APTAC Test Procedure for DIERS Round Robin Testing of Vinyl Acetate Polymerization

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ioMosaic Corporation
93 Stiles Road
Salem, New Hampshire
03079 U.S.A.

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Possible Scenario's

1. Introduction

As part of the ongoing DIERS Round Robin study of vinyl acetate polymerization, it was determined that a detailed test procedure applicable to Automatic Pressure Tracking Adiabatic Calorimeters (APTACs™) was needed. The included test procedure is intended to study the free radical initiated (dilauroyl peroxide as a free radical initiator) and the thermal polymerization reactions (if any) of vinyl acetate solution polymerization in toluene. In addition, the procedure also allows for the study of the polymer decomposition reaction, which occurs at higher temperatures (>200 ℃). Because of the many options for APTAC operation, test parameters for two scenarios are specified in the procedure below. These scenarios include adiabatic runaway and external heating induced runaway. The sample preparation and head space replacement for the test cell are the same for both scenarios.

- Scenario #1: Adiabatic runaway starting at 50 ℃
- Scenario #2: Runaway simulating external heating of 1.5 ℃/min

2. Recipe Information: Vinyl Acetate Solution Polymerization

(Adapted from July 23, 2012 Memo by Joseph C. Leung)

- 60% wt. vinyl acetate (VAM)
- 39% wt. toluene
- 1% wt. dilauroyl peroxide (99% assay, available from Sigma)
- 50 ℃ onset temperature (*note the onset self heat rate is in the vicinity of 0.1 ℃/min*)

Note 1: It should be okay to premix the monomer, the initiator, and the solvent at ambient temperature, but the solution should be used immediately.

Note 2: For a 129 ml test cell, the suggested sample size is 75 grams. For other test cell sizes, please use the same charge loading – 58 grams per 100 ml test cell volume.

Note 3: If the test apparatus can be used to simulate fire heating at the prescribed rate, it will further provide valuable data for modeling at a later time.

Note 4: There is a potential for high pressure at higher temperatures in a closed test cell due to decomposition of the polymer.

Note 5: Evacuate the air and/or replace with nitrogen, since VAM can form peroxide with air and alter the kinetics.

Note 6: For Scenario #1, a certain amount of time (induction time) will be needed at 50 ℃ before self heating is observed. This induction time is due to the presence of the initiator, which comes with VAM from the supplier. For those who have the ability to remove the inhibitor, please specify what method is used. This kind of uninhibited VAM data will also be useful for modeling comparison later.

Note 7: It is important to know the type and precise amount of inhibitor in the VAM. Induction time and temperature are dependent on the inhibitor used. A VAM sample with hydroquinone (HQ) at a concentration of 8–12 ppm will be preferable over 3–20 ppm for our study.

Sample Preparation

Weigh the appropriate amount of vinyl acetate, toluene, and lauroyl peroxide (LPO) in an APTAC titanium test cell (with stirrer). Chill the test cell and sample to subzero temperature using an acetone/ice mixture to reduce sample loss during the headspace replacement with nitrogen. Connect the test cell quickly to the APTAC and repeat pressurization (150 psia) and depressurization (20 psia) five (5) times and then bring down to ambient pressure. Record the sample pressure and temperature before commencing the test.

Test Parameters

The APTAC instrument is calibrated with the control thermocouple inside the test cell. Make sure the drift at 50 ℃ is <0.005 ℃/min (important for iso-aging at 50 ℃ in the Scenario #1 test). Make sure the wall thermocouple is in good contact with the test cell wall, the nitrogen supply is adequate in the high pressure cylinder and the stirrer is off during the cool down data collection.

Scenario #1: Adiabatic Runaway Starting at 50 °C

Test Parameters	APTAC Closed Test
Test Cell Material	Stainless Steel
Test Cell Volume (ml)	~129
Test Cell Weight (g)	~93
Stirrer (g)	~4
Sample Thermocouple	Inside Test Cell
Head Space	Nitrogen
Start Temperature (°C)	50
Heat Mode	Iso-Aging Followed by HWS
Isothermal Mode (Isofixed/Isotrack)	Isofixed Mode
Iso-Aging Time (Minutes)	**400***
Isothermal Window (°C)	0.2
Stirrer Speed (rpm)	300
Exotherm Threshold (°C/min)	0.04
Heat Step (°C) During HWS	5
At the End of Exotherm go to HWS Mode	Yes
End Temperature (°C)	400
End Temperature in Case of Exotherm (°C)	400
Cool Down Temperature (°C)	<40
Shutdown Criteria	
Temperature (°C)	405
Heating Rate (°C/min)	1,000
Pressure (Psia)	**2,000****
Pressure Rise Rate (psia/min)	5,000

*An induction time of ninety two (92) minutes was measured for 60% VAM (3–20 ppm inhibitor) in toluene initiated by lauroyl peroxide at iso-aging temperature of 50 °C in a stainless steel test cell. The induction time may depend on the type and amount of inhibitor in VAM. Iso-Aging time of four hundred (400) minutes is a maximum limit, although exotherm may be detected earlier.

**The APTAC manufacturer recommends a maximum pressure limit of 2,000 psia but the user should use the pressure limit within their comfort zone.

Scenario #2: Runaway Simulating External Heating of 1.5 °C/min

Test Parameters	APTAC Closed Test
Test Cell Material	Stainless Steel
Test Cell Volume (ml)	~129
Test Cell Weight (g)	~93
Stirrer (g)	~4
Sample Thermocouple	Inside Test Cell
Head Space	Nitrogen
Start Temperature (°C)	50
Heat Mode	Heat Ramp Constant Rate (dT/dt) with Adiabatic Mode Selection
Heat Rate ((°C/min)	1.5
Adiabatic Mode on Exotherm	Yes
Stirrer Speed (rpm)	300
Exotherm Threshold (°C/min)	0.04
End Temperature (°C)	400
End Temperature in Case of Exotherm (°C)	400
Cool Down Temperature (°C)	40
Shutdown Criteria	
Temperature (°C)	400
Heating Rate (°C/min)	1,000
Pressure (Psia)	**2,000***
Pressure Rise Rate (psia/min)	5,000

*The APTAC manufacturer recommends maximum pressure limit of 2,000 psia but the user should use the pressure limit within their comfort zone.

End of Test Measurements

At the end of the test, relieve the pressure in the test cell to ambient using the APTAC software. Record the final weight (test cell + spent). Slowly pour out the liquid (use filter paper to capture small solid particles that may be suspended in the liquid). Dry the test cell under vacuum at room temperature until a constant weight is achieved. Determine the weight of solid product including any captured on the filter paper. Calculate the percent solids as a percent of the available VAM.

Items to Submit

1. Determine and record the ppm HQ (inhibitor) in the VAM, and mention whether the inhibitor was removed prior to conducting the test.
2. Give details about the sample size, close or open system test, and whether the test cell was rid of nitrogen to start.

3. Submit data in Excel format, showing time (min), T (°C), P (psia or bara), dT/dt (°C/min), dP/dt (psi/min, or bar/min) with clear header identifying each column.
4. Submit data plots showing T(°C) and P (psia or bara) vs time (min), dT/dt (°C/min) and dP/dt (psi/min, or bar/min) vs – 1000/TK Arrhenius type plots, and log P vs 1/TK chart display.
5. Measure and record the percent solids as a percent of the available VAM after the test. This will be useful for the modeling effort later.