

PERSPECTIVE

The Swollen Polymer Network Model of Hydrogel Design: Opportunities in Limitations

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ABSTRACT

Hydrogels are water-swollen polymer networks (SPNs) with applications as biomaterials, adhesives, and signal transducers. The SPN model coordinates fundamental theories to predict hydrogel physical properties of swelling, stiffness, and solute transport based on the hydrogel's structure. Having shown that the SPN model is effective for decoupling stiffness and solute transport in multi-arm poly(ethylene glycol) hydrogels, the next objectives are to further refine the fundamental accuracy of the SPN model, its breadth of applicability to different hydrogel systems, and the properties that can be accurately predicted through the model. To support a broader effort of hydrogel structure–property modeling, this article discusses limitations and opportunities for the SPN model and shares an outlook for model-based hydrogel design.

1 | Rational, Modular Design of Hydrogels

Hydrogels are water-swollen polymer networks (SPNs) [1]. They are used primarily in biomedical applications, such as drug delivery [2–6], wound healing [7–9], tissue engineering [10–13], and disease modeling [14–16], although they have additional applications in agriculture, environmental engineering, and hygiene [17, 18]. This broad application space drives the development of diverse hydrogel formulations, each with unique physical and chemical properties. As the hydrogel design space expands, advances in fundamental hydrogel modeling are needed to coordinate insight across the field and optimize the design of hydrogels toward application-specific desirable properties [19].

Fundamental hydrogel modeling connects the structure and chemical composition of hydrogels to their physical and chemical properties [1, 19, 20]. Effective modeling enables accurate prediction of hydrogel properties from the hydrogel's network structure and chemical composition. Predictable hydrogel properties accelerate the design process, leading to application-ready hydrogels with reduced trial-and-error in their development. Furthermore, the structure-based prediction of hydrogel

properties supports modular design, wherein components of a hydrogel can be exchanged to alter specific properties without affecting other desirable properties [19–21]. In situations where changing structural parameters affects multiple properties, such as polymer concentration affecting both swelling and stiffness, fundamental modeling can identify alternative combinations of structural parameters that decouple property changes, yielding a desirable final combination of properties [20]. In this way, fundamental hydrogel design allows systematic multi-property optimization that would not be feasible without a predictable, fundamental, and mathematically defined model for hydrogel structure–property relationships.

Hydrogel design modeling emerged from the modeling of polymer network swelling and stiffness, pioneered by Flory and colleagues [22, 23]. Much of their approach is conserved in current swelling and stiffness modeling, with modifications to address differences between water and organic solvents and the formation of hydrogels from dilute aqueous polymer solutions [1]. Because solute transport is a common priority in aqueous solutions and biomedical applications, models of specific solutes moving through hydrogels were developed and subsequently

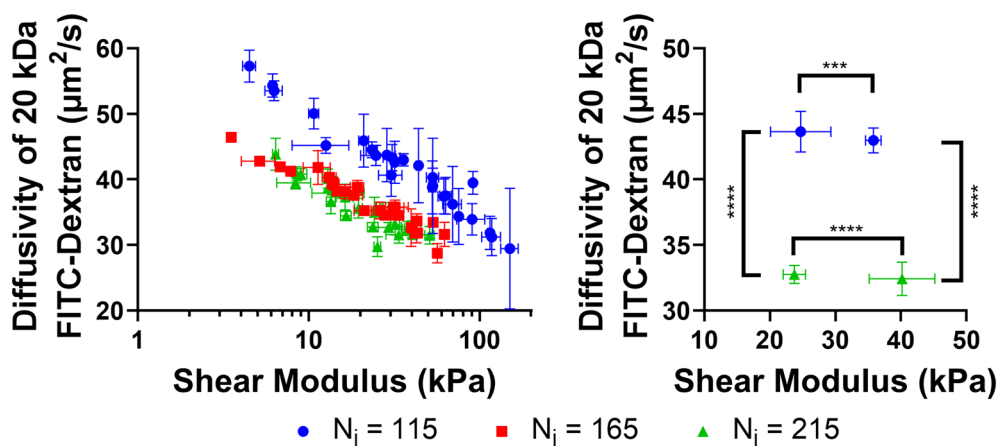


FIGURE 1 | Four structural parameter-based designs yielded decoupled stiffness and solute transport in multi-arm PEG hydrogel formulations. Initially, 73 structurally distinct hydrogel formulations were characterized, and a set of four formulations was proven to be statistically structurally decoupled with orthogonal control of shear modulus and solute diffusivity. Figures adapted from Richbourg and Peppas [1] with permission from Elsevier.

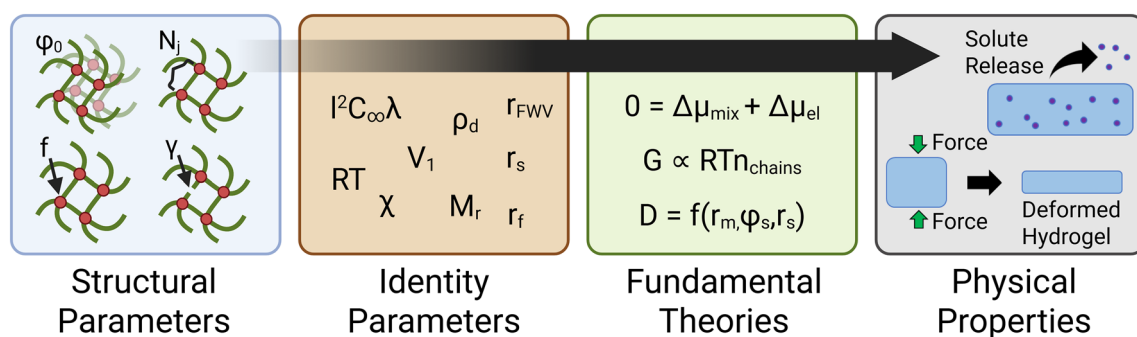


FIGURE 2 | The swollen polymer network (SPN) model connects hydrogel structure to properties via structural parameters, identity parameters, and fundamental theories. This figure is a conceptual schematic of the use of parameters and theories to predict hydrogel properties, including the diffusion of solutes through hydrogels (solute release) and force-deformation relationships.

refined [24–27]. The development of the current SPN model from the fundamental theories, including Flory-Rehner equilibrium swelling theory and rubberlike elasticity theory, is described in detail in our previous publication [1], including the underlying principles of thermodynamics, free energy, and chemical potential balancing. Readers are highly encouraged to review that publication for further details, as recounting them here is beyond the scope of this forward-looking article. A more accessible introduction to these concepts is provided on our tutorial website, HydrogelDesign.org.

Whereas prior theories and models primarily aimed to more accurately describe structure–property relationships within hydrogels, the recently proposed SPN model reorganizes structure–property-relating models into a coordinated, predictive tool [1, 19]. With the SPN model, structural parameters, which are defined by hydrogel synthesis conditions, predict a hydrogel formulation's physical properties, facilitating a priori hydrogel design. The utility of this structure-driven design approach was demonstrated by decoupling stiffness and solute transport in multi-arm poly(ethylene glycol) (PEG) hydrogels by simultaneously varying four structural parameters (Figure 1) [20]. Complementary studies in poly(vinyl alcohol) (PVA) hydrogels did not facilitate the same extent of structural control over junction functionality and the frequency of chain-end defects but

demonstrated the applicability of the SPN model beyond a single polymer system [28, 29].

By addressing the current state of fundamental modeling for modular hydrogel design, this article aims to make advanced, application-specific hydrogel design accessible for a broad scientific audience. First, the article describes the SPN model in both conceptual and mathematical terms that enable the reader to critically assess its utility, limitations, and opportunities for further development. It then discusses other well-established models related to fundamental hydrogel design with a perspective toward future coordination with the SPN model. Next, it presents the three major use cases of fundamental hydrogel design modeling (forward, sideways, and backward), addressing their advantages and drawbacks. The article ends with a comment on the importance of robust hydrogel data management and sharing.

2 | The SPN Model

The SPN model is an ongoing effort to refine fundamental hydrogel design modeling. The SPN model posits that four universal structural parameters and a set of material identity parameters predict the swelling, stiffness, and solute transport properties of

a hydrogel (Figure 2) [1, 19, 30]. The four structural parameters are the initial polymer volume fraction (ϕ_0), the degree of polymerization between junctions (N_j), the junction functionality (f), and the frequency of chain-end defects (γ). These four parameters can be defined for any hydrogel, often as controllable variables for hydrogel synthesis. The material identity parameters are established parameters specific to the polymer, solution, and any relevant solutes [1]. Each material identity parameter is independently verifiable. The specific physical properties predicted by the SPN model are the equilibrium-swollen polymer volume fraction (ϕ_s), the shear modulus of the equilibrium-swollen hydrogel (G), and the diffusion coefficient of a specific solute within the hydrogel (D). The following equations describe the current mathematical form of the SPN model [20]

$$\phi_s^{-\frac{1}{3}} [\ln(1 - \phi_s) + \phi_s + \chi \phi_s^2] = -1 \left(1 - \frac{2}{f}\right) (1 - \gamma) \frac{V_1 \rho_d}{M_r N_j} \phi_0^{\frac{2}{3}} \quad (1)$$

$$G = RT \left(1 - \frac{2}{f}\right) (1 - \gamma) \frac{\rho_d}{M_r N_j} \phi_0^{\frac{2}{3}} \phi_s^{\frac{1}{3}} \quad (2)$$

$$\xi = \phi_s^{-\frac{1}{3}} \left[\left(1 - \frac{2}{f}\right) \bar{l}^2 C_\infty \lambda N_j \right]^{\frac{1}{2}} \quad (3)$$

$$r_m = \begin{cases} \frac{\sqrt{6}}{3} \xi & f=4 \\ \frac{1}{2} \xi & f=6 \\ \frac{\sqrt{2}}{4} \xi & f=8 \end{cases} \quad (4)$$

$$\frac{D}{D_0} = \operatorname{erf} \left(\frac{r_{FWV}}{r_s} \right) \exp \left[-1 \left(\frac{r_s}{r_{FWV}} \right)^3 \left(\frac{\phi_s}{1 - \phi_s} \right) \right] + \operatorname{erfc} \left(\frac{r_{FWV}}{r_s} \right) \exp \left[-\frac{\pi}{4} \left(\frac{r_s + r_f}{r_m} \right)^2 \right] \quad (5)$$

Equation (1) describes the swollen polymer volume fraction as a function of hydrogel structure. Equation (2) describes the shear modulus as a function of hydrogel structure and the swollen polymer volume fraction. Equations (3–5) are used in series to describe the hydrogel mesh size (ξ), mesh radius (r_m), and the diffusion coefficient of a solute within the hydrogel, respectively. In these equations, the identity parameters used are the polymer-solvent interaction parameter (χ), the molar volume of water (V_1), the dry density of the polymer (ρ_d), the molecular weight of the repeating polymer unit (M_r), the ideal gas constant (R), the absolute temperature (T), the average bond length in the polymer chain ($\bar{l}$), the Flory characteristic ratio (C_∞), the number of backbone bonds per repeating unit (λ), the diffusion coefficient of the solute in solution (D_0), the free volume radius of water (r_{FWV}), the radius of the solute (r_s), and the fiber radius of the polymer (r_f) [1].

An important result of Equations (1) and (2) in the SPN model is the invariant relationship between swelling and stiffness. For a hydrogel in the equilibrium swollen state that perfectly follows the SPN-modeled relationships, any shear modulus

corresponds to a single swollen polymer volume fraction, despite the multiple network structures that may yield those properties. In other words, unlike the established capability to decouple stiffness and solute transport, the model does not indicate a way to decouple stiffness at equilibrium swelling and the extent of swelling. However, to support a priori prediction of both stiffness and equilibrium swelling, Equations (1) and (2) are presented as functions of the structural parameters, and equilibrium swelling must be calculated first to predict the shear modulus from structural parameters. This relationship does not diminish the four structural parameters as independent influences from each other on stiffness, swelling, and solute transport, but it suggests further potential avenues of research into how to decouple stiffness and swelling at equilibrium.

The SPN model is based on a fundamental modeling perspective that aims to maintain self-consistency while progressing toward further model improvement. Because a model can be quantitatively accurate despite incorrect underlying concepts and assumptions, accuracy to an experimental dataset is not the singular determinant of model quality. Therefore, improvements to the SPN are developed based on validating fundamental structure–property relationships and broadly evaluating whether those relationships persist or predictably change when other input parameters or non-quantitative factors are adjusted [20, 28–32]. With this perspective, establishing accurate structure–property trends is more important for the SPN model than improving the R^2 value of a fit to a dataset.

The emphasis on defined, specific structure–property relationships and a fundamental theoretical framework sets the SPN model up for rigorous hypothesis testing and ongoing improvement. The equations in the SPN model are the results of an ongoing process that combines and distills important relationships. Although this process is more labor-intensive than fitting raw data via a machine learning algorithm, it provides a testable foundation for all hydrogel design and yields interpretable rationales for observed relationships. To ensure the continuing relevance of this fundamentals-first approach amid the accelerating expansion of hydrogel formulations, creative, rigorous, and well-informed hypothesis-driven experimentation is needed to further refine the SPN model. This article aims to facilitate further development by highlighting the most promising and challenging opportunities for SPN model refinement.

3 | Critical Limitations of the SPN Model

Despite its fundamental basis and rigorous development, the SPN model retains several well-defined limitations in its modeling approach that restrict its accuracy and/or applicability to different systems. The most relevant and challenging limitations are briefly described here (Figure 3), although an exhaustive list of model limitations is beyond the scope of this article. Currently, these limitations mean that the SPN model is most applicable to simple, well-defined hydrogels such as the model multi-arm PEG hydrogels presented in Figure 1. However, by overcoming the limitations discussed here and other more advanced limitations, it is plausible that the SPN will eventually become applicable to all types of hydrogels, including composite, biopolymer, polyelectrolyte, and dynamically crosslinked hydrogels. These

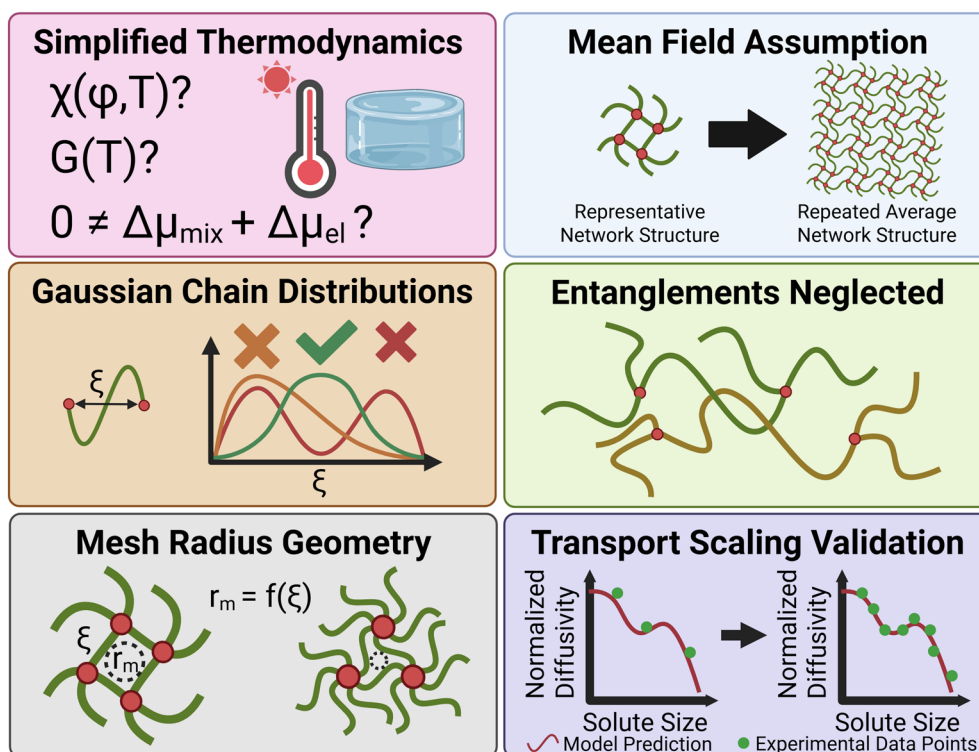


FIGURE 3 | Key limiting assumptions in the SPN model.

six limitations are discussed as critical obstacles to developing a broader and more accurate fundamental understanding of how hydrogel structure informs properties.

The SPN model as it is presented in Equations (1–5) hides several thermodynamic assumptions associated with equilibrium swelling, statistical chain mechanics, and rubberlike elasticity theories. Whereas these assumptions are addressed in more detail elsewhere [1], it is worthwhile to briefly highlight some as points of potential development or contention. First is the context-dependence of the polymer-solvent interaction parameter. Although the SPN model uses the polymer-solvent interaction parameter (χ) as an invariant identity parameter, it is sensitive to both polymer volume fraction and temperature [20, 33]. Indeed, our own swelling results suggest that a polymer volume fraction dependence of the interaction parameter would improve prediction accuracy compared to the static value for PEG hydrogels [20]. Furthermore, the unperturbed dimensions of polymer chains are sensitive to temperature, which is not addressed in the mesh size calculation [34, 35]. It is implied in the derivation of the SPN model that temperature sensitivity is neutralized by evaluating characteristics in the same thermal state as the reference values and that temperature is not changed substantially during swelling [1], but these are practically limiting assumptions. Additionally, there may be cases wherein the additivity of elastic and mixing chemical potentials is fundamentally challenged, either through nonindependence or substantial contributions of additional chemical potential terms [1, 36, 37]. Temperature and thermodynamic non-idealities should be explicitly reintroduced to the SPN model to evaluate their effects on hydrogel properties.

The mean-field assumption simplifies the polymer network structure into repeating average voxels with consistent properties

for each voxel. This approach greatly simplifies the molecular complexity of the network and helps to parse it into standardized parameters, but it fails to capture the characteristics of materials that have heterogeneities larger than the mean-field unit voxel. Hydrogels with multiscale heterogeneities, such as crystallized regions, have useful characteristics that cannot be accurately represented within the SPN model [38]. Because the mean-field assumption is central to the SPN model, developing an alternative approach would require a complete reevaluation of all model concepts and mathematical implementations and would introduce layers of complexity that may provide no additional benefit for hydrogels that already fit the mean-field assumption.

The Gaussian chain distribution assumption requires that all mesh sizes in the network form a Gaussian distribution instead of bimodal or otherwise non-Gaussian distributions. The resulting average degree of polymerization between junctions and mesh size are therefore accurate representations of the network chains. For flexible polymers without higher-order interactions (such as the regular hydrogen bonding into a helical structure found in DNA), the Gaussian distribution further justifies the treatment of polymer chains in the network as entropic springs, which is critical for the SPN model. Some efforts at addressing non-Gaussian chain distributions have been attempted but have not been effectively incorporated into the SPN model or validated [39]. Hydrogels with bimodal chain lengths and otherwise non-Gaussian distributions likely provide unique opportunities for manipulating fatigue characteristics and nonlinear profiles for permissible solute sizes and therefore warrant further investigation and accurate modeling.

The SPN model neglects any effects associated with polymer entanglements in the network. This approach is partially justified

by the phantom-like network deformation model, the relatively dilute polymer concentrations in hydrogels, and the condition that most hydrogels are synthesized in aqueous solution instead of as a polymer melt [1]. Many gels are formulated and used at such low polymer concentrations that the effects of entanglements on network properties are negligible. However, especially interesting properties emerge when many entanglements are intentionally introduced to water-SPNs [40]. Higher polymer concentrations and kneading of high-polymer-concentration gel precursors increase the rate of entanglements within a network and their effects on hydrogel properties [41]. A robust conceptual and mathematical framework for how entanglements would affect hydrogel structure–property modeling has not been developed, although substantial steps have been taken in terms of slipping crosslink models [42] and quantification of modifications to hydrogel properties resulting from kneading the polymer network [41].

The mesh radius term (r_m) that Richbourg et al. proposed and validated with solute transport studies in multi-arm PEG hydrogels improves the model predictions of large solute transport within hydrogels, but it introduces new limitations to the SPN model's applicability [20, 30, 31]. The relationship between mesh size and mesh radius is only defined for junction functionalities of 4, 6, and 8 [30]. Some practical softening of the rigid lattice structures used to represent four-, six-, and eight-arm networks is needed to evaluate how mesh radius and mesh size are related in a broader set of hydrogel formulations. An imperfect intermediate solution would be to use the mesh size in place of the mesh radius when junction functionalities are expected to be much higher than 8, although the geometric effect underpinning the mesh radius concept suggests that mesh radius would be a small fraction of mesh size at high junction functionalities and that forming such high-functionality junctions would be unlikely.

Beyond the mesh radius concept, mesh transport is the least developed of the three underlying theories in the SPN. Because of the complexities added by introducing a diffusing solute to the hydrogel, both conceptually and experimentally, modeling solute diffusion within hydrogels has not converged on a reliable universal approach. Some shortcomings are immediately evident within the SPN model. First, the scaling within Equation (3) references the dry state for unperturbed polymer dimensions instead of the initial state of the polymer in solution, like the rubberlike elasticity relation. This can be remedied with an initial polymer volume fraction term but should be cross-evaluated conceptually and experimentally. The characteristic ratio for PEG was determined in water, suggesting that the pre-gel solution is an appropriate reference state for mesh size [23]. Another scaling issue emerges from the nonmonotonic response of normalized diffusivity to solute radius resulting from the error function weighting in the multiscale diffusion model (Equation 5). Specifically, Axpe et al. justified the model through a dataset containing only three solute sizes [27], which is insufficient information to validate a nonmonotonic relationship. The weighting function presents a powerful approach for scaling solute transport in hydrogels, but a robust experimental analysis with multiple solute sizes distributed throughout the nonmonotonic region is needed to further refine modeling of solute transport, proving or disproving the predicted nonmonotonicity

before further addressing the plausibility of other transport model components and alternatives.

4 | Other Hydrogel Modeling Approaches

Incorporating insights from other hydrogel modeling approaches will enhance the SPN model (Figure 4a). There are practical and technical hurdles to doing so, such as resolving related assumptions and downstream effects on associated modeling components. For example, incorporating the Real Elastic Network Theory (RENT) [44] into the SPN model will affect both the rubberlike elasticity component and the dependent equilibrium swelling component.

RENT addresses how loop defects in a network affect the overall elasticity of the material [44–49]. Initially, RENT addressed isolated primary loop defects wherein a single network junction is rendered elastically ineffective because it is only connected to the overall network via a single chain [44]. This modeled relationship was complemented by the molecular simulation-based observation that the frequency of these primary loops is predictive of a network's frequency of secondary and tertiary loops [45]. Subsequent developments increase the fundamental accuracy of the defect-sensitive modification to hydrogel elasticity modeling, including addressing the contributions of secondary and tertiary loops [44], accounting for the nonlinear effects of increasing junction functionality [46], experimentally validating the relationship between primary and secondary loop frequencies [47], accounting for the influence of third- and fourth-order loops and prestrain applied to the network [48], and finally overcoming the “ideal loop gas” assumption of isolated loops having independent, additive effects on overall elasticity [49]. These studies develop precise mathematical treatments for loop defect structures within networks that increase the accuracy of modulus modeling to an exceptional degree. This mathematical approach would substantially improve the relatively simplistic modeling of the effect of the frequency of chain-end defects within the SPN model. The apparent limitation of RENT for broad application is the need to measure or predict the frequency of primary loops in the network, which is addressed in their work by designing specifically degradable hydrogels and using mass spectrometry to quantify primary and secondary loops [44, 47]. Like the SPN model, this approach also does not directly address the role of entanglements, making it primarily applicable to hydrogels synthesized in dilute aqueous solutions. Finally, the mathematical modifications necessary to implement RENT within the SPN may be unwieldy and therefore may be most relevant in situations where a known high fraction of loops are present and/or highly accurate elasticity modeling is especially important.

The Lake–Thomas model presents a molecular rationale for the fatigue and fracture characteristics of a polymer network [50]. Specifically, the Lake–Thomas model connects the force of bulk material fracture to the force needed to break a single polymer chain at the site of crack propagation. In hydrogels, Equation (6) has been proposed as a mathematical form of the Lake–Thomas model [50]. In Equation (6), Γ_0 is the cyclic-strain fatigue threshold, a specific form of toughness with units of energy per unit area. In a cyclic stretching experiment

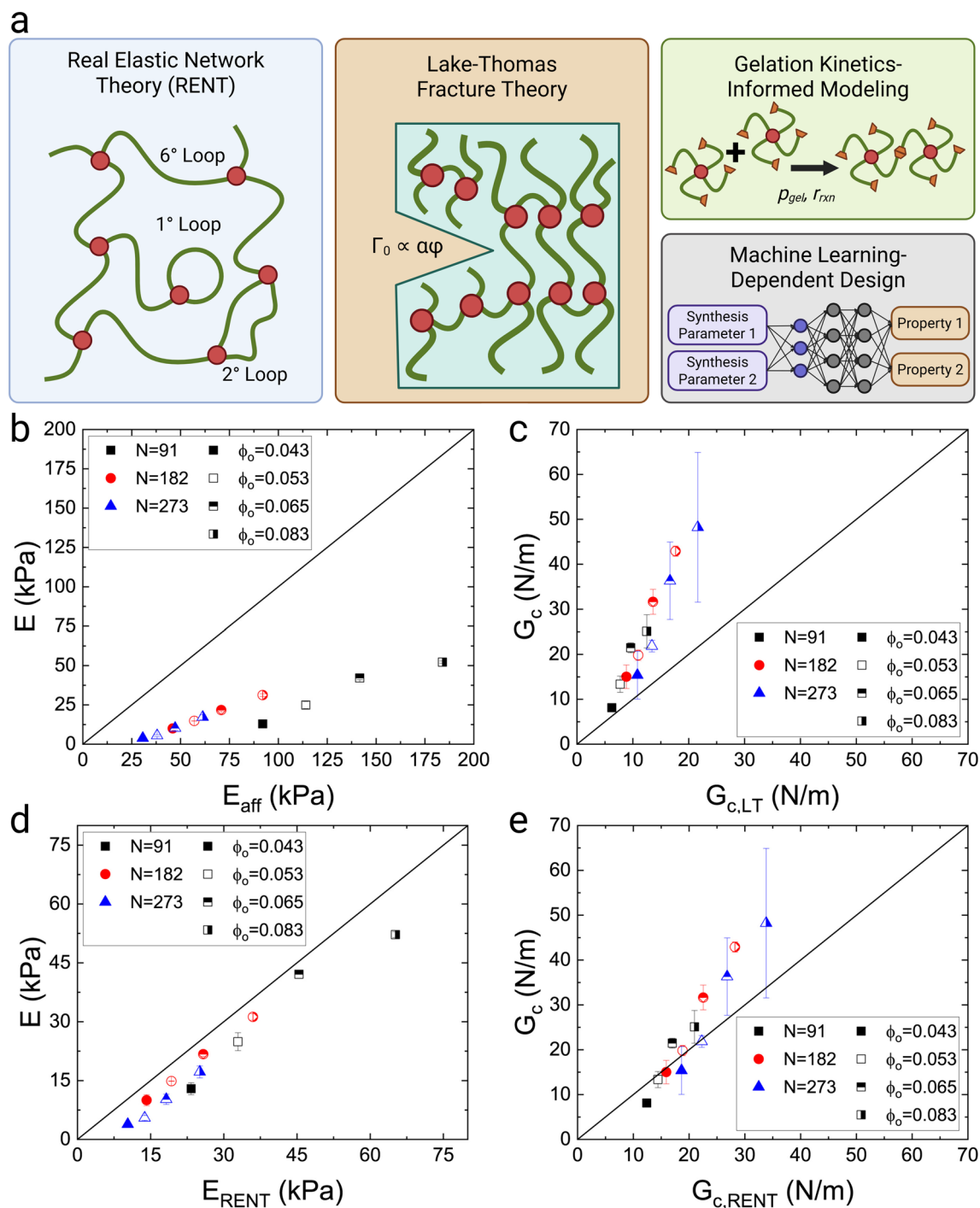


FIGURE 4 | Alternative hydrogel modeling approaches that may complement and refine the SPN model (a). Refining the Lake-Thomas model using RENT improved predictions of both the Young's modulus (d) and the fracture energy (e) compared to prior models (b, c) for structurally varied tetrafunctional PEG hydrogels. N is the degree of polymerization between junctions and ϕ_0 is the initial polymer volume fraction. Figure adapted from Barney et al. [43] with permission from the USA National Academy of Sciences.

with a precut crack, the crack does not grow when the amplitude of the energy release rate is below the threshold. α is an arbitrary prefactor near unity, l_m is the length of the monomer, J is the single carbon-carbon bond energy, and V is the volume of the monomer unit. Aside from the undetermined prefactor, Equation (6) suggests that a hydrogel's cyclic-strain fatigue threshold is fully defined by the network structure and is compatible with the SPN model. Some updates can be immediately

applied to this equation from the SPN model, such as the phantom deformation and weighted-average corrective components of the mesh size equation for different monomers [1]. In monomers like PEG, which do not have a simple carbon-carbon backbone, it is possible that chain breaks may occur at other bond types (e.g., carbon-oxygen), but since the carbon-carbon bond is weaker than the carbon-oxygen bond, this effect may be negligible. It is also important to note that under

extended or cyclic deformation, the force applied to the network will shift the equilibrium from the swollen state, and the changes to polymer entropy under the extreme deformations necessary to produce chain breakage may also disrupt the underlying assumptions related to the polymer chains being in an entropic spring state. For context, the rubberlike elasticity theory is only considered applicable for small deformations of less than 20% change in one dimension [28]. These considerations from the SPN model approach are complemented by a discussion of the limitations of the Lake–Thomas model from the fatigue and toughness modeling perspective [51]. Critically, recent investigations have further refined the Lake–Thomas model to account for loop defects in PEG hydrogels by incorporating RENT, refining estimates of both the Young’s modulus and fracture energy [43]. This study rationalized the α prefactor via the junction functionality-dependence of RENT, which aligns with the phantom deformation correction used in the SPN model (Figure 4b–e). Modeling of how chain breakage affects subsequent force distribution via “loop-opening” also improves model–experiment accuracy for PEG gels and suggests further structure–property insight [52]. The Lake–Thomas model holds potential for extending the utility of the SPN model to cases of fatigue and fracture, but thorough experimental validation, coordination of mechanistic concepts within and beyond the current SPN model, and accounting for high deformation effects are needed.

$$\Gamma_0 = \alpha \varphi_s^{\frac{2}{3}} \varphi_0^{\frac{1}{3}} l_m \sqrt{N_j} \left(\frac{J}{V} \right) \quad (6)$$

Gelation kinetics modeling is an interesting complement to thermodynamics-based SPN modeling. Whereas SPN modeling is state-based and assumes high-fidelity, thorough gelation to relate structure to properties, gelation kinetics and percolation theory analysis aim to evaluate local spatial and temporal contributions during the gelation process to network topology, integrity, and deviations from ideal behavior [53–57]. Although it is difficult to reconcile the two approaches, RENT appears to draw insight from both gelation kinetics and state-based hydrogel modeling, potentially paving a path toward a more universal perspective. For now, it is important to consider that gelation kinetics and percolation theory may have answers where SPN modeling falls short.

Molecular simulation, design of experiments analysis, artificial intelligence (AI), and coarse-grained models each provide alternatives to fundamental modeling for predictive design of hydrogel properties [58–60]. These approaches may be more effective than fundamental modeling in certain cases, such as when developing hydrogels with known complexities that break the assumptions used in fundamental modeling. For example, the

SPN model is far from being able to predict the properties of an interpenetrating network hydrogel, but an appropriately trained AI model may be able to make some useful predictions [61]. However, the associated lack of fundamental insights yields a form of uncertainty in the predictions and a lack of applicability to other systems that run contrary to the goals of the SPN model [62]. Further examples and discussion of these approaches can be found elsewhere [63–65].

5 | Forward, Sideways, Backward: Model Use and Utility

The meta-structure of the SPN model, with structural parameters linked to physical properties by fundamental modeling and identity parameters, yields three major use cases, described here as forward, backward, and sideways applications (Figure 5). Forward application of the model uses structural parameters to predict physical properties. Backward application uses a hydrogel’s measured properties to infer details of its structure. Sideways applications use one hydrogel property and some knowledge of the hydrogel structure to estimate another property of the hydrogel.

Forward use of the SPN model enables a priori design of hydrogels with specific properties by controlling their structure at synthesis. Forward use has the greatest opportunity for practical applications, but it requires high confidence in the model and in the control of structural parameters by hydrogel synthesis conditions. An example of forward model use is designing hydrogels with decoupled stiffness and solute transport by changing structural parameters at hydrogel synthesis [20].

Backward use of the SPN model helps to draw conclusions about structural features of a hydrogel that are impossible to directly observe, such as the mesh size. Backward use may help suggest fundamental relationships that could be broadly applied through universal structures, but it requires accurate measurements and high confidence in the applicability of the model to the hydrogel formulation. An example of backward model use is measuring a hydrogel’s stiffness to estimate its degree of polymerization between junctions.

Sideways use of the SPN model expands the utility of a single characterization experiment. Sideways use can help to estimate the values of additional properties of a hydrogel, but it is the most dependent of the three use cases on the accuracy of the model since it effectively involves a backward and then a forward application of the model. An example of sideways use is predicting a hydrogel’s stiffness from its swelling data.

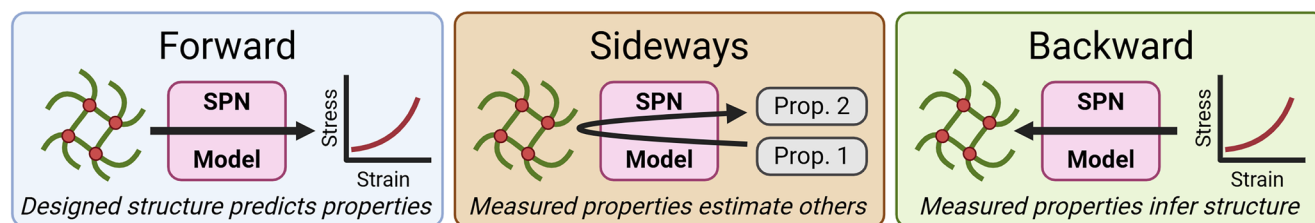


FIGURE 5 | Forward, sideways, and backward uses of the SPN model connect structure and properties.

Each use case requires a high degree of confidence in the model, so how does one validate and improve the model? By combining the other key features of each use case—precise structural control, accurate measurement methods, and multiple complementary property measurements for each hydrogel formulation—it is possible to evaluate the accuracy and limitations of the model itself. If the model is not accurate in all three directions, then something is wrong, and the precise, comprehensive characterization of structurally defined hydrogel formulations can help to identify what causes the mistakes and how they can be addressed.

To compare, the forward case is most likely to be relevant in developing new hydrogels, and the sideways case is the most likely to yield unreliable results since it obfuscates the model's assumptions and limitations. Given that most hydrogel physical properties can be decoupled by altering multiple structural parameters, there is not necessarily a one-to-one correlation between two different measured properties [20]. Without additional context, backward model use is aimless. For example, calculating a mesh size from a hydrogel's stiffness without comparing it to similar hydrogels or alternative methods of calculating mesh size or commenting on how that value differs from expectations is not a meaningful result since it cannot be externally validated. Critically, a backward use from a measured shear modulus could not fully predict the combination of four structural parameters that yielded that property, whereas forward use from a complete network structure can fully define the predicted hydrogel properties.

6 | Hydrogel Characterization and Data Access

Given that hydrogel modeling is best improved by robust characterization of a wide variety of well-defined hydrogel formulations, reliable reporting of hydrogel structures and associated

properties could greatly refine hydrogel modeling. Most hydrogel research in the literature is presented as application-oriented studies that include an incomplete description of hydrogel formulations coupled to characterizations that narrowly apply to solving a specific problem. While this siloed approach may demonstrate viable solutions to individual problems, it undercuts progress that could be shared across the field of hydrogel design [19]. Because hydrogel structure–property modeling aims to encode the translatable characteristics of all hydrogels, model refinement needs detailed information on developed hydrogel formulations and their properties. The first step toward broadly usable hydrogel data is minimizing ambiguities in how hydrogels are formulated, such as by defining each structural parameter and identity parameter relevant to a hydrogel formulation. This level of reporting would ensure that the description is compatible with the SPN model. However, too often the initial polymer concentration of a hydrogel formulation is reported but not the molecular weight of the polymer, or a similar omission, rendering the information unusable for robust structure–property modeling. Ideally, characterization methods should be consistent with literature standards where possible and include thorough reporting of methods to support later comparisons [66].

Second, it is always useful to clearly pair characterization results with the fully defined hydrogel formulation. Doing so will help to validate the mapping of the hydrogel structural design space to the hydrogel property space (Figure 6). For an example of a freely available [67], tidy (i.e., following the principles of tidy data for universal analysis) [68] dataset of hydrogel formulations and associated characterizations, see the “essential Richbourg-Peppas dataset” at <https://hydrogeldesign.org/tools>. By presenting the raw experimental data and not just the model-dependent interpretations, the data is adaptable to other interpretations. To this end, reporting a swelling ratio is acceptable (alongside a defined equation for a swelling ratio), but presenting both the

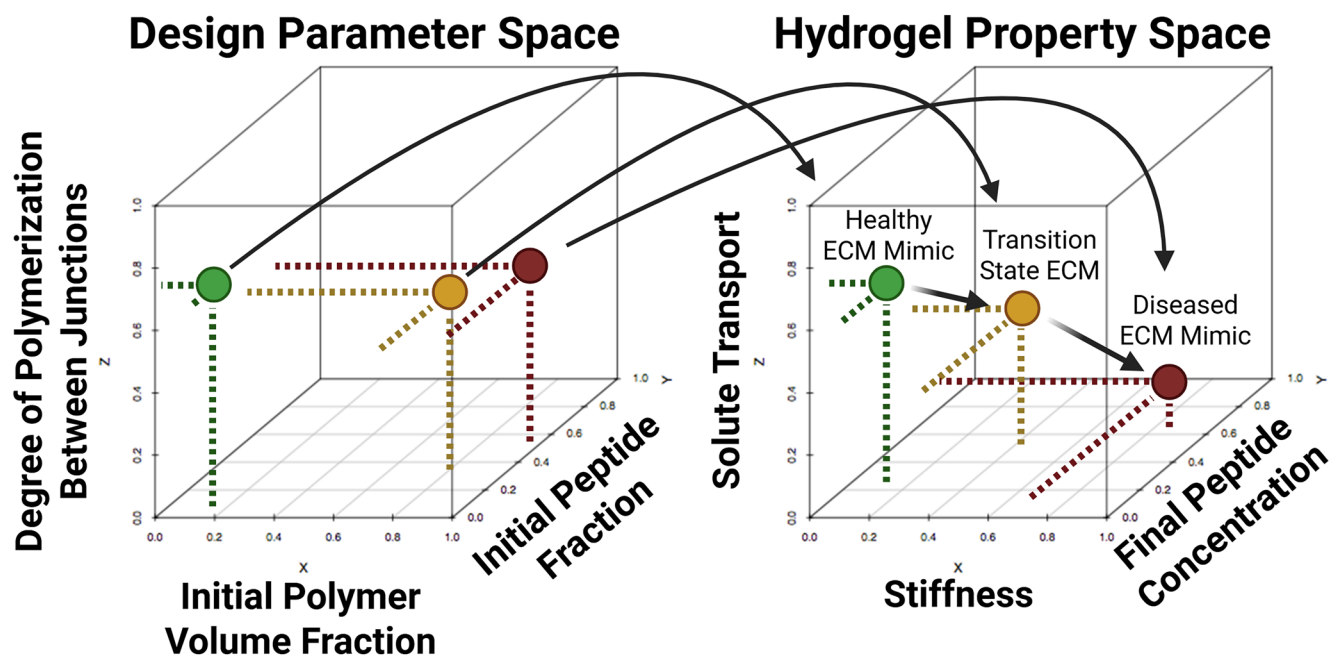


FIGURE 6 | Modeling and modularity capture the nonlinear relationships between the hydrogel design parameter space and the hydrogel property space and enable multi-property optimization and controlled adaptation of biomaterials for diverse applications.

initial polymer volume fraction and the equilibrium-swollen polymer volume fraction maximizes the utility for reanalysis [32].

An overarching problem for hydrogel design modeling is the ever-growing gap between fundamental hydrogel design and application-specific hydrogel design [69–72]. Novelty bias rewards formulation complexity even if it is not justified, and hydrogels that use well-established polymers are therefore devalued in a research context, even if they are highly adaptable and applicable to many problems. Fundamental hydrogel modeling is an exception to this trend, wherein increasingly well-defined, simple systems are developed to draw conclusions about how hydrogels work [73]. The result is a broadening gap, where the models are increasingly accurate for these simple hydrogels, but these models have limited applicability to the incredibly complex hydrogels being developed for varying applications. Addressing the limitations and opportunities discussed above may help to bridge this gap.

Simplicity in applied hydrogel design presents two primary advantages: modularity and modelability [19]. Relatively simple hydrogel formulations can be modified easily to alter their properties, supporting hypothesis testing of how specific property changes affect biological responses to a material (Figure 6). When these changes are within a model-predictable regime, then the desired properties can be achieved readily without extensive experimentation. In many cases, a modular hydrogel approach can achieve the desirable capabilities of a more complex hydrogel formulation without introducing additional variables and unknown changes. The advantages of modeling and modularity scale exponentially with increases in the number of design criteria that must be met for an application.

7 | Conclusions and Outlook

The SPN model is a framework for thought, a tool for practical hydrogel design, and an opportunity to further develop and refine the collective understanding of hydrogels. The potential applications of the SPN model go well beyond the scope of a single lab, so this discussion is intended to inform other groups on the state of the SPN model so they can further explore and develop it with their own insights and use cases. All hydrogel researchers are encouraged to test the SPN model, question its assumptions, tentatively apply its insights to new systems, and share their results toward a better, shared understanding of these fantastic materials.

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Conflicts of Interest

The author declares no conflicts of interest.

Data Availability Statement

Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

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