CHEMICAL ENGINEERING SENIOR LABORATORY
CHEG 4139

Initiated Chemical Vapor Deposition

Objective:
The objective of this experiment is to determine the effect of process variables on the deposition of thin polymeric films using the initiated chemical vapor deposition technique. This experiment touches on multiple aspects of chemical engineering, including vapor phase flow, reaction kinetics, mass transfer, and polymer chemistry. As a vapor-phase polymerization technique, one of the additional goals is to compare results with conventional liquid-phase polymerization techniques.

Major Topics Covered: Vapor-phase fluid mechanics, mass transfer, reaction kinetics, polymer chemistry.

Theory:
Initiated chemical vapor deposition (iCVD) is a vapor-phase polymerization technique first discovered in the early 2000's at MIT. As a technique, it allows fabrication of nano- and micro-scale thin polymer films that can be used for a variety of surface modification applications, depending upon the chemistries selected. One of the primary advantages of iCVD is that it is a conformal, solventless, gentle process that can allow the coating of substrates that are not typically accessible to conventional polymerization schemes (i.e. thermally or solvent sensitive susbstrates, such as fabrics or paper, or substrates with 3-D high-aspect-ratio features, such as nanoscale devices.). For a review of the iCVD process, see **References 1 and 2.**

Safety Precautions:
1. Reagents used in this experiment (alkyl acrylates and organic peroxides) can be harmful. Review the MSDS sheets for the specific chemicals used in your experiment and observe all recommended safety precautions.
2. The filament used to activate the precursors uses moderately high voltages for heating. Always ensure that the filament is powered down and unplugged before opening the reactor. Always ensure that the filament is not making electrical connectivity to the chamber before powering up.
3. Keep acetone as far away from the heat sources in the CVD. Do not store acetone bottles in the CVD cabinet.
4. This experiment uses a HeNe laser to measure thin film growth in real-time. Use caution when working around the reactor, as reflective surfaces can redirect the beam.

Available Variables: Monomer feed flowrate, initiator feed flowrate, substrate temperature.

Procedure: See iCVD operation manual and iCVD Operational Checklist.

Analysis:
Your analysis **must include:**

1. Comparison of the reaction (polymerization) rates made by the variation of one of the variables.

2. Discussion of what the results signify with respect to the overall polymerization mechanism.

3. Calculation of the apparent activation energies for the polymerization reaction, and comparison to the literature values.

4. *Only when explicitly instructed, a second comparison of the reaction (polymerization) rates made with another variable. Confirm with your instructor*.

Report:
Describe the design of your experiments and the results obtained, including an error analysis. Provide thoughtful and quantitative discussion of results, explain trends using physical principles and relate your experimental observations to predicted results. Express any discrepancies between observed and predicted results in terms of quantified experimental uncertainties or limitations of the correlations or computational software used.

Pro Tips:

1. There is generally an offset between the chiller set point and the actual stage temperature, so be aware of this when planning experiments.
2. Don't forget to start the datalogging for the system when you start your experiment.
3. Always check the leak rate of the chamber prior to starting the day's experiments – if it is too high, see an instructor.
4. Start the chiller at the lowest temperature you are testing, then increase. It takes longer for the chiller to cool down than it does to warm up.
5. Always clean the chamber before and after you use the system.
6. If you need to determine the angle of incidence manually, you can use a string and ruler to measure the required distances.

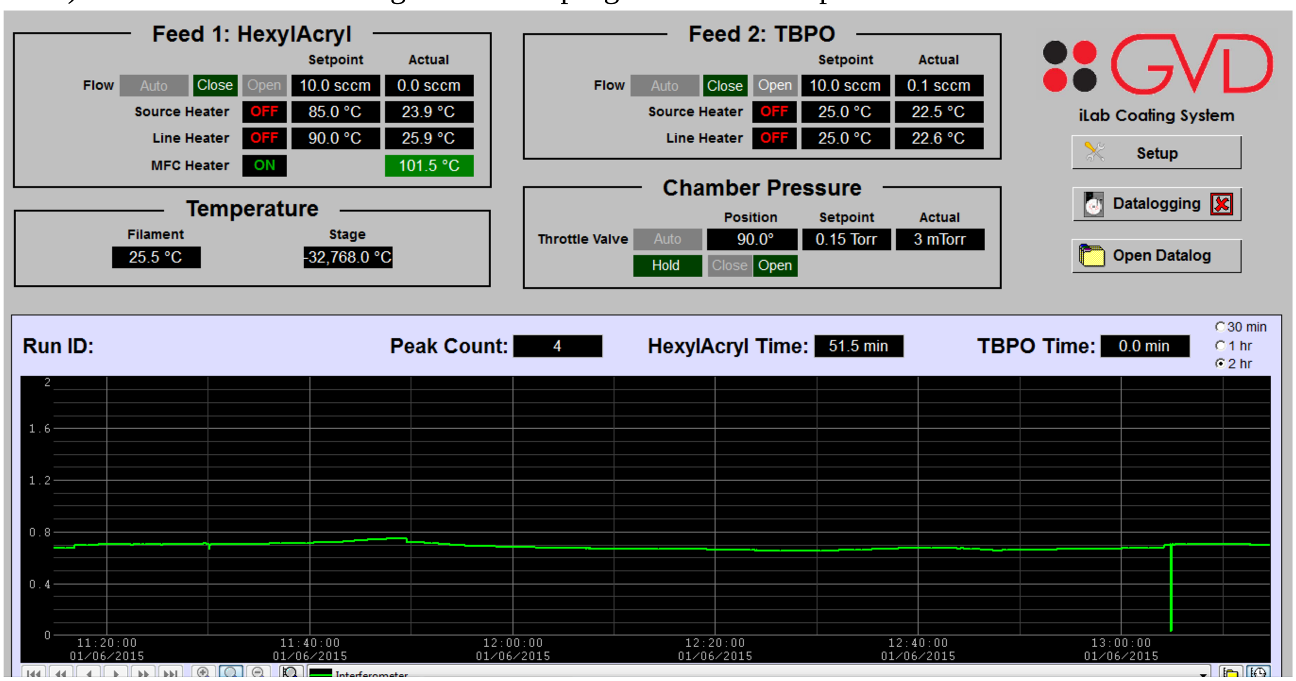
References:

1. Tenhaeff, W.E., Gleason, K. K., "Initiated and Oxidative Chemical Vapor Deposition of Polymeric Thin Films: iCVD and oCVD", *Advanced Functional Materials*, **2008,** *18*, 979-992.
2. Baxamusa, S.H., Im, S.G, Gleason, K.K., "Initiated and oxidative chemical vapor deposition: a scalable method for conformal and functional polymer films on real substrates", *Physical Chemistry Chemical Physics,* **2009,** *11*, 5227-5240.
3. Lau, K.K.S., Gleason, K.K., "Initiated Chemical Vapor Deposition (iCVD) of Poly(alkyl acrylates): An Experimental Study", *Macromolecules*, **2006,** *29*, 3688-3694.
4. Fogler, H.S., *Elements of Chemical Reaction Engineering*, 4th Ed., Prentice Hall, New Jersey, (2005).

Standard operating procedure for initiated chemical vapor deposition (iCVD) using hexyl acrylate and tert-butyl peroxide (TBPO)

The instructor or TA will fill the vessels with Hexyl Acrylate and TBPO prior to each lab session.

1) Make sure that the metal plate to which the vent lines of the chamber and the vacuum pump are connected is attached to the fume hood
   - The fume hood will not be used for anything else when the iCVD experiment is running.
2) Open the sash in the front of the enclosure housing the chamber
3) Make sure that the valves upstream and downstream of both mass flow controllers (MFCs) are closed
4) Check for the following in the iLab program on the computer screen:



- Feed 1: HexylAcryl (MFC MKS 1152)
  - Source heater should be ON and read 85ºC
  - Line heater should be ON and read 90 ºC
  - MFC heater should be ON and read ~104 ºC
- Feed 2: TBPO (MFC MKS 1479)
  - Source heater should be OFF and read room temperature
  - Line heater should be OFF and read room temperature
- The chamber will be under vacuum with the actual pressure less than 100 mTorr

5) Hexyl acrylate will be loaded in the vessel corresponding to Feed 1 (MFC MKS 1152)

6) TBPO will be loaded in the vessel corresponding to Feed 2 (MFC, MKS 1479)
7) Turn on the chiller kept under the instrument and set the desired stage temperature
8) Close throttle valve #1 attached to the chamber using the iLAB program (click "CLOSE"). The reading should go from 90^o to 0^o
9) Manually close valve #2 that is located outside the enclosure between the pump and the chamber
10) Purge the chamber by opening valve #3 (green needle valve) that is attached to the chamber and connected to the nitrogen cylinder
    - Once the lid can be opened easily, close valve #3
11) Open the chamber and clean the stage and lid with acetone. Ask the TA to remove the filaments.
12) Set up the substrate, connect the filament bank to the leads inside the chamber and then close the chamber
    - Substrate should be placed shiny side up
    - TA can cut the first substrate as a demonstration. The remaining cuts, if necessary, can be performed by your group.
13) Check the resistance of the leads using a voltmeter
    - Set the voltmeter to 200 Ω
    - Hold the voltmeter probes against each other to confirm it is properly working
    - Hold the probes against the leads that protrude from the chamber to check for current
    - Hold one probe against a lead and the other probe to the side to check that there is no current
14) Confirm that the laser used to determine the thickness of the deposited film is incident on the substrate and not affected by the filaments, and that the reflected beam is centered on the detector window
15) Confirm that the chiller has reached the desired set point
16) Open valve #1 by 5^o using the iLAB program and manually open valve #2 fully. Wait for the pressure to drop below 1000 mTorr and then open valve #1 fully (90^o)
17) Under the Throttle Valve controls in iLab, select "Auto."
18) Open the green N_2 gas valve as little as possible. Watch the "Position" of the Throttle Valve; the goal is to achieve a chamber pressure of 0.150 Torr. This will likely correspond to a Throttle Valve Position between 20-50^o. Wait until the position and pressure are stable.

19) Connect the orange filament leads outside the chamber to the rheostat outside and bring filament temperature to the desired setpoint by adjusting the knob on the rheostat. The filament temperature can be read in the iLab program on the computer screen
20) Check that the materials, stage, and filaments are heated to the setpoints
    - If not done yet, change the flow rate of the monomer or initiator to desired values
21) Manually open the valves upstream and downstream of MKS 1152 and MKS 1479
22) Once the system has stabilized, start datalogging, stop nitrogen flow by closing valve #3, and immediately start the desired flow of the hexyl acrylate monomer and TBPO using the iLAB program
    - Start the HA and TBPO flows by selecting "Auto" under Feed 1 & Feed 2 control panels
23) Set the desired chamber pressure using the iLab program if it is different than 150 mTorr
24) Watch for a sinusoidal curve in the iLab program. If you do not see a sinusoidal curve, ask an instructor or TA.
25) The run will be complete after 3-5 sinusoidal waves. Begin your count from the first low point in the sinusoidal wave.
26) When the run is complete, perform the following steps:
    - Stop datalogging
    - Turn off the filament heater: turn dial to zero AND turn off power switch.
    - Stop the flow of the monomer and TBPO
    - Open valve #1 (90^o)
    - Close the valves upstream and downstream of MKS 1152 and MKS 1479
    - Turn off the chiller
27) Follow the previously mentioned procedure to purge and open the chamber, remove the substrate and clean the chamber (stage and lid) with acetone or methanol
28) Dispose of all gloves and kimwipes in the waste disposal bin
29) Dispose of all processed wafers in a designated waste container or in the sharps container
30) If it is the last run of the day, perform the following steps:
    - Bring the chamber under vacuum; both valves #1 and #2 should be fully open and the valves upstream and downstream of MKS 1152 and MKS 1479 should be closed
    - Turn the source and line heaters corresponding to Feed 1 off using the iLAB program
    - Turn the chiller off

Note: If you plan to run more experiments on during a later laboratory period. You may begin setting up the experiment before you leave the laboratory. Refer to your instructor/teaching assistant for further instructions.