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Model to Determine The Diameter of an Electrospun Fiber

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Abstract. The purpose of this paper is to explore the different parameters that affect the overall final radius of a fiber when a polymer is electrospun. Through the implementation of a Python Model that calculates the final radius of a fiber of PAN (Polyacronitrile) inside DMF (dymethylformamide), sensitivity analysis is performed to determine the local and global effects of each one of the variables. Two equations developed by different groups are tested to check the accuracy of them predicting the final radius, and then these are compared to laboratory measured data of PAN inside DMF. More in depth analysis is then performed to determine if the power of certain terms in the equations were correctly determined by the MIT Zoom Lab and by R Stephanyan et. all [1]. Main findings showed that the ratio of the flow rate over the current of the system is the main factor affecting the diameter of the fiber produced.

1 Pandas and Plotly Libraries Exploration for PAN Data Analysis

Originally, the idea was to have a big data set with lots of data regarding a particular polymer. However, a small data set for PAN [2] was all that we could find even though many hours where spent trying to find this. Most papers only had figures to explain their results and no data was given. Even though we had this problem, we still wanted to explore and learn how to read data from files and be able to use it to generate graphs. Pandas commands where implemented to show how data can be read in jupyter notebooks, and other commands where used to perform statistics in the data from the different columns. **Figure [1]** shows different measured parameters at different weight percents for PAN. The most important ones are the viscosity η, the rate of evaporation k, the surface tension γ, the final diameter df, and the ratio between the flow rate Q and the voltage V that is applied to the system.

$$rf \sim (k\rho\eta)^{\frac{1}{3}} \times (\frac{Q}{I})^{\frac{2}{3}} \tag{1}$$

where rf is the radius of the fiber (nm); k is the evaporation rate ($10^{-5} kg/s*m^2$); ρ is the density of the solution that was calculated using the previous formula.

(kg/m^3);η is the solution viscosity (cp); Q is the fiber flow rate (m^3/s), and I is the current in the system (A).

But as it can be seen, to be able to determine the final radius of the fiber, the density of the solution needs to be calculated since this data was not found in Table 1.A. as a result it was determined that the best way to approximate the density of the solution was to find the densities at room temperature of both PAN and DMF [2]. It was assumed that the density dependency on temperature should not have a big impact in the final results. Using partial properties:

$$\rho_t = \frac{(PAN_w \times \rho_p) + (DMF_w \times \rho_s)}{100} \tag{2}$$

Where ρ_t is the density of the solution (kg/m^3); PAN_w is the weight percent of Polyacronytrile(PAN); ρ_p is the density of Polyacronytrile (PAN, $1.184kg/m^3$); DMF_w is the weight percent of the solvent DMF; ρ_s is density of the solvent DMF($0.944kg/m^3$)

PAN (wt %)	η_o (cP)	κ (μS/cm)	cone height (mm)	jet length (mm)	d_j (μm)	d_f (nm)	l_f/l_j	v_j (m/s)
5.0	47	35.3	1.54	1.21	3.99 ± 0.28	213 ± 47[b]		6.7
5.5	109	35.5	1.94	1.30	3.93 ± 0.20	-		6.9
6.0	171	36.0	1.49	2.24	3.25 ± 0.19	240 ± 81	8.80	10.0
6.5	194	42.8	2.13	1.37	3.78 ± 0.08	281 ± 57	9.50	7.4
7.0	338	45.4	1.25	1.88	3.84 ± 0.26	304 ± 62	9.09	7.2
8.0	515	46.2	1.49	2.80	4.04 ± 0.20	353 ± 71	8.51	6.5
10.5	1446	50.0	1.28	4.72	5.38 ± 0.23	552 ± 45	8.17	3.7
12.0	2753	51.5	1.07	12.29		1064 ± 175		

[a] γ remained constant at 36.3 dyn/cm and processing variables were fixed at $Q = 0.3$ mL/h, $H = 7$ cm, 6 kV, and the o.d. of needle is 1.47 mm. [b] Beaded fibers. d_f was determined by the fiber diameter between the spindles (beads).

Fig. 1. Table with PAN data [2]

Furthermore, equation (1) was developed since the MIT Zoom lab had already developed an expression to approximate the final diameter of a fiber , but there was concern that this group had not considered the effects of the mixture viscosity in their expression.

$$df \sim \gamma^{\frac{1}{3}} \times (\frac{Q}{I})^{\frac{2}{3}} \times (\omega p)^{\frac{1}{2}} \tag{3}$$

γ is the surface tension of the polymer solution(dyn/cm), ωp is the polymer volume fraction(range from 0 to 1,and here we treat polymer solutions as ideal solutions), Q is the ow rate(m^3/s), and I is the electric current in the system(A).

As it can be seen this relation does not account for the viscosity of the solution.

It was decided that the first step to take was to calculate the solution density using equation (1), and then generate a plot illustrating the dependency of the final diameter as a function of the solution density that we calculated. Values were put in the .csv file and it was possible to read the data into the document and do an initial assessment. To be able to generate nice interactive plots that, in our opinion, look much better than the ones generated in Matplotlib, we

decided to dig in and explore this library [3]. We spent a lot of time reading documentation and watching videos [4], but the result was very nice.

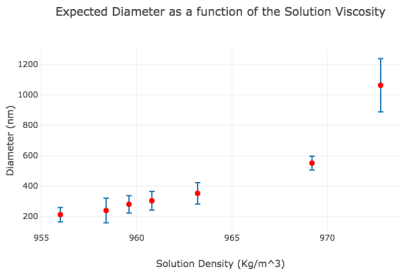

Fig. 2. Experimental diameter of the fiber as a function of calculated density

Figure[2] depicts the experimental diameter as a function of the solution density calculated. Please recall the diameter was measured experimentally and the solution of the density had to be approximated. But as the density of the solution increases at a particular weight percent, so does the diameter. The error bars of the plot where generated using the experimental errors given.

It was also important to determine the relation between the solution viscosity and the experimental diameter for the same weight percents of the polymer (the ones the data was given). So a similar plot could be generated to have an initial assessment of the dependency of the fiber diameter on the viscosity in the same plot as the solution density depicted before.

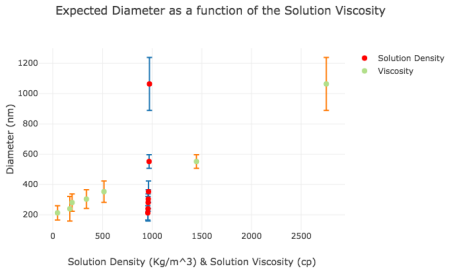

Fig. 3. Experimental diameter of the fiber as a function of the calculated solution density and the experimental solution viscosity

In **Figure [3]** we can see that the solution density did not vary much at different weight percents compared to the the solution viscosity, on the other hand solution viscosity is much more spread in the x axis. Considering this

range variation , this may not be the best way to depict the effects both solution viscosity and density have in the final diameter of the fiber.

After more time was spent looking into the Plotly Library [3], we were able to generate a plot that depicts the measured diameter as a function of the calculated solution density, but we added a third dimension, the color of each point in the graph is a function of the solution viscosity.

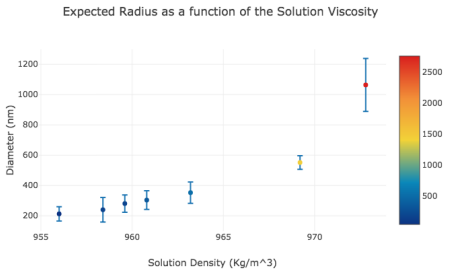

Fig. 4. Experimental diameter of the fiber as a function of the calculated solution density and the experimental solution viscosity

Figure [4] shows the dependency on solution density on the axis. But each color represents a different viscosity. As solution density increases, radius of the fiber increases and so does the solution viscosity, which ranges from 500 cP to around 2300 cP.

2 Determination of Density and Viscosity of Power in "Fiber Diameter in Electrospinning" approximation of diameter

Fridrikh et. all [2] stated that the nal ber diameter is dependent on the evaporation rate k and the solution viscosity η with a power law exponent 1/3, and make a scaling formula for the fiber's terminal radius, as shown in equation (1) Cause the concentrations of the solutions are not so big and the experiments should be controlled at room temperature.Also Q and I are constant in all experiments. So the equation(1) can be simplified as :

$$rf = A \times (\rho\eta)^{\frac{1}{3}} \tag{4}$$

$$A = (k)^{\frac{1}{3}} \times (\frac{Q}{I})^{\frac{2}{3}} \tag{5}$$

And then we can define the function to evaluate the power of $\rho\eta$ term by using the method:parameters, covariance = scipy.optimize.curve _ fit(function, x_data, y_data) in Jupyter notebook. From the results we got A=13.580(based

on nanometers), and the exponential power to the $(\rho\eta)$ is 0.5. First, we choose the power to be 1/3 as mentioned in the article and substitute the value of A to our equation(4). Then we can compare the measured diameters and calculated diameters with the theoretical exponential power to the $(\rho\eta)$. The results are shown in **Figure [5]**. Second, we choose our calculated exponential power of 0.5 to calculate the final diameters.Using the same constant A to our equation(4). Also we can compare the measured diameters and calculated diameters with this new exponential power to the $(\rho\eta)$. The results are shown in **Fig [6]**.The graphs illustrate that the predicted diameters of fiber based on exponential power of 0.5 fit better with the measured results than the one based on theoretical power. This is reasonable because we simply take the evaporation rate of solution as a constant. However, the evaporation rate changes within the concentrations of solution. And in sensitivity analysis we can clearly see that even very small change added to this rate makes the final diameter of the fiber changes a lot.

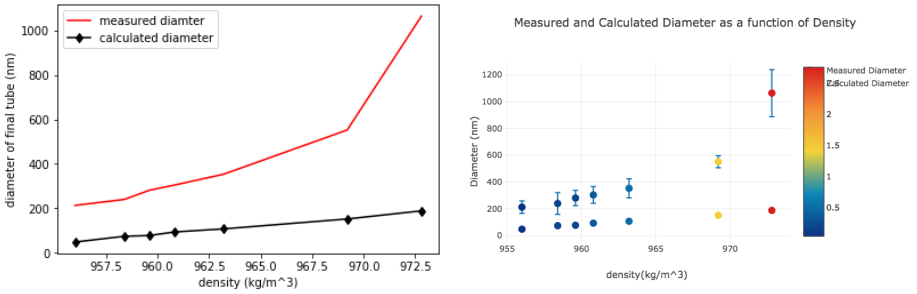

Fig. 5. Diameters of final fiber change with the increase of PAN solutions' densities. The power is set to be 1/3.

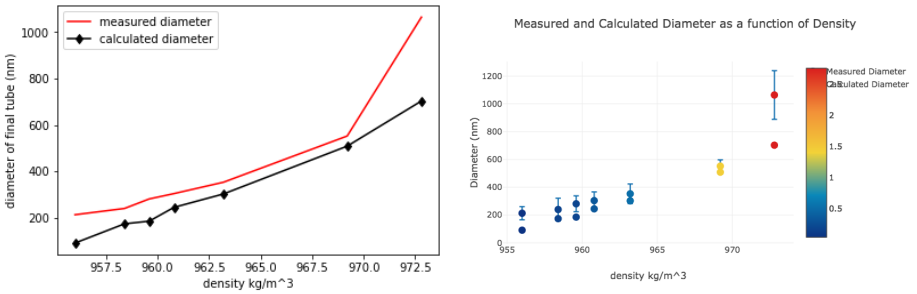

Fig. 6. Diameters of final fiber change with the increase of PAN solutions' densities. The power is set to be 0.5.

Another alternative model is developed at MIT and is built around an assumption that the terminal ber's diameter is determined by an equilibrium between the Coulombic repulsion between the charges on the jet's surface and the liquid's surface tension equation(3)
We regard the surface tension as a constant value.Also Q and I are constant in all experiments. So the formula(3) can be simplified as,

$$df = B \times (\omega)^{\frac{1}{2}} \tag{6}$$

$$B = \gamma^{\frac{1}{3}} \times (\frac{Q}{I})^{\frac{2}{3}} \tag{7}$$

To determine the exponential power to the ωp term, we still use the method of scipy.optimize.curve _ fit(function, x_data, y_data) to deal with the data in **Figure [1]**. From the results we got $B = 1.5093 \times 10^{-4}$(based on nanometers), and the exponential power to the (ωp) is 2. First, we choose the power to be 0.5 as mentioned in the formula(3) and substitute the value of B to our equation(6). Then we can compare the measured diameters and calculated diameters with the theoretical exponential power to the (ωp). The results are shown in **Figure [7]**. Second, we choose our calculated exponential power of 2 to calculate the final diameters.Using the same constant B to our equation(6). Also we can compare the measured diameters and calculated diameters with this new exponential power to the (ωp). The results are shown in **Figure [8]**. The results show that both two calculated final diameters within different exponential power fail to match the measured diameters well. This could be the changeable value of the surface tension of the solution that lead to the inaccurate prediction. However, it's more likely to say that this model is too simple to deal with the problem cause it only takes volume fractions into consideration and ignore the important factors such as viscosity, density and solvent evaporation rate.

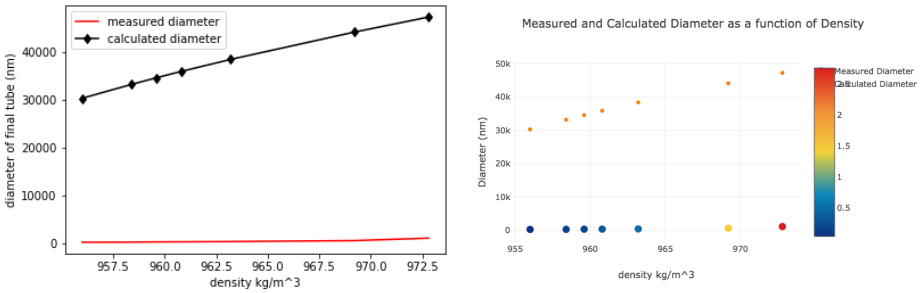

Fig. 7. Diameters of final fiber change with the increase of PAN solutions' densities.The results are calculated within volume fractions, and the power here is set to be 0.5.

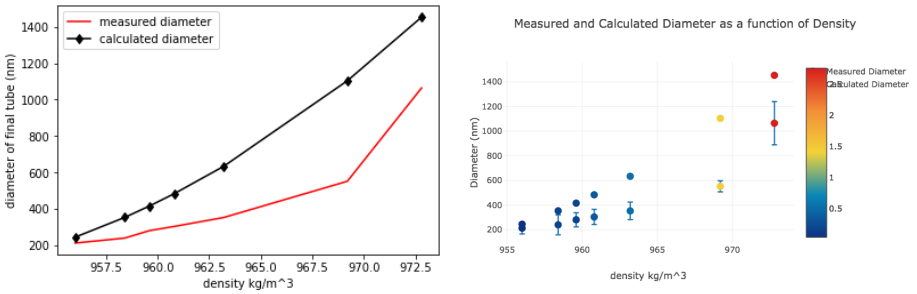

Fig. 8. Diameters of final fiber change with the increase of PAN solutions' densities.The results are calculated within volume fractions, and the power here is set to be 2.

3 Sensitivity Analysis

A main component of this investigation is to model the diameter of a fiber based on different parameters in equations already developed by two groups. For the PAN final measured diameter, the experiments were conducted at a constant surface tension and at a fixed flow rate. In this investigation we decided to use the equation developed by R Stephanyan et. all [1] to study the effects of changing these variables as well as the other ones for a bigger range of inputs. To interrogate the model, both local sensitivity and global sensitivity analysis where implemented. For the local analysis we had to use the Numpy Library and import some interactive widgets as well as the Seaborn Library. We input the data for both density and weight percent given in **Figure** [**1**] to compute our density in the solution. Once we had those values, a separate function was created that returns the density. Following this, a function based on R Stephanyan et. all [1] formula(1) was also created in python to return the expected radius of the fiber.

Parameters	Lower limit	Upper limit	Step
k (kg/s*m^2)*10^-5	1.00E-06	0.1	1.00E-05
density (kg/m^3)	944	1184	1
viscosity (cP)	4.70E-02	2.75E+00	1.00E-05
Q/l (m^3/s A)	1.00E-08	1.00E-02	1.00E-06
E (J/mol)	1.51E+04	2.79E+04	100
T (K)	2.98E+02	3.73E+02	1

Fig. 9. Table that shows the parameters to vary during local sensitivity analysis for model I

3.1 Model I

Here we try to study the effect of solution density(ρ), viscosity(η), ratio of Q/I and evaporation rate k in order to determine the overall effect of this factors in the terminal radius of the fiber for the formula(1). Then temperature effects and activation energy effects are considered as well, following C. Wang et. all [2]

$$\eta(T) = \eta(T_0) \times e^{\frac{\Delta E}{R} \times (\frac{1}{T} - \frac{1}{T_0})} \tag{8}$$

where T is the temperature in Kelvin; $\eta(T)$ is the viscosity of polymer solutions at temperature T; $\eta(T_0)$ is the referenced viscosity at $298K$; R is the gas constant($8.314J*mol^{-1}*K^{-1}$); and ΔE is the activate energy. We created some sliders that indicate the variation of the diameter as a function of each of these values separately. Please consider that the value of the evaporation rate K had to be approximated following the data found for the evaporation rate of DMF at a temperature of 60 to120C due to the lack of studies found for temperature lower than this range [5]. By approximating at least the order of magnitude, we could generate a radius, in the same order of magnitude as the expected diameter found in **Figure[1]**. Another variable was also created for the Q/I term, but considering the data on **Figure [1]** was calculated at constant flow rate of 0.3 ml/s, we were able to identify that most likely this term was very small since it had to be divided by the current. These ranges can be found in **Figure [9]**. An initial sensitivity analysis did not consider the activation energy dependence in temperature. A snap of the results found follows: By changing each input it is

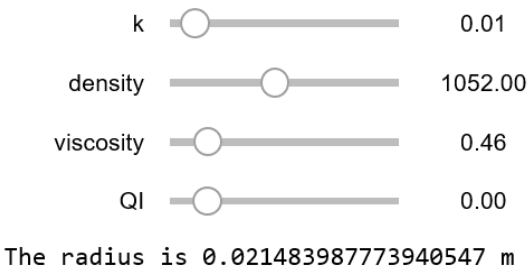

Fig. 10. Snapshot of the local sensitivity analysis performed without considering activation energy temperature dependence

possible to determine how the radius changes. Once this analysis was performed, we followed on a similar kind of analysis but accounting for the effect that changing the temperature would have in the activation energy, following equation(8) and these were the results found:

Even though a local sensitivity analysis is well suited for small data sets, it still does not take into account the interaction between parameters, for this reason we tried implementing The Morris Method. Which is a more computationally

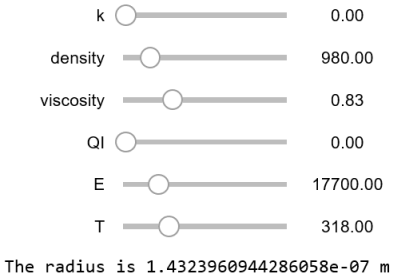

Fig. 11. Snapshot of the local sensitivity analysis performed considering activation energy temperature dependence

demanding method but, will indeed handle better nonlinear relations (good for our relations with exponents) and account for interactions between inputs. To be able to implement this method, we had to import SALib. We defined a Morris Problem, and we proceeded to check the dependence by generating a sample using the ma.analyze command and generating a sample of 120000 inputs. From there, we were able to create some plots and to determine the effect of each parameter accounting for the interactions between parameters themselves.

Name	mu	mu_star	sigma
k	0.03	0.03	0.03
density	0.00	0.00	0.00
viscosity	0.00	0.00	0.00
QI	0.04	0.04	0.03
E	- 0.00	0.00	0.00
T	- 0.01	0.01	0.01

Fig. 12. Snapshot of mu, mu-star, sigma values for Model I

By looking at the results it can be inferred that the Q/I term is the one that is most determinant to predict the radius. It is then followed by the evaporation rate K. This results will be more clear in the next figure.

On the left side it can be seen that the radius of the fiber is the most sensitive to changes in Q/I, then its followed by changes in K and then the other terms are not as significant. Density and viscosity in this analysis are not very important compared to the other parameters in the equation. On the right the fact that the dots align with the continuous lines is a good indication.

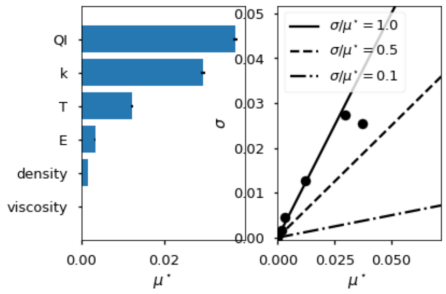

Fig. 13. Morris Method outcome for Model I

3.2 Model II

For the second model, we try to study the effect of the variables accounted in formula(3). This is the model independent on solution viscosity. The variables to account for in this model and the ranges for their local sensitivity analysis can be found in the following **Figure [14]**. for the surface tension, we centered the ranges around 36.3 dyn/cm considered the PAN experiment was done at this surface tension. For Q/I, we decided to keep the lower and upper limit the same as the ones used for the previous model. For the volume fraction, we varied it between a value between 0 and 1.

Parameters	Lower limit	Upper limit	Step
γ(dyn/cm)	1.00E+00	100	1.00E+00
wp	0.01	0.99	1.00E-02
Q/I (m^3/s A)	1.00E-08	1.00E-02	1.00E-06

Fig. 14. Showing the Parameters to vary local sensitivity analysis for model 2

Once those ranges were input and widgets were used, sliders could be generated to study the effect of each parameter in the final diameter.

But again, local sensitivity does not consider the interaction between parameters so Morris Method was implemented to the MIT Zoom Lab equation(3) just as in the first Model.

Mu in this case indicates that once again the most significant parameter is Q/I. But both surface tension and the volume fraction of the polymer are also very important and have a very big impact on the final radius, relative to the Q/I term. This can be said considering mu is 0.4 for Q/I and 0.3 for the other two parameters. These results can be better visualized in the following figure.

In this **Figure [17]** the results for the Morris Method for Model II can be seen. as mentioned before, Q/I is the most significant parameter, but from the

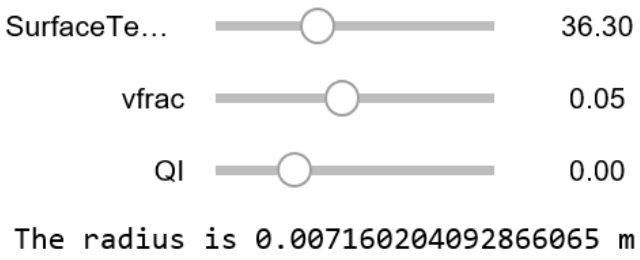

Fig. 15. Showing the Parameters to vary local sensitivity analysis for model II

Name	mu	mu_star	sigma
SurfaceTension	0.03	0.03	0.03
vfrac	0.03	0.03	0.03
QI	0.04	0.04	0.03

Fig. 16. Snapshot of mu, mu-star, sigma values for Model II

plot it can be seen that the volume fraction of the polymer is more significant than the Surface tension.

3.3 Model Conclusions

Regarding the sensitivity analysis performed for the two models, the main finding is that the MIT Zoom lab and R Stephanyan et. all [1] both develop different equations to be able to identify the most significant parameters affecting the size of the diameter and they get the same parameter as being the most determinant. In both scenarios, Morris method indicated that the most significant parameter is the flow rate over the current term. For Model I, the evaporation rate K, the temperature and solution and the activation energy were also significant to calculate the final diameter, but viscosity and density ended up not being as significant. Particular attention should be paid to the fact that temperature is used to calculate activation energy, so the Morris Method for this two variables could be a misleading considering they might depend on each other and maybe only activation energy should have been taken into account to perform The Morris Method For Model II, both volume fraction of the polymer and also the surface tension of the solution ended up being significant in the final diameter.

3.4 Future Work

To continue the work on this project it will be very important to find a larger data set. It would be a good idea to find data for different polymers or just one big data set for a particular polymer so our results can be more reliable. Having

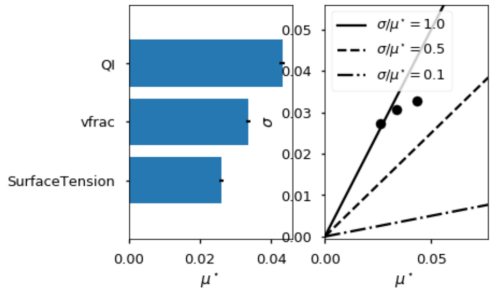

Fig. 17. Morris Method outcome for Model II

a sample as this size is not the best for the sensitivity analysis. Besides the size of the sample, it would also work if this project can be done in a lab, and data can be collected just to check if the model is predicting the correct results. Once several sets of data are collected for the same polymer, the model can be verified, and maybe there won't be a need to do the physical experiments in a laboratory simply because the model is accurate enough.

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