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Moisture Sorption and Swelling of Sylgard-184

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Contents

1. Introduction....................5
2. Moisture Sorption....................5
3. Comparison with other moisture sorption models for Sylgard-184....................9
4. Polymer swelling....................9
5. Thermal Expansion....................13
6. Summary....................13

1. Introduction

The report summarizes the quantitative assessment of moisture sorption by Sylgard-184. It is an important ingredient in many of our materials. Moisture sorption for this material has been extensively studied with data from 9 different samples available for analysis. These samples varied in size and geometry. Seven of the 9 samples were thin slabs. The remaining 2 were cylinders, one of which had comparable height and diameter and is therefore considered a 3-D sample. All the samples, except 2 (1D_slab4.06mm and 1D_Sylgard_2016_Sharma) belonged to lot number A1606324. They were all prepared by Tony Rodrigues in the plastics shop in the Summer of 2016 and tested by Hom Sharma between October 2016 and June 2017. 1D_slab4.06mm was also prepared by Tony Rodrigues in the plastics shop in Summer of 2016, however, the sample did not have a lot number. 1D_Sylgard_2016_Sharma was prepared by Hom Sharma in February 2016 and tested potentially around May - June 2016.

2. Moisture Sorption

The amount of water taken up by Sylgard-184 was measured by measuring the change in sample mass as a function of time, upon exposure to different humidity conditions. These measurements were made using the Hiden Isochemia IGAsorp instrument.

Data was collected at 20, 30, 40, 50, and 60 ^{o}C. Only the data stored in the folder Sylgard-184(IGASORP) was analyzed as the data in other folders were collected from test runs for instruments. Over 40 experimental datasets were collected. Some of them were excluded from the analysis for various reasons. **Table 1** gives a summary of all the datasets and reasons for excluding certain datasets.

Table 1. Datasets excluded from the parameterization process.

Folder name	Names of excluded datasets	Reason
1D_cylinder	-	
1D_slab_0.5mm	*Sylgard184_slab_1D_05mmSD40C_3-9-17.DAT*	Atypical hysteresis
1D_slab_0.7mm	*Sylgard-184-1D-07cm-4-10-17-SD40C.DAT* – partially excluded	Unexpected drop in measured mass
1D_slab_0.7mm	*Sylgard-184-1D-07cm-4-12-17-SD40C.DAT*	Unexpected increase in measured mass
1D_slab_2mm	*Sylgard184_slab_1D_2mmSD40C_5-25-17.DAT* – partially excluded	Unexpected behavior of measured RH
1D_slab_3mm	*Sylgard-1D30C.txt*	No temperature data
1D_slab_3mm	*Sylgard184_slab_1D_3mmSD40C_6-19-17.DAT*	Lack of equilibration
1D_slab1.18mm	-	-
1D_slab4.06mm	All datasets were excluded	Lack of equilibration
1D_Sylgard_2016_Sharma	-	-
Sylgard3D/Cylinder	All 30 and 40 ^{o}C datasets were excluded	Lack of equilibration
Sylgard3D	All datasets except folder *Cylinder* excluded	No sample information file

For each dataset included in the parameterization process, a Matlab script was used to compute the equilibrium concentration of water within the polymer at each RH step. These values are plotted in **Figure 1**. The figure shows considerable scatter in the moisture uptake data for the same temperatures. Despite the scatter, a systematic temperature trend is present in the data in **Figure 1**.

The triple mode model was used to fit the data, consisting of the Henry, Langmuir, and Pooling modes. After testing several models, the best model with the least number of parameters was given by the following equation:

$$\boldsymbol{c_{poly} = \left(k_{d,0} + k_{d,1}T\right) \times RH + \frac{S_0 \cdot \beta \cdot RH}{1 + \beta \cdot RH} + \alpha(RH)^n} \quad (1)$$

where c_{poly} is the moisture concentration in the polymer in mg/cc, $k_{d,0}$ and $k_{d,1}$ are the parameters associated with the temperature dependent Henry's solubility model, T is temperature in Celsius, RH is relative humidity, S_0 is Langmuir capacity in mg/cc, β is the Langmuir affinity, α is the pooling parameter in mg/cc and n is the pooling exponent. Henry's solubility is assumed to have a linear dependence on temperature:

$$\boldsymbol{k_d = k_{d,0} + k_{d,1}T} \quad (2)$$

Theoretically, k_d is expected to have an exponential dependence on temperature. The temperature range of interest spans 40 ^{o}C and moisture uptake curves do not change dramatically over this temperature range. Hence, an exponential function can be approximated well by a linear function.

RH in Eq. (1) is defined as p/p_{sat} where p is the partial pressure of moisture in the environment and p_{sat} is the saturation pressure for water at the temperature of interest. Relative humidity in **Figure 1** is reported in percentages instead of the fraction definition in Eq. (1). The fitted values for the parameters in Eq. (1) are reported in **Table 2**. The performance of the model fit against the experimental data is shown in **Figure 2** where the curves represent the model predictions, and the markers show the experimental data. The distribution of the errors between the model predictions and experimental data is shown in **Figure 3.**

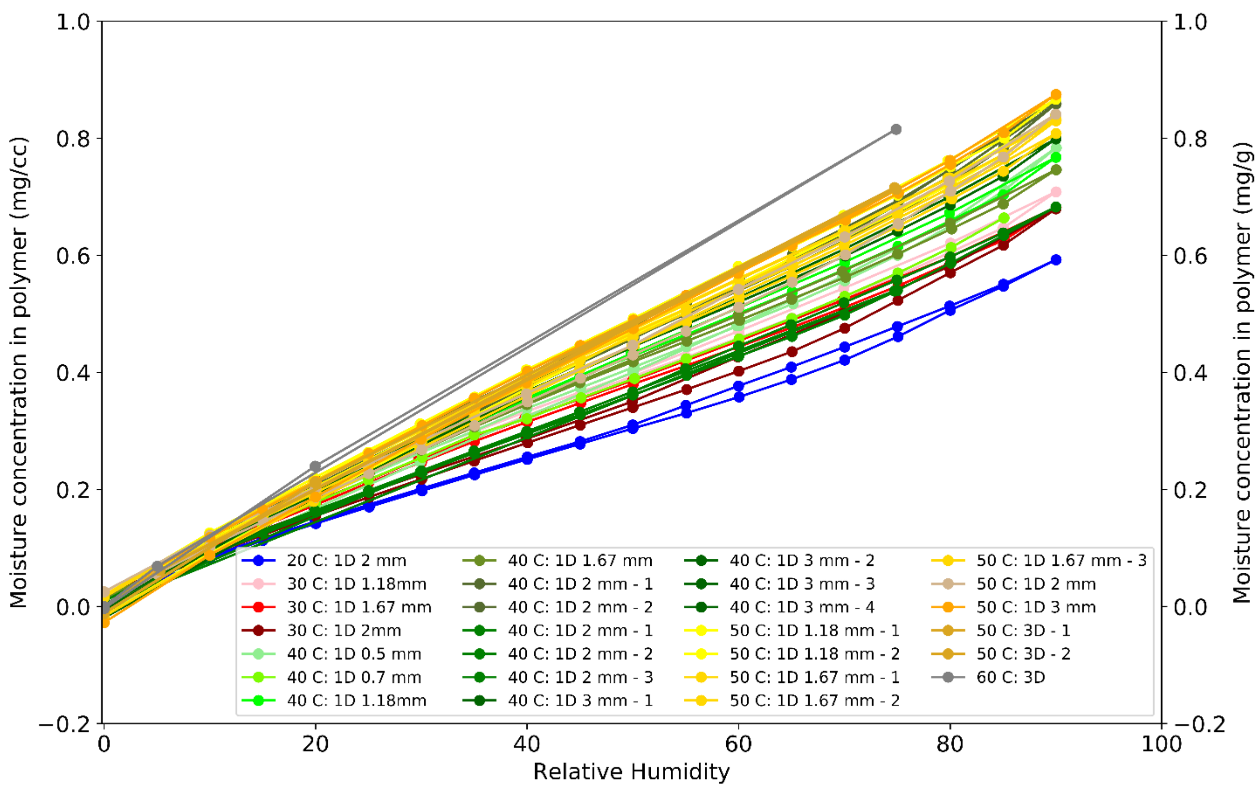

Figure 1. Equilibrium moisture concentration as a function of relative humidity for Sylgard-184. The secondary y-axis is obtained by dividing the primary y-axis by the average density of Sylgard-184 (1.00 g/cc)

Table 2. Equilibrium moisture uptake parameters for Sylgard-184 using the model described in Eq. (1).

Parameter Name	Parameter Value
Henry's solubility parameter 1, $k_{d,0}$ (mg/cc)	0.361
Henry's solubility parameter 2, $k_{d,1}$ (mg/cc/°C)	9.35E-3
Langmuir capacity, S_0 (mg/cc)	0.0644
Langmuir affinity, β ()	8.55
Pooling parameter, α (mg/cc)	0.160
Pooling exponent, n	10.8

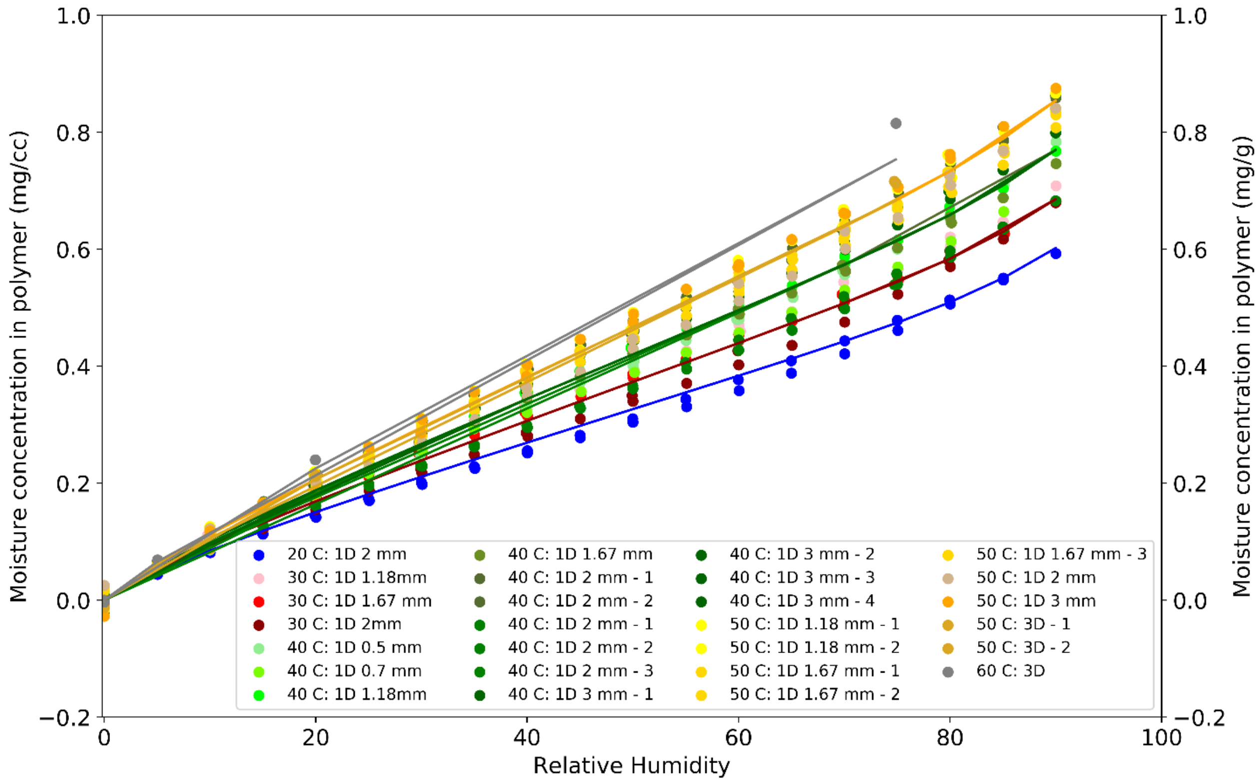

Figure 2. Comparison between predictions of moisture uptake using model parameters in **Table 2** (solid curves) and experimental data (markers) for Sylgard-184. The secondary y-axis is obtained by dividing the primary y-axis by the average density of Sylgard-184 (1.00 g/cc)

For the purposes of implementation in Diablo, the moisture uptake model is written in terms of ambient moisture concentration instead of RH as defined in Eq. (1).

$$c_{poly} = Kc_{gas} + \frac{S_0'\beta' c_{gas}}{1 + \beta' c_{gas}} + \alpha'\left(c_{gas}\right)^{n'} \quad (3)$$

Parameter values in **Table 2** can be converted into the form of the model described in Eq. (3) by using the saturation pressure for water and ideal gas law to convert RH into ambient moisture concentration. Values of the model parameters in the context of Eq. (3) are tabulated in **Table 3**.

Solubility of different gases in a polymer can be related to each other using information about their critical temperature and pressure. To use water vapor solubility to infer solubility of other gases, K defined in Eq. (3) above is converted into S which is defined as:

$$c'_{poly} = Sp \quad (4)$$

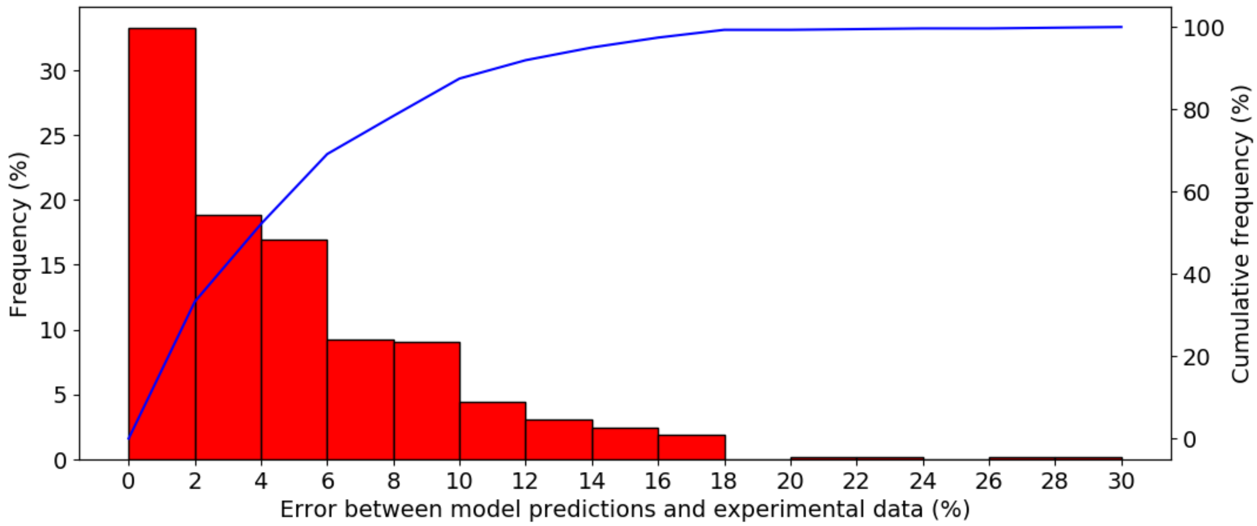

Figure 3. Distribution of error between the model predictions and the experimental data shown in **Figure 2.** The x-axis is the percentage error between the model predictions and experimental data. Each red bar shows the percentage of data points (left y-axis) that have an error in the corresponding interval on the x-axis. For example, the fourth red bar shows that 9 % of the model predictions are within 6 to 8 % of the experimental data. The blue curve shows the cumulative percentage of data points (right y-axis) that have an error less than the corresponding % value on the x-axis. For example, 87 % of the data has an error less than 10 %.

Table 3. Equilibrium moisture uptake parameters for Sylgard-184 using the model described in Eq. (3). The numbers in this table were computed using the values in **Table 2**.

Temperature	K ( )	S_0' (mg/cc)	β' (cc/mg)	α'	n'
20 °C	31.8	6.44E-2	496	1.93E+18	10.8
30 °C	21.2	6.44E-2	282	4.37E+15	10.8
40 °C	14.4	6.44E-2	168	1.56E+13	10.8
50 °C	10.0	6.44E-2	103	8.38E+10	10.8
60 °C	7.1	6.44E-2	66	6.51E+08	10.8

where c'_{poly} has units of cc at STP of water vapor/cc of polymer, S is the Henry's solubility with units of cc at STP of water vapor/cc of polymer/atm and p is the partial pressure of water vapor in the units of atm. K and S are related. Values for S are reported in **Table 4**.

A plot of $\ln(S)$ as a function of $\left(\frac{T_c}{T}\right)^2$ for Sylgard-184 is shown in **Figure 4**. T_c in **Figure 4** is the critical temperature of water and is equal to 647.14 K. The curve in **Figure 4** is linear with a slope of 1.48.

Table 4. Solubility values for moisture uptake in Sylgard-184. The units of ***S***, defined in Eq. (4) are cc at STP of water vapor/cc of polymer/atm where standard temperature is 0 °C and standard pressure is 1 atm. The numbers in this table were computed using the values in **Table 3**.

Temperature	20 °C	30 °C	40 °C	50 °C	60 °C
S **(cc of water at STP/cc of polymer)**	29.6	19.1	12.6	8.5	5.8

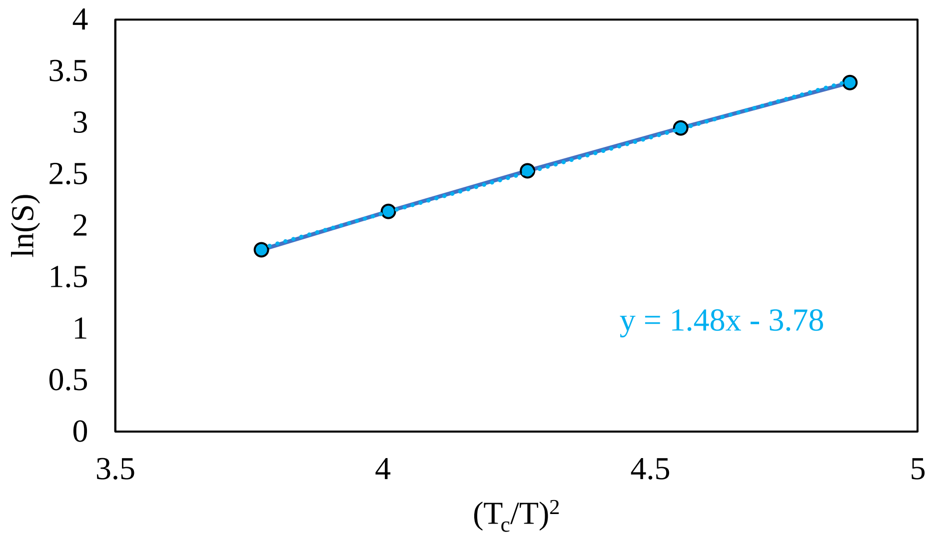

Figure 4. Plot of $\mathbf{ln}(\boldsymbol{S})$ as a function of $\left(\frac{T_c}{T}\right)^2$ for Sylgard-184. The slope of the curve is 1.48.

3. Comparison with other moisture sorption models for Sylgard-184

There are at least 3 other models for moisture sorption that have been developed using the some of the experimental data shown in **Figure 1**. There are reported in two manuscripts published in 2017 and 2020 and work done by Pratanu Roy. While the model parameters reported here were obtained by fitting all available equilibrium datasets, the other models were developed by considering both the equilibrium and transient data together and parameterizing experimental data one dataset at a time.

A comparison between the different model parameters is shown in **Figure 5**. The definitions and dimensions of the parameters from different sources are different. As a result, the parameters have been appropriately modified to allow for a reasonable comparison. The values of Henry's solubility estimated by all four studies are consistent as shown in **Figure 5 (a)**. This is encouraging because Henry's mode is the main mode of sorption for Sylgard-184, and consistent Henry's solubility across the four studies suggests that choosing any of the four models would give reasonable predictions for most RH values.

The values of the Langmuir parameters are different between models, especially the values from the 2017 study. This suggests that at low relative humidites the predictions made by the 2017 model could be significantly different from that made by the other models. However, since Langmuir mode's contribution to the overall moisture sorption is low, this discrepancy between the different models will be significant only at low relative humidities.

Finally, the pooling parameters for all four models are very different. This is partly due to the small contribution of the pooling term to the overall moisture sorption. As a result, the difference in the values of the pooling parameters would have a significant impact only at high relative humidity values. The large discrepancies in the values of α' do not have as large an impact on the magnitude of the pooling contribution. The pooling term has a power law dependence on concentration due to which small changes in the value of n' result in large changes in the values of α'. In other words, an increase in α' by 10 orders of magnitude would not yield a similar increase in the pooling contribution if the associated n' values are also higher.

4. Polymer swelling

Change in the volume of Sylgard-184 in response to moisture sorption was measured using the NETZSCH

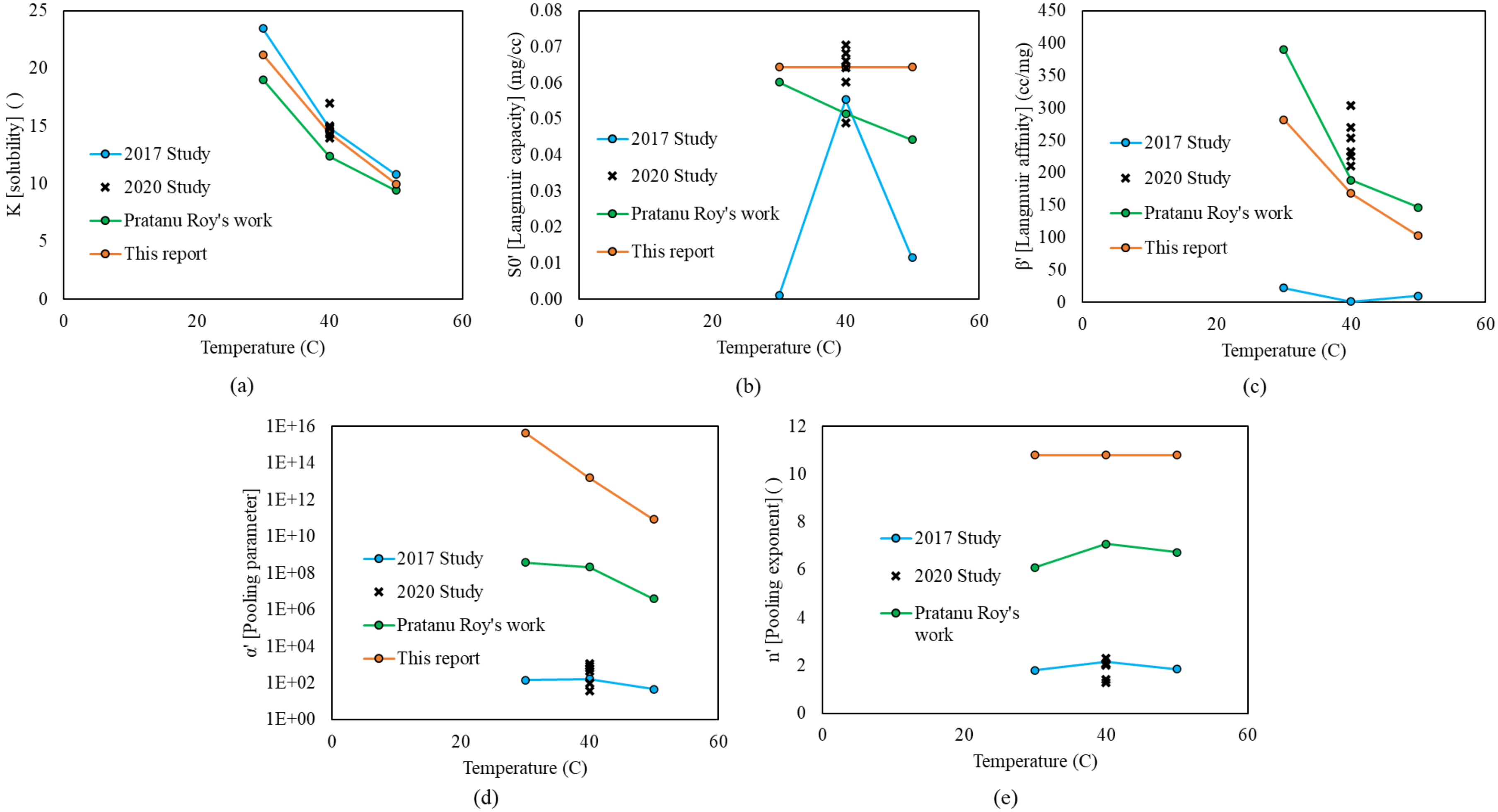

Figure 5. Comparison of model parameters estimated by four different studies namely the 2017 study, the 2020 study, the work done by Pratanu Roy, and this study. (a) Henry's solubility, $\boldsymbol{K}$, (b) Langmuir capacity, $\boldsymbol{S_0}'$, (c) Langmuir affinity, $\boldsymbol{\beta}'$, (d) the pooling parameter, $\boldsymbol{\alpha}'$, and (e) the pooling exponent $\boldsymbol{n}'$.

Thermo-mechanical Analyzer. Fang Qian did more than 20 individual experiments on Sylgard-184 as it was the first material for which the instrument was used to measure swelling in response to change in humidity. The experiments were largely run at 50 ºC with a few runs at 30 and 60 ºC.

Several of the initial experiments done in February, March and April of 2021 could not be used for any analysis as the sample did not dry enough to give a constant baseline at dry conditions. This has been observed in many polydimethylsiloxane-based materials that have been tested subsequently. Experiments done in May and June of 2021 had to be manually processed as the recorded data file did not record the humidity of the experimental chamber. Finally, most of the experiments done in 2022 with the tensile modulus showed an unexpected drop in strain at the highest RH. The reasons behind this drop in 3 out of the 4 humidity experiments are unclear. Consequently, these datasets were also not used in the hygroscopic analysis presented in this report.

Reasonable experimental datasets were either analyzed manually or using a Matlab script to compute the equilibrium strain at each RH step. The computed strains are plotted as a function of RH in **Figure 6**. The figure shows that except for the dataset from 7th May, 2021, all other datasets are consistent with each other (they all are at 50 ºC).

All the data in **Figure 6** except the dataset from 5/7/2021 were used to estimate a coefficient of hygroscopic expansion, β_H, and $\beta_{H,RH}$ based on the following definitions:

$$\boldsymbol{\beta_H} = \frac{\partial \boldsymbol{\epsilon_{hygroscopic}}}{\partial \boldsymbol{c_{poly}}} \tag{5}$$

$$\boldsymbol{\beta_{H,RH}} = \frac{\partial \boldsymbol{\epsilon_{hygroscopic}}}{\partial RH} \tag{6}$$

where $\epsilon_{hygroscopic}$ is the hygroscopic strain and c_{poly} is the moisture concentration in the polymer. The moisture sorption model described above was used to convert the temperature and relative humidity

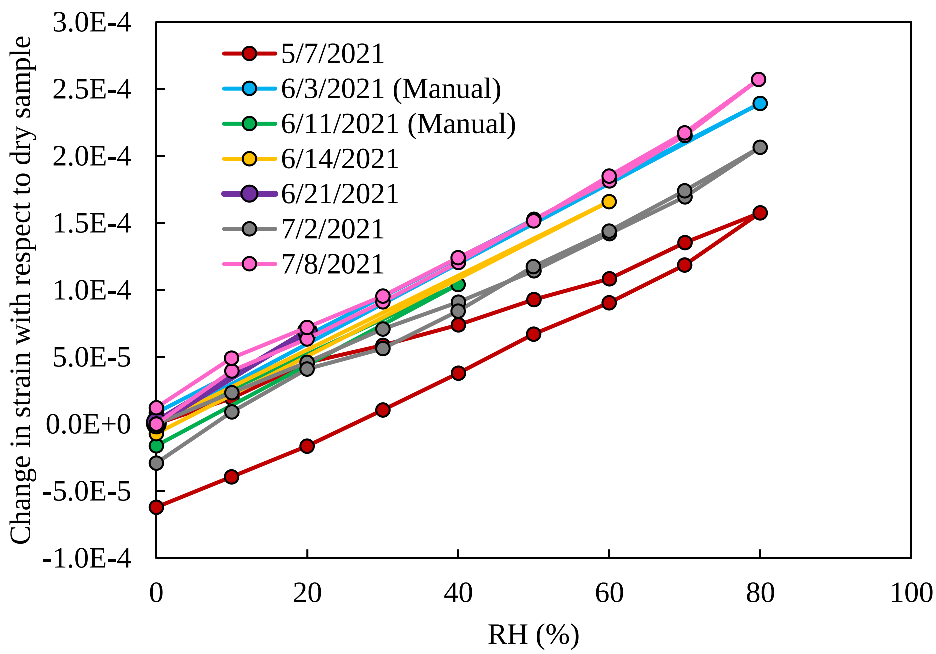

Figure 6. Hygroscopic strain experienced by Sylgard-184 as a function of RH at 50 ºC. The word “Manual” in the legend is used to denote experiments for which the humidity was not recorded by the instrument and was manually assigned based on the knowledge of the settings in the instrument.

conditions to the amount of moisture absorbed by the sample, c_{poly}, to estimate β_H.

In addition to the two definitions above, a third definition, implement in Diablo, is of the form:

$$\boldsymbol{\beta_{H,Diablo}} = \frac{\partial \boldsymbol{\epsilon_{hygroscopic}}}{\partial \boldsymbol{c_{poly,Henry}}} \tag{7}$$

where $\beta_{H,Diablo}$ is the coefficient of hygroscopic expansion as defined in Diablo, and $c_{poly,Henry}$ is the concentration of moisture in the polymer that is attributed to Henry's mode. The values the coefficient of hygroscopic expansion, for the different definitions, have been summarized in **Table 5.** The trendline fits used to estimate the values in **Table 5** are shown in **Figure 7.** All three fits seem equally good based on the R^2 value.

Table 5. Estimates for the coefficient of hygroscopic expansion for Sylgard-184 (see Eqs. (5-(7 for the definitions).

β_H	2.98×10^{-4} cc/mg
$\beta_{H,Diablo}$	3.35×10^{-4} cc/mg
$\beta_{H,RH}$	2.77×10^{-6}

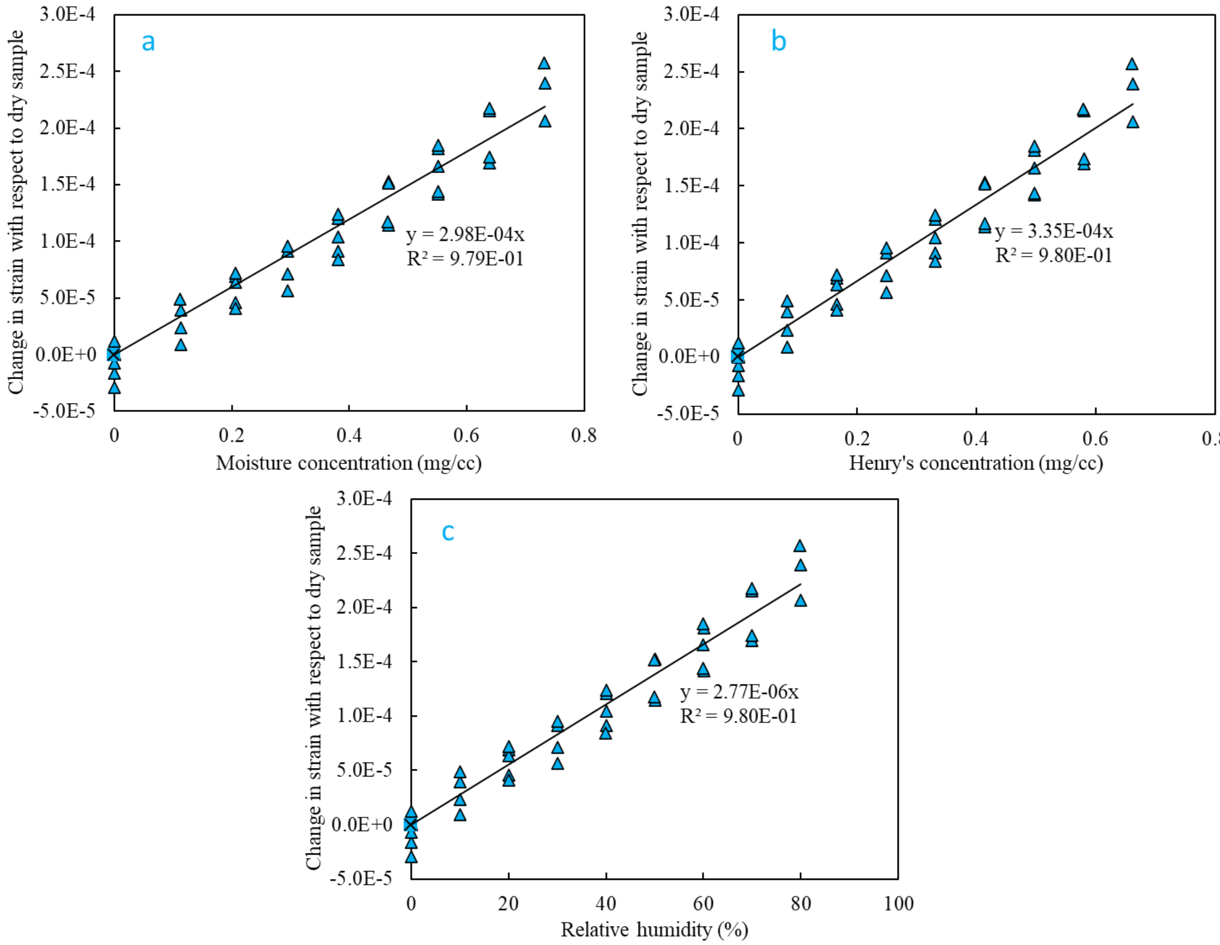

Figure 7. Linear fits used to estimate (a) $\boldsymbol{\beta_H}$, (b) $\boldsymbol{\beta_{H,Diablo}}$ and (c) $\boldsymbol{\beta_{H,RH}}$. Refer to Eqs. (5 - (7 for the definitions.

5. Thermal Expansion

Change in the size of Sylgard-184 in response to temperature change was measured using the NETZSCH Thermo-mechanical Analyzer. All datasets from experiments conducted using the compression module were used to estimate the coefficient of thermal expansion, α_T defined as:

$$\boldsymbol{\alpha_T = \frac{\partial \epsilon_{thermal}}{\partial \mathrm{T}}} \tag{8}$$

where $\epsilon_{thermal}$ is the thermal strain and T is the temperature. α_T is estimated by computing the slope of the strain vs temperature curve. The average value of the linear coefficient of thermal expansion for Sylgard-184 was estimated to be $3.0 \pm 0.2 \times 10^{-4}$ ºC^{-1}. This is consistent with what is reported in the literature. The method used to estimate α_T assumes that the sample achieves thermal equilibrium at time scales much shorter than the time scales at which the temperature is being changed in the experiment.

6. Summary

The findings of this report show that the measured moisture uptake for Sylgard-184 between 20 and 60 ºC increases with temperature at a given RH. The moisture uptake was characterized by the triple mode model that includes temperature dependent Henry's mode and temperature independent Langmuir and Pooling modes. The model was able to predict 87 % of the datapoints with an error less of than 10 %. Henry's solubility estimate in this report agrees well with the previously published estimates for Henry's solubility. The estimates for other parameters associated with the Langmuir and Pooling modes did not always match with previous estimates. This could partly be due to the smaller contribution of the Langmuir and pooling modes compared to Henry's mode. This study differs from other studies at it uses all the experimental datasets in trying to estimate the model parameters associated with moisture sorption.

Coefficients of hygroscopic expansion (at 50 ºC) and thermal expansion were also estimated. Sylgard-184's mechanical response to thermal changes is significantly stronger that its mechanical response to hygroscopic changes. For example, the strain experienced by Sylgard-184 due to a temperature change of 10 ºC is two orders of magnitude higher than the strain change due to a RH change of 10 %.