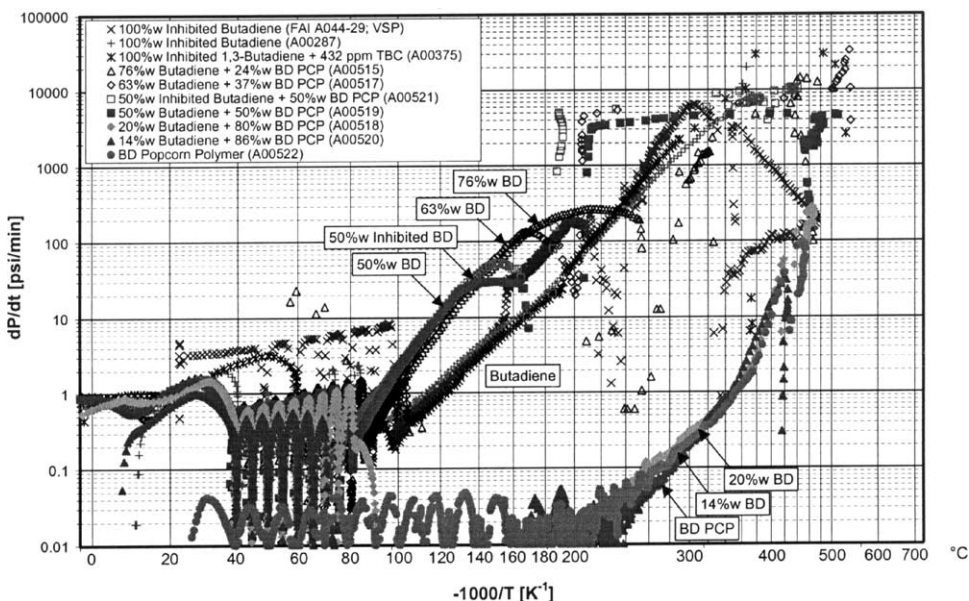


Fig. 16. Pressure rate versus temperature behavior of combinations of butadiene and butadiene popcorn polymer #2; APTAC experiments, in nitrogen.

corn polymer. With only 6 wt.% butadiene in the sample, the time-to-maximum rate profile tracks that of the neat polymer once the initial exotherm is complete.

3.3. Mixtures of butadiene with popcorn polymer #2

To examine the sensitivity of the butadiene + popcorn polymer reactivity results, to the specific popcorn polymer sample employed, another series of APTAC tests was conducted with a second batch of popcorn polymer. This second sample was also harvested from an olefins manufacturing unit.

The temperature–time behavior for butadiene–popcorn polymer compositions ranging from 14 wt.% to 76 wt.% butadiene qualitatively look similar to those for the first popcorn polymer sample. Again, for butadiene amounts of 50 wt.% or more, the trends resemble those for butadiene alone. For 20 wt.% and 14 wt.% butadiene, the occurrence of more than one exotherm is evident. However, the 14 wt.% butadiene parallels the neat popcorn polymer behavior above 200 °C. The 20 wt.% butadiene shows behavior characteristic of both neat butadiene and neat popcorn polymer. The pressure–time plots show similar trends. The tests with butadiene concentrations at or above 50 wt.% resemble those of neat butadiene.

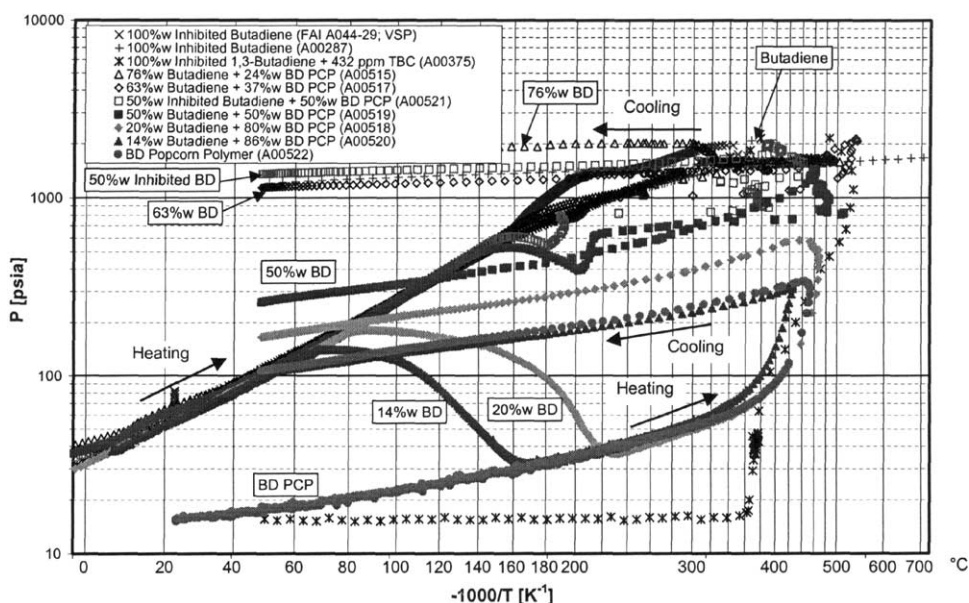


Fig. 17. Pressure versus temperature behavior of combinations of butadiene and butadiene popcorn polymer #2; APTAC experiments, in nitrogen.

The 14 wt.% butadiene test resembles the neat popcorn polymer while the 20 wt.% exhibits behavior intermediate to neat butadiene and neat popcorn polymer.

The self-heat rate behavior (minus heat-wait-search steps) of mixtures of butadiene with popcorn polymer #2 is shown in Fig. 15 (without the heat-wait-search steps). As was the case for the first popcorn polymer sample, the reactivity of butadiene with this sample of popcorn polymer is greater than for butadiene alone. In addition, it appears that the reactivity with this popcorn polymer sample is greater than with the first sample, as indicated by the greater separation between the popcorn polymer-containing and the neat butadiene curves. Depletion of butadiene is evident by the limited temperature rise and peak heat rate at low butadiene concentrations followed by the secondary exotherm characteristic of neat popcorn polymer. Note also that the 50 wt.% butadiene curves with and without *tert*-butylcatechol inhibitor are essentially indistinguishable up to about 180 °C.

The pressurization rate trends for the butadiene + popcorn polymer mixtures depicted in Fig. 16 are consistent with those for popcorn polymer #1. For butadiene concentrations at or above 50 wt.%, significant pressurization rates in excess of those for neat butadiene, even surpassing 10,000 psi/min, can be observed. In contrast, for 20 wt.% butadiene or less, the pressurization rate is apparently negative from 90 °C to 200 °C while butadiene in the vapor phase is consumed by reaction. Above 200 °C, pressurization rates characteristic of the neat popcorn polymer are displayed.

As was the case for popcorn polymer sample #1, the samples with higher concentrations of butadiene, that is, 50 wt.% or higher, show pressure behavior as a function of temperature akin to that of neat butadiene (Fig. 17). The residual elevated pressure upon cool-down to 50 °C reflects the generation of non-condensable species attributable to high temperature decomposition. At the lower butadiene concentrations,

the pressure–temperature profile initially follows the curve of neat butadiene, but reverts to that of the popcorn polymer once the butadiene has been exhausted. There is considerably less residual pressure in the tests with reduced butadiene concentrations suggesting that less extensive decomposition is taking place.

Fig. 18 clearly demonstrates reduced times to reach peak reaction rates for the higher butadiene content samples. This behavior is sustained nearly the entire duration of these tests. The 20 wt.% sample exhibits at about 85 °C a 225 min time-to-maximum rate—consistent with what is expected from higher butadiene percentages. However, the curve quickly transitions, as the butadiene is depleted, to one near the neat popcorn polymer. At even lower butadiene concentrations, such as 14 wt.%, the time-to-maximum rate parallels that of the neat popcorn polymer. The impact of the first exotherm for the 14 wt.% test on the overall reaction time frame does not appear in the graph because the initial and subsequent exotherms were interrupted by additional heat-wait-search steps (the exotherm proceeded essentially to completion).

It is evident from the tests in this study that the extent of reaction of butadiene with popcorn polymer depends on the popcorn polymer sample employed. The variation in rate can be attributed to the nature of and/or accessibility to free radical sites on the popcorn polymer. Factors such as the specific type of free radical site, its surroundings, its concentration, and the structure/porosity of the popcorn polymer may affect the observed reactivity.

3.4. Mixtures of butadiene with lauroyl peroxide

To examine the impact a more-controlled free radical source would have on reactivity, several tests were performed on 1,3-butadiene dosed with lauroyl peroxide. The choice of lauroyl peroxide as an initiator arises from its inherent de-

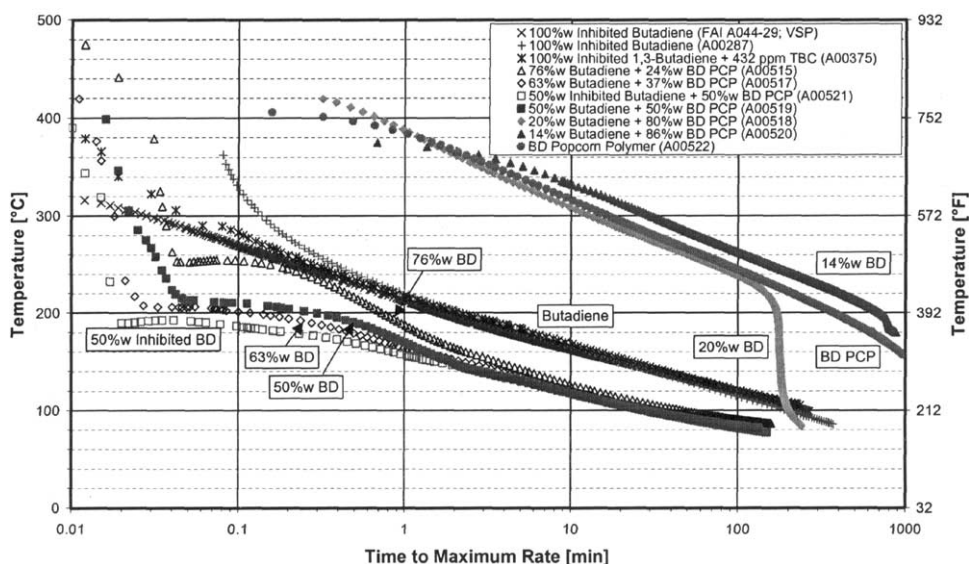


Fig. 18. Time to maximum rate of combinations of butadiene and butadiene popcorn polymer #2; APTAC experiments, in nitrogen.

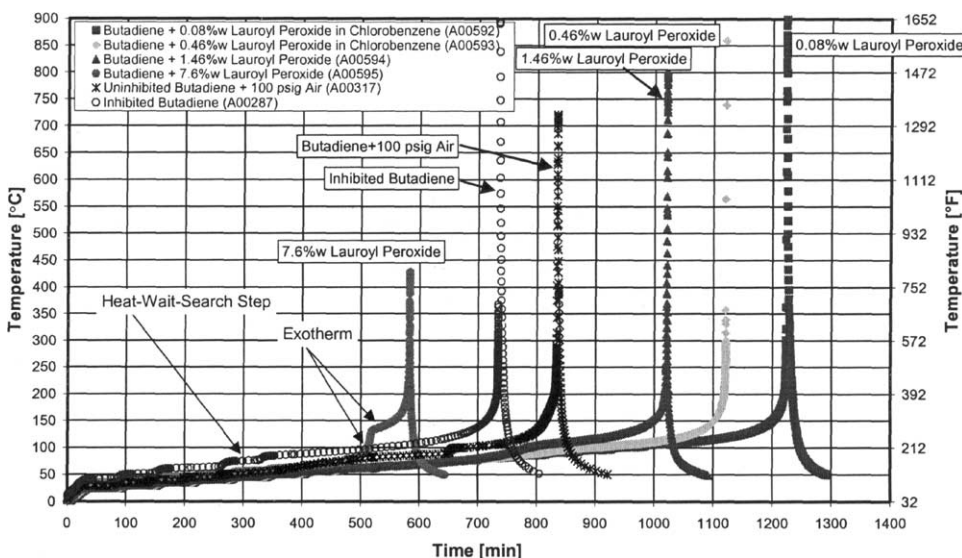


Fig. 19. Temperature history of butadiene with lauroyl peroxide; APTAC experiments, in nitrogen.

composition rate in organic solvents to provide free radicals at temperatures above room temperature, but below the observed onset temperature of neat butadiene. From decomposition rates in *aromatic* solvents supplied in the literature [17], lauroyl peroxide is expected to have a half-life of the order of 15 h at 60 °C, 4-1/2 h at 70 °C, and 1/2 h at 85 °C.

The temperature–time profiles for butadiene in combination with various amounts of lauroyl peroxide are illustrated in Fig. 19. In addition, to explore conditions under which peroxide might form and affect results, data for *uninhibited* butadiene subjected to an initial pressurization with 100 psig air through a submerged dip-tube are included for comparison. All of the tests show a steep rise in temperature with

time once reaction has initiated. In tests A00594 and A00595, in which the highest concentrations of lauroyl peroxide are employed (1.5 to 7.6 wt.%, respectively), two exotherms are clearly visible. Similar behavior is observed for the corresponding pressure curves.

The self-heat rate behavior of Fig. 20 (without the heat-wait-search steps) shows the presence of a low temperature reaction peak beginning at about 60 °C. There is a steady progression in the magnitude of this peak with increasing peroxide content, with a maximum self-heat rate of about 6.6 °C/min in the 7.6 wt.% peroxide test. At low peroxide concentrations, this additional reaction appears to die out prior to the start of butadiene dimerization. This may be due to

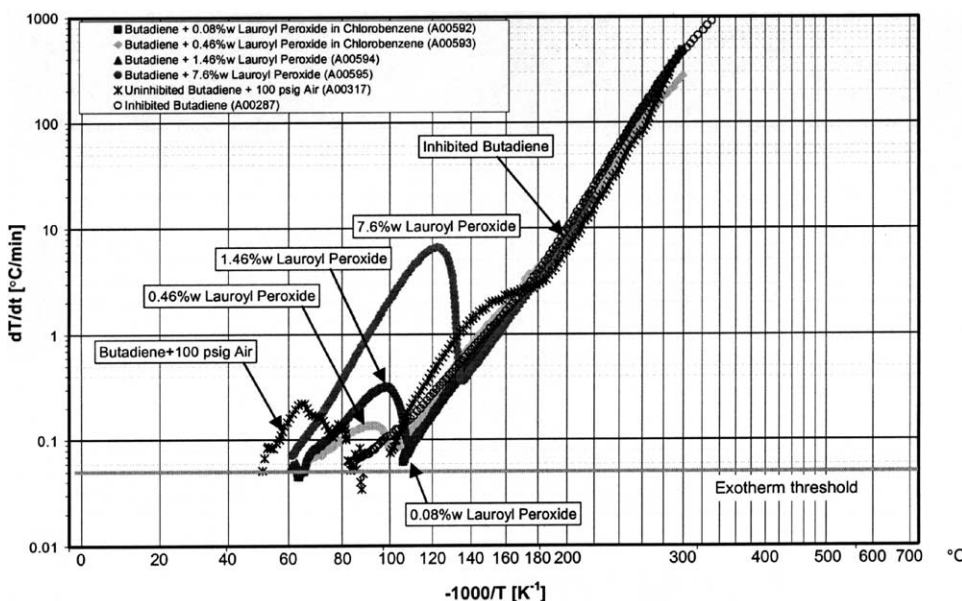


Fig. 20. Self-heat rate–temperature relationship of butadiene with lauroyl peroxide; APTAC experiments, in nitrogen; heat-wait-search steps removed.

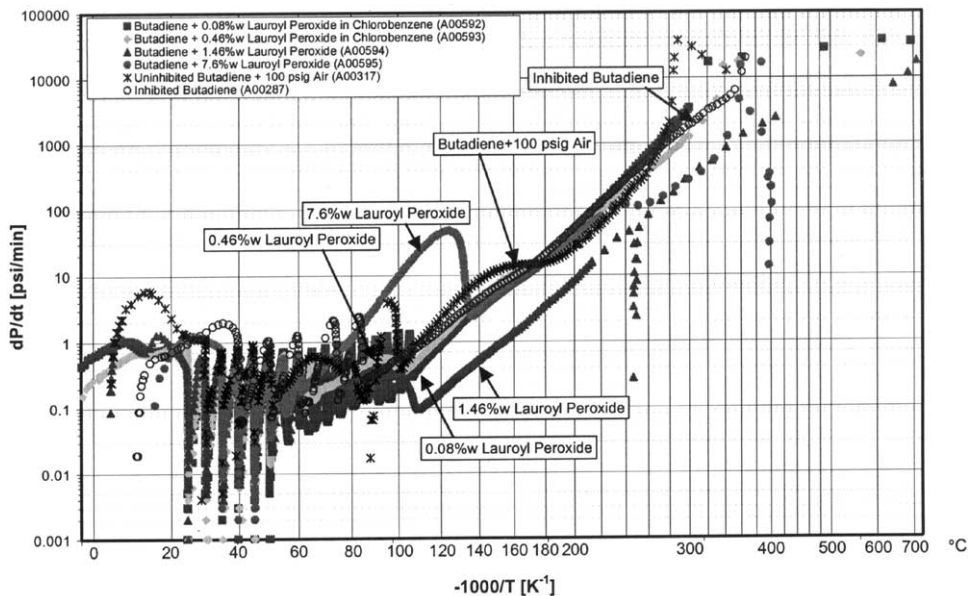


Fig. 21. Pressurization rate–temperature relationship of butadiene with lauroyl peroxide; APTAC experiments, in nitrogen.

free radical termination leading to dead end polymerization. At the highest peroxide concentration, the peak is sustained until about 135 °C—well beyond the onset of the dimerization reaction. Note that the lauroyl peroxide is not expected to have an effect on Diels–Alder reaction dimerization.

For the case where 100 psig air has been added, two additional reaction peaks are observed. One occurs between 50 °C and 90 °C, with a maximum rate of about 0.2 °C/min; the second appears as a shoulder superimposed upon the butadiene dimerization curve between 100 °C and 170 °C. The contact of butadiene with air presumably yields peroxide species. The pressurization rate versus temperature profiles are depicted

in Fig. 21 and show trends that mirror those of the self-heat rate. Test A00594 (1.5 wt.% lauroyl peroxide) is an exception to this in that the pressurization rates for this test inexplicably lie below those of the other tests. It is believed that this could be the result of a problem with the pressure transducer (such as partial pluggage).

The pressure versus temperature trends of Fig. 22 show all of the tests (with the exception of test A00317 which started with 100 psig of air) to coincide closely with neat butadiene. This implies that the additional low temperature exotherm has little actual impact on the system pressure. Once this initial exotherm has been completed, the self-heat rate

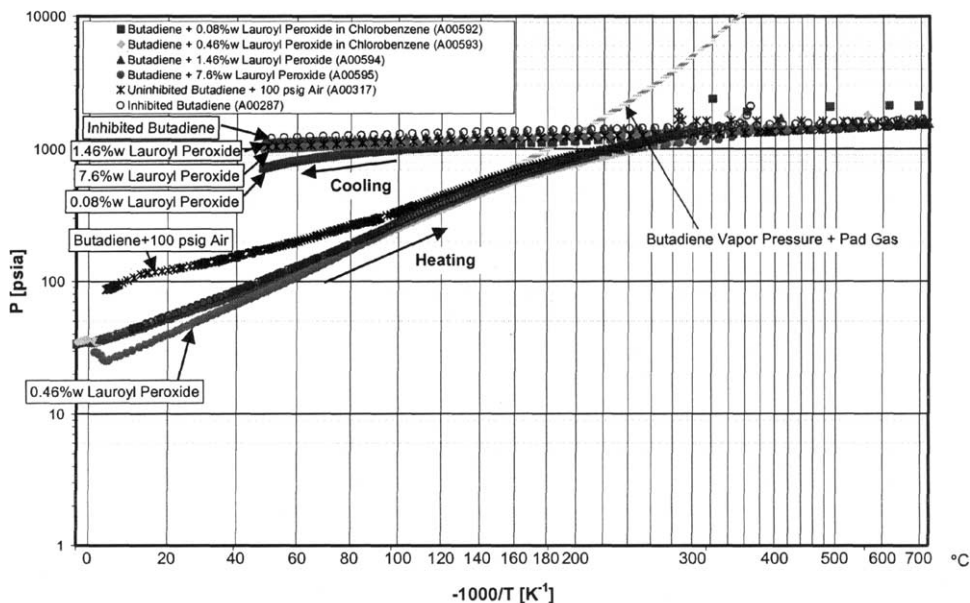


Fig. 22. Pressure versus temperature behavior of butadiene with lauroyl peroxide; APTAC experiments, in nitrogen.

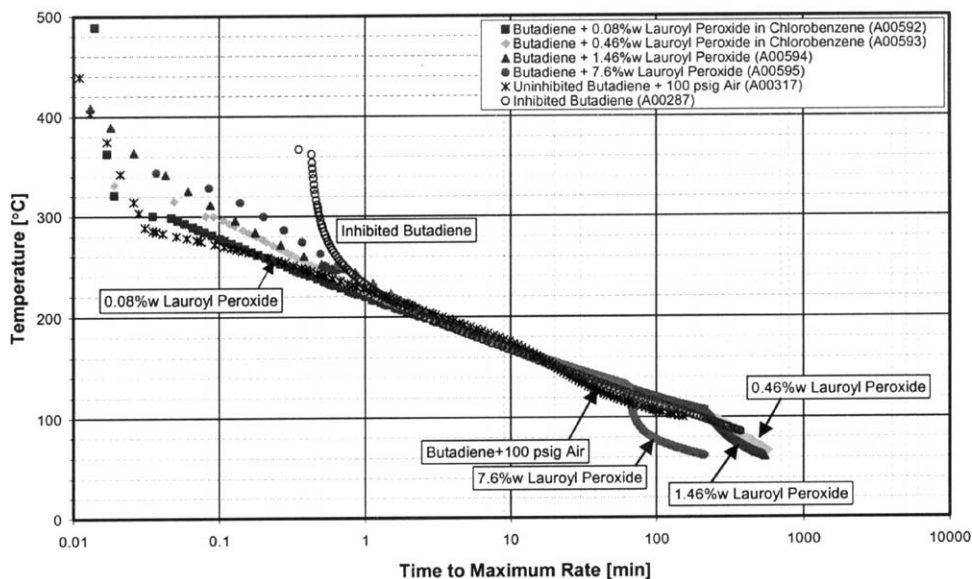


Fig. 23. Time to maximum rate of butadiene with lauroyl peroxide; APTAC experiments, in nitrogen.

and pressurization rate behavior of these systems look nearly identical to neat butadiene.

Finally, in the time-to-maximum rate plots shown in Fig. 23, the lauroyl peroxide serves to reduce the time to reach the peak rate for temperatures below 100–120 °C. Thereafter, the curves lie closely toward neat butadiene. This behavior is expected since the reaction appears in the low temperature range, effectively acting as a “stepping stone” for subsequent butadiene dimerization (and oligomerization).

3.5. Thermal inertia effects

In this study’s experiments, the thermal inertia or phi factor (ϕ), ranges between 1.12 to 1.30 (see Tables 1–4). This means that the sample container has a thermal capacitance of 12–30% of that of the sample, or expressed differently, about 7–23% of the total of the cell plus sample. The actual temperature rise experienced in a large-scale adiabatic environment, in which the relative wall thermal capacitance might be very small, would be higher by the thermal inertia factor or an additional 12–30%. Thus, the extent of each exotherm would be greater and may hasten the transition between exotherms. Furthermore, a greater pressure build-up can be expected to accompany the increased temperature rise. In addition to the impact of thermal inertia on temperature rise, the self-heat rates associated with the exotherms would be greater at the commercial scale than those observed in the experiments by a factor larger than the thermal inertia factor. This means that the timeframe for a temperature/pressure excursion beginning at some initial temperature would be correspondingly shorter.

To adjust the current study’s results properly for equipment with a lower thermal inertia, a dynamic simulation that takes into account the observed reaction kinetics cou-

pled with material and equipment properties would be required.

4. Summary

The reactivity of butadiene-derived popcorn polymer harvested from manufacturing-scale butadiene extraction facilities has been examined through adiabatic calorimetry. In the absence of butadiene, samples of the popcorn polymer are found to exhibit exothermic behavior at elevated temperatures. This behavior resembles that of a commercially-available polybutadiene and is accompanied by production of non-condensable gas species indicating the possible occurrence of decomposition. At least two distinct activation energies for exothermic popcorn polymer reaction are found suggesting multiple mechanisms for degradation or the presence of other effects (such as mass transfer limitations).

Low concentrations of 1,3-butadiene (e.g., less than 20 wt.%) with popcorn polymer result in modest exothermic behavior with an onset temperature much lower than that for popcorn polymer reaction (ca. 180+ °C) or for (thermal) dimerization of butadiene (ca. 90 °C). Once the butadiene has been consumed, this combination continues with the high temperature exotherm found for popcorn polymers alone.

High concentrations of 1,3-butadiene (e.g., 50+ wt.%) with popcorn polymer yield exothermic behavior more reminiscent of thermal dimerization of 1,3-butadiene, but with the appearance of an added low temperature exotherm beginning around 70 °C.

The reactivity with butadiene varies with the history and/or source of the popcorn polymer. This may relate to the density of free radical sites in the popcorn polymer, the nature of these sites, or the accessibility of these sites.

Uninhibited 1,3-butadiene with 100 psia air pressured into the sample cell through the liquid exhibits additional, but modest exothermic behavior between 50 °C and 90 °C. Dosing of neat 1,3-butadiene with lauroyl peroxide introduces a low temperature exotherm appearing at 60 °C. The peak reaction rate is proportional to the amount of peroxide in the system. This combination also shows exothermic behavior similar to that of butadiene with popcorn polymer.

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