

# Absorption and Diffusion of Water in the Components of PBX 9501 and Estane Degradation Modeling

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With Experimental contributions from:

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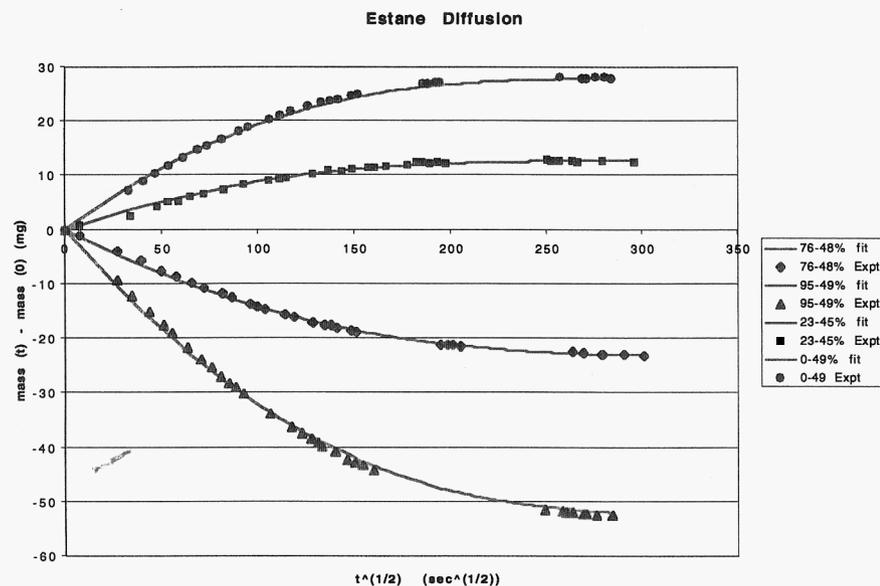
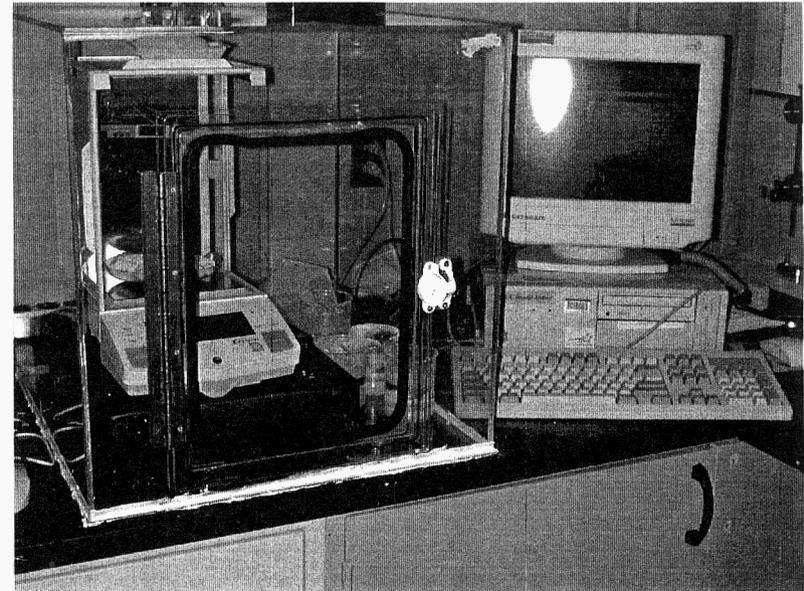


# Introduction

- Model various methods of Estane degradation: hydrolysis, thermolysis, radiolysis
- Hydrolysis modeling
  - requires knowledge of the concentration of absorbed water in the components of PBX 9501 and the rate at which water diffuses through these components

# Experimental Design

- Dessicate sample thoroughly
- Measure dry mass and place in either 23, 76, or 95% RH environments.
- Allow sufficient time to establish equilibrium at higher RH



- Place sample in 45%RH environment and measure mass at a function of time
- Fit data to Fickian model of diffusion to extract diffusion coefficient, D.
- Calculate  $A_{0 \rightarrow X\%RH}$  and  $A_{0 \rightarrow 45\%RH}$  from dry mass, mass at X%RH, and mass at 45%RH.

# Moisture Study Components

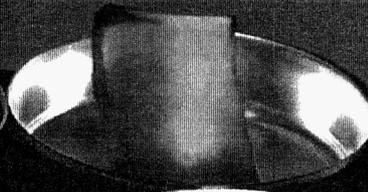
**HMX**



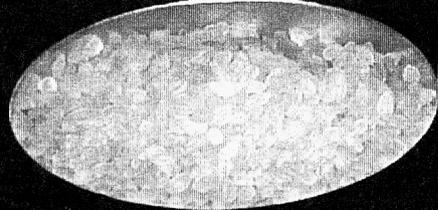
**Nitroplasticizer**



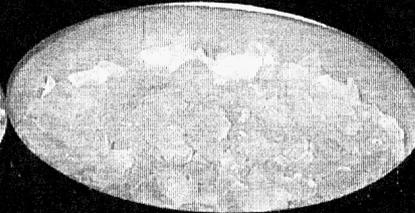
**Formulated Binder  
(Estane + NP)**



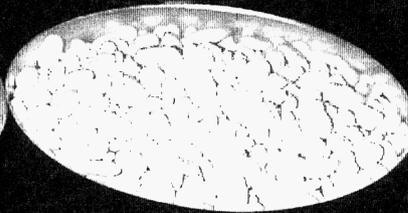
**Pressed and  
Machined  
PBX 9501  
Cylinders**



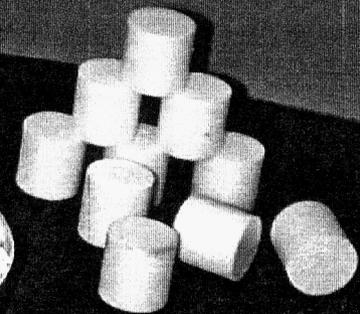
**Pelletized  
Estane**



**Flaked  
Estane**

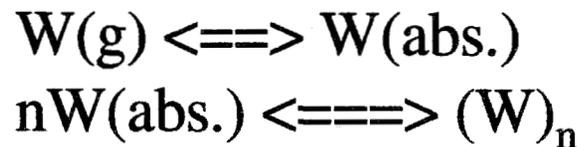
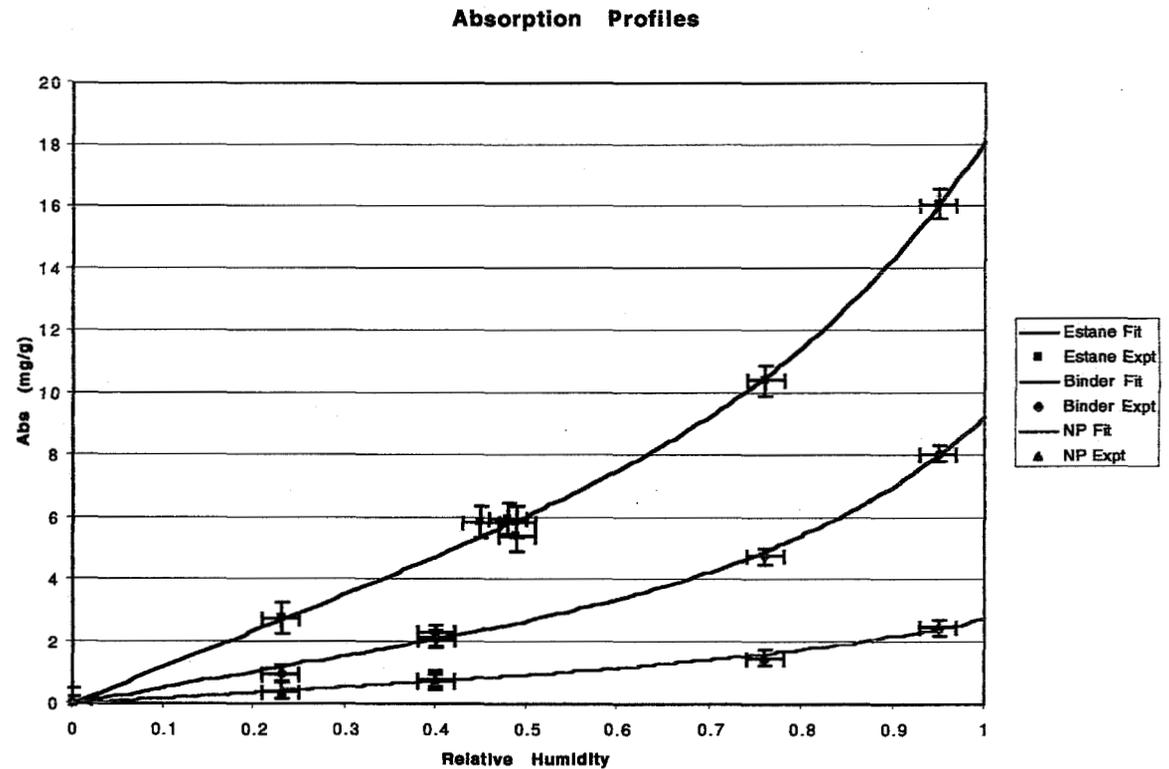


**PBX 9501  
Molding Powder**



# Absorption of Water in Estane, Binder, and Nitroplasticizer

- Estane absorbs the most water.
- Linear absorption profiles below ~50% RH, then nonlinear behavior is observed.
- Nitroplasticizer demonstrates the least amount of nonlinear behavior.
- Data fit with a water clustering model.

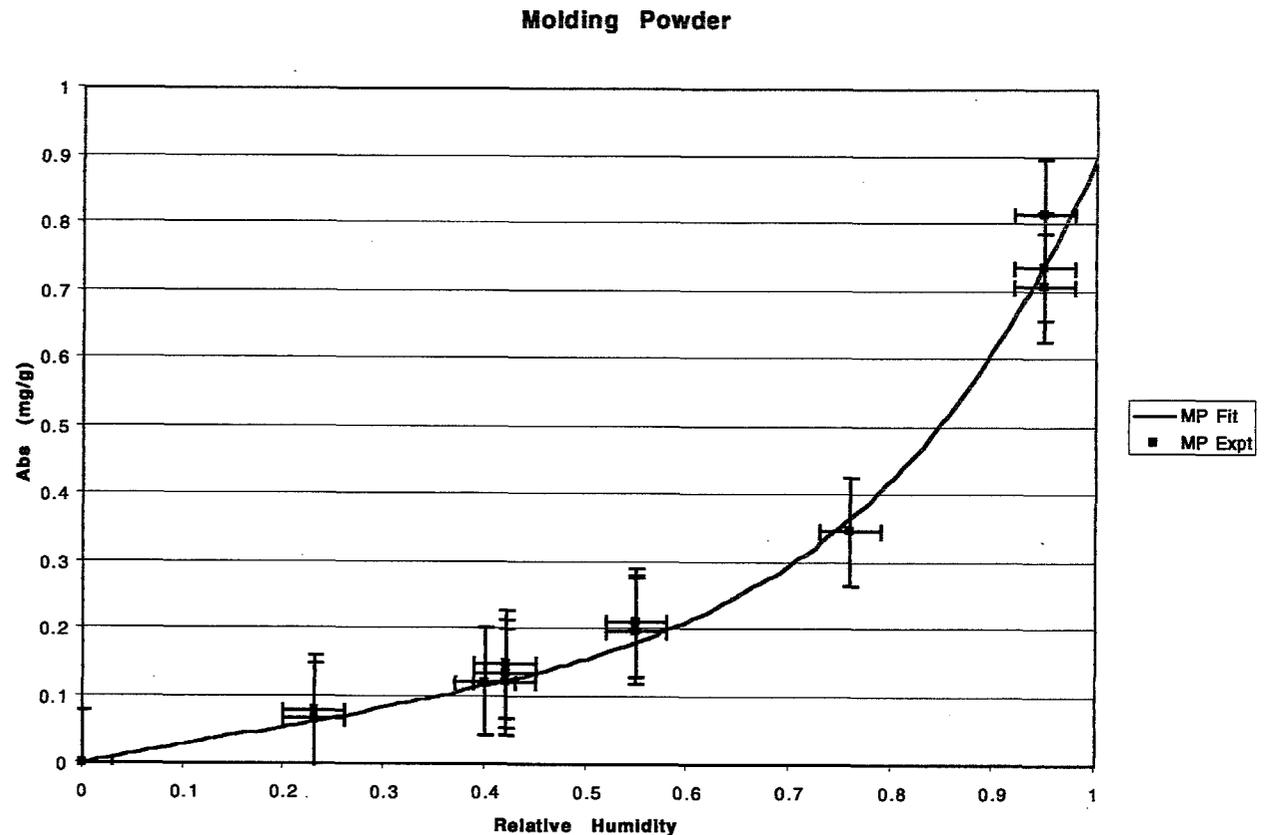


# Absorption of Water in PBX 9501 Molding Powder

- Approximate spherical shape with avg. diameter =  $0.18 \pm 0.15$   $\mu\text{m}$

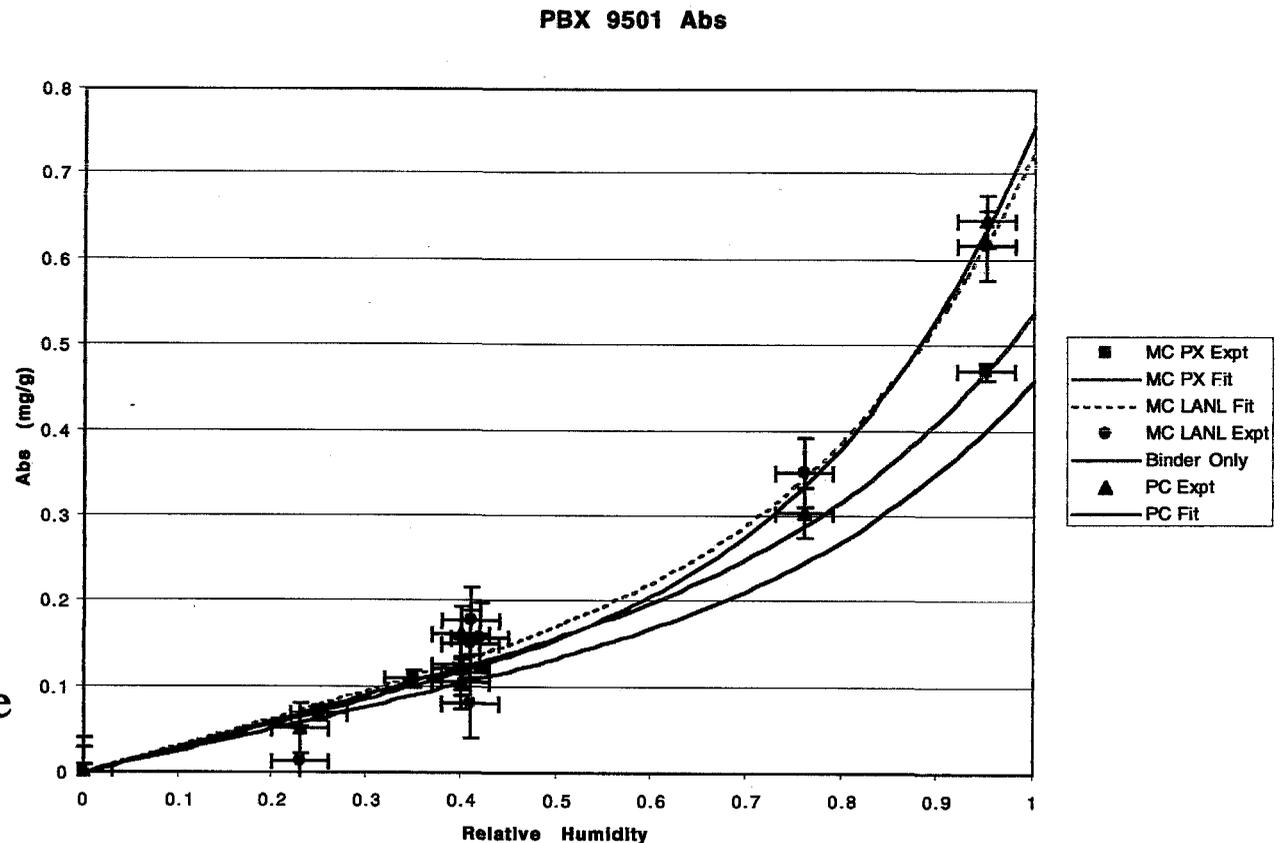


- Linear absorption below  $\sim 50\%RH$  followed by nonlinear behavior
- Cluster model fits data well



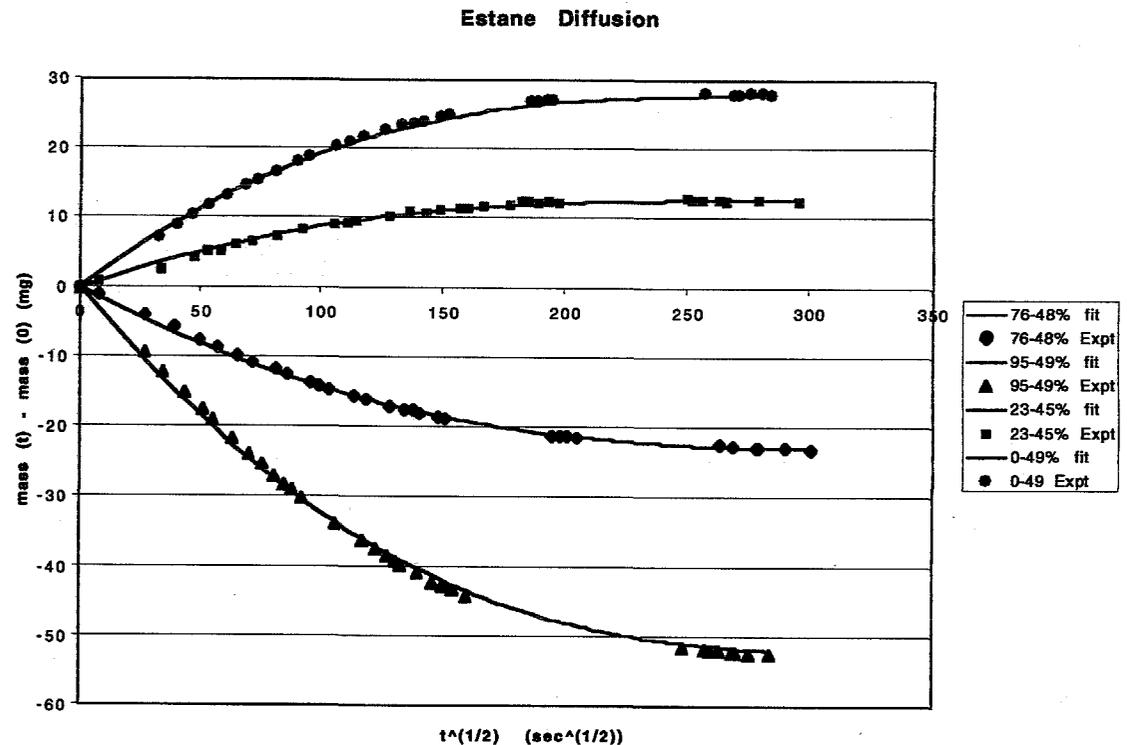
# Absorption of Water in Pressed PBX 9501

- PX Expts. Pressed and machined 1" diameter by 1" long cylinders
- LANL Expts. 0.5" diameter by 0.5" long cylinders
- Good agreement below ~50%RH.
- All experiments absorb more water than what is predicted from the binder above ~50%RH.
- LANL data at high RHs are extrapolated values



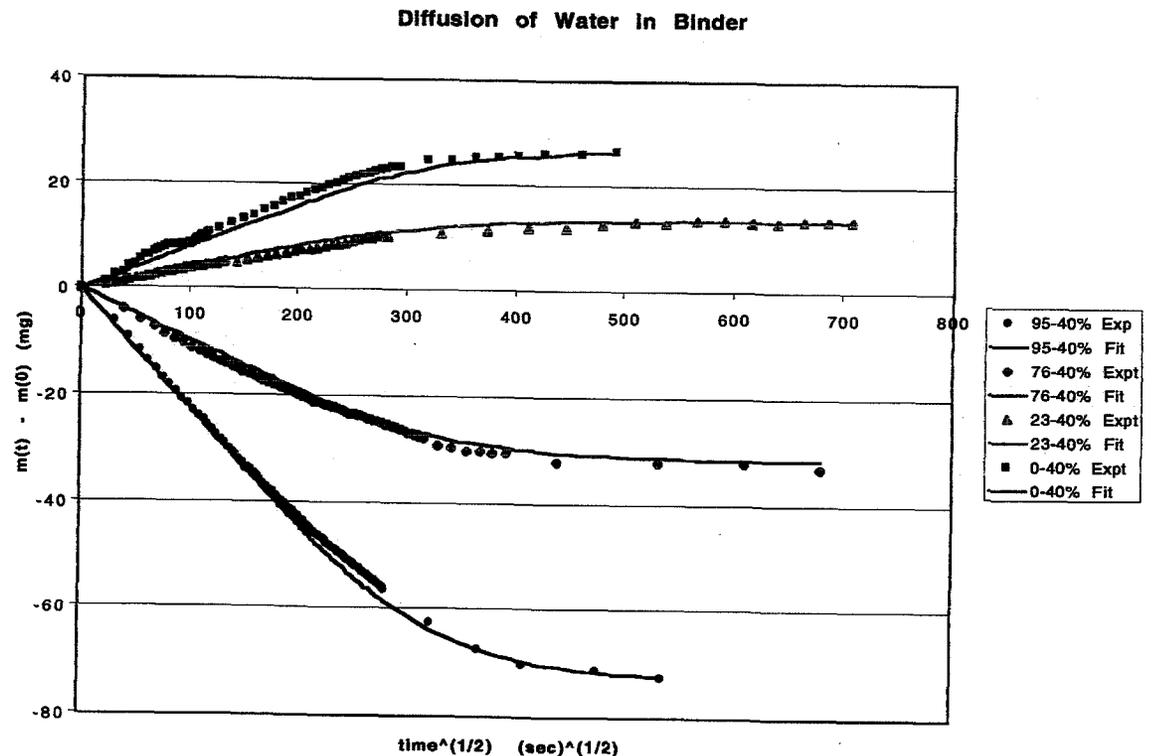
# Diffusion of Water through Estane

- Sample shapes were approximated as cylinders.
- Classic Fickian diffusion
- $D = 1.1 \pm 0.3 \times 10^{-7} \text{ cm}^2/\text{sec}$



# Diffusion of Water through the Binder

- Sample was a thin film with an average thickness of 0.59 cm.
- Classic Fickian diffusion
- $D = 2.5 \pm 0.5 \times 10^{-6} \text{ cm}^2/\text{sec}$



# Diffusion of Water through Nitroplasticizer

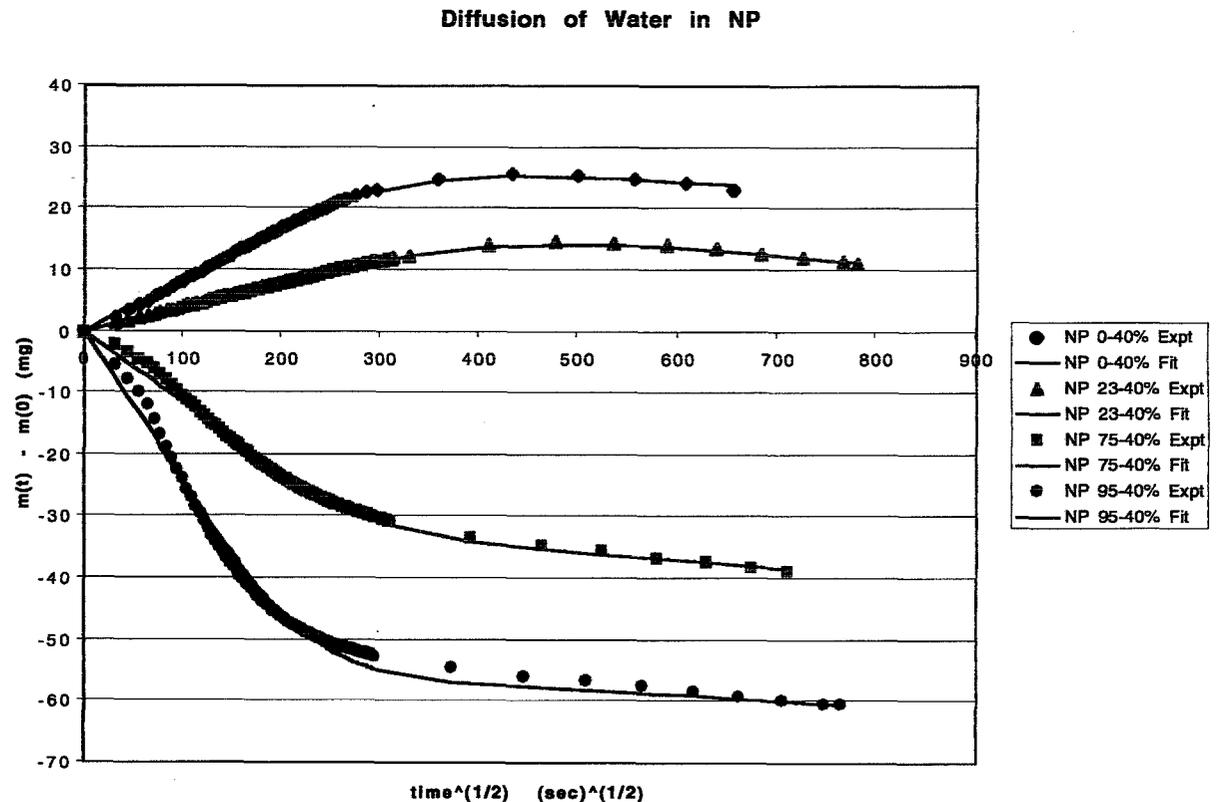
- Nitroplasticizer evaporates off causing mass loss
- $m_{NP}(t) = m_{NP}(0)e^{-kt}$

$$m(t) = m_W(t) + m_{NP}(t)$$

$$k = 2.3 \times 10^{-10} \text{ sec}^{-1}$$

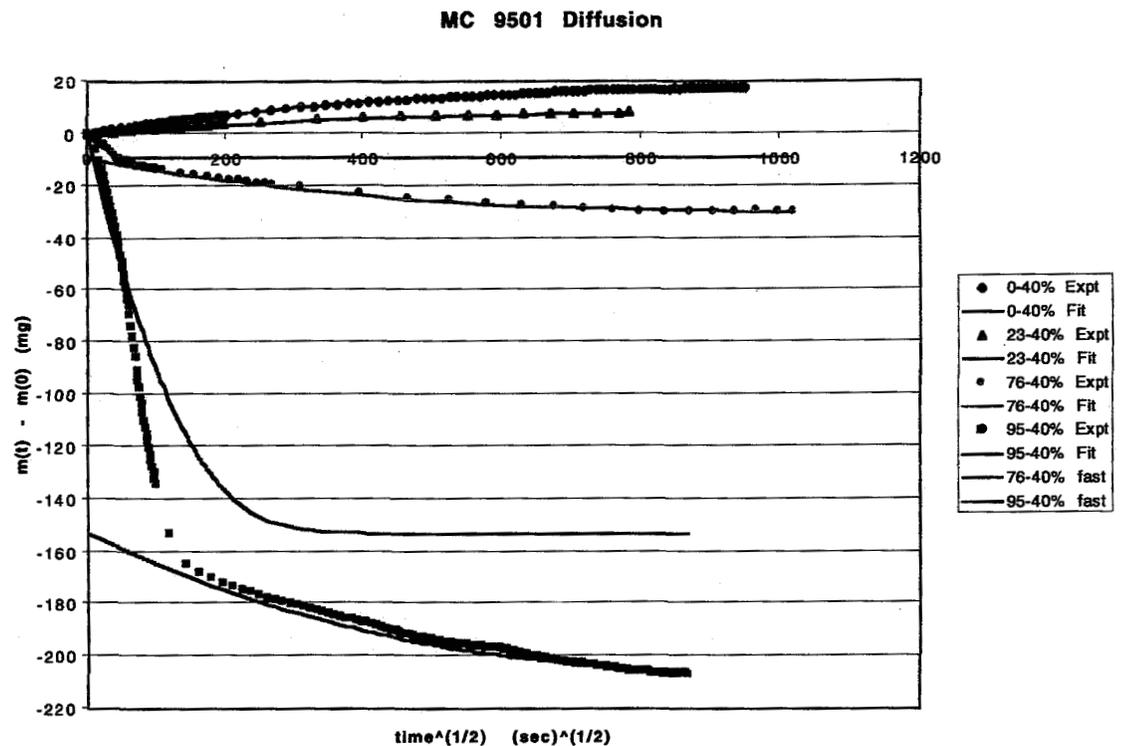
$$D_{\text{gain}} = 3.5 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$D_{\text{loss}} = 7.3 \times 10^{-6} \text{ cm}^2/\text{sec}$$



# Diffusion of Water through PBX 9501 Pressed and Machined Cylinders - LANL Expts.

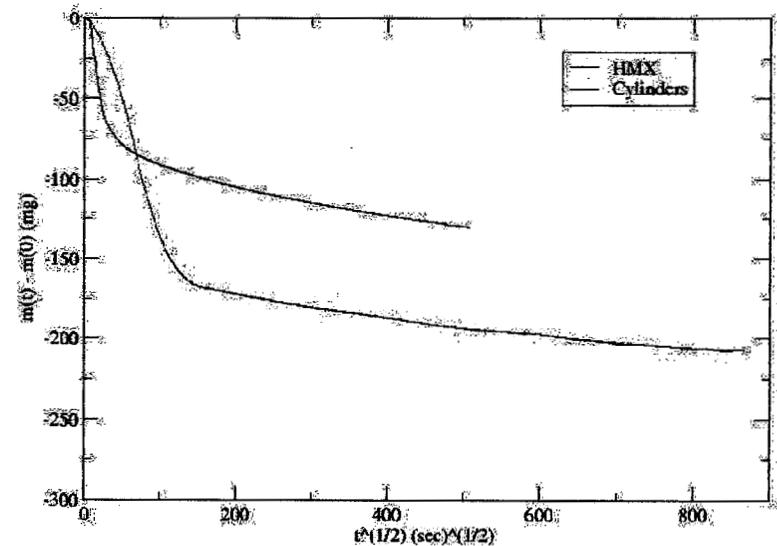
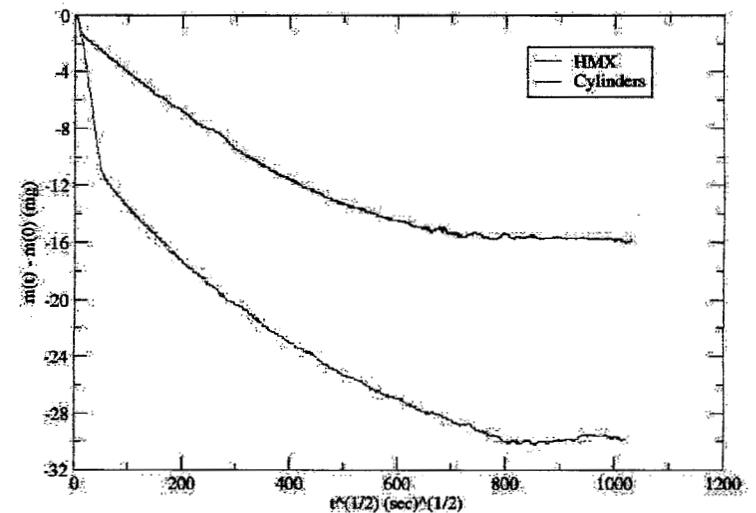
- non-Fickian behavior at higher RHs
- total absorption of water at higher RHs is much more than what is predicted from binder-only absorption



# Diffusion of Water through HMX

- HMX not expected to absorb significant amounts of water
- In fact, we find that HMX does absorb large amounts of water at high RHs
- Very similar diffusion plots between HMX and PBX 9501 cylinders

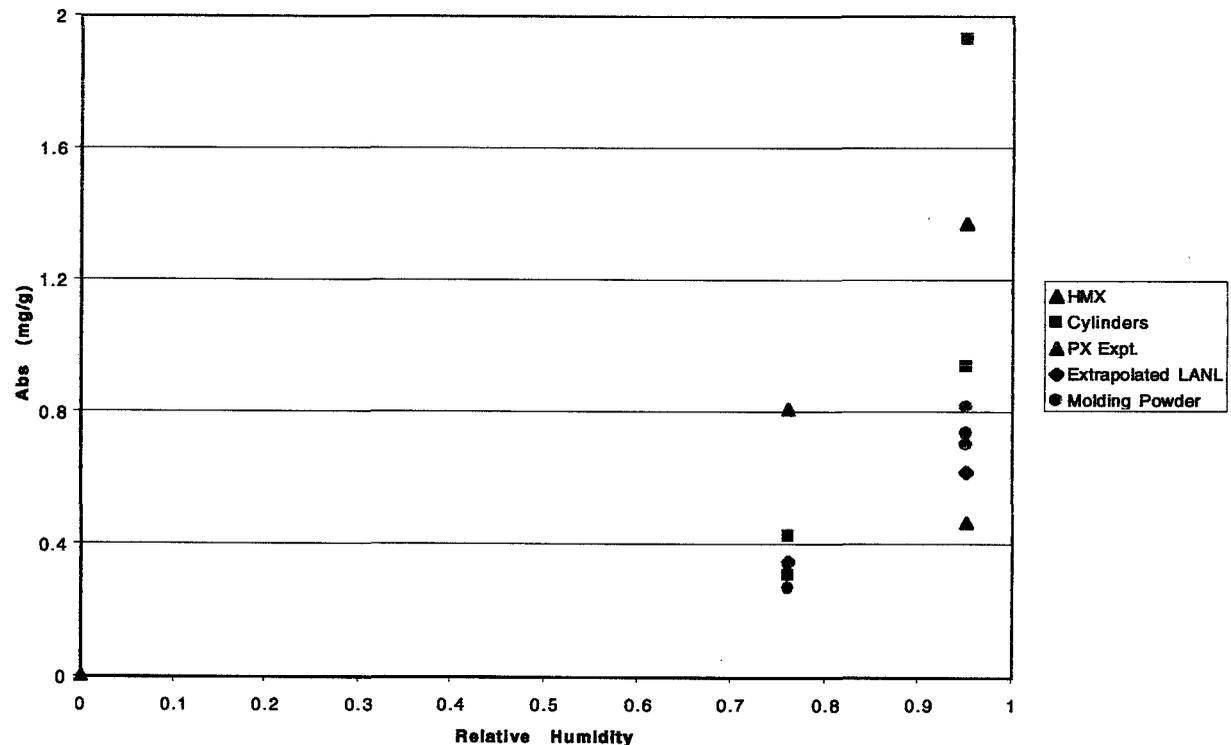
76-40% Expt.



# High RHs Absorption Profiles for HMX and PBX 9501

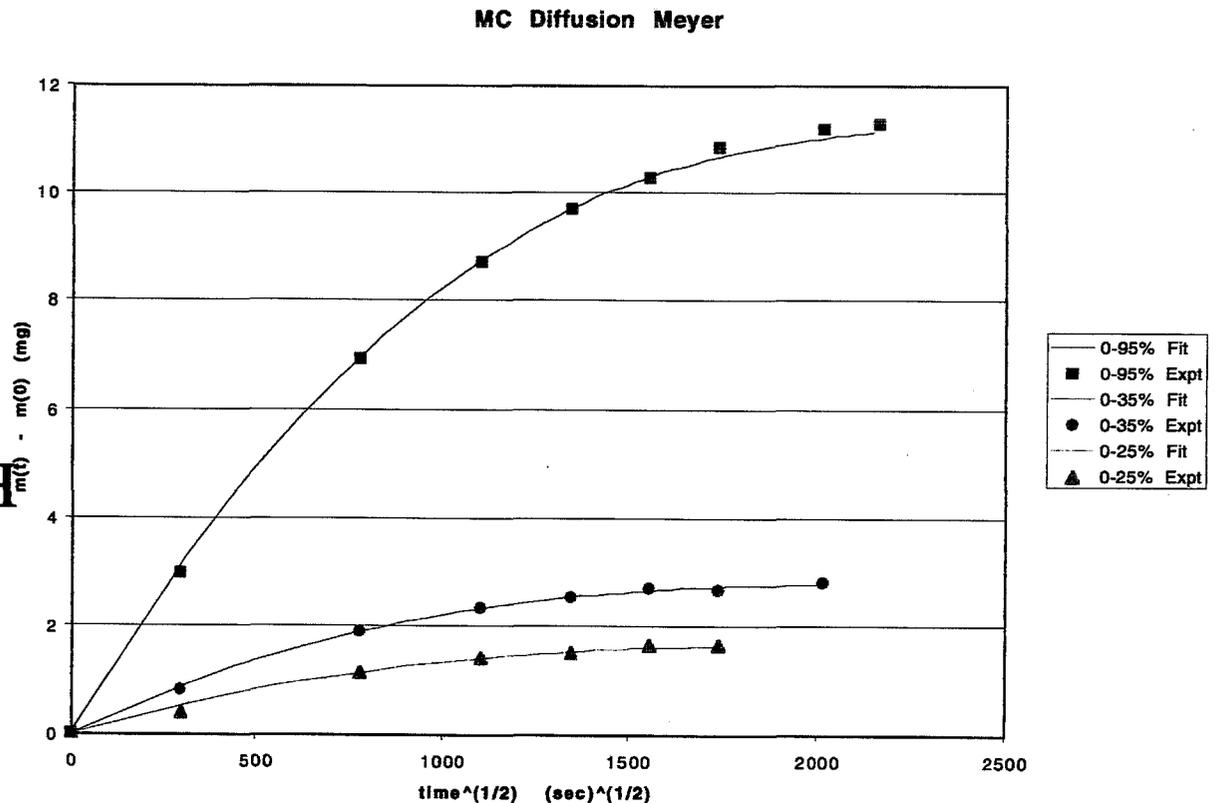
- Large scatter in total absorption at 95%RH
- HMX is responsible for almost all the total absorption

Total HMX and PBX 9501 Cylinder Absorption



# Diffusion of Water through PBX 9501 Pressed and Machined Cylinders - Pantex Expts.

- classic Fickian behavior
- single diffusion coefficient fits all the data
- Absorption at 95%RH is slightly more than expected from binder-only absorption

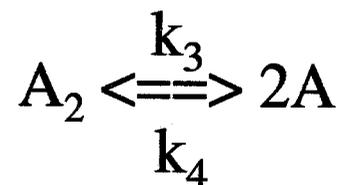
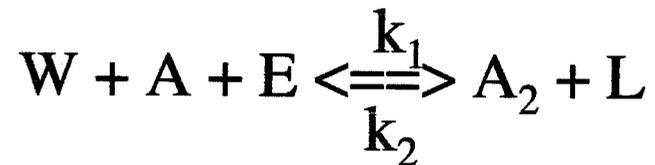


# Summary of Water Absorption and Diffusion by PBX 9501 Component

- Most components show classic Fickian diffusion properties at all RHs
- HMX and pressed and machined PBX 9501 show non-Fickian behavior at higher RHs
- HMX absorbs significant amounts of water at high RHs
- Not clear why PX experiments show smaller water absorption at higher RHs than LANL experiments

# Estane Hydrolysis Model

$A_{AC2}$  Mechanism or Reversible Hydrolysis

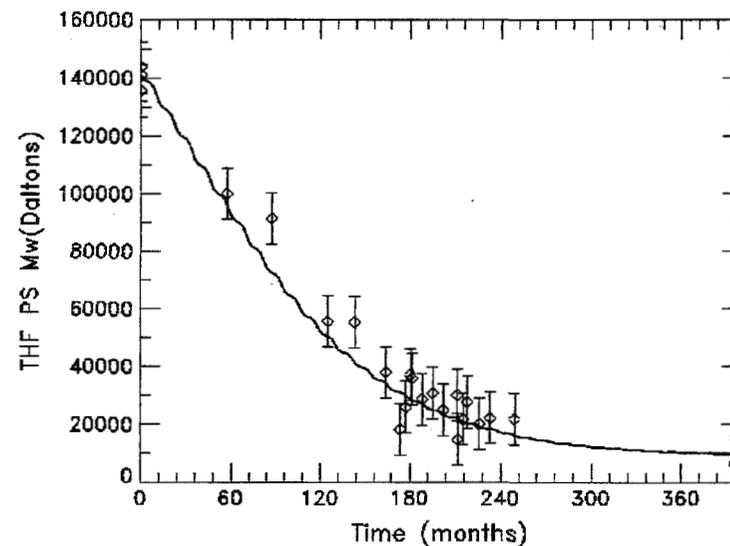
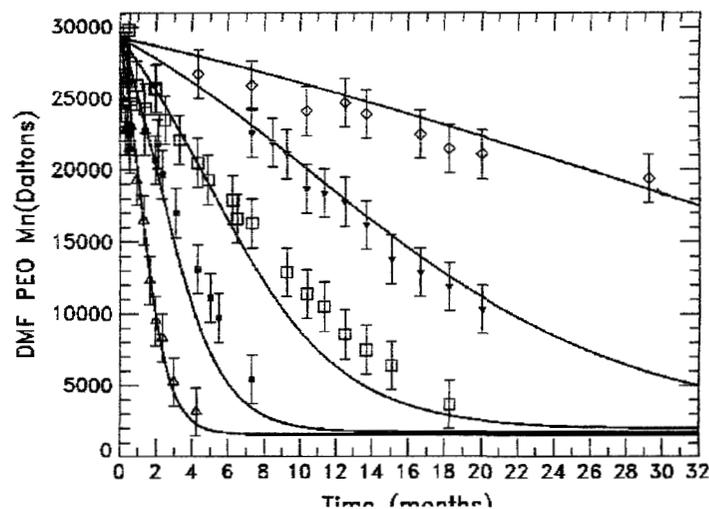


acid catalyzed and acid producing,  
thus autocatalytic

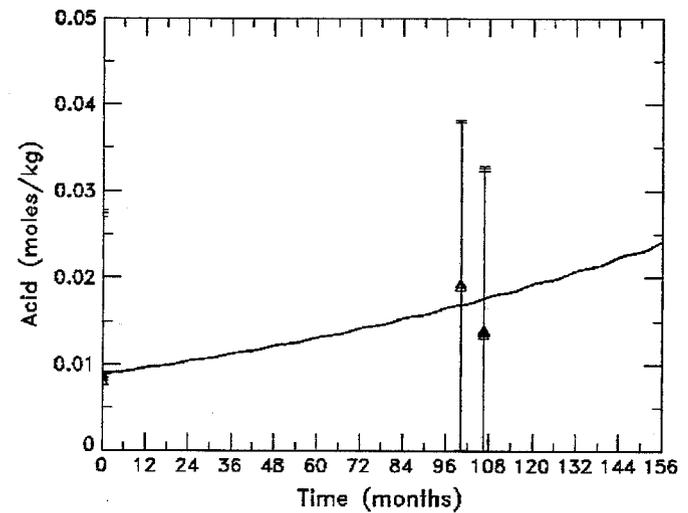
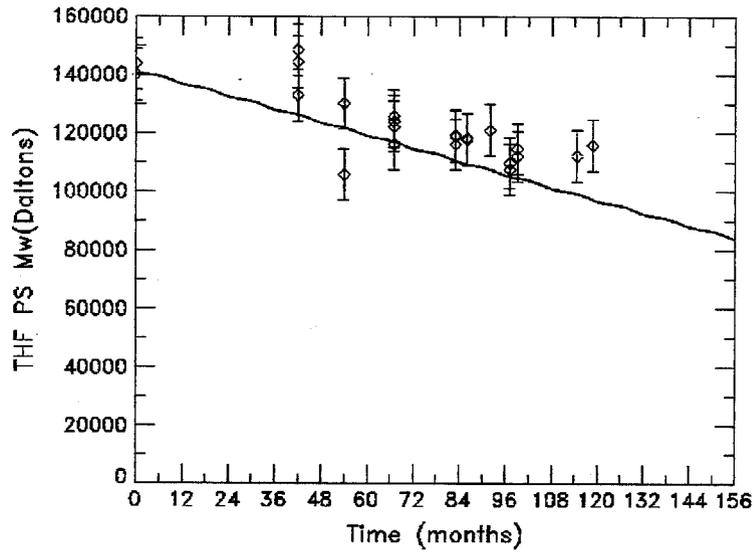
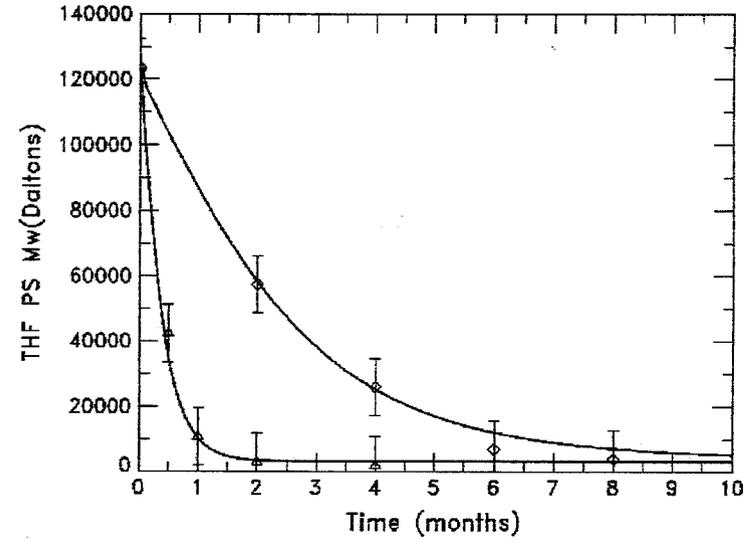
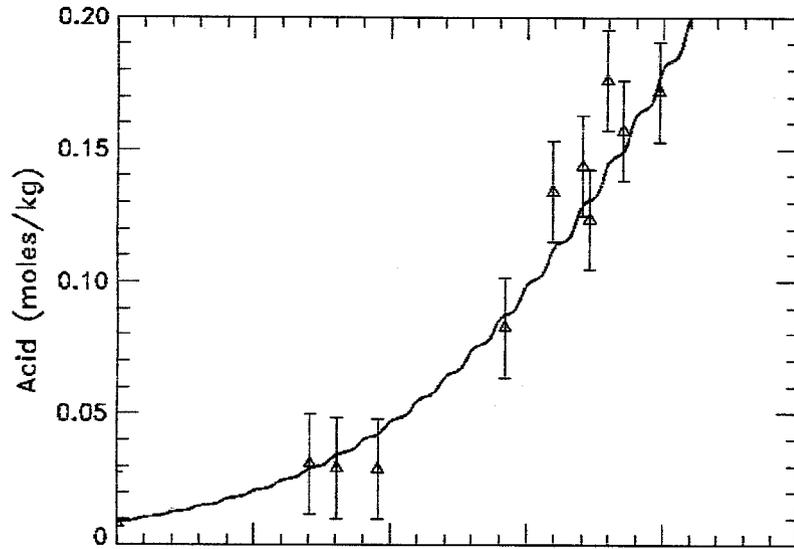
[W] is maintained via the water clustering  
model

# Experiments

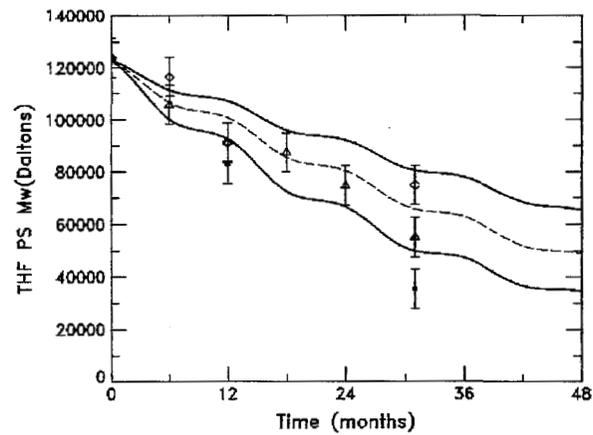
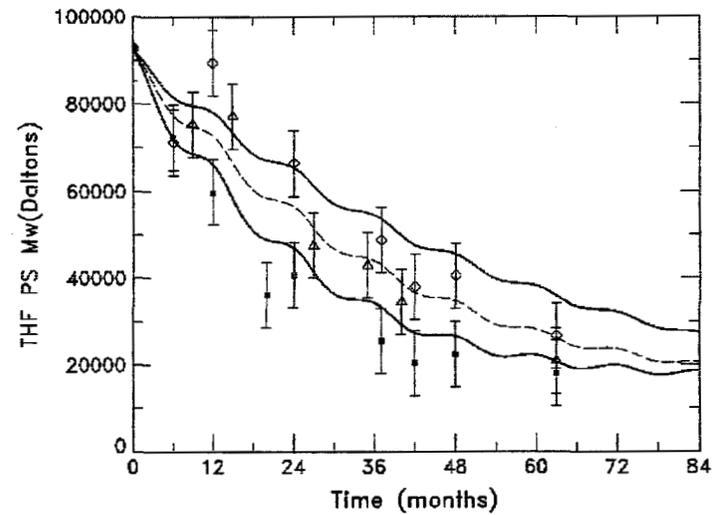
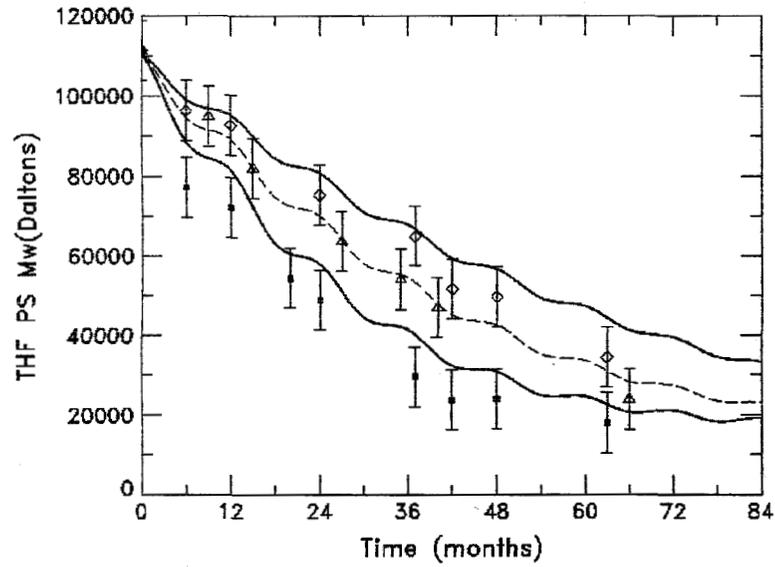
- Experimental data which ranged over RH, temperature, and starting molecular weight
- Measurements ranged from Mw, Mn, acid concentration, and NMR analysis of end groups
- Fitting a single experiment with the model is not difficult; however, fitting all the diverse experiments with a single set of rate coefficients was a challenge.



# More Experiments



# Further Experiments



# Summary of Hydrolysis Modeling

- Able to fit diverse experiments with a single set of rate coefficients.
- Data ranged over temperatures from room temperature to 95°C and RHs from dry to ambient to 100%RH.
- Fitting these data yields confidence in having a reliable hydrolysis model.