JCIM JOURNAL OF CHEMICAL INFORMATION AND MODELING
Article
Cite This: *J. Chem. Inf. Model.* XXXX, XXX, XXX−XXX
pubs.acs.org/jcim

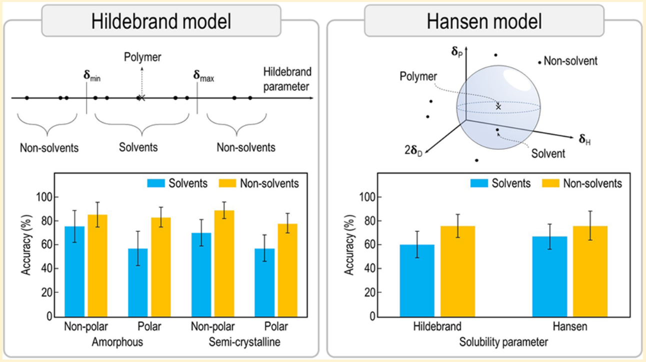
Critical Assessment of the Hildebrand and Hansen Solubility Parameters for Polymers

Shruti Venkatram, Chiho Kim, Anand Chandrasekaran, and Rampi Ramprasad*

School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive NW, Atlanta, Georgia 30332, United States

S *Supporting Information*

ABSTRACT: Solubility parameter models are widely used to select suitable solvents/nonsolvents for polymers in a variety of processing and engineering applications. In this study, we focus on two well-established models, namely, the Hildebrand and Hansen solubility parameter models. Both models are built on the basis of the notion of "like dissolves like" and identify a liquid as a good solvent for a polymer if the solubility parameters of the liquid and the polymer are close to each other. Here we make a critical and quantitative assessment of the accuracy/utility of these two models by comparing their predictions against actual experimental data. Using a data set of 75 polymers, we find that the Hildebrand model displays a predictive accuracy of 60% for solvents and 76% for nonsolvents. The Hansen model leads to a similar performance; on the basis of a data set of 25 polymers for which Hansen parameters are available, we find that it has an accuracy of 67% for solvents and 76% for nonsolvents. The availability of the Hildebrand parameters for a large polymer data set makes it a widely applicable capability, as the Hildebrand parameter for a new polymer may be determined using this data set and machine learning methods as we have done before; the predicted Hildebrand parameter for a new polymer may then be used to determine suitable solvents and nonsolvents. Such predictions are difficult to make with the Hansen model, as the data set of Hansen parameters for polymers is rather small. Nevertheless, the Hildebrand approach must be used with caution. Our analysis shows that while the Hildebrand model has a predictive accuracy of 70−75% for nonpolar polymers, it performs rather poorly for polar polymers (with an accuracy of 57%). Going forward, determination of solvents and nonsolvents for polymers may benefit by developing classification models built directly on the basis of available experimental data sets rather than utilizing the solubility parameter approach, which is limited in versatility and accuracy.



INTRODUCTION

Solvent selection is critical to applications involving polymers.[1] For instance, polymer recycling requires designer solvents that degrade polymers in a controlled manner with environmentally compatible byproducts. Drug delivery systems require chemically permeable polymers to effectively operate in biological environments. Solvent selection is critical to avoid phase segregation during polymer synthesis and to develop stable formulations that meet environmental, safety, and quality standards.[1−3]

The need to identify suitable (non)solvents for polymers has led to the development of quantitative models of polymer−solvent compatibility governed by the notion of "like dissolves like".[4,5] In essence, a solvent with a cohesive energy density similar to that of a polymer is expected to be a good solvent for the polymer. The cohesive energy density of a condensed substance is a measure of the intramolecular bond strength and is defined as the energy necessary to isolate a unit volume of the molecules making up the substance from each other.

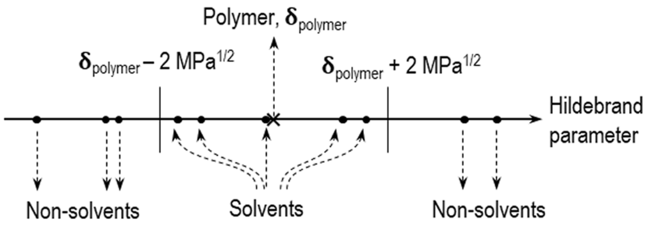
Two widely used measures of solvent−polymer compatibility are the Hildebrand[1,5−7] and Hansen[4−7] solubility parameters. The Hildebrand model utilizes a single parameter, δ, defined as the square root of the cohesive energy density, to determine whether a substance is a good solvent or nonsolvent for a polymer. Solvents with δ values different from that of a polymer by more than 2 MPa$^{1/2}$ are deemed nonsolvents, and those within ±2 MPa$^{1/2}$ of the polymer δ value are considered good solvents; the factor 2 MPa$^{1/2}$ was determined on the basis of empirical considerations. Figure 1a pictorially depicts the Hildebrand solubility criterion.

The Hansen model utilizes three parameters, δ_D, δ_P, and δ_H, to quantify solvent−polymer compatibility. These three parameters represent the dispersion, polar, and hydrogen-bonding components, respectively, of the Hildebrand parameter δ, such that, $\delta^2 = \delta_D{}^2 + \delta_P{}^2 + \delta_H{}^2$. If visualized as a three-dimensional plot, the axes being $2\delta_D$, δ_P, and δ_H, the polymers

Received: August 6, 2019
Published: September 23, 2019

DOI: 10.1021/acs.jcim.9b00656

(a) Hildebrand solubility model



(b) Hansen solubility model

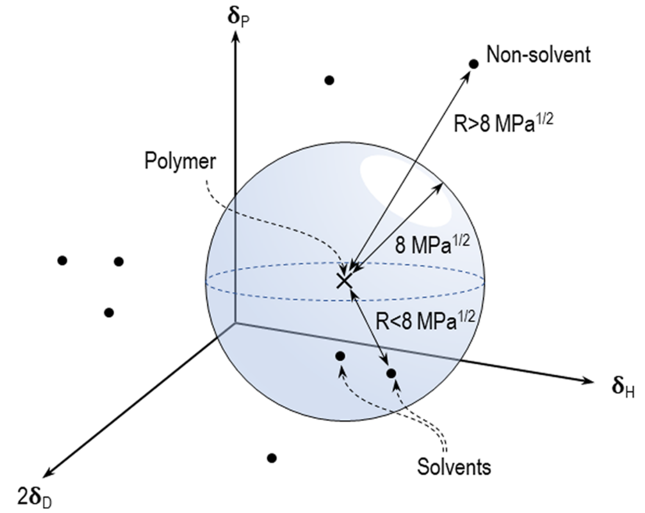


Figure 1. Solubility criteria of (a) the Hildebrand solubility parameter (δ), where the solvent Hildebrand values are within ±2 MPa$^{1/2}$ of the polymer Hildebrand value ($\delta_{polymer}$) and the nonsolvent Hildebrand values are differ by more than 2 MPa$^{1/2}$, and (b) the Hansen solubility model, where the three axes represent the dispersion (δ_D), polar (δ_P), and hydrogen-bonding (δ_H) components, and solvents and nonsolvents fall within or outside a sphere of radius R = 8 MPa$^{1/2}$ centered on the polymer, respectively.

and solvents are represented by points in this space. Those solvents within a sphere of radius R = 8 MPa$^{1/2}$ centered at a point corresponding to a polymer are deemed to be good solvents for that polymer, and those solvents falling outside the sphere are considered nonsolvents. Again, the factor 8 MPa$^{1/2}$ was determined on the basis of empirical considerations. Figure 1b pictorially depicts the Hansen solubility criterion.

In this study, we critically assess the performance of both the Hildebrand and Hansen models by directly comparing their predictions against actual experimental data (collected from the *Polymer Handbook*) on solvents and nonsolvents for a benchmark set of polymers. The model predictions were based on the criteria described above and portrayed in Figure 1. A challenge we had to overcome in this study is that the Hildebrand and Hansen solubility parameters are available for only limited numbers of polymers (although the solubility parameters are available for numerous solvents). For those polymers for which experimental data on solvents and nonsolvents were available but the Hildebrand parameter was not available, a previously developed machine learning (ML) model[8] was used first to predict the Hildebrand parameter, followed by application of the criterion discussed above to predict solvents and nonsolvents. The Hansen model values were available for only 25 polymers—too few to train a ML model. Thus, Hansen model assessments were performed only for these 25 polymers.

Overall, we conclude that both the Hildebrand and Hansen parameters provide limited accuracy. For a data set of 75 polymers, we find that the Hildebrand model predicts solvents with an accuracy of 60% and nonsolvents with an accuracy of 76%. The Hansen model is similarly evaluated using a data set of 25 polymers for which the Hansen values are available. We find that its predictive capability is similar to that of the Hildebrand model, with a predictive accuracy of 67% for solvents and 76% for nonsolvents. The quantity and diversity of polymers for which the Hildebrand parameters are available (and the Hansen parameters are not) makes it a suitable candidate to predict solvents and nonsolvents for polymers. For new polymers, this data set and ML methods can be used to predict the Hildebrand parameter. However, the performance of the Hildebrand parameter is not uniform across the chemical space of polymers. From this study, we find that the Hildebrand model's predictive capability is better for nonpolar polymers (with an accuracy of 70–75%) than for polar polymers (with an accuracy of 57%). To overcome these limitations, the next steps for more accurate solvent predictions for polymers could be to use the experimental data sets as is with classification models rather than go through the intermediate route with solubility parameters. This approach may lead to a higher success in capturing complex relationships between polymers and solvents.

■ METHODS AND DATA SETS

Experimental Data on Solvents and Nonsolvents. Experimental data on solvents and nonsolvents for polymers are well-documented in the *Polymer Handbook* by Brandup et al.[9] In some cases, solvents and nonsolvents are specified as generic organic substances like alcohols, esters, ethers, ketones, acids, and hydrocarbons. However, solubility models are defined for specific organic compounds. Therefore, to apply solubility models, generic compounds (e.g., alcohols) found in data sources were replaced by specific common organic solvents (e.g., methanol, ethanol, etc.) to allow for the application of solubility models. For the example of poly(ethylene oxide), the generic groups tabulated in the *Polymer Handbook* as (non)solvents were replaced by specific substances as follows (highlighted in bold in Table 1):

Table 1. Solvents and Nonsolvents with Generic Compounds and Specific Organic Compounds for Poly(ethylene oxide)

Solvents and Nonsolvents from the Literature[9] (Generic Compounds in Bold)
Solvents: acetonitrile, **alcohols**, benzene, chloroform, cyclohexanone, dimethylformamide, **esters**, water (cold)
Nonsolvents: **aliphatic hydrocarbons**, water (hot), **ethers**, dioxane
Expanded Solvents and Nonsolvents with Specific Solvents[9−11] (Generic Compounds Replaced by Specific Solvents in Bold)
Solvents: acetonitrile, **methanol**, **ethanol**, ***tert*-butyl alcohol**, **methyl isobutyl carbinol**, **diethylene glycol**, **2-ethylhexanol**, **furfuryl alcohol**, **benzyl alcohol**, benzene, chloroform, cyclohexanone, dimethylformamide, **ethyl acetate**, **propyl acetate**, ***tert*-butyl acetate**, **hexyl acetate**, **isoamyl acetate**, water (cold)
Nonsolvents: **hexane**, **heptane**, **pentane**, water (hot), **tetrahydrofuran**, **diethyl ether**, **ethylene glycol dimethyl ether**, **dipropylene glycol methyl ether**, **diethylene glycol monomethyl ether**, dioxane

Table 2. Data Set for the Assessment of the Hildebrand Solubility Model across Different Polymer Classes[9,12−40]

polymer class	polymers
amorphous nonpolar	atactic polypropylene, atactic polystyrene, poly(phenylene oxide), *cis*-polyisoprene, poly(1,3-butadiene), atactic poly(1-butene), atactic poly(cyclohexylethylene), poly(α-methylstyrene), low-mol.-wt. poly(phenylacetylene), atactic poly(cyclohexenylethylene), poly(4-acetoxystyrene), poly(1-hexene)
amorphous polar	poly(vinyl chloride), poly(ether imide), polycarbonate, poly(methyl methacrylate), polyurethane, atactic poly(acrylic acid) , poly(ethyl methacrylate), poly(vinyl methyl ether), poly(isobutyl vinyl ether), poly(*tert*-butyl vinyl ether), polyacetaldehyde, poly(2,6-dimethyl-1,4-phenylene oxide), poly(vinyl acetate), poly(2-chlorobutadiene), poly(4-hydroxystyrene), poly(*n*-propyl methacrylate)
semicrystalline nonpolar	isotactic polypropylene, isotactic polystyrene, poly(methylpentene), high-density polyethylene, poly(phenylene sulfide), polyallene, poly(1,2-butadiene), high-mol.-wt. poly(phenylacetylene), polyacetylene, *cyclo*-poly(methylene) polyisobutene, isotactic poly(cyclohexenylethylene), poly(2-*tert*-butyl-1,3-butadiene), poly(dicyclopentadiene), poly(5,7-dimethyl-1,6-octadiene), poly(1,4-diphenyl-1,3-butadiene), isotactic poly(1-butene), isotactic poly(4-methyl-1-pentene), poly(cyclopentene), poly(acenaphthylene), poly(1,3-cyclohexadiene)
semicrystalline polar	polyacrylonitrile, nylon-6,6, polyethylene terephthalate, poly(oxymethylene), poly(vinyl alcohol), isotactic poly(acrylic acid) , poly(1-methoxybutadiene), poly(2-chlorobutadiene), poly(2-chloromethylbutadiene), poly(ethylene oxide), poly(ε-caprolactone), poly(ε-caprolactam), poly(vinyl methyl ketone), poly(vinyl fluoride), poly(vinylidene chloride), poly(vinyl bromide), poly[bis(methylthio)acetylene], poly(*p*-chlorostyrene), poly(styrenesulfonic acid), poly(methacrylonitrile), poly(vinyl formal), poly(vinyl trifluoroacetate), poly(2-vinylpyridine), poly(propylene oxide), polyurethane

- **alcohols**: methanol, ethanol, *tert*-butyl alcohol, methyl isobutyl carbinol, diethylene glycol, 2-ethylhexanol, furfuryl alcohol, benzyl alcohol
- **esters**: ethyl acetate, propyl acetate, *tert*-butyl acetate, hexyl acetate, isoamyl acetate
- **aliphatic hydrocarbons**: hexane, heptane, pentane
- **ethers**: tetrahydrofuran, diethyl ether, ethylene glycol dimethyl ether, dipropylene glycol methyl ether, diethylene glycol monomethyl ether

All of the generic substances present in this study and their associated specific organic solvents used for the purpose of the assessment of the solubility parameters are listed in the Supporting Information.

Hildebrand and Hansen Solubility Parameters. To assess the solvent prediction capability of the Hildebrand model, a benchmark polymer data set (shown in Table 2) containing 75 polymers classified into four categories, viz., 12 amorphous nonpolar polymers, 17 amorphous polar polymers, 21 semicrystalline nonpolar polymers, and 25 semicrystalline polar polymers was used. Since the Hildebrand solubility parameters were not available for all of the polymers (although the solubility parameters are available for most solvents), the Hildebrand values for the polymers in the data set were predicted using a previously developed Gaussian process regression (GPR) ML model.[8]

To train the machine learning model, 113 polymers were used, and all of them are plotted in Figure 2. The model performance was assessed using a learning curve in the work by Kim et al.[8] However, the final model used for the prediction of the solubility parameter uses all 113 data points to ensure maximum diversity, and therefore, there is no validation set. The root-mean-square error for the model prediction is 0.49 MPa$^{1/2}$, and the model performance plot is shown in Figure 2. Each polymer in this data set has corresponding experimentally determined solvents and nonsolvents that are documented in the *Polymer Handbook* by Brandup et al.[9,12−40]

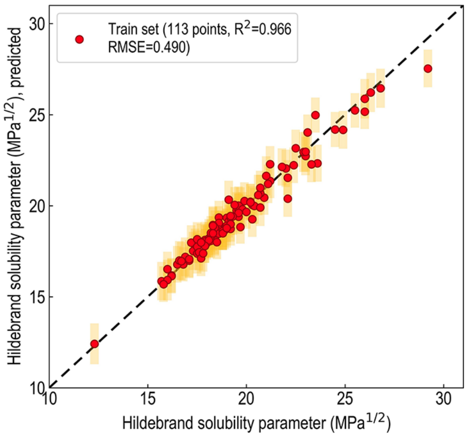


Figure 2. Performance of the Hildebrand solubility machine learning model developed using Gaussian process regression (GPR) for the prediction of unknown polymer Hildebrand solubility values.

The evaluation of the solvent prediction capabilities of the Hansen model was conducted using 25 polar and nonpolar polymers (shown in Table 3). The size of the polymer data set was constrained by the scarcity of data for the Hansen parameter. The Hansen parameters for polymers were collected from the official Hansen parameter website.[41,42] For comparison, the data set was also assessed using the Hildebrand model, where the parameter values were obtained using the ML model described above. Each polymer in this data set has corresponding experimentally determined solvents and nonsolvents that are documented in the *Polymer Handbook* by Brandup et al.[9] The Hildebrand and Hansen parameter values for all of the solvents and nonsolvents were obtained from the literature.[9,42]

Assessment Procedure. To assess the Hildebrand model, the benchmark polymer data set and its associated experimental solvents and nonsolvents (as described above) were evaluated using the miscibility criterion depicted in Figure 1a. Similar Hildebrand parameters indicate miscibility, i.e., the difference between the Hildebrand parameters of a miscible solvent−polymer pair should not exceed ± 2 MPa$^{1/2}$. For nonsolvent−polymer pairs, the difference between the Hildebrand parameters must be greater than ± 2 MPa$^{1/2}$. The (non)solvent prediction accuracy was calculated using this miscibility criterion for each (non)solvent−polymer pair.[6,7]

Likewise, the Hansen model was evaluated using the aforementioned data set and its associated solvents and nonsolvents. The miscibility criteria depicted in Figure 1(b) is used to assess the model where miscible polymer−solvent pairs are within ± 8 MPa$^{1/2}$ and polymer-nonsolvents are greater than ± 8 MPa$^{1/2}$. Each (non)solvent−polymer pair was evaluated using this criterion.[4,41−43]

For every polymer in the Hildebrand and Hansen data sets, the (non)solvent prediction accuracy was calculated as the percentage of (non)solvents correctly predicted by the solubility models. Then, to estimate the performance of these models across the polymer space, the population statistics for each data set was determined using a well-established statistical resampling method called bootstrapping. The bootstrap method is a statistical technique for estimating the mean and standard deviation of a population by averaging

Table 3. Data Set for the Assessment of the Hansen Solubility Model[41,42]

polyethylene, polypropylene, polystyrene, poly(vinyl chloride), polyacrylonitrile, poly(methyl methacrylate), poly(ethyl methacrylate), polycarbonate, polycaprolactone, poly(vinyl acetate), nylon-6,6, poly(ethylene terephthalate), poly(vinyl butyral), poly(vinylidene fluoride), poly(phenylene oxide), polyurethane, polysulfone, poly(ether sulfone), poly(oxymethylene), poly(vinylpyrrolidone), poly(ethylene oxide), poly(propylene oxide), poly(vinyl alcohol), ethylene vinyl alcohol, poly(lactic acid)

estimates from a smaller data set. In this method, larger data sets, representative of the population, are constructed by randomly duplicating entries in the smaller data set. This allows a given sample to be included in the larger data set more than once and is commonly called sampling with replacement. These larger data sets can then be used to calculate the population statistics, namely, the mean and the standard deviation. By this method, larger data sets representative of the polymer population were constructed for both the Hildebrand and Hansen data sets. The larger data sets comprised 1000 samples and were constructed by randomly sampling each smaller original data set with replacement. These data sets were used to assess the (non)solvent prediction accuracy for each polymer, and the associated error bars arise from the bootstrapping process. Although we did not explicitly account for the uncertainty from the ML predictions, the RMSE of the ML model is low (0.49 $\mathrm{MPa}^{1/2}$), and we believe that the bootstrapping process captures the statistical uncertainty that arises from the (non)solvent prediction variability in the data set. Furthermore, we also believe that the prediction trends will remain unchanged given the inherent capability of the Hildebrand parameter to capture only the van der Waals forces for a given system and the lack of data on the Hansen parameter for polymers.

■ RESULTS AND DISCUSSION

Assessment of the Hildebrand Solubility Parameter Across Different Polymer Classes. The performance of the Hildebrand parameter for solvents and nonsolvents for the four distinct classes of polymers is shown in Figure 3. The Hildebrand parameter was originally developed for amorphous nonpolar polymers, and its prediction capability is known to falter for semicrystalline and polar polymers.[7] Here we evaluated its prediction capabilities quantitatively across four different polymer classes: amorphous polar, amorphous nonpolar, semicrystalline polar, and semicrystalline nonpolar. The Hildebrand approach predicts solvents for nonpolar polymers more accurately than for polar polymers. The solvent predictions for amorphous nonpolar and semicrystalline nonpolar polymers reach accuracies of 77% and 72%, respectively. However, the performance deteriorates for polar polymers: 59% for amorphous polar polymers and 57% for semicrystalline polar polymers. At greater than 78%, the parameter performance is uniformly satisfactory for nonsolvent prediction for all polymer classes.

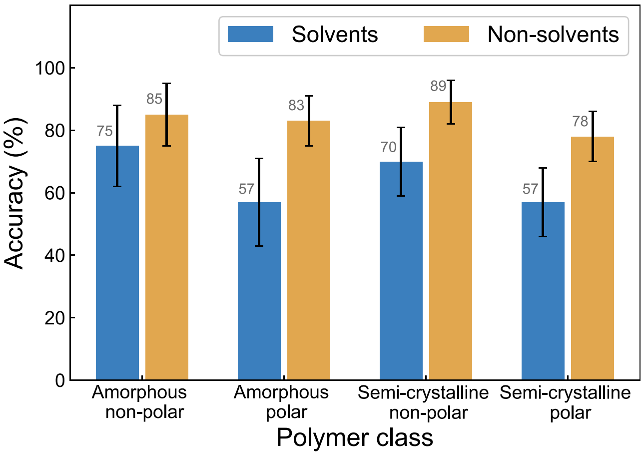


Figure 3. Performance of the Hildebrand parameter for 75 polymers across polymer classes for solvents and nonsolvents.

The performance trend of the parameters for solvents can be explained by the nature of the interactions captured by the Hildebrand parameter and the interactions at play for various classes of polymers. The Hildebrand parameter essentially captures the total cohesive interactions, which include the dispersion forces, dipole−dipole interactions, and hydrogen-bonding interactions for a molecule. For nonpolar polymers, which do not have noteworthy polar or hydrogen-bonding contributions, the total cohesive energy suffices as the primary criterion for solubility. For polar polymers, specific interactions like hydrogen bonding play a crucial role that the Hildebrand parameter, as a single parameter, is unable to explicitly capture. For instance, polycarbonate (PC) and poly(methyl methacrylate) (PMMA) are well-known polar amorphous polymers. Acetone is a solvent for PMMA but is a nonsolvent for PC, and yet the three systems have similar Hildebrand parameters. Acetone is a polar aprotic solvent and therefore does not have hydrogen atoms that can form hydrogen bonds during solvation. Therefore, the PMMA−acetone solubility can be explained by a polymer-specific polar or hydrogen-bonding interaction that is absent in the PC−acetone interaction, which the single-parameter Hildebrand model is incapable of predicting.[1,7,44] Additionally, the solvent and nonsolvent temperatures also play an important role in solubility by altering the free energy of mixing, which the parameter does not consider. For nonsolvents, the Hildebrand parameter has a reasonable level of accuracy since the criterion is based on exclusion.

Despite its disadvantages, the Hildebrand parameter can be used to predict solvents for nonpolar polymers with reasonable accuracy and to predict nonsolvents for all classes of polymers. Additionally, the Hildebrand parameter has an expansive data set for polymers, and we have utilized this to train an ML model that predicts the parameter values for a new polymer or polymers absent from the data set. This development has led to a user-friendly ML-based screening tool to predict solvents and nonsolvents for a queried polymer using the Hildebrand parameter. This tool is implemented at www.polymergenome.org.

Assessment of the Hansen Solubility Parameter and Its Comparison to the Hildebrand Parameter. The performance of the Hansen and Hildebrand solubility parameters for 25 polymers and their associated solvents and nonsolvents is shown in Figure 4. As expected, we find that the average solvent prediction accuracy of the Hansen model (69%) is higher than that of the Hildebrand model (60%). The nonsolvent accuracies of the two methods are equal (76%).

The Hansen parameter was developed to overcome a major inadequacy of the Hildebrand parameter by the inclusion of

DOI: 10.1021/acs.jcim.9b00656
J. Chem. Inf. Model. XXXX, XXX, XXX−XXX

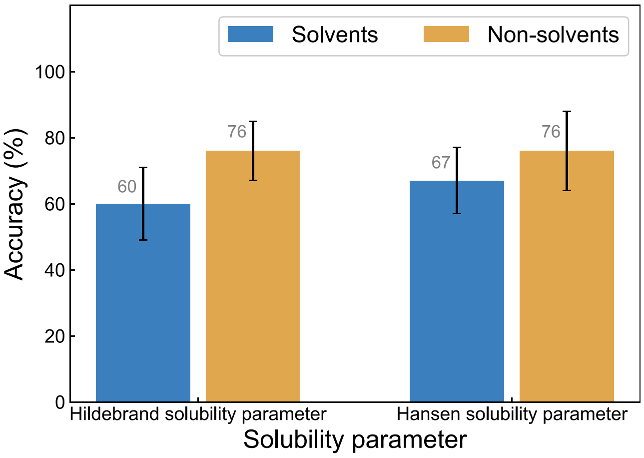


Figure 4. Performance of the Hildebrand and Hansen solubility parameters for 25 polymers for solvents and nonsolvents.

the polar and hydrogen-bonding contributions.[42] However, the difference between the accuracies of the parameters for polymer systems, especially polar polymers, is not striking. We find that the Hildebrand parameter is equivalent to or outperforms the Hansen parameter in solvent predictions for 12 polar polymers, which constitute 48% of the Hansen data set. The reasonable nonsolvent accuracy implies that the parameters can be used interchangeably for this purpose.

The Hansen parameter's lack of significant improvement can be attributed to two reasons. First, the parameter is heavily biased toward its dispersion component, which captures the nonpolar interactions of a molecule. The dispersion component has a multiplier of 2 attached to it, which diminishes the contributions of the polar and hydrogen-bonding parameters. Second, polymer solubility is a complex process involving swelling, diffusion, and solvation processes that are often dependent on the polymer structure and other physical attributes like the solvation temperature and solvent concentration.[1] These parameters are not represented in the Hansen model or the Hildebrand model, and their inclusion could be used to develop a better solubility model.

OUTLOOK

The heuristic nature of the Hildebrand and Hansen models renders them easy to use but results in significant drawbacks and limitations. Polymer solubility is an inherently complex process and depends on a multitude of chemical, morphological, thermodynamic, and kinetic factors. Quantifying such a phenomenon using a limited number of manually fitted parameters is an exceptionally challenging endeavor.[45] For instance, both the Hildebrand and Hansen solubility parameters are completely unable to capture the specific nature of the interaction of water with polymers.[1,41] Another major drawback is the limited availability of the model parameter values for polymers, especially for the Hansen model.[4] Indeed, in some cases conflicting values of the Hansen parameter have been reported for the same polymer.[46] Moreover, for a newly designed polymer, it is difficult to obtain a measurement of the Hildebrand parameter or an estimate of the Hansen solubility parameter. Other solubility models, like the χ parameter, have specific values/parameters for polymer−solvent pairs at given temperatures and concentrations, making it difficult to generalize to unexplored chemical space.[47]

To overcome these drawbacks, the solvent/nonsolvent data could be directly used to train an ML classifier and therefore bypass the requirement of obtaining intermediary solubility parameters. Such an approach is likely to possess significant advantages over the Hildebrand and Hansen criteria because of its ability to learn from a larger chemical space without the requirement of generating empirically derived parameters. Modern ML algorithms like deep neural networks could capture the highly nonlinear multivariate mapping between the characteristics of a polymer and its solubility in a given solvent.

CONCLUSIONS

This study critically examines and establishes a predictive baseline for two well-established solubility models (based on the Hansen and Hildebrand solubility parameters) that are widely utilized to characterize polymer solubility in solvents. This comparative study could be used to make informed decisions when utilizing the models for solvent predictions and could also be used as a baseline for new polymer solubility models. Key findings from this study are summarized below:

- We find that the Hildebrand model has a better solvent prediction accuracy for nonpolar polymers than for polar polymers. The nonsolvent prediction accuracy is uniformly high for all polymer classes. The higher solvent prediction accuracy for nonpolar polymers can be attributed to the accurate representation of van der Waals forces by the Hildebrand parameter. The lower solvent prediction accuracy for polar polymers occurs because polar and hydrogen-bonding contributions are lacking in the single-parameter Hildebrand model.
- We find that the Hildebrand and Hansen models have similar prediction accuracies for solvents and nonsolvents for polymers. Considering that the Hansen model was developed as an improvement of the Hildebrand model, the insignificant difference in the two models' performance can be attributed to the scarcity of available data for the Hansen model and the complexity of polymer solubility, as neither model captures factors like temperature, concentration, or polymer molecular weight.

Traditional solubility parameters provide a simple and powerful gateway to understand polymer solubility by utilizing parameters that attempt to capture forces pertinent to solvation. This is particularly true of the Hildebrand approach, which may be widely used for a large portion of the polymer chemical space (e.g., using ML methods, as has been done at https://www.polymergenome.org). However, the limited number of parameters such models contain are insufficient to capture the full complexity of polymer−solvent interactions. In the future, we aim to bypass the use of traditional solubility-parameter-based models and utilize experimental data as is with numerous potentially relevant features and ML algorithms to determine a unique structure−property mapping of solvent and polymer structures to their miscibility.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jcim.9b00656.

Polymer SMILES strings (XLSX)

Table of broad solvent classes and the associated specific solvents used in this validation study (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: rampi.ramprasad@mse.gatech.edu.

ORCID

Shruti Venkatram: 0000-0003-0306-8222
Chiho Kim: 0000-0002-1814-4980
Rampi Ramprasad: 0000-0003-4630-1565

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We would like to thank Dr. Lihua Chen for her valuable inputs to this work. This work was supported by the Office of Naval Research 417 through Grants N00014-17-1-2656 and N00014-16-1-2580.

REFERENCES

(1) Miller-Chou, B. A.; Koenig, J. L. A Review of Polymer Dissolution. *Prog. Polym. Sci.* **2003**, *28*, 1223−1270.

(2) Srivastava, A.; Nauman, E. Kinetics of Solvent Induced Melting of Semi-crystalline Polymers. *Polym. Mater.: Sci. Eng.* **1993**, 307−308.

(3) Kufner, M.; Kufner, S. *Micro-optics and Lithography*; Vu University Press: Amsterdam, 1997.

(4) Hansen, C. M. The Universality of the Solubility Parameter. *Ind. Eng. Chem. Prod. Res. Dev.* **1969**, *8*, 2−11.

(5) Barton, A. F. Solubility Parameters. *Chem. Rev.* **1975**, *75*, 731−753.

(6) Burke, J. *Solubility Parameters: Theory and Application*; The Book and Paper Group of the American Institute for Conservation, 1984.

(7) Gilbert, M. *Brydson's Plastics Materials*, 8th ed.; Elsevier, 2017; pp 75−102.

(8) Kim, C.; Chandrasekaran, A.; Huan, T. D.; Das, D.; Ramprasad, R. Polymer Genome: A Data-Powered Polymer Informatics Platform for Property Predictions. *J. Phys. Chem. C* **2018**, *122*, 17575−17585.

(9) Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R. *Polymer Handbook*; Wiley: New York, 1989; Vol. 7.

(10) Murov, S. Properties of Solvents Used in Organic Chemistry. http://murov.info/orgsolvents.htm (accessed Sept 18, 2019).

(11) Cartwright, H. DOSE. The Dictionary of Substances and Their Effects, Edited by Sharat Gangolli. The Royal Society of Chemistry, Cambridge, England, 1999. Seven volumes with access to online electronic chemical safety database. 1295 (set of hardcopy volumes plus site-wide licence to electroic database). ISBN 0−85−85404−803−0. *Chem. Educ.* **2000**, *5*, 98−99.

(12) Rennie, A. *Mechanical Properties and Testing of Polymers*; Springer, 1999; pp 23−24.

(13) Ehrenstein, G. W. *Polymeric Materials: Structure, Properties, Applications*; Carl Hanser Verlag GmbH Co KG, 2012.

(14) Tadokoro, H.; Takahashi, Y.; Otsuka, S.; Mori, K.; Imaizumi, F. Structure of Crystalline Polyallene. *J. Polym. Sci., Part B: Polym. Lett.* **1965**, *3*, 697−701.

(15) Mariani, A.; Fiori, S.; Chekanov, Y.; Pojman, J. A. Frontal Ring-opening Metathesis Polymerization of Dicyclopentadiene. *Macromolecules* **2001**, *34*, 6539−6541.

(16) Natta, G.; Corradini, P. The Structure of Crystalline 1, 2-polybutadiene and of Other Syndyotactic Polymers. *Rubber Chem. Technol.* **1956**, *29*, 1458−1471.

(17) Marconi, W.; Mazzei, A.; Cucinella, S.; Cesari, M. Stereo-specific Polymerization of 2-substituted-1, 3-butadienes. I. Crystalline Polymers of 2-tert-butyl-1, 3-butadiene. *J. Polym. Sci., Part A: Gen. Pap.* **1964**, *2*, 4261−4270.

(18) Kargin, V.; Kabanov, V.; Mirlina, S. Y.; Vlasov, A. Isotactic Polyacrylic acid and its Salts. *Polym. Sci. U.S.S.R.* **1962**, *3*, 28−34.

(19) Vrentas, J.; Duda, J.; Hou, A.-C. Anomalous Sorption in Poly (ethyl methacrylate). *J. Appl. Polym. Sci.* **1984**, *29*, 399−406.

(20) Akaishi, T.; Miyasaka, K.; Ishikawa, K.; Shirakawa, H.; Ikeda, S. Crystallinity of Bulk Polyacetylene. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 745−750.

(21) Maynard, J.; Mochel, W. The Structure of Neoprene. VI. Crystallization. *Rubber Chem. Technol.* **1954**, *27*, 634−647.

(22) Hasegawa, R.; Takahashi, Y.; Chatani, Y.; Tadokoro, H. Crystal Structures of Three Crystalline forms of Poly (vinylidene fluoride). *Polym. J.* **1972**, *3*, 600.

(23) Yang, W.; Tabata, M.; Kobayashi, S.; Yokota, K.; Shimizu, A. Synthesis of Ultra-high-molecular-weight Aromatic Polyacetylenes with [Rh (norbornadiene) Cl] 2-triethylamine and Solvent-induced Crystallization of the Obtained Amorphous Polyacetylenes. *Polym. J.* **1991**, *23*, 1135.

(24) Malanga, M.; Vogl, O. Head to Head Polymers. XXV: Properties of Head to Head Polyisobutylene. *Polym. Eng. Sci.* **1983**, *23*, 597−600.

(25) Hayano, S.; Takeyama, Y.; Tsunogae, Y.; Igarashi, I. Hydrogenated Ring-Opened Poly (e ndo-dicyclopentadiene) s Made via Stereoselective ROMP Catalyzed by Tungsten Complexes: Crystalline Tactic Polymers and Amorphous Atactic Polymer. *Macromolecules* **2006**, *39*, 4663−4670.

(26) Glaser, R.; Dendi, L. R.; Knotts, N.; Barnes, C. L. Ab Initio and Crystal Structures of (E, E)-1, 4-Diphenylbutadiene: A New Type of Arene- Arene Double T-Contact and an Interesting Interlayer Cooperation Involving Diastereoisomeric Contacts. *Cryst. Growth Des.* **2003**, *3*, 291−300.

(27) Erdem, H. B. The Crystallization Behaviour of Isotactic Polybutene-1. Ph.D. Thesis, Bilkent University, Ankara, Turkey, 2002.

(28) Marconi, W.; Cesca, S.; Fortuna, G. D. Crystalline Poly-4-vinylcyclohexene-1. *J. Polym. Sci., Part B: Polym. Lett.* **1964**, *2*, 301−305.

(29) Collins, S.; Kelly, W. M. The Microstructure of Poly (cyclopentene) Produced by Polymerization of Cyclopentene with Homogeneous Ziegler-Natta Catalysts. *Macromolecules* **1992**, *25*, 233−237.

(30) Kuo, S.-W.; Huang, W.-J.; Huang, C.-F.; Chan, S.-C.; Chang, F.-C. Miscibility, Specific Interactions, and Spherulite Growth Rates of Binary Poly (acetoxystyrene)/Poly (ethylene oxide) Blends. *Macromolecules* **2004**, *37*, 4164−4173.

(31) Lin, F.; Stivala, S.; Biesenberger, J. Physical-chemical Studies of Polyhexene-1. Some Dilute Solution Properties. *J. Appl. Polym. Sci.* **1973**, *17*, 1073−1090.

(32) Wang, J.; Cheung, M. K.; Mi, Y. Miscibility and Morphology in Crystalline/Amorphous Blends of Poly (caprolactone)/poly (4-vinylphenol) as Studied by DSC, FTIR, and 13C Solid State NMR. *Polymer* **2002**, *43*, 1357−1364.

(33) Hart, R.; Janssen, R. Structure of Poly (styrenesulfonic acid) Prepared by Sulfonation of Polystyrene. *Makromol. Chem.* **1961**, *43*, 242−244.

(34) Schatschneider, B.; Mathers, R. T.; Gee, R. H.; Wonderling, N. M. Exploration of the Transition Temperatures and Crystal Structure of Highly Crystalline Poly (1, 3-cyclohexadiene): An Experimental and Computational Investigation. *Polymer* **2014**, *55*, 6085−6090.

(35) Reichel, B.; Marvel, C.; Greenley, R. Transannular Polymerization of 1, 5-cyclooctadiene. *J. Polym. Sci., Part A: Gen. Pap.* **1963**, *1*, 2935−2943.

(36) Wall, L. A.; Fetters, L. J.; Straus, S. Polymerization and Pyrolysis of Poly-1, 2-dihydronaphthalene. *J. Polym. Sci., Part B: Polym. Lett.* **1967**, *5*, 721−733.

(37) Beiner, M.; Schröter, K.; Hempel, E.; Reissig, S.; Donth, E. Multiple Glass Transition and Nanophase Separation in Poly (n-alkyl methacrylate) Homopolymers. *Macromolecules* **1999**, *32*, 6278−6282.

(38) Joh, Y.; Kotake, Y.; Yoshihara, T.; Ide, F.; Nakatsuka, K. Stereospecific Polymerization of Methacrylonitrile. I. Characterization of Crystalline Polymethacrylonitrile. *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5*, 593−603.

(39) Bohn, C.; Schaefgen, J.; Statton, W. Laterally Ordered Polymers: Polyacrylonitrile and Poly (vinyl trifluoroacetate). *J. Polym. Sci.* **1961**, *55*, 531−549.

DOI: 10.1021/acs.jcim.9b00656
J. Chem. Inf. Model. XXXX, XXX, XXX−XXX

(40) Burnett, G.; Ross, F.; Hay, J. Crystalline Poly (vinyl bromide). *J. Polym. Sci., Part B: Polym. Lett.* **1967**, *5*, 271−276.

(41) Hansen, C. Hansen Solubility Parameters - Official Website. www.hansen-solubility.com (accessed Sept 18, 2019).

(42) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press, 2002.

(43) Lv, H.-l.; Wang, B.-g.; Kong, Y. Prediction of Solvent Diffusivities in Amorphous Polymers by Free-volume Theory: Group Contribution and PALS methods. *Polym. J.* **2009**, *41*, 1049.

(44) Hultin, D. P. A Guide to Solvents and Reagents in Introductory Organic Chemistry for students in 2.222. https://home.cc.umanitoba.ca/~hultin/chem2220/Support/solvents_and_reagents.pdf (accessed Sept 18, 2019).

(45) Sanchez-Lengeling, B.; Roch, L. M.; Perea, J. D.; Langner, S.; Brabec, C. J.; Aspuru-Guzik, A. A Bayesian Approach to Predict Solubility Parameters. *Adv. Theory Simul.* **2019**, *2*, 1800069.

(46) Vayer, M.; Vital, A.; Sinturel, C. New Insights into Polymer-Solvent Affinity in Thin Films. *Eur. Polym. J.* **2017**, *93*, 132−139.

(47) Orwoll, R. A.; Arnold, P. A. *Physical Properties of Polymers Handbook*; Springer, 2007; pp 233−257.

DOI: 10.1021/acs.jcim.9b00656