Communications



Estimation of the Flory-Huggins interaction parameter of polymer-solvent mixtures using machine learning

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Abstract

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The Flory-Huggins interaction parameter χ for polymer-solvent mixtures captures the nature of interactions and provides insights on solubility. χ is usually estimated using experimental or (empirical) computational methods, which may be expensive, time-consuming or inaccurate. Here, we built a machine learning (ML) model to instantly predict temperature-dependent χ for a given polymer-solvent pair. The ML model was trained using 1586 experimental polymer-solvent datapoints, and a hierarchical polymer and solvent fingerprinting scheme. Extensive testing has been performed to verify the accuracy and generality of this model. This work demonstrates an ML model that can progressively be improved as new data emerges.

Introduction

Understanding polymer-solvent interactions is critical in several contexts, e.g., during polymer synthesis,^[1] designing polymer-blends,^[2] building polymer membranes,^[3,4] and polymer recycling.^[5] The polymer-solvent interaction parameter χ , also alternatively known as Flory-Huggins interaction parameter, is a quantitative measure of the degree of interaction between the polymer and solvent molecules.^[6–8] A lower χ implies higher polymer-solvent interaction and thus indicates higher solubility. Furthermore, by knowing χ , one can express other properties that depend on polymer-solvent interaction, some of which include viscosity, miscibility and swelling equilibria.^[9] In the future, we hope this work serves as guideline for polymer design for desired polymer-solvent interaction related properties.

The conventionally used experimental methods to estimate χ are osmotic pressure, vapor sorption, or inverse gas chromatography measurements.^[10] However, these methods are usually time-intensive. For example, sorption studies are time consuming as they require allowing the solvent to fully absorb the polymer until saturation. Previously, computational approaches involving classical force fields molecular dynamics (MD)^[11–13] and density functional theory (DFT)^[14] have been used to calculate χ . However, these methods are either not reliable enough or are computationally expensive.

An alternate simple approach the community has adopted is to estimate χ from the Hildebrand solubility parameter of the solvent (δ_s) and that of the polymer (δ_p) as follows:^[15]

$$\chi_{\text{Hildebrand}} = (v_p v_s)^{1/2} (\delta_p - \delta_s)^2 / RT + \beta$$
(1)

 v_p and v_s stand for the molar volume of the polymer and solvent, *R* is the universal gas constant, *T* is the temperature, and β is a constant with a commonly used value of 0.34. The Hildebrand parameter of a system is the square root of its cohesive energy per unit volume.

Figure 1 makes a comparison of $\chi_{\text{Hildebrand}}$ with $\chi_{\text{experimental}}$ values at room temperature for a number of polymer-solvent pairs. More details on the literature-sourced $\chi_{\text{experimental}}$ values are covered in "Dataset" section. While some correlation does indeed exist between $\chi_{\text{Hildebrand}}$ with $\chi_{\text{experimental}}$, it is not quantitative enough to be useful for general polymer-solvent combinations. Moreover, Eq. (1) is too simplistic an approach to capture the full breadth of polymer-solvent interactions. Hence, other more reliable and practical methods must be explored to estimate χ .

In this contribution, we have developed a Gaussian Process Regression (GPR) based machine learning model to instantly predict χ values of the polymer-solvent pairs. To train this model, we used a dataset of experimentally measured χ values. The temperature of measurement and the chemical features of the polymer and solvent were used to define our total feature space. Extensive testing of the strengths and limitations of the model was performed. Given that the dataset has a larger diversity and number of solvents than polymers, generalizability was better for unseen solvents. Nevertheless, the model can be progressively improved as newer data on polymer-solvent pairs become available. We hope that this work serves as an initial step towards a data-driven, quantitative predictive capability for describing polymer-solvent interactions.^[16,17]





Figure 1. (a) Comparison of χ obtained from Eq. (1) (χ Hildebrand) with corresponding experimental values (χ experimental) at room temperature, (b) same comparison in a log–log plot.



Figure 2. Distribution of χ as a function of temperature for each unique polymer and solvent.

Technical details Dataset

Experimental χ values corresponding to unique polymersolvent pairs at various temperatures have been collected from literature sources and online databases.^[10,19-29] Figure 2 illustrates our 1586 data points corresponding to 58 polymers and 140 solvents, within a temperature range of 273-526 K. The experimental methods commonly used to report χ are osmotic pressure measurements, sorption studies, and inverse gas chromatography. It has been observed that χ decreases with an increase in temperature.^[30] When multiple values of χ were available, the average value was considered. Our dataset also contains negative values of χ , which are fairly uncommon. These arise due to excess negative entropy contributions, commonly seen in exothermic mixing.^[31] Further, our dataset contains mostly simple synthetic organic polymers and a few natural polymers, such as polystyrene (318), polybutadiene (172), poly(dimethylsiloxane) (123), polyisobutylene (86), polycarbonate (67) and polyethylene (56). The solvents belong to various classes like aromatic, linear aliphatics, and cyclic aliphatics.

Fingerprints

To numerically represent polymers and solvents, this study uses a unique fingerprinting scheme to define the chemical features of the polymer and solvent.^[18,32] The fingerprinting scheme derives features from various hierarchical levels including atomic level descriptors, block-level descriptors and morphological descriptors, as described in Ref. 18. The atomic level fingerprints consider the atomic triples (fragments of three contiguous atoms). The block-level fingerprints consider the blocks from a larger scale, like benzene rings. Additionally, the morphological descriptors deal with features such as shortest topological distance between rings, fraction of atoms that are part of side-chains, and the length of the largest side-chain. Finally, the morphological descriptors also include quantitative structure-property relationship (QSPR) type descriptors such as Van der Waals volume, surface area and the topological polar surface area (TPSA). Moreover, the temperature at which χ was measured is another essential feature. In total, 400 features were used to train our machine learning model.

Machine learning

Gaussian process regression (GPR) was utilized as the method of choice owing to various advantages. First, as a Bayesian approach, one of the critical advantages of using GPR is its ability to provide uncertainty on the predictions. The uncertainty acts as a good metric on whether one can trust the prediction or not. Second, GPR converges well on a small dataset. Our model was built using radial basis function kernel (RBF), and five-fold cross-validation.

To assess the impact of sampling methods on the model accuracy, we have tested four sampling methods: (1) random split, (2) group shuffle split based on polymer groups, (3) group shuffle split based on solvent groups, and (4) polymer and solvent one-holdouts.^[33] For the group shuffle splits, each unique polymer (or solvent) is assigned to a unique group, and these specific groups are split into training and testing sets. These group splits are critical to deciphering the model performance for polymers/solvents chemically distinct from the ones in our trainset. On the other hand, the one hold-out splits is a particular case of the group split, where only one polymer (with all its associated solvents) or one solvent (with all its associated polymers) is held out. This helps us to understand the model performance for that specific targeted held-out polymer/solvent. For small dataset sizes, the machine learning model performance changes drastically with the choice of sampling, but this dependence should vanish as the number of distinct polymers and solvents increases in the dataset.

The model performance was checked with the following two error metrics: root mean square error (RMSE) and the coefficient of determination (\mathbb{R}^2). The RMSE as a function of trainset size is visualized in the form of a learning curve to check against overfitting. The trainset size was varied from 50 to 100% of the full dataset size, and for each trainset size, five runs were performed.

Results and discussion

Firstly, the most critical step is data validation, which is done by comparing the experimental χ values to the available solubility data. Next, this validated dataset was then converted into a machine-readable form via fingerprinting. Thereafter, a GPRbased machine learning model was constructed, considering different sampling methods. Lastly, the generality and accuracy of the developed model was validated by testing on two novel polymers, never seen by the ML model during training: PIM-1 and SBAD-1.

Dataset validation

For the dataset accumulated over various sources, dataset validation was done to ensure its viability. From the definition of χ , it follows that the smaller the value of χ , the greater is the reduction in Gibb's free energy of polymer-solvent mixing.^[10] This implies that the χ values may be expected to be small for good solvents for a particular polymer. To ascertain that such a trend occurs, we compared our polymer-solvent χ data with two available polymer-solvent solubility datasets, as portrayed in Fig. 3.

The first comparison was made with solubility data found from Hansen's Solubility Parameters: A user's handbook.^[34] This handbook classifies the solubility levels of polymer-solvent mixtures on a 6-level scale: (1) soluble; (2) almost soluble; (3) strongly swollen, slight solubility; (4) swollen; (5) little swelling; (6) no visible effect, insoluble. Comparing with the solvent-polymer pairs in our dataset, we find 8 common polymers (polystyrene, polyisopropene, polyisobutylene, poly(vinyl chloride), poly(vinyl acetate), poly(methyl methacrylate), poly(cis-1,4-butadiene), cellulose acetate) and 41 common solvents corresponding to 367 datapoints at room temperature. The violin plots in Fig. 3 show that, as expected, the median values of χ of our dataset increase with an increasing level of insolubility as per Hansen's solubility data.

The second comparison was made using newer accumulated solubility data.^[35] This new dataset represented solubility at two levels: insoluble and soluble. Figure 3(b) compares our χ data with this new solubility data for the polymer-solvent

combinations that occur in both datasets (corresponding to 11 polymers and 12 solvents, with a total of 45 data points). As expected, with increasing χ values, the level of insolubility increases. These comparisons provide us confidence that our χ dataset is reliable and shows expected trends in terms of correlations with available solubility data.

Machine learning model performance

Next, we move on to discuss the trained GPR-based ML model utilizing the 1586 χ data points corresponding to 58 polymers and 140 solvents, trained using 400 features. Because χ is impacted by both polymer and solvent types, different types of sampling methods are used to understand the strengths and limitations of the models. We used four sampling splits to train our model: (1) random split, (2) group shuffle split based on polymer groups, (3) group shuffle split based on solvent groups (4) polymer and solvent one-holdouts, details provided in "Machine learning" section and Supplemental Information.

Figure 4 shows the parity plots corresponding to random split, the polymer group split, and solvent group split, followed by the learning curve plotted for five runs. The learning curve is a great tool to check if the model is overfitting. It is evident from the learning curve that the performance for the model with the random split is the best, closely followed by solvent group splits, followed at last by polymer group splits. Further, with increasing trainset size, the model performance improves.

We also note from Fig. 4 that when the random split is used, the model may get a glimpse of the polymers (and solvents) present in the test set. That polymer may have already been paired with another solvent, or even with the same solvent at another temperature. The high test R^2 values (0.83) and low RMSE (0.27) values attest to the satisfactory performance of the model, as can be seen from Fig. 4. For the solvent-based splits, the performance does not change drastically as a function of the held-out solvent. This is because the solvent space spanning about 140 solvents is quite diverse. For polymer group splits, the performance changes dramatically as a function of held-out polymers. The polymer space consisting of 58 examples is relatively small and not diverse enough. Therefore due to the data imbalance, the model performance fluctuates dramatically for polymers that are chemically different from the polymers in the trainset.



Figure 3. Violin plots to visualize (a) χ comparison with 6-level solubility classes (experimental data referenced from Hansen's Solubility Parameters Handbook),^[34] (b) χ comparison with newer 2-level solubility classification (experimental data).^[35]



Figure 4. Parity plot (for 90 % trainset size) with data split using (a) random split, (b) polymer group split, and (c) solvent group split, along with d) learning curve comparing the three splits.

In addition to the three sampling methods discussed above, we did another exercise pertaining to the polymer and solvent hold-outs included in the Supplemental Information. This exercise compares the model performance as a function of one-heldout polymer (and solvent) at a time. It emphasizes the fact that for held-out polymers that are chemically similar to the ones present in the trainset, the predictions are quite satisfactory. However, the predictions are less accurate for the ones that are not chemically similar. This analysis is crucial to realize the strengths and weaknesses of the model.

Further model validation

One of the major goals of any machine learning algorithm is extrapolative prediction. Thus, there is a need to validate the model by checking its generalizability. To ensure the model's validity, we tested the model performance on two novel polymers, SBAD-1 (spirobifluorene aryl diamine) and PIM-1 (polymer of intrinsic microporosity).^[4] The experimentally measured χ at room temperature has been recently reported for these two polymers with 12 solvents, leading to a total of 14 data points. None of these new datapoints were part of our χ training set. The model built using random split (see Fig. 4) was used to make predictions on SBAD-1 and PIM-1. Unfortunately, the model greatly underpredicts χ values for these polymers. This is an expected result as PIM-1 and SBAD-1 are ladder and semi-ladder polymers (see Fig. 5), which are very different from the more straightforward linear or branched polymers present in our dataset. The principal component analysis (PCA) plot in Figure 6 contrasts the difference in chemistry corresponding to the polymers from our dataset with SBAD-1 and PIM-1 polymers. This difference in chemistries clearly explains why the model does not perform an excellent job at making predictions for PIM-1 and SBAD-1 polymers.

To aid better predictions for these drastically different polymers, we iteratively augmented the PIM-1 and SBAD-1 data (see Fig. 7). The driving force for this exercise is to create a model with some data to just learn enough about these different polymers. As a part of this exercise, out of the 14 new datapoints, just datapoints for which the predictions showed the highest uncertainty and errors were appended to the original training dataset. We proceed to add data points sequentially: first, we added one data point each for SBAD-1 and PIM-1 polymers. The augmented data points were also chosen consciously so as to balance the solvent chemistry. The validating dataset contained solvents of the type aromatic, linear aliphatics, and cyclic aliphatics. After retraining the model, it was seen that PIM-1 predictions became quite satisfactory on the addition of only one new data point. On the other hand, the behavior for SBAD-1 was still not learned by the model, and we continued to add 4 more data points for SBAD-1. With these 5 appended data points, the model learns the behavior of PIM-1 and SBAD-1 for the solvents not added to the dataset. This exercise clearly demonstrates the limitation of the machine learning models, but also points to a pathway to understand the limitations and overcome them (via suitable data augmentation and infusion, when possible).

We proceeded to retrain our final production model with all data pertaining to PIM-1 and SBAD-1 polymers. This model built on 1600 datapoints shows an average CV train RMSE of 0.211 and average CV test RMSE of 0.333. Details of this model have been included in the Supplemental Information.

Conclusion

A knowledge of χ enables us to decipher and understand polymer-solvent interactions. Here, we have developed a machine learning model for instantaneous χ predictions for polymersolvent pairs. Based on 1586 experimental χ values, 400 features were generated for polymers and solvents using the

Figure 5. Structure of (a) PIM-1 polymer, (b) SBAD-1 polymer.^[4]

Figure 6. (a) Comparison of the chemical space of polymers SBAD-1 and PIM-1 with the polymers present in our trainset, (b) Similar comparison for solvents used. Here PC0 and PC1 denote the first and second principal components derived from PCA analysis.

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Figure 7. Model Validation, column (a) predictions for PIM-1 and SBAD-1 polymers, (b) retrained model predictions with appended 1 PIM-1 and 2 SBAD-1 datapoints (c) retrained model predictions with appended 1 PIM-1 and 4 SBAD-1 datapoints. Appended datapoints are denoted by red filled marker.

Polymer Genome fingerprint scheme and were used to train our GPR model.^[29] We further assessed the model performance by considering various sampling methods and testing on unseen polymer-solvent pairs. Although the data scarcity problem limits the model's accuracy and generality, it can be progressively improved by exposing the model to new data.

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Data availability

The compiled χ dataset has been made available in the Supplemental Information.

Declarations

Conflict of interest

The authors declare no competing interests.

Supplementary Information

The online version of this article (https://doi.org/10.1557/ s43579-022-00237-x) contains supplementary material, which is available to authorized users.

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