Hydrolysis Kinetics and Lifetime Prediction for Polycarbonate and Polyesters

James E. Pickett

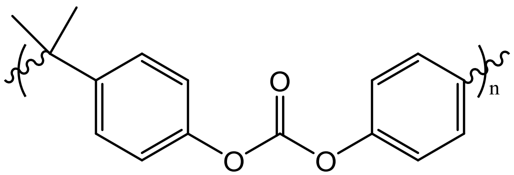
GE Global Research
Niskayuna, NY 12309
pickett@ge.com

Acknowledgements

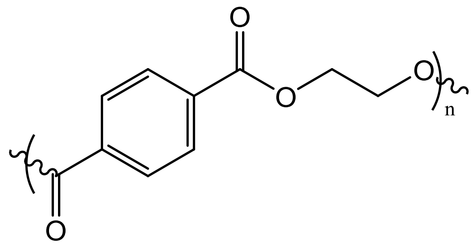
Dennis Coyle

GE Energy
U.S. Department of Energy Award DE-FC36-07GO17045

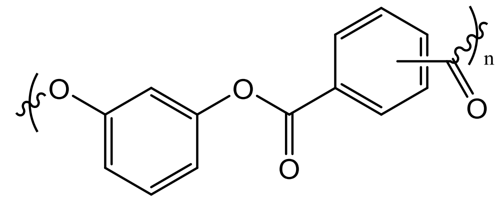
Service Life Prediction of Polymeric Materials: Vision for the Future
Monterey, California
March 3-8, 2013



BPA polycarbonate
(PC)



poly(ethylene terephthalate)
(PET)



resorcinol polyarylate
(RPA)

- Candidates for front sheet of flexible PV modules
- UV stability a separate consideration
- **Do they have enough hydrolytic stability?**

Outline

- Lifetime prediction model based on climatic data
- Kinetics of hydrolysis under humidity aging conditions
- Application of kinetics to the model
- Effect of variables on the prediction
- Folly of single-condition testing

Lifetime Prediction Model

Step	Need to know
Time-parsed climatic data for 1 year	Typical Meteorological Year (TMY) data http://rredc.nrel.gov/solar/old_data/nsrdb/1991-2005/tmy3/
Calculate conditions for object at each time interval	Models for temperature and RH
Calculate degradation for each time interval relative to reference conditions e.g. 85 °C and 85% RH	Knowledge of the kinetics - activation energy (E_a) - kinetic equation $k = A\, exp(-E_a/RT)[H_2O]^n$
Sum over entire year	
This is tells how much exposure under reference conditions = 1 year	Life data at reference conditions - e.g. 85 °C and 85% RH

TMY3 Miami Data

- http://rredc.nrel.gov/solar/old_data/ nsrdb/1991-2005/tmy3/
- downloaded as csv file into EXCEL; download User's Manual to decode headers

722020	MIAMI INTL AP FL		-5	25.817	-80.3	11	
Date (MM/DD/ YYYY)	Time (HH:MM)	ETR (W/m^2)	ETRN (W/m^2)	GHI (W/m^2)	GHI source	GHI uncert (%)	DNI (W/m^2)
1/1/1995	1:00	0	0	0	1	0	0
1/1/1995	2:00	0	0	0	1	0	0
1/1/1995	3:00	0	0	0	1	0	0
1/1/1995	4:00	0	0	0	1	0	0
1/1/1995	5:00	0	0	0	1	0	0
1/1/1995	6:00	0	0	0	1	0	0
1/1/1995	7:00	0	0	0	1	0	0
1/1/1995	8:00	98	1191	39	1	10	262
1/1/1995	9:00	369	1415	218	1	10	694
1/1/1995	10:00	606	1415	394	1	10	768
1/1/1995	11:00	785	1415	540	1	10	747
1/1/1995	12:00	896	1415	411	1	10	230
1/1/1995	13:00	928	1415	503	1	10	324
1/1/1995	14:00	882	1415	514	1	10	517
1/1/1995	15:00	759	1415	396	1	10	107
1/1/1995	16:00	568	1415	313	1	10	117
1/1/1995	17:00	323	1415	116	1	10	152
1/1/1995	18:00	61	955	16	1	10	22
1/1/1995	19:00	0	0	0	1	0	0
1/1/1995	20:00	0	0	0	1	0	0
1/1/1995	21:00	0	0	0	1	0	0
1/1/1995	22:00	0	0	0	1	0	0
1/1/1995	23:00	0	0	0	1	0	0
1/1/1995	24:00:00	0	0	0	1	0	0

… 44 more columns
irradiance
temperature
RH, dew point
atmospheric pressure
wind speed and direction
cloud cover, visibility
precipitation

… 8736 more rows: selected typical months to make an average year

Temperature and Humidity Models

- **Temperature**
  - sophisticated models exist; T = f(Irradiance, T_{amb}, wind, material properties, …)
  - used simple transfer function from black panel temperature data

    see J.E. Pickett and J.R. Sargent, *Polymer. Degrad. Stab.*, **94**, 189-195 (2009)

    adjusted to give various maximum temperatures

    $$\boldsymbol{T}_{mod} = \boldsymbol{T}_{amb} - 3.843 \times 10^{-6}\,\boldsymbol{I}^2 + 0.521\,\boldsymbol{I} - 3.25$$ where $\boldsymbol{I}$ = irradiance (W/m^2)

- **Relative humidity / moisture content**
  - assuming thin film that equilibrates quickly (< 1 hr) so $[H_2O] \propto RH$
  - important RH is that of boundary layer at surface *at the surface temperature*
  - $$\boldsymbol{RH}_{mod} = \frac{\boldsymbol{p}_{H_2O}}{\boldsymbol{p}_{sat}} = \frac{\boldsymbol{RH}_{amb} \times \boldsymbol{p}_{sat,T_{amb}}}{\boldsymbol{p}_{sat,T_{mod}}}$$ *where RH* is fractional relative humidity
  - Magnus Equation: $$\boldsymbol{p}_{sat,T} = exp\left(6.4154 + \frac{17.62\,\boldsymbol{T}}{243.12 + \boldsymbol{T}}\right)$$ in *pascals* where $\boldsymbol{T}$ is in °C

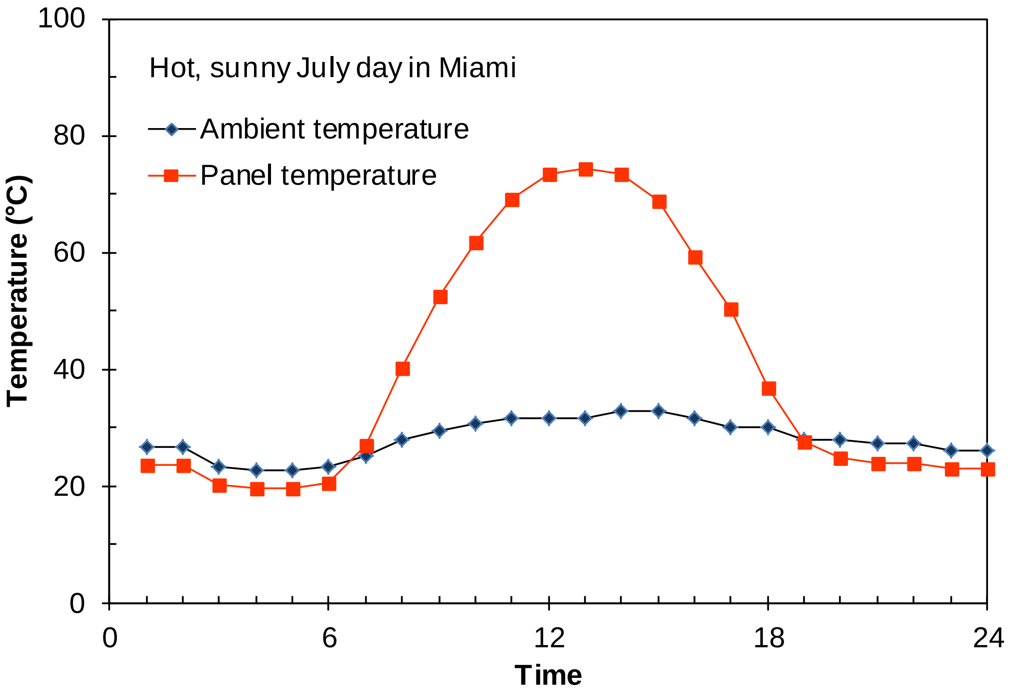
Climatic Data – Miami TMY3

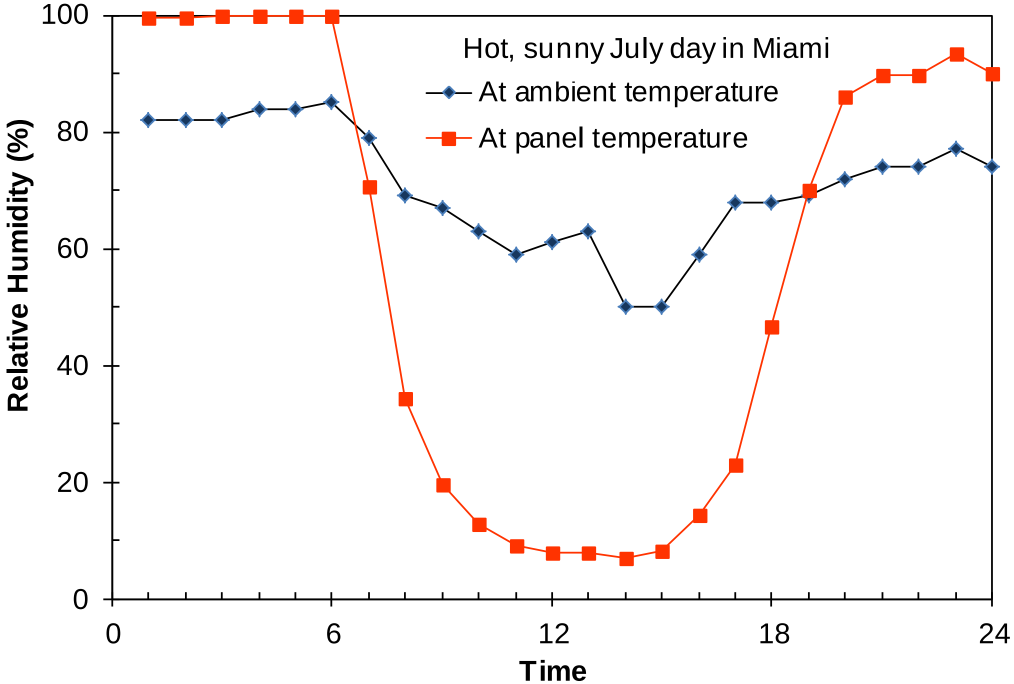
- use data to calculate module temperature and module RH for each hour
- e.g. data for hot, sunny July day

Date	Time	Global Irradiance (W/m^2)	Dry-bulb (°C)	Rel Hum (%)	Calculated: Module surface (°C)	Calculated: RH at module (%)
7/4/1990	1:00	0	26.7	82	23.5	99.5
7/4/1990	2:00	0	26.7	82	23.5	99.5
7/4/1990	3:00	0	23.3	82	20.1	100
7/4/1990	4:00	0	22.8	84	19.6	100
7/4/1990	5:00	0	22.8	84	19.6	100
7/4/1990	6:00	9	23.3	85	20.5	100
7/4/1990	7:00	100	25.0	79	26.9	70.5
7/4/1990	8:00	309	27.8	69	40.3	34.4
7/4/1990	9:00	525	29.4	67	52.5	19.7
7/4/1990	10:00	696	30.6	63	61.8	12.7
7/4/1990	11:00	832	31.7	59	69.2	9.1
7/4/1990	12:00	927	31.7	61	73.5	7.8
7/4/1990	13:00	944	31.7	63	74.2	7.8
7/4/1990	14:00	902	32.8	50	73.5	6.8
7/4/1990	15:00	803	32.8	50	68.9	8.3
7/4/1990	16:00	618	31.7	59	59.2	14.3
7/4/1990	17:00	469	30.0	68	50.4	22.9
7/4/1990	18:00	195	30.0	68	36.8	46.5
7/4/1990	19:00	58	27.8	69	27.6	70.0
7/4/1990	20:00	4	27.8	72	24.8	86.2
7/4/1990	21:00	0	27.2	74	24.0	89.7
7/4/1990	22:00	0	27.2	74	24.0	89.7
7/4/1990	23:00	0	26.1	77	22.9	93.5
7/4/1990	24:00	0	26.1	74	22.9	89.9

Calculated module temp and RH

- e.g. data for hot, sunny July day
- module temp rises with irradiance





- RH_{amb} decreases as T_{amb} increases
- RH_{mod} decreases to < 10%

Lifetime Prediction Model

Step		Need to know
Time-parsed climatic data for 1 year	←	Typical Meteorological Year (TMY) data http://rredc.nrel.gov/solar/old_data/nsrdb/1991-2005/tmy3/
↓		
Calculate conditions for object at each time interval	←	Models for temperature and RH
↓		
Calculate degradation for each time interval relative to reference conditions e.g. 85 °C and 85% RH	←	Knowledge of the kinetics - activation energy (E_a) - kinetic equation
↓		

$$k = A\, exp(-E_a/RT)[H_2O]^n$$

Hydrolysis Kinetics

Key points:

- $[H_2O]$ in polymer $\propto$ p_{H2O} / p_{sat} = relative humidity
- E_a for PET is much higher than E_a for PC
- hydrolysis in polymer film is *second order* in water

JE Pickett and DJ Coyle, Hydrolysis kinetics of condensation polymers under humidity aging conditions, submitted to *Polymer Degradation and Stability*

Hydrolysis Experiment

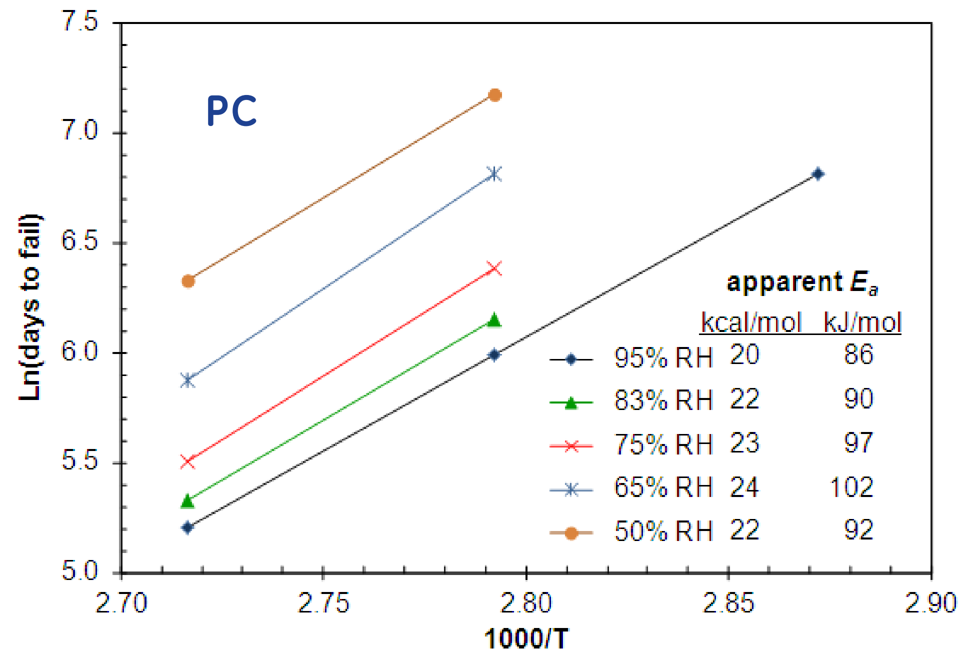
- 7-10 mil films of polycarbonate, Melinex PET, and resorcinol polyarylate
- test by bend around ¼" diameter rod
- constant humidity jars at 95, 83, 75, 50, (23) %RH
- in ovens at 95, 85, 75, (and 65) °C
- also 85 °C / 85% RH climatic chamber

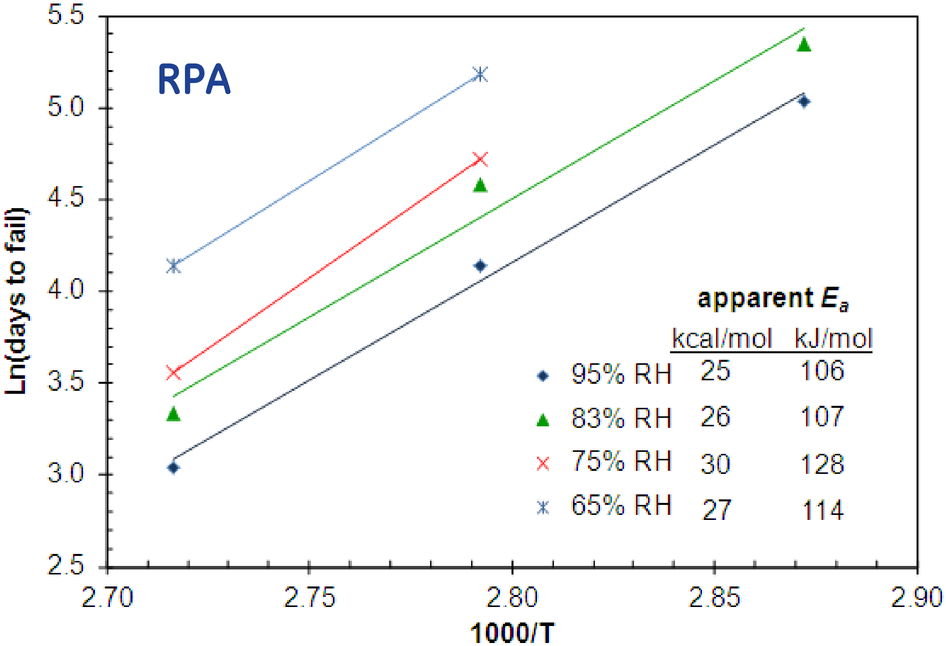
temp (°C)	RH (%)	PC (days)	PET-A (days)	PET-B (days)	PET-C (days)	PET-D (days)	RPA-A (days)	RPA-B (days)	RPA-C (days)
95	95	182	21	25	21	19	11	21	32
	83	206	25	28	25	25	14	28	35
	75	245	32	28	32	28	19	35	42
	65	357	56	49	49	49	25	63	70
	50	560	70	63	63	63	28	77	88
	23	-	119	112	112	102	102	140	168
85	95	399	84	84	84	77	28	63	-
	85	483	98	98	98	70	42	77	-
	83	469	98	105	98	98	42	98	-
	75	591	126	133	126	105	49	112	-
	65	907	207	207	207	175	84	178	-
	50	1301	266	266	266	231	105	259	-
75	95	907	231	221	231	207	84	154	-
	83	-	294	287	294	252	112	210	-
	75	-	357	343	357	280	112	-	-
65	95	-	-	-	-	-	189	-	-

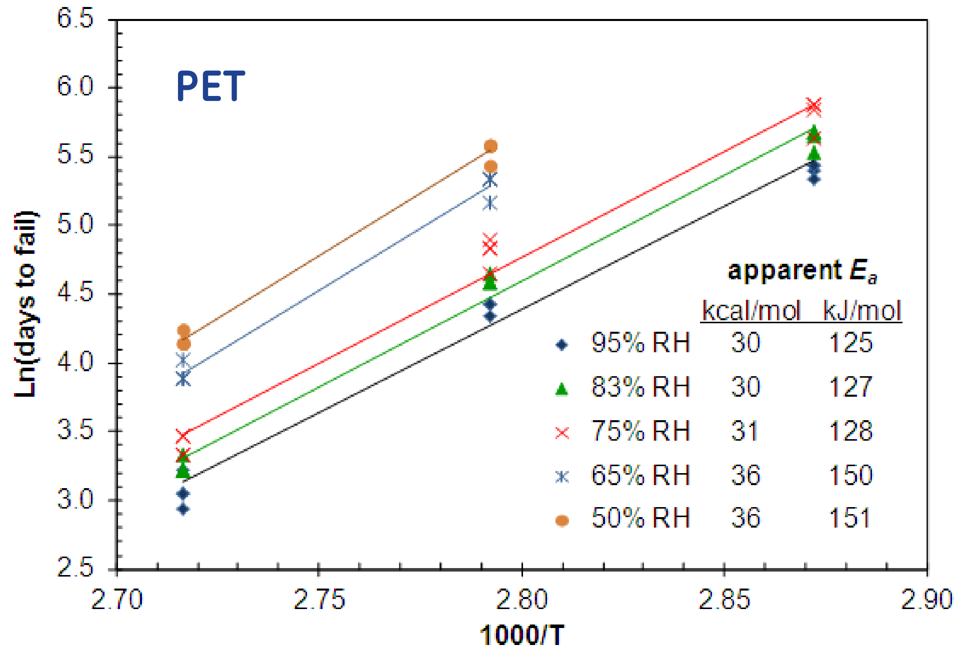
Temperature Effects

	Average E_a (kcal/mol)
PC	22
PET	32
RPA	27

will treat in a more sophisticated manner below

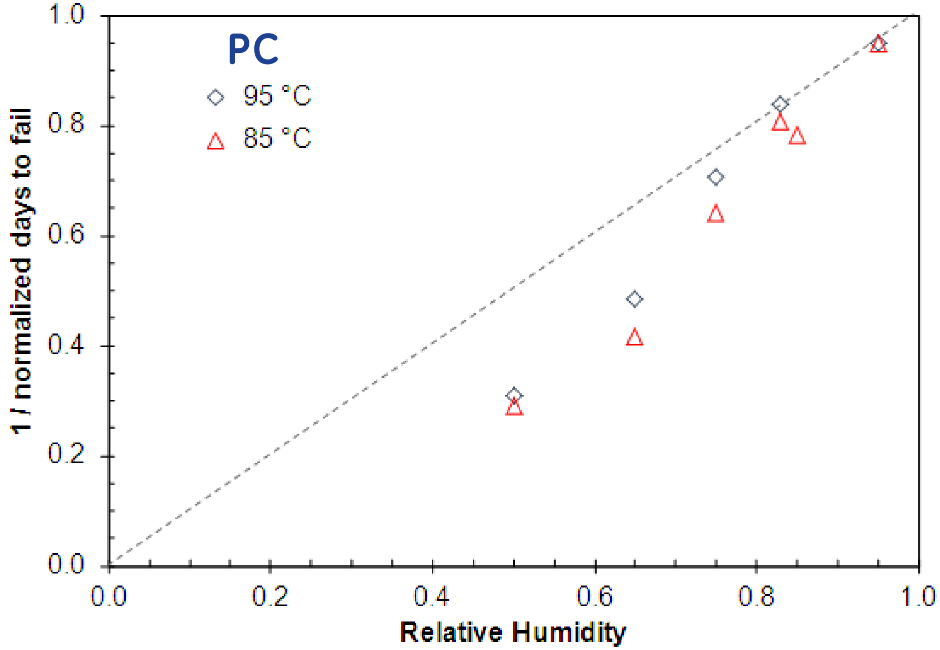


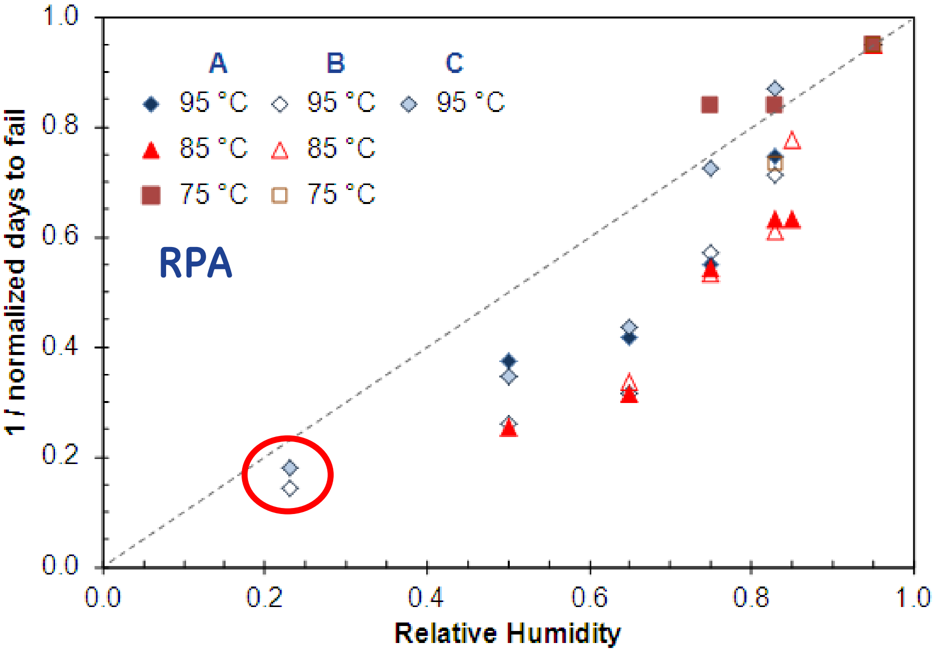


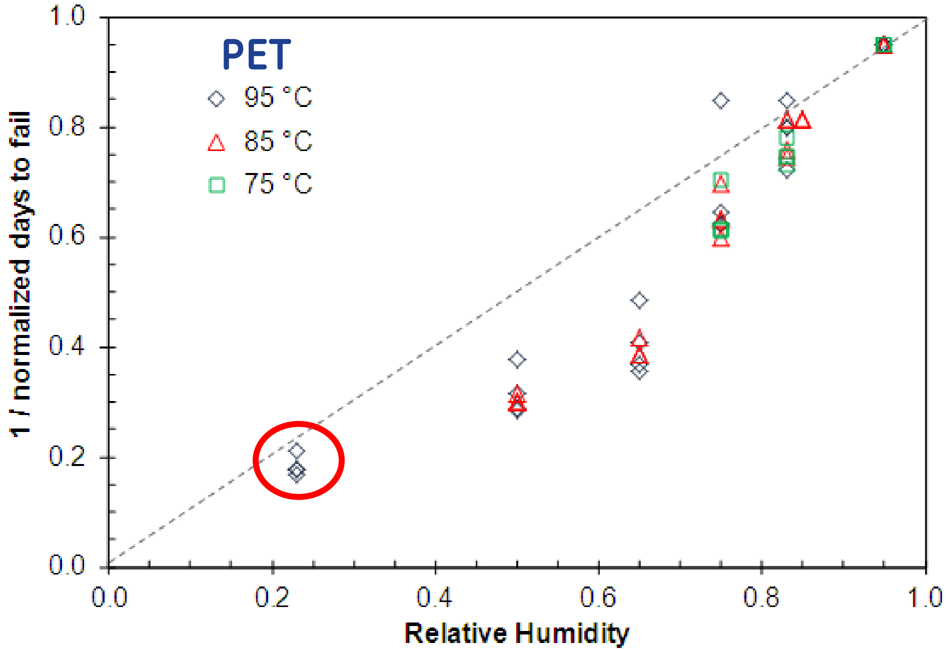


Humidity Effects

normalized rates are not linear with RH



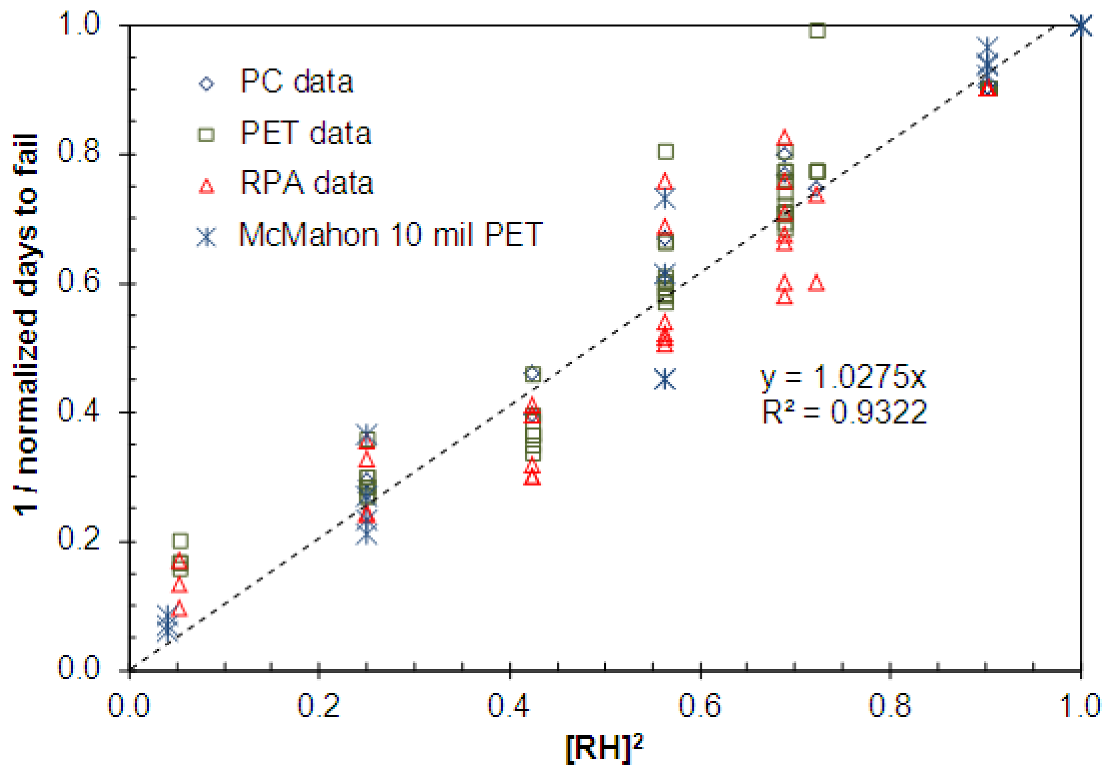




Humidity Effects

But… normalized rates appear linear with $[RH]^2$

Second order in water?



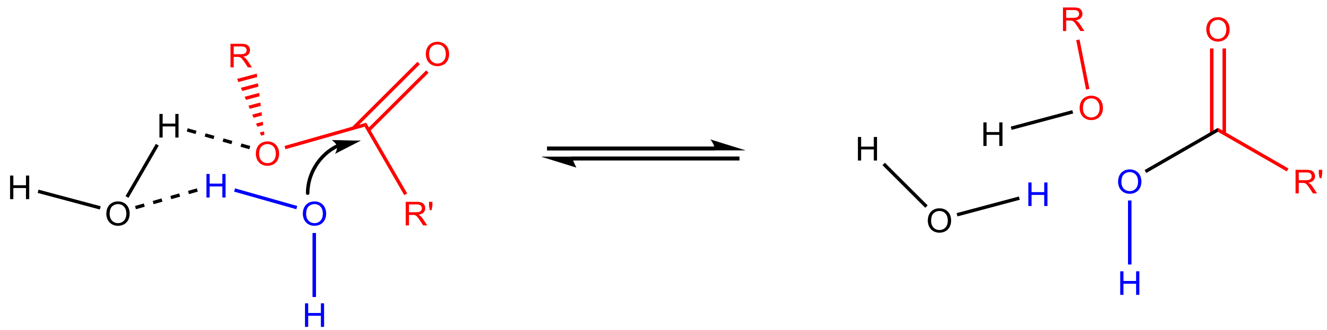
W McMahon, HA Birdsal, GR Johnson, CT Camilli, *J. Chem. Eng. Data*, **4**, 57-79 (1959)

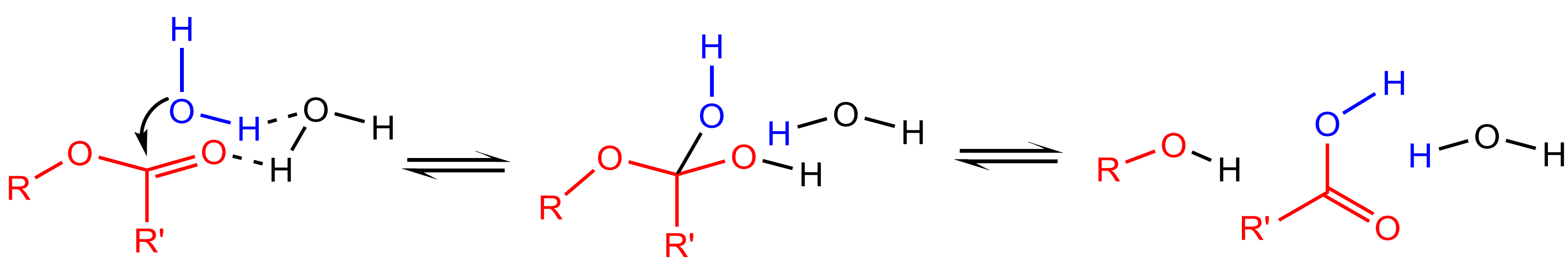
Humidity dependence

$$\frac{-d[P]}{dt} = k[P][H_2O]^2$$

- Ester hydrolysis requires a catalyst to move the protons around or polarize the carbonyl
- A clean polymer has no catalysts
- ***Under neutral conditions, another molecule of water serves as the catalyst***

e.g. W.P. Jencks and J. Carriuolo, *J. Amer. Chem. Soc.*, **83**, 1743-1750 (1961)
E.K. Euranto and N.J. Cleve, *Acta Chem. Scand.*, **17,** 1584-1594 (1963)
Z. Shi, *et al.*, *Can. J. Chem.*, **87**, 339-543, 544-555 (2009)





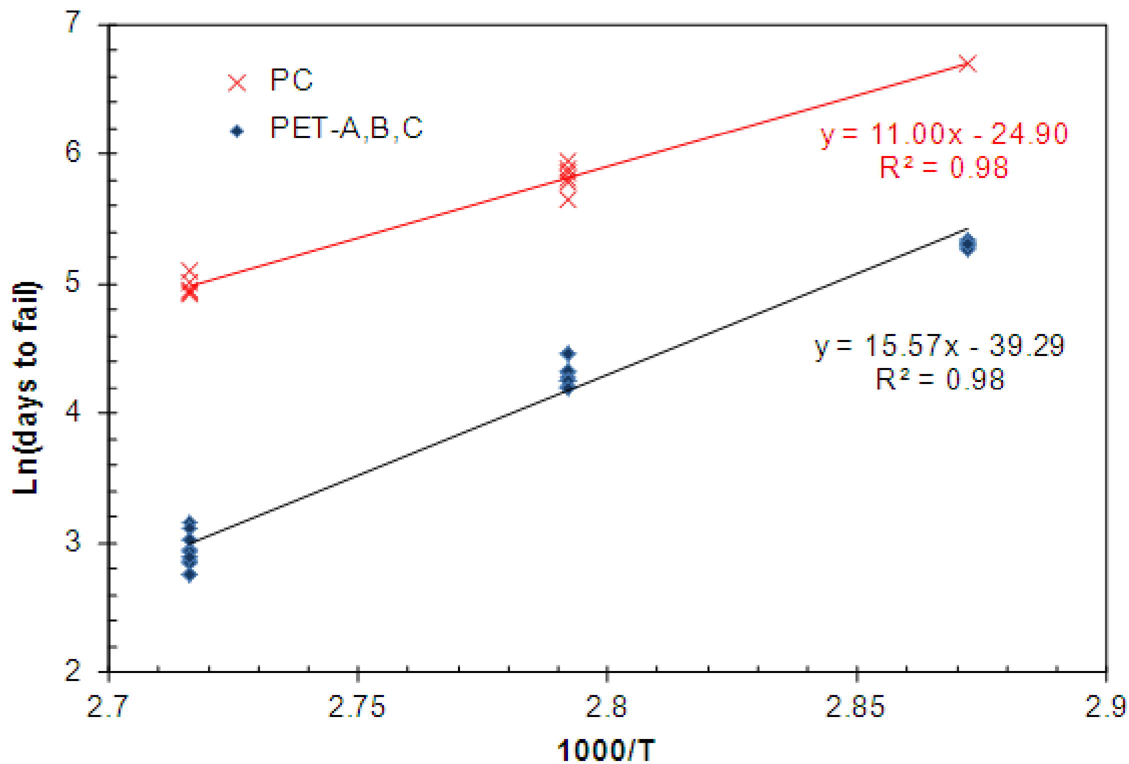
Kinetic analysis

$$t_{fail} = \frac{\exp(E_a/RT)}{A[RH]^2}$$

Assume 2nd order in RH to normalize all data sets at one T, but several RH to 100% RH

Allows some statistics ranges at 95% confidence

series	E_a kcal/mol	ln(*A*)	mean error %	R^2
PC	21.9 ± 2.3	24.9 ± 3.2	5.0	0.99
PET-A,B,C	30.9 ± 1.6	39.3 ± 2.2	12.1	0.96
PET-D	30.6 ± 1.4	38.9 ± 2.0	16.4	0.95
RPA-A	25.0 ± 2.6	31.8 ± 3.7	11.9	0.95
RPA-B,C	24.3 ± 2.9	30.0 ± 4.0	13.2	0.96



Optimized parameters

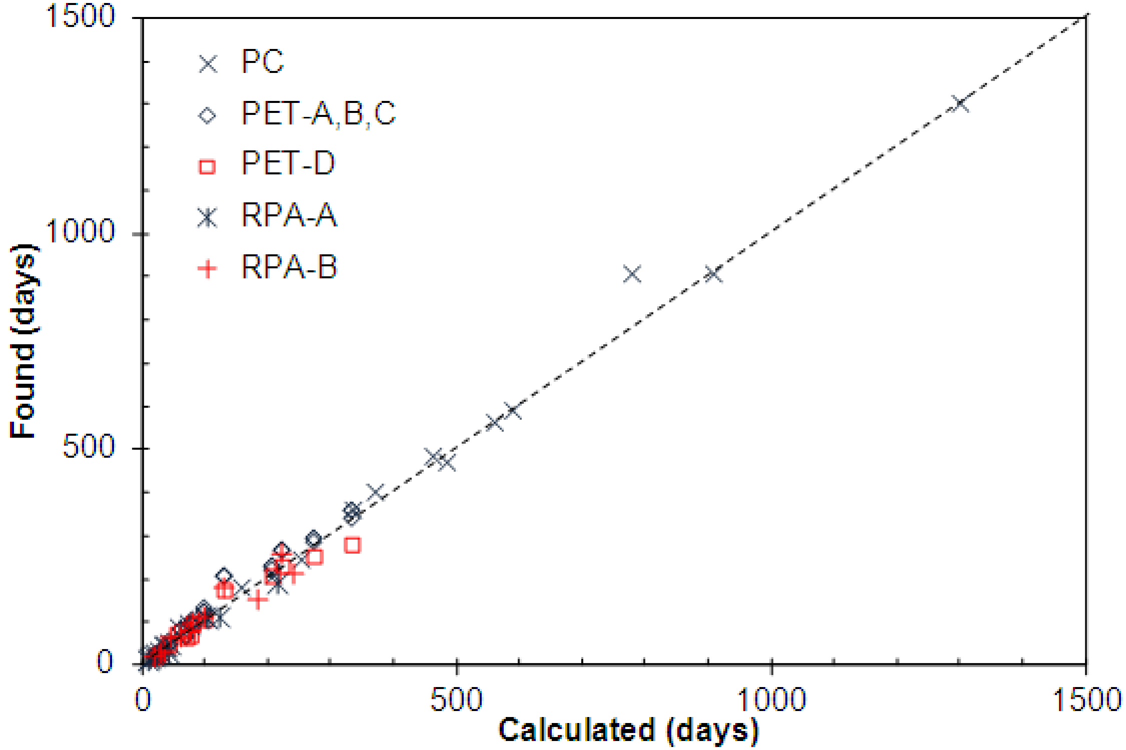
$$t_{fail} = \frac{\exp(E_a/RT)}{A[RH]^n}$$

series	E_a kcal/mol	ln(*A*)	*n*	mean error %	R^2
PC	22.1	25.21	1.95	4.3	0.99
PET-A,B,C	30.5	38.68	2.13	11.5	0.97
PET-D	30.4	38.74	2.03	10.6	0.96
RPA-A	24.0	30.46	1.98	11.7	0.96
RPA-B,C	23.5	29.06	2.29	12.4	0.97

Let Solver in EXCEL find best E_a, *A*, and *n* for each data set by minimizing mean error

Note that Solver found n ≅ 2

All within error of previous analysis



Calculate degradation

- for each time interval relative to the reference conditions

		Calculated		Rates relative to 85 °C/85% RH	
Date	Time	Module surface (°C)	RH at module (%)	PC	PET
7/4/1990	1:00	23.5	99.5	1.72E-02	5.02E-05
7/4/1990	2:00	23.5	99.5	1.72E-02	5.02E-05
7/4/1990	3:00	20.1	100	1.29E-02	2.54E-05
7/4/1990	4:00	19.6	100	1.24E-02	2.29E-05
7/4/1990	5:00	19.6	100	1.24E-02	2.29E-05
7/4/1990	6:00	20.5	100	1.35E-02	2.80E-05
7/4/1990	7:00	26.9	70.5	1.16E-02	5.01E-05
7/4/1990	8:00	40.3	34.4	8.07E-03	1.46E-04
7/4/1990	9:00	52.5	19.7	6.49E-03	3.91E-04
7/4/1990	10:00	61.8	12.7	5.18E-03	7.37E-04
7/4/1990	11:00	69.2	9.1	4.31E-03	1.17E-03
7/4/1990	12:00	73.5	7.8	4.17E-03	1.64E-03
7/4/1990	13:00	74.2	7.8	4.38E-03	1.83E-03
7/4/1990	14:00	73.5	6.8	3.18E-03	1.25E-03
7/4/1990	15:00	68.9	8.3	3.53E-03	9.41E-04
7/4/1990	16:00	59.2	14.3	5.50E-03	6.19E-04
7/4/1990	17:00	50.4	22.9	7.59E-03	3.73E-04
7/4/1990	18:00	36.8	46.5	1.12E-02	1.41E-04
7/4/1990	19:00	27.6	70.0	1.20E-02	5.59E-05
7/4/1990	20:00	24.8	86.2	1.44E-02	4.88E-05
7/4/1990	21:00	24.0	89.7	1.46E-02	4.51E-05
7/4/1990	22:00	24.0	89.7	1.46E-02	4.51E-05
7/4/1990	23:00	22.9	93.5	1.44E-02	3.93E-05
7/4/1990	24:00	22.9	89.9	1.33E-02	3.63E-05

$$k = A\,exp(-E_a/RT)(RH)^n$$

$$\boldsymbol{k}_{rel} = \boldsymbol{k}_{T,RH}/\boldsymbol{k}_{T_{ref},RH_{ref}}$$

$$\Delta\, Deg_{rel} = k_{rel}\,\Delta t$$

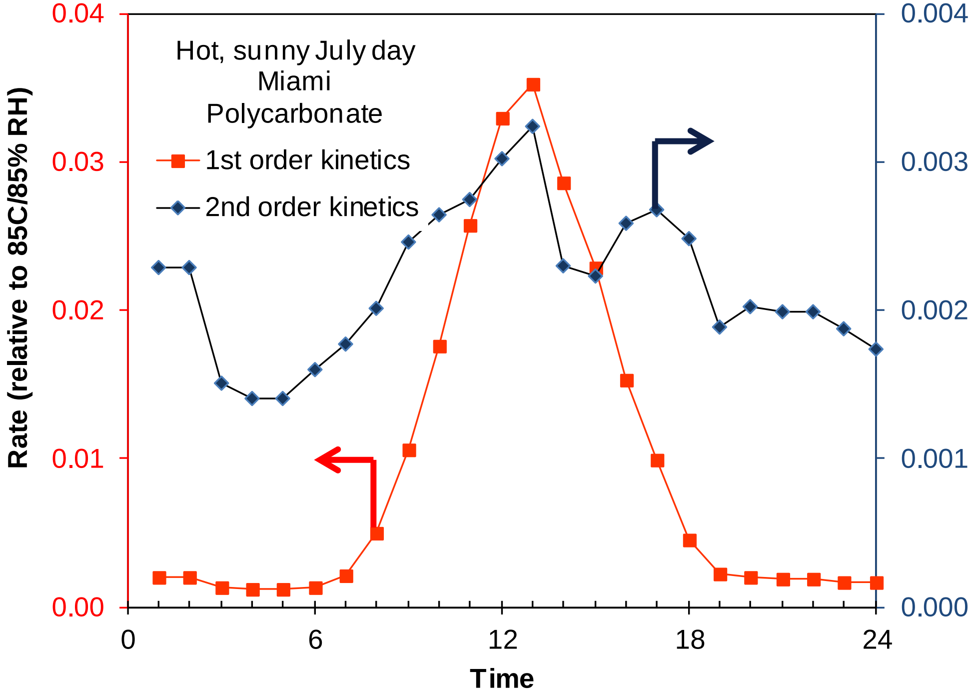
1 hr at 27.6 °C and 70% RH = 0.012 hr at 85 °C and 85% RH for PC

Sum for entire year to get # of hours on test = 1 year

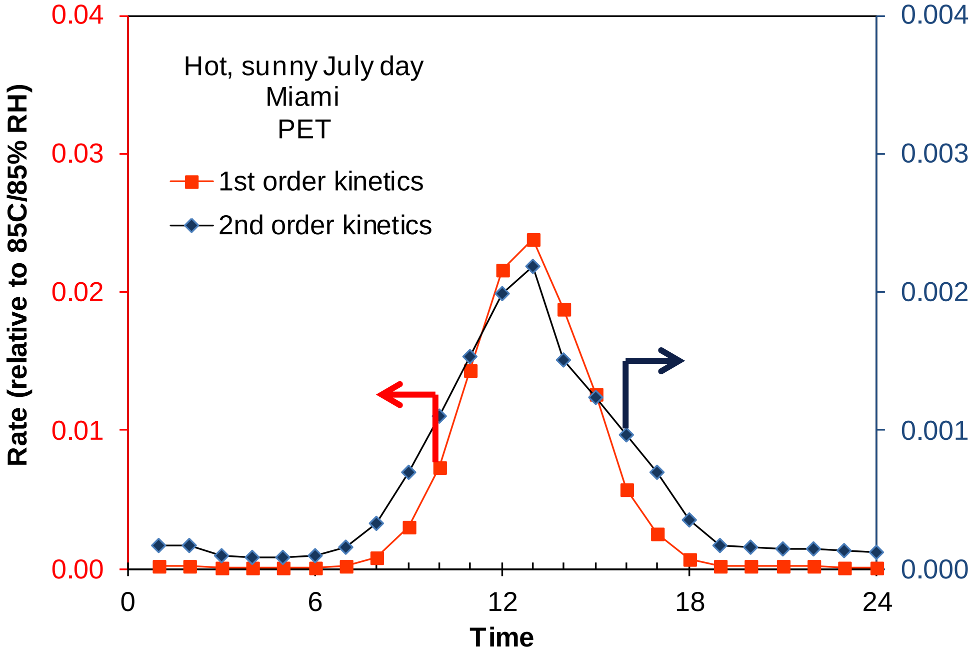
Calculate degradation

For PC with lower E_a, temperature effect not enough to make up for lower RH when panel is hot—relatively constant rate of hydrolysis (if 2nd order).

Temperature dominates if kinetics are 1st order in RH and rates are much higher.



For PET with higher E_a, temperature effect dominates for both 1st and 2nd order kinetics; rates 10x faster for 1st order kinetics.



Calculation Results

- All three polymers should have more than enough stability for > 25 years
- Unlikely to last that long, but hydrolysis does not appear to be an issue
- This is despite "PET's hydrolytic stability problem" in 85°C/85% RH testing

	PC	PET	RPA
E_a (kcal/mol)	21.9	30.9	24.3
hr 85 C/85% RH per yr-eq	13.8	2.3	8.1
days 85/85 to fail	483	98	77
hr 85/85 to fail	11592	2352	1848
calc. years in module	837	1023	230

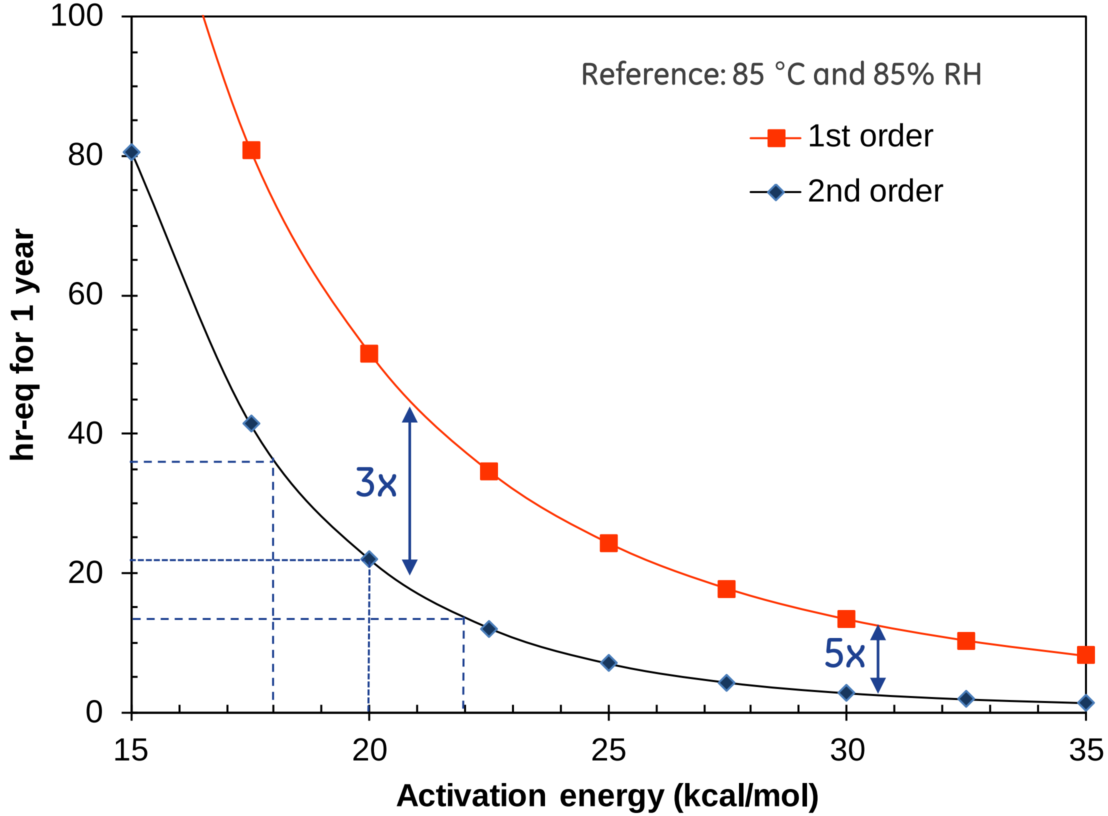
Qualifications

Assuming linear Arrhenius plots (extrapolating from 75 °C to 25 °C)

Assuming 2nd order in RH (extrapolating from 50% RH to 5% RH)

Effects of the variables
Activation energy

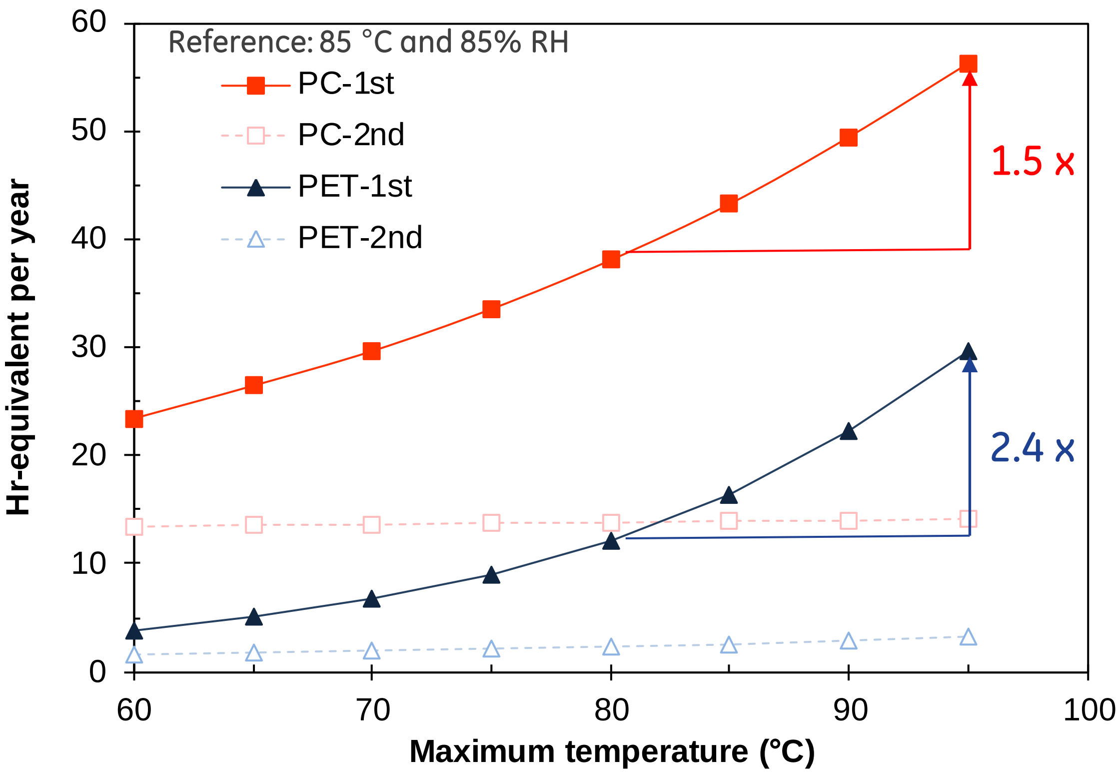
- “Correlation” increases ~ exponentially with lower E_a
- Reaction order has larger fractional effect with higher E_a



20 ± 2 kcal/mol → 13 – 36 hr-eq/year life

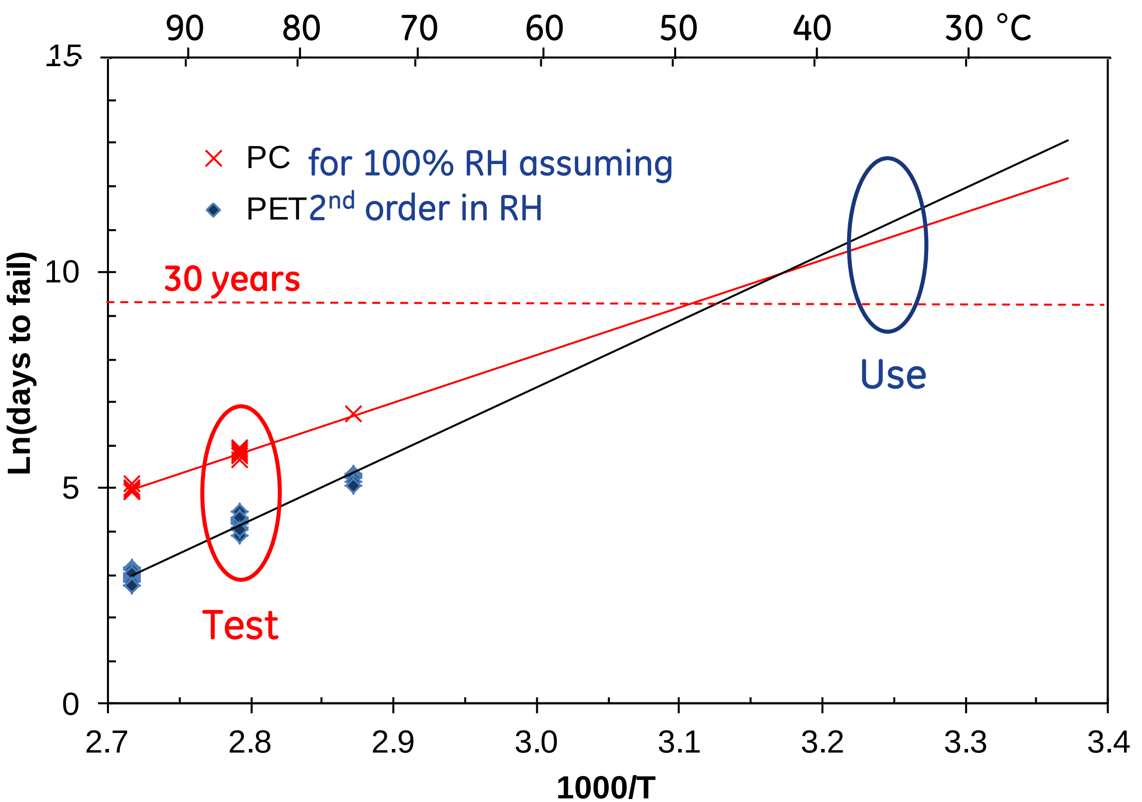
Effects of the variables
Temperature

- 2^{nd} order in RH → little effect from temperature model
- 1^{st} order in RH → greater fractional effect with higher E_a
    - need more accurate temperature model



Folly of the qualification test

- 85 °C and 85% RH (1000 hours) carved into stone
- But… need two more pieces of information to be useful
  - slope (E_a, assuming Arrhenius extrapolation is valid)
  - effective use temperature and other conditions
- PC hydrolysis slower than PET at 85 °C, but faster < 43 °C



Conclusions

- Lifetime prediction models require:
  - good data for use conditions, preferably time-parsed
  - good models for calculating environmental stresses on article
  - good kinetic models for relating use stresses to reference conditions

- Polyester and polycarbonate hydrolysis is second order in moisture
  - large effects on predictions at low RH from data at high RH

- Even notoriously "hydrolytically unstable" polymers appear suitable for high temperature, long duration use
  - high temperature $\rightarrow$ low humidity, so hydrolysis rate slows dramatically
  - all bets are off if water can become trapped

- 1-condition qualification tests cannot be predictive

References

PC:
Golovoy A, Zinbo M. Polym Eng Sci 1989: 29; 1733-1737.
Zinbo M, Golovoy A. Polym Eng Sci 1992: 32; 786-791.
Pryde CA, Kelleher PC, Hellman MY, Wentz RP. Polym Eng Sci 1982: 22; 370-375.
Gardener RJ, Martin JR. J Appl Polym Sci 1978: 24; 1269-1280.
Pryde CA, Hellman MY. J Appl Polym Sci 1980: 25; 2573-2587.
Factor A. In: LeGrand DG, Bendler JT, eds. Handbook of polycarbonate science and technology. Marcel Dekker; 2000.

PET:
McMahon W, Birdsall HA, Johnson GR, Camilli CT. J Chem Eng Data 1959: 4; 57-79.

BPA polyarylate:
Golovoy A, Cheung MF. J Appl Polym Sci 1988: 35; 1511-1521.
Golovoy A, Cheung MF, Zinbo M. J Appl Polym Sci 1988: 35; 2001-2008.
Golovoy A, Zinbo M. J Appl Polym Sci 1990: 39; 189-197.