SUPPLEMENTARY INFORMATION

RISK ASSESSMENT FOR REDUCING THERMOSET WASTE: PREDICTIVE MODELING OF WATER AGEING IN EPOXY INFRASTRUCTURE

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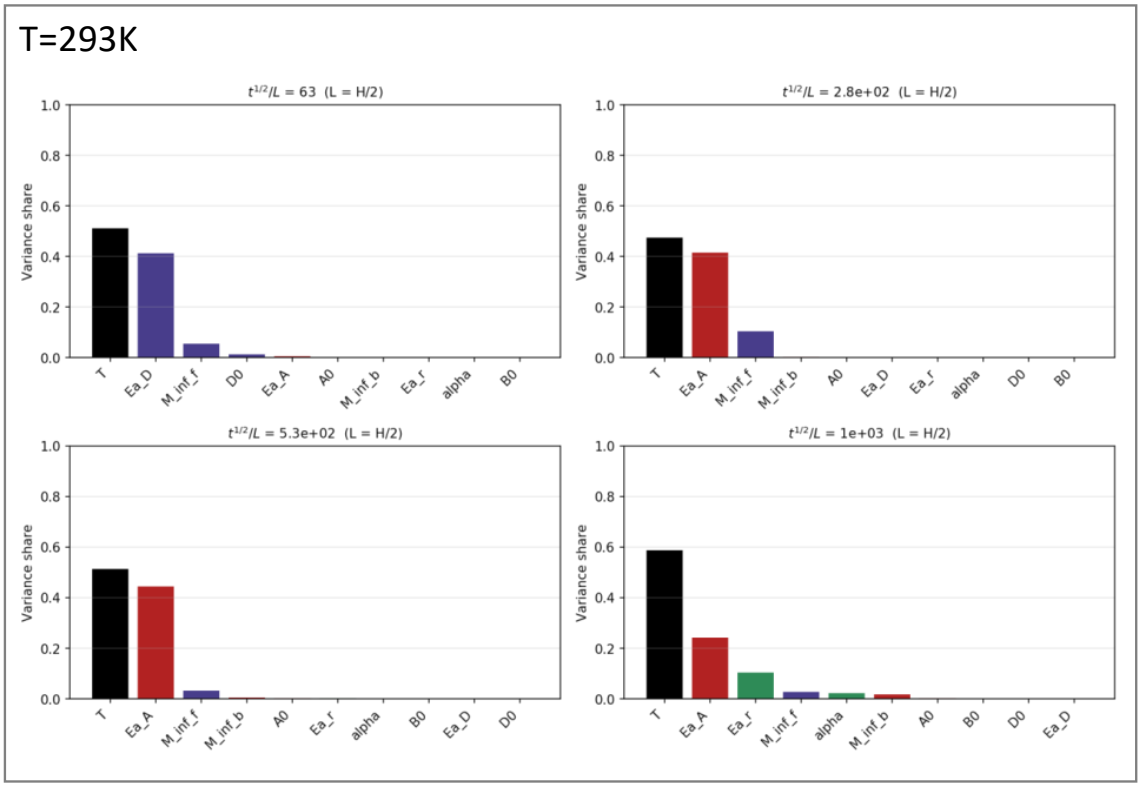
KEYWORDS: polymer ageing, water diffusion; hydrolysis; degradation, AI.

S1. Model sensitivity analysis.

To identify which physical parameters are governing our model's output at each stage of sorption, we performed a variance-based Monte-Carlo sensitivity study. Putting it in simple terms, the analysis is intended to answer the question *"At any moment, which inputs dominate the predicted uptake?"*.

With this aim, we perturb every adjustable quantity by a small, independent log-normal factor and propagate the effect into the predicted mass-uptake curve. We then collect all kinetic and thermodynamic parameters (diffusivity pre-exponent D, equilibrium sorption $M_{\infty,f}$ and $M_{\infty,l}$, Arrhenius activation energies, pre-exponents, α, and the absolute temperature). Our procedure therefore returns the fractional contribution (variance share) of every parameter at each selected sampling instant.

The results for DGEBA-Dicure system (at 295 and 366K) are presented in Figure S1, and can be summarized as follows: a) Temperature determination is the most relevant parameter across all x and temperature values, and therefore temperature control accross experiments is decisive. b) At low temperatures and early times water absorption is almost purely diffusion-controlled; activation energy for Fickian transport (Ea_D) and the maximum Fickian uptake ($M_{\infty,f}$) dominate (once the effect of T is factored out). c) At larger times a transition regime emerges where the activation energies of both the sorption sites (Ea_b) and of the hydrolysis (Ea) gain influence. d) Finally, at higher temperatures hydrolysis parameters become dominant (hydrolysis overtakes diffusion: Ea and α together explain most of the variance).



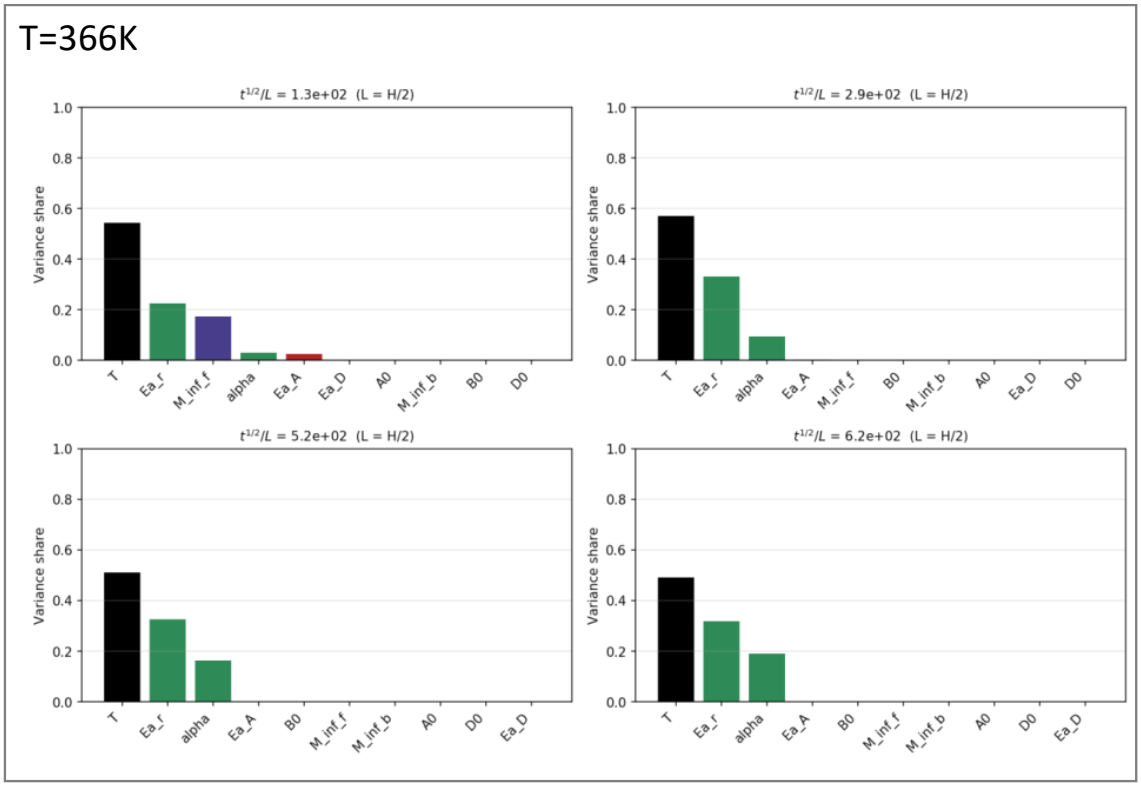


Figure S1. Fractional variance of each model parameter for different reduced times x (early, intermediate, and final stages of the mass gain). a) T=295K. b) T=366K

S2. Water uptake and FTIR signal.

Figure S2 shows DGEBA-Dicure (top) and DGEBA-Jeffamine (bottom) near-infrared (NIR) spectra (4000–6000 cm^{-1}) obtained on samples after immersion in deionised water at 93 and 50 °C, respectively, for increasing exposure times. The ageing intervals are labelled in days for DGEBA-Dicure (2 d to 104 d) and as sequential states A0–A8 for DGEBA-Jeffamine. All spectra were normalised with respect to the aromatic C–H overtone at 4 624 cm^{-1}, characteristic of the DGEBA backbone, in order to highlight the relative evolution of the water-related bands during absorption.

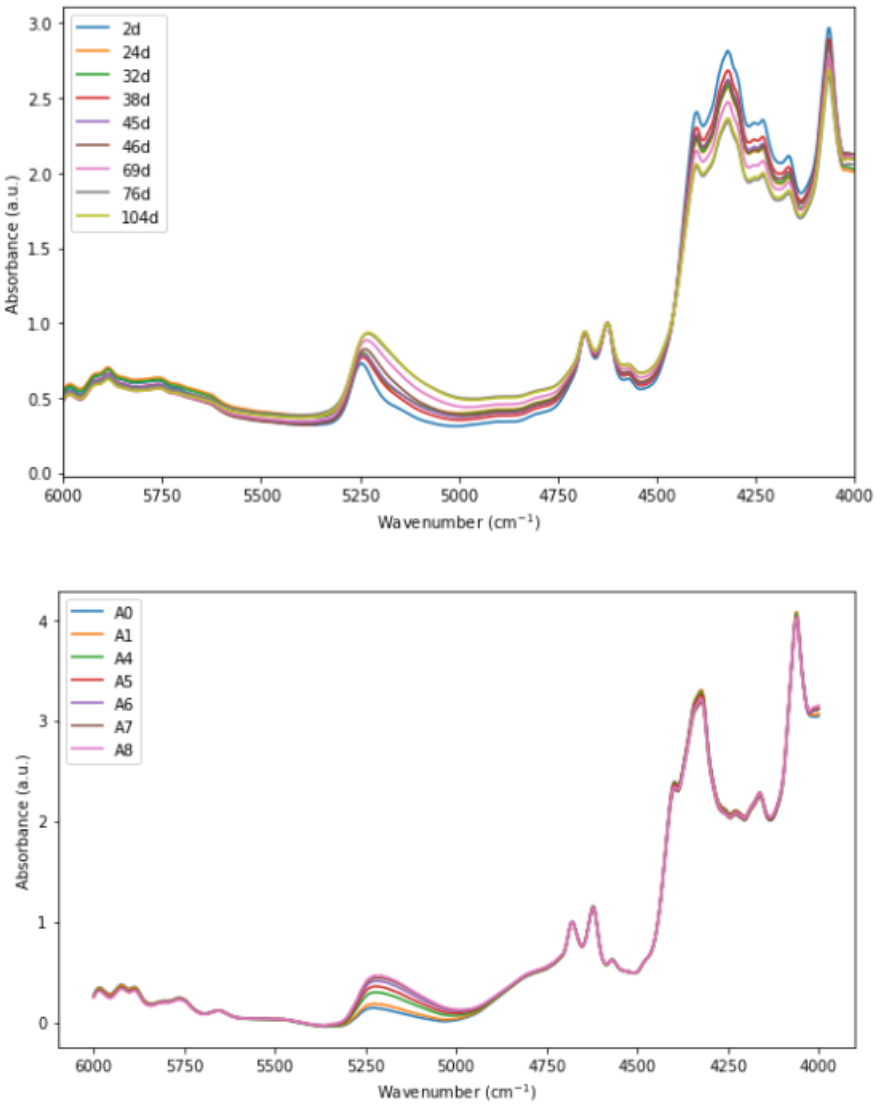


Figure S2. FTIR spectra of thermosetting samples immersed in water: a) DGEBA-Dicure (93°C) and b) DGEBA-Jeffamine (50°C), parametric with time.

S3. Ancamine results.

Figure S3 shows the gravimetric experimental results (filled dots) and the model contributions (blue, red and green lines represent Fickian, Sorption and Hydrolysis contributions, respectively). Black line represents the sum of contributions, which as shown closely describes the experimental data at 23, 80 and 93 C. The obtained parameters are summarized in the bar plots shown in Figure S4.

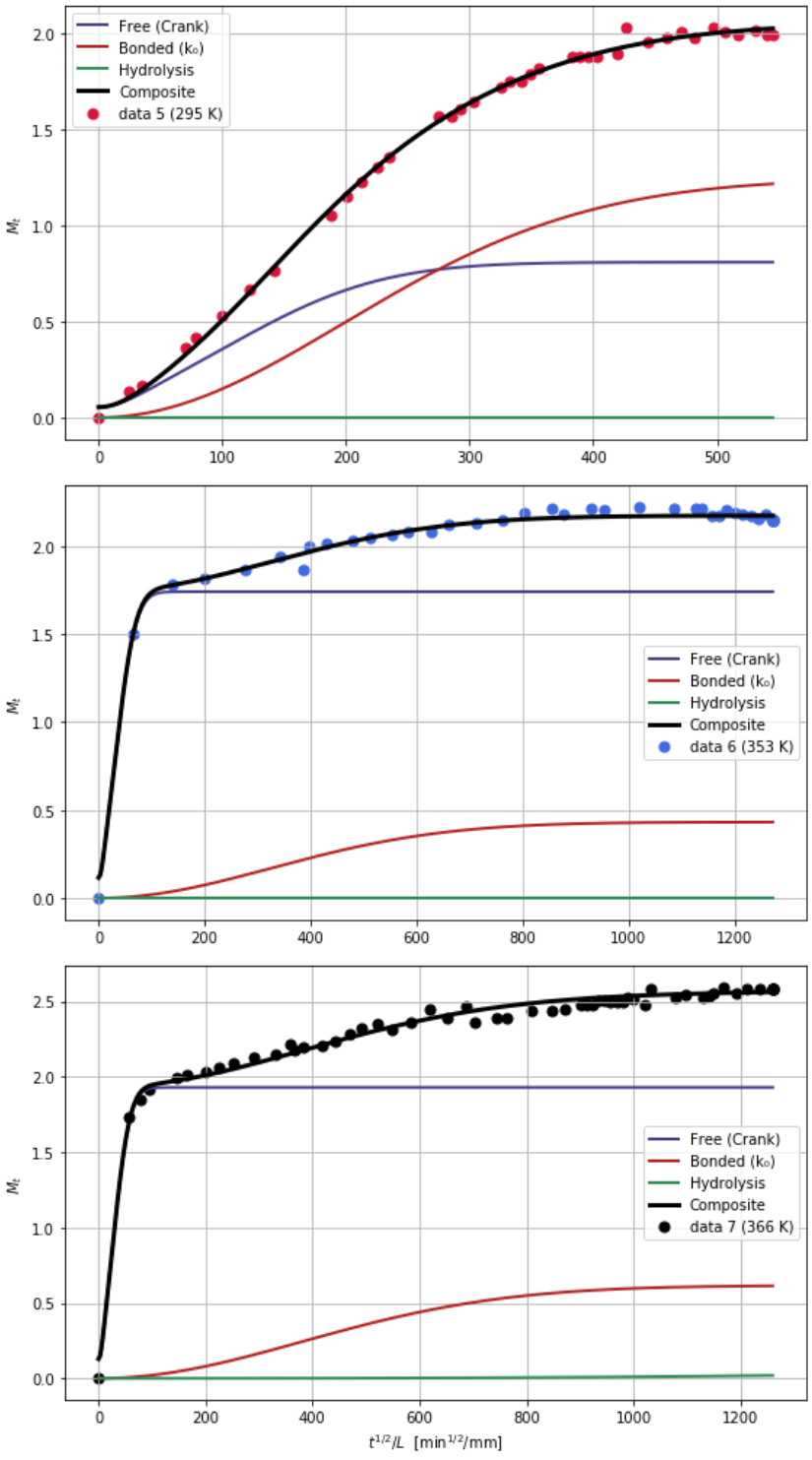


Figure S3. Comparison of the gravimetric experimental data (dots) with model curves for DGEBA-Ancamine thermoset. Black solid line corresponds to the sum of the model contributions.

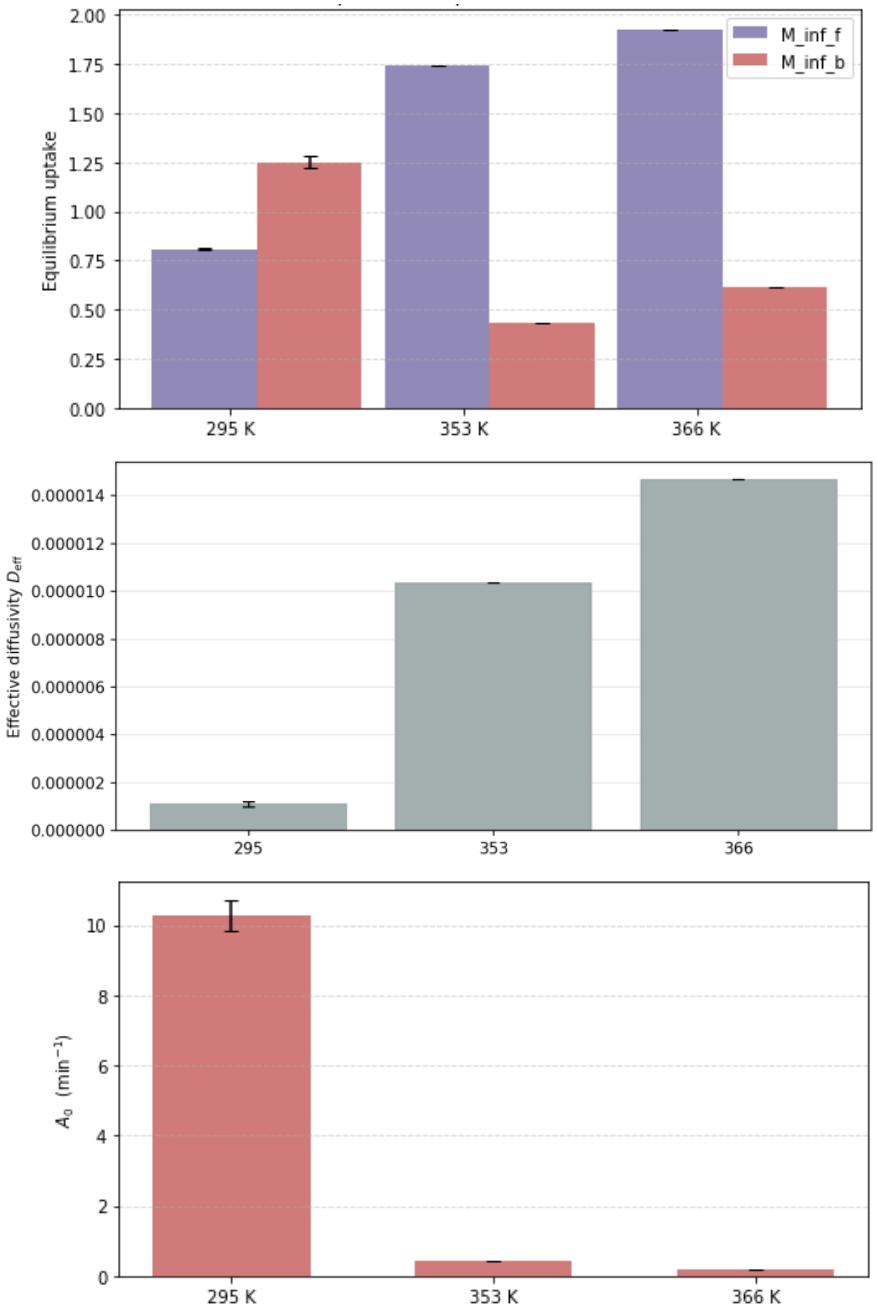


Figure S4. Parameters values for the Fick and Sorption contribution models as a function of absolute temperature

S4. Lindride results.

Figure S5 shows the gravimetric experimental results (filled dots) and the model contributions (blue, red and green lines represent Fickian, Sorption and Hydrolysis contributions, respectively). Black line represents the sum of contributions, which as shown closely describes the experimental data at 23, 80 and 93 C. The obtained parameters are summarized in the bar plots shown in Figure S6.

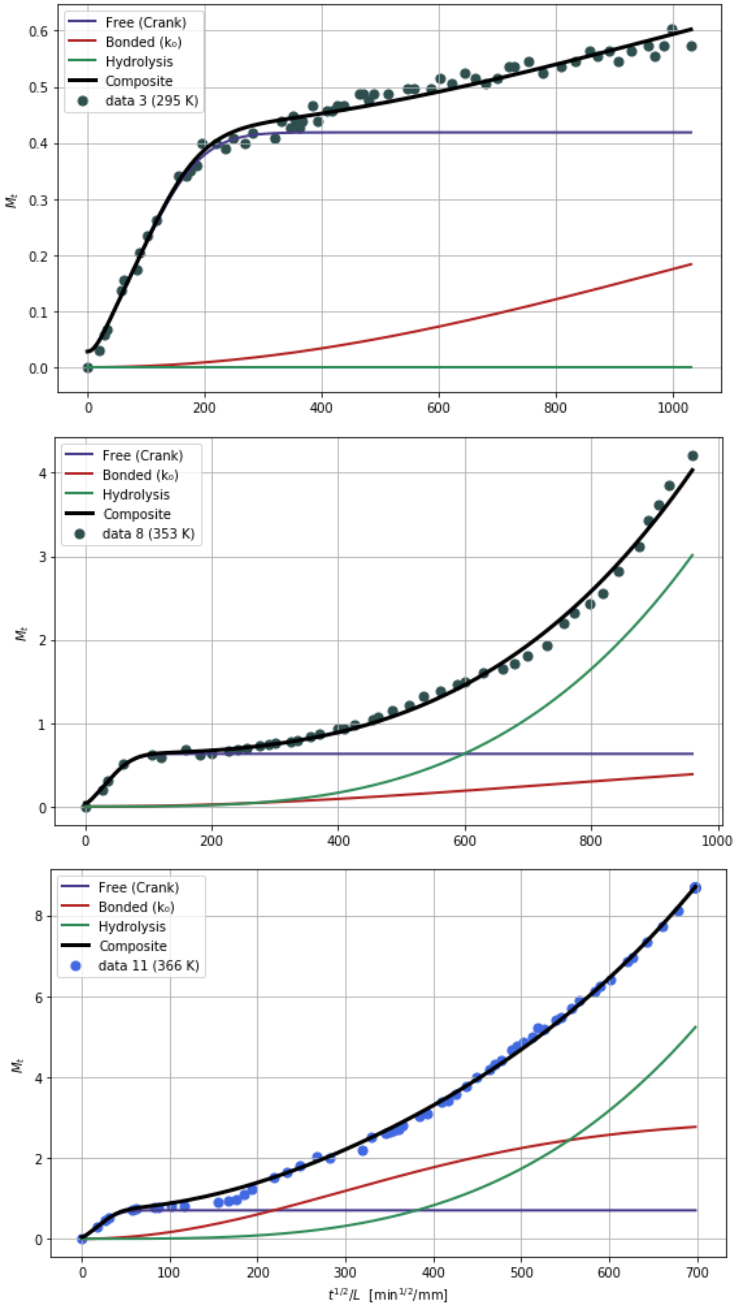


Figure S5. Comparison of the gravimetric experimental data (dots) with model curves for DGEBA-Lindride thermoset. Black solid line corresponds to the sum of the model contributions

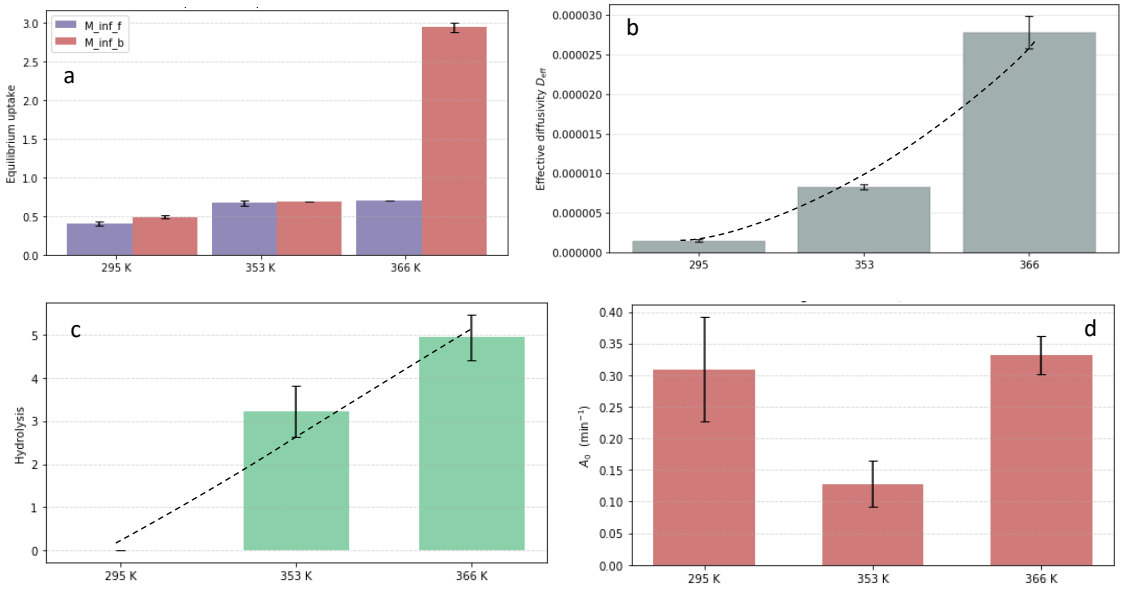


Figure S6. Parameters values for the Fick, Sorption and Hydrolysis contribution models as a function of absolute temperature

S5. Glass transition of aged samples.

Figure S7 shows the observed glass transition temperatures of the water absorbed samples at different absorption times (i.e. different water contents) and experimental time in days. As shown, at Mt values larger than 1.5 the plasticization effect increases (observed as a sharp decrease in the observed glass transition temperature).

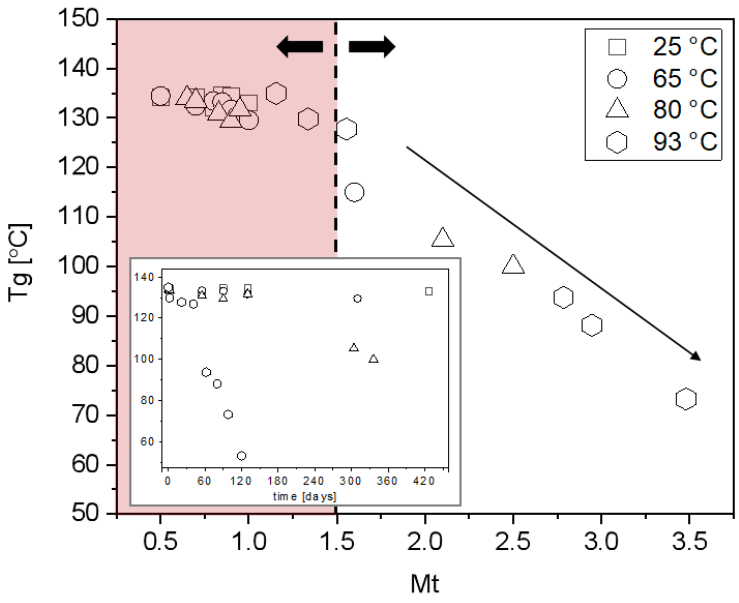
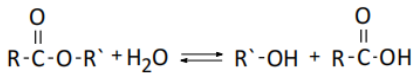


Figure S7. Glass transition temperature as a function of water content. INSET: glass transition as a function of time (days) for DGEBA-Dicure system

S6. Hydrolysis.

Ester hydrolysis in epoxy-anhidride systems (see below): an ester linkage reacts with water to form an alcohol and a carboxylic acid. Both products introduce OH groups, so mid-IR spectra display signatures of the alcohol and carboxylic-acid products.



S7. Fitting results.

Lindride (all curves):

Dataset 1

R2 = 0.9372 # Coefficient of determination

RMSE = 0.1836 # Root-mean-square error

MAE = 0.1719 # Mean absolute error

NRMSE = 0.3009 # Normalised RMSE (RMSE ÷ data range)

Dataset 2

R2 = 0.8894 # Coefficient of determination

RMSE = 0.1466 # Root-mean-square error

MAE = 0.1337 # Mean absolute error

NRMSE = 0.2982 # Normalised RMSE

Dataset 3

R2 = 0.8724 # Coefficient of determination

RMSE = 0.1877 # Root-mean-square error

MAE = 0.1757 # Mean absolute error

NRMSE = 0.3111 # Normalised RMSE

Dataset 4

R2 = 0.7503 # Coefficient of determination

RMSE = 0.1727 # Root-mean-square error

MAE = 0.1566 # Mean absolute error

NRMSE = 0.3153 # Normalised RMSE

Dataset 5

R2 = 0.947 # Coefficient of determination

RMSE = 0.1744 # Root-mean-square error

MAE = 0.1613 # Mean absolute error

NRMSE = 0.3155 # Normalised RMSE

Dataset 6

R2 = 0.9056 # Coefficient of determination

RMSE = 1.105 # Root-mean-square error

MAE = 0.8112 # Mean absolute error

NRMSE = 0.261 # Normalised RMSE

Dataset 7

R2 = 0.9153 # Coefficient of determination

RMSE = 1.157 # Root-mean-square error

MAE = 0.8317 # Mean absolute error

NRMSE = 0.2647 # Normalised RMSE

Dataset 8

R2 = 0.9289 # Coefficient of determination

RMSE = 1.119 # Root-mean-square error

MAE = 0.7838 # Mean absolute error

NRMSE = 0.2662 # Normalised RMSE

Dataset 9

R2 = 0.9435 # Coefficient of determination

RMSE = 1.516 # Root-mean-square error

MAE = 1.058 # Mean absolute error

NRMSE = 0.2841 # Normalised RMSE

Dataset 10

R2 = 0.5 # Coefficient of determination

RMSE = 3.279 # Root-mean-square error

MAE = 2.639 # Mean absolute error

NRMSE = 0.423 # Normalised RMSE

Dataset 11

R2 = 0.9702 # Coefficient of determination

RMSE = 3.574 # Root-mean-square error

MAE = 2.872 # Mean absolute error

NRMSE = 0.4108 # Normalised RMSE

Dataset 12

R2 = 0.9769 # Coefficient of determination

RMSE = 3.732 # Root-mean-square error

MAE = 2.987 # Mean absolute error

NRMSE = 0.4136 # Normalised RMSE

Dataset 13

R2 = 0.9671 # Coefficient of determination

RMSE = 3.462 # Root-mean-square error

MAE = 2.849 # Mean absolute error

NRMSE = 0.4373 # Normalised RMSE

– Local parameters (per curve) –

curve 1 (T = 295 K): M_inf_f = 0.4227 , M_inf_b = 0.4784 , D0 = 0.000231 , A0 = 0.406 , B0 = 0.00576 , k0(T) = 4.81e-07 , beta = 2.26e-07 , gamma = 2.55e-07

curve 2 (T = 295 K): M_inf_f = 0.3599 , M_inf_b = 0.5221 , D0 = 0.000252 , A0 = 0.235 , B0 = 0.141 , k0(T) = 2.78e-07 , beta = 1.13e-07 , gamma = 1.65e-07

curve 3 (T = 295 K): M_inf_f = 0.4187 , M_inf_b = 0.4746 , D0 = 0.0002 , A0 = 0.389 , B0 = 0.00478 , k0(T) = 4.61e-07 , beta = 2.16e-07 , gamma = 2.45e-07

curve 4 (T = 295 K): M_inf_f = 0.4272 , M_inf_b = 0.475 , D0 = 0.000229 , A0 = 0.242 , B0 = 0.00105 , k0(T) = 2.87e-07 , beta = 1.36e-07 , gamma = 1.51e-07

curve 5 (T = 295 K): M_inf_f = 0.407 , M_inf_b = 0.4879 , D0 = 0.0002 , A0 = 0.273 , B0 = 0.0359 , k0(T) = 3.23e-07 , beta = 1.47e-07 , gamma = 1.76e-07

curve 6 (T = 353 K): M_inf_f = 0.71 , M_inf_b = 0.69 , D0 = 0.000538 , A0 = 0.166 , B0 = 529 , k0(T) = 1.85e-06 , beta = 9.37e-07 , gamma = 9.1e-07

curve 7 (T = 353 K): M_inf_f = 0.6932 , M_inf_b = 0.69 , D0 = 0.000537 , A0 = 0.131 , B0 = 527 , k0(T) = 1.46e-06 , beta = 7.3e-07 , gamma = 7.26e-07

curve 8 (T = 353 K): M_inf_f = 0.6316 , M_inf_b = 0.6956 , D0 = 0.000568 , A0 = 0.0792 , B0 = 501 , k0(T) = 8.83e-07 , beta = 4.2e-07 , gamma = 4.63e-07

curve 9 (T = 353 K): M_inf_f = 0.6496 , M_inf_b = 0.69 , D0 = 0.000517 , A0 = 0.138 , B0 = 630 , k0(T) = 1.54e-06 , beta = 7.46e-07 , gamma = 7.92e-07

curve 10 (T = 366 K): M_inf_f = 0.7001 , M_inf_b = 2.989 , D0 = 0.00167 , A0 = 0.288 , B0 = 813 , k0(T) = 4.81e-06 , beta = 9.12e-07 , gamma = 3.89e-06

curve 11 (T = 366 K): M_inf_f = 0.7045 , M_inf_b = 2.951 , D0 = 0.00152 , A0 = 0.342 , B0 = 930 , k0(T) = 5.71e-06 , beta = 1.1e-06 , gamma = 4.61e-06

curve 12 (T = 366 K): M_inf_f = 0.7091 , M_inf_b = 2.999 , D0 = 0.00142 , A0 = 0.336 , B0 = 997 , k0(T) = 5.62e-06 , beta = 1.08e-06 , gamma = 4.55e-06

curve 13 (T = 366 K): M_inf_f = 0.7 , M_inf_b = 2.86 , D0 = 0.00164 , A0 = 0.358 , B0 = 869 , k0(T) = 5.98e-06 , beta = 1.18e-06 , gamma = 4.8e-06

Dicure (all curves):

Dataset 1

R2 = 0.9842 # Coefficient of determination

RMSE = 0.2085 # Root-mean-square error

MAE = 0.2015 # Mean absolute error

NRMSE = 0.2701 # Normalised RMSE

Dataset 2

R2 = 0.9459 # Coefficient of determination

RMSE = 0.2089 # Root-mean-square error

MAE = 0.2018 # Mean absolute error

NRMSE = 0.2639 # Normalised RMSE

Dataset 3

R2 = 0.9089 # Coefficient of determination

RMSE = 0.207 # Root-mean-square error

MAE = 0.1994 # Mean absolute error

NRMSE = 0.273 # Normalised RMSE

Dataset 4

R2 = 0.9567 # Coefficient of determination

RMSE = 0.2376 # Root-mean-square error

MAE = 0.2259 # Mean absolute error

NRMSE = 0.1999 # Normalised RMSE

Dataset 5

R2 = 0.9927 # Coefficient of determination

RMSE = 0.2547 # Root-mean-square error

MAE = 0.2417 # Mean absolute error

NRMSE = 0.2016 # Normalised RMSE

Dataset 6

R2 = 0.9758 # Coefficient of determination

RMSE = 0.2401 # Root-mean-square error

MAE = 0.2254 # Mean absolute error

NRMSE = 0.2002 # Normalised RMSE

Dataset 7

R2 = 0.9845 # Coefficient of determination

RMSE = 0.238 # Root-mean-square error

MAE = 0.224 # Mean absolute error

NRMSE = 0.1945 # Normalised RMSE

Dataset 8

R2 = 0.9766 # Coefficient of determination

RMSE = 0.2501 # Root-mean-square error

MAE = 0.235 # Mean absolute error

NRMSE = 0.1961 # Normalised RMSE

Dataset 9

R2 = 0.9623 # Coefficient of determination

RMSE = 0.9195 # Root-mean-square error

MAE = 0.8067 # Mean absolute error

NRMSE = 0.38 # Normalised RMSE

Dataset 10

R2 = 0.9383 # Coefficient of determination

RMSE = 0.8337 # Root-mean-square error

MAE = 0.751 # Mean absolute error

NRMSE = 0.3657 # Normalised RMSE

Dataset 11

R2 = 0.7174 # Coefficient of determination

RMSE = 0.6317 # Root-mean-square error

MAE = 0.5924 # Mean absolute error

NRMSE = 0.3123 # Normalised RMSE

Dataset 12

R2 = 0.5747 # Coefficient of determination

RMSE = 0.5579 # Root-mean-square error

MAE = 0.5269 # Mean absolute error

NRMSE = 0.2825 # Normalised RMSE

Dataset 13

R2 = 0.6915 # Coefficient of determination

RMSE = 0.5357 # Root-mean-square error

MAE = 0.5093 # Mean absolute error

NRMSE = 0.2922 # Normalised RMSE

Dataset 14

R2 = 0.4549 # Coefficient of determination

RMSE = 1.17 # Root-mean-square error

MAE = 0.9876 # Mean absolute error

NRMSE = 0.3654 # Normalised RMSE

Dataset 15

R2 = 0.9899 # Coefficient of determination

RMSE = 1.613 # Root-mean-square error

MAE = 1.378 # Mean absolute error

NRMSE = 0.455 # Normalised RMSE

Dataset 16

R2 = 0.9766 # Coefficient of determination

RMSE = 1.638 # Root-mean-square error

MAE = 1.406 # Mean absolute error

NRMSE = 0.45 # Normalised RMSE

Dataset 17

R2 = 0.9984 # Coefficient of determination

RMSE = 1.758 # Root-mean-square error

MAE = 1.486 # Mean absolute error

NRMSE = 0.4545 # Normalised RMSE

– Local parameters (per curve) –

curve 1 (T = 295 K): M_inf_f = 0.4465 , M_inf_b = 0.5038 , D0 = 0.00661 , A0 = 3.53 , B0 = 0.0294 , k0(T) = 4.19e-06 , beta = 1.97e-06 , gamma = 2.22e-06

curve 2 (T = 295 K): M_inf_f = 0.4465 , M_inf_b = 0.4666 , D0 = 0.00818 , A0 = 4.65 , B0 = 0.0176 , k0(T) = 5.51e-06 , beta = 2.69e-06 , gamma = 2.82e-06

curve 3 (T = 295 K): M_inf_f = 0.4512 , M_inf_b = 0.4926 , D0 = 0.00652 , A0 = 3.45 , B0 = 0.00018 , k0(T) = 4.09e-06 , beta = 1.96e-06 , gamma = 2.14e-06

curve 4 (T = 338 K): M_inf_f = 0.5867 , M_inf_b = 0.6549 , D0 = 0.0194 , A0 = 1.03 , B0 = 24.7 , k0(T) = 6.91e-06 , beta = 3.27e-06 , gamma = 3.65e-06

curve 5 (T = 338 K): M_inf_f = 0.6295 , M_inf_b = 0.7255 , D0 = 0.018 , A0 = 0.942 , B0 = 36.6 , k0(T) = 6.34e-06 , beta = 2.95e-06 , gamma = 3.4e-06

curve 6 (T = 338 K): M_inf_f = 0.625 , M_inf_b = 0.7215 , D0 = 0.0187 , A0 = 0.862 , B0 = 9.71 , k0(T) = 5.8e-06 , beta = 2.69e-06 , gamma = 3.11e-06

curve 7 (T = 338 K): M_inf_f = 0.5905 , M_inf_b = 0.7011 , D0 = 0.0257 , A0 = 0.92 , B0 = 30.5 , k0(T) = 6.19e-06 , beta = 2.83e-06 , gamma = 3.36e-06

curve 8 (T = 338 K): M_inf_f = 0.6586 , M_inf_b = 0.7074 , D0 = 0.0207 , A0 = 0.894 , B0 = 41.1 , k0(T) = 6.01e-06 , beta = 2.9e-06 , gamma = 3.11e-06

curve 9 (T = 353 K): M_inf_f = 0.8956 , M_inf_b = 0.735 , D0 = 0.00644 , A0 = 0.0555 , B0 = 957 , k0(T) = 6.2e-07 , beta = 3.4e-07 , gamma = 2.79e-07

curve 10 (T = 353 K): M_inf_f = 0.8994 , M_inf_b = 0.7005 , D0 = 0.00667 , A0 = 0.135 , B0 = 771 , k0(T) = 1.5e-06 , beta = 8.46e-07 , gamma = 6.59e-07

curve 11 (T = 353 K): M_inf_f = 0.8234 , M_inf_b = 0.7025 , D0 = 0.0117 , A0 = 0.617 , B0 = 383 , k0(T) = 6.89e-06 , beta = 3.72e-06 , gamma = 3.17e-06

curve 12 (T = 353 K): M_inf_f = 0.8075 , M_inf_b = 0.9847 , D0 = 0.0146 , A0 = 0.436 , B0 = 180 , k0(T) = 4.86e-06 , beta = 2.19e-06 , gamma = 2.67e-06

curve 13 (T = 353 K): M_inf_f = 0.8161 , M_inf_b = 0.7435 , D0 = 0.0118 , A0 = 0.497 , B0 = 235 , k0(T) = 5.54e-06 , beta = 2.9e-06 , gamma = 2.64e-06

curve 14 (T = 366 K): M_inf_f = 0.8356 , M_inf_b = 0.8466 , D0 = 0.0305 , A0 = 1.61 , B0 = 4.63e+03 , k0(T) = 2.7e-05 , beta = 1.34e-05 , gamma = 1.36e-05

curve 15 (T = 366 K): M_inf_f = 1.267 , M_inf_b = 0.7339 , D0 = 7.15e-05 , A0 = 248 , B0 = 6.09e+03 , k0(T) = 0.00415 , beta = 0.00263 , gamma = 0.00152

curve 16 (T = 366 K): M_inf_f = 1.055 , M_inf_b = 0.775 , D0 = 9.9e-05 , A0 = 202 , B0 = 5.95e+03 , k0(T) = 0.00339 , beta = 0.00195 , gamma = 0.00143

curve 17 (T = 366 K): M_inf_f = 0.9744 , M_inf_b = 0.8311 , D0 = 0.0146 , A0 = 0.393 , B0 = 6.88e+03 , k0(T) = 6.58e-06 , beta = 3.55e-06 , gamma = 3.03e-06

curve 18 (T = 366 K): M_inf_f = 1.045 , M_inf_b = 0.8342 , D0 = 0.00519 , A0 = 0.219 , B0 = 6.94e+03 , k0(T) = 3.66e-06 , beta = 2.04e-06 , gamma = 1.63e-06

curve 19 (T = 366 K): M_inf_f = 1.024 , M_inf_b = 0.8306 , D0 = 0.00513 , A0 = 0.407 , B0 = 6.06e+03 , k0(T) = 6.82e-06 , beta = 3.76e-06 , gamma = 3.05e-06

Ancamine (all curves):

Dataset 1

R2 = 0.9264 # Coefficient of determination

RMSE = 0.865 # Root-mean-square error

MAE = 0.8139 # Mean absolute error

NRMSE = 0.4156 # Normalised RMSE

Dataset 2

R2 = 0.9331 # Coefficient of determination

RMSE = 0.862 # Root-mean-square error

MAE = 0.8102 # Mean absolute error

NRMSE = 0.4241 # Normalised RMSE

Dataset 3

R2 = 0.9225 # Coefficient of determination

RMSE = 0.8688 # Root-mean-square error

MAE = 0.8158 # Mean absolute error

NRMSE = 0.4112 # Normalised RMSE

Dataset 4

R2 = 0.7497 # Coefficient of determination

RMSE = 0.7767 # Root-mean-square error

MAE = 0.7317 # Mean absolute error

NRMSE = 0.3903 # Normalised RMSE

Dataset 5

R2 = 0.948 # Coefficient of determination

RMSE = 0.8717 # Root-mean-square error

MAE = 0.8166 # Mean absolute error

NRMSE = 0.4295 # Normalised RMSE

Dataset 6

R2 = 0.8906 # Coefficient of determination

RMSE = 0.2552 # Root-mean-square error

MAE = 0.1642 # Mean absolute error

NRMSE = 0.1149 # Normalised RMSE

Dataset 7

R2 = 0.9826 # Coefficient of determination

RMSE = 0.3735 # Root-mean-square error

MAE = 0.294 # Mean absolute error

NRMSE = 0.1439 # Normalised RMSE

– Local parameters (per curve) –

curve 1 (T = 295 K): M_inf_f = 0.809 , M_inf_b = 1.279 , D0 = 0.000467 , A0 = 10.3 , B0 = 3.06e+04 , k0(T) = 1.22e-05 , beta = 4.71e-06 , gamma = 7.44e-06

curve 2 (T = 295 K): M_inf_f = 0.809 , M_inf_b = 1.252 , D0 = 0.000431 , A0 = 10.5 , B0 = 0.00833 , k0(T) = 1.24e-05 , beta = 4.86e-06 , gamma = 7.52e-06

curve 3 (T = 295 K): M_inf_f = 0.809 , M_inf_b = 1.277 , D0 = 0.000447 , A0 = 10.2 , B0 = 5.87e+04 , k0(T) = 1.2e-05 , beta = 4.67e-06 , gamma = 7.36e-06

curve 4 (T = 295 K): M_inf_f = 0.799 , M_inf_b = 1.2 , D0 = 0.000512 , A0 = 9.62 , B0 = 9.43e+03 , k0(T) = 1.14e-05 , beta = 4.56e-06 , gamma = 6.84e-06

curve 5 (T = 295 K): M_inf_f = 0.809 , M_inf_b = 1.245 , D0 = 0.000394 , A0 = 10.8 , B0 = 1.62 , k0(T) = 1.28e-05 , beta = 5.04e-06 , gamma = 7.75e-06

curve 6 (T = 353 K): M_inf_f = 1.741 , M_inf_b = 0.4321 , D0 = 0.00158 , A0 = 0.423 , B0 = 2.84e-05 , k0(T) = 4.71e-06 , beta = 3.78e-06 , gamma = 9.37e-07

curve 7 (T = 366 K): M_inf_f = 1.93 , M_inf_b = 0.616 , D0 = 0.00188 , A0 = 0.208 , B0 = 103 , k0(T) = 3.48e-06 , beta = 2.64e-06 , gamma = 8.41e-07