Acid Catalyzed Degradation of PCL Thin Films for Use as a pH Indicator of Acidic Aerosols

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Introduction

- Acidic aerosols have adverse effects to health and the environment. They can be as small as 2.5 μm, thus it is difficult to measure the pH directly.¹
- Polycaprolactone (PCL) is a polymer that is susceptible to acid-catalyzed ester hydrolysis.²
- The following seeks to calibrate the degradation of PCL thin films in acid to determine if it is a viable candidate as a pH indicator.

Methods

Flow Coating
Substrate moves beneath blade to spread PCL in toluene solution

Spin Coating
Substrate is spun to spread PCL in toluene solution

Film Casting

Melt and Recrystallize
The film is heated then cooled isothermally to allow rearrangement into a thermodynamically favorable morphology.

Degradation
Films are left in a sulfuric acid solution which contains 30 mM MgSO₄ and taken out over various periods of time.

Characterization
- Images of morphology via optical microscope
- Thickness measurement via spectral reflectance (Filmetrics spectrometer, right)

Results

Figure 1. Optical microscope images at 20X of a film a) before degradation (517.1 nm) b) after 4 days in pH 2 acid solution (515.8 nm) and c) Profile image at 50X of a branched crack after 8 days in pH 2 acid solution (167 μm X 167 μm image).

Figure 2. Change in PCL film thickness over time with the flow coating and spin coating methods. Time (days)

Figure 3. Change in PCL film thickness over time in pH 0 and pH 2 sulfuric acid solution. Time (days)

Figure 4. Atomic Force Microscope images of PCL films a) 6 nm, as cast b) 100 nm, melted and recrystallized, and c) 250 nm, SVA with THF.

References

² Spinney, G.L., Degradation Kinetics of Polylactides: PLA and PCL. Polymers from Renewable Sources (Doe 2001, 239-231)

Conclusion

The degradation of the PCL did not change the morphology of the film in pH 0 solution. In pH 2 solution, the films developed branched cracks as shown by the optical images. The occurrences did not necessarily increase over time. Degradation is evident by a decrease in the film thickness over time, however it is difficult to measure the decrease precisely. Due to their uniformity and stability, the degradation of spin coated films was measured more precisely than in flow coated films. However, the standard deviation is still 42.9% of the measurement on average. Preliminary trials show a significant difference in degradation rates in pH 0 and pH 2 solutions. Thus, PCL thin films remain a potential pH indicator.

Future Work

- Continued optimization of the methodology to obtain precise results
- Calibration of degradation to an analytical level
- Continued observation of branched cracks
- More experiments to test the effects of...
  - Film thickness
  - Solvent vapor annealing (SVA)
  - Ionic strength of acid solution
  - Type of salt in acid solution

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