

9 Summary and Discussion

9.1 Summary of the Current Work

The use of supercritical fluids for the extraction of organic compounds has been a commercial process for many years. More recently, supercritical fluids are receiving wide attention in manufacturing processes as cleaning solvents and reaction media. This research work has investigated the use of supercritical solvents in yet another area of potential manufacturing application: the removal of polymer coatings by (supercritical) solvent swelling.

The Supercritical Fluids Facility at LANL has engaged in experimental work on a wide range of polymer coatings, applied to a range of substrates. Historically, the experimental approach has been largely trial and error, since no method was available to predict, the effect of a given solvent composition, at arbitrary processing conditions, on an arbitrary polymer/substrate combination. This meant that the amount of necessary experimentation is usually quite large. The situation was doubly problematic since even the data obtained from successful experiments could not be used to benefit subsequent applications, involving other polymers and/or solvent systems. Consequently, the focus of this work has been the development of a model framework, which explains the past experimental results, and which can incorporate these results so that predictions could be made on untested polymer/substrate combinations.

This raises the question as to what the ultimate goal of such a predictive model framework should be. It is intended that the model developed in this work be able to reduce the amount of experimental trials required to achieve a particular supercritical solvent/polymer interaction. Because of the nature of the equipment required to conduct high-pressure experiments/processes, eliminating even a few experimental runs represents a significant cost savings, not only in terms of manpower, but also more importantly in terms of equipment, as high-pressure systems are relatively expensive to maintain and operate.

The model framework, developed and presented in the previous chapters of this dissertation, is built upon (1) the assumption that the molecular interactions present in a three-component system (solvent/cosolvent/polymer) can be accurately described by a suitable combination of the molecular interactions present in a matrix of two-component systems, (2) a means of describing the molecular interactions present in the various two-component systems that is valid over a wide range of temperatures and pressures, and (3) the method used to describe the molecular interactions in the pure components is largely independent on the identity of the pure component. The method chosen to describe the molecular interactions for the pure components is the three-component solubility parameter concept proposed originally by Crowley⁵⁸⁰ and Hansen (HSP).⁵⁸¹ This particular approach was chosen over several alternate possibilities (Section 4-2) because it has been shown to provide a relatively good description of the solubility behavior of a wide range of liquid and gaseous solvents and polymer systems. As a result, a fairly large industrial following has been built up, including the publishing of numerous compilations

of measured and/or calculated solubility parameters, as well as well-developed calculation methods, in the absence of tabulated values.

The development of the model required the development of a methodology for expressing HSP values for solvents and cosolvents in the gaseous, liquid, and supercritical fluid phases, as well as polymers. The approach adopted in this work was to first determine a set of ambient-condition HSP's for the solvent, and then to devise a method of extending this single point in solubility parameter space to any arbitrary temperature and pressure. This entailed the verification of previously available temperature derivative functions, and, for the derivation of novel pressure derivative functions. Such a methodology was developed and demonstrated for pure solvents and cosolvents, using CO₂ as an example. CO₂ has been extensively studied and its use as a supercritical fluid is well established in high-pressure chromatography and fluid extraction applications. The resulting ability to express molecular interactions, in terms of HSP's, for a pure fluid solvent in a way which unites the liquid, gas, and supercritical phases, represents an advancement in understanding the role of solvents in both existing applications, as well as the new, proposed, application (polymer coatings removal). It is important to note that the equations developed are not specific to any particular compound and are applicable to any solvent, cosolvent, or polymer HSP's.

Following the development of temperature- and pressure-dependent HSP's for the pure components, methodologies were developed to combine these pure component HSP's to describe the six, unique pairs of components present in a ternary system (Section 2.3). Also required at this step was the development of a method to describe the

influences of not only temperature and pressure, but also swelling into the resulting polymer HSP's.

Finally, the various two-component HSP descriptions were used to model the behavior of two coatings removal applications involving different solvent/cosolvent/polymer systems. Several organic compounds were evaluated as model cosolvents, including at least one example each of a non-polar fluid, a Lewis acid, and a Lewis base. These examples, allow the evaluation of the relative magnitude of intermolecular effects that can be expected when dealing with a generalized supercritical fluid/polymer system. With the solvent and cosolvent(s) thus fully described by HSP's, mixture values are developed.

The polymers evaluated in this work were selected from two example applications. These polymers are pure and relatively well characterized. In addition, existing experimental data was available for evaluating polymer/solvent interactions, specifically polymer swelling in a supercritical fluid. This is necessary in order to incorporate the change in polymer volume (due to swelling) into the polymer HSP values. Further, as was the case for the polymers evaluated here, the behavior of polymers in a supercritical fluid environment can vary. As will be discussed in the following section, a particular polymers behavior may be predicted with an appropriate polymer/fluid EOS, however, for the development of a descriptive methodology, the use of experimental data alleviates the potential of overlapping models generating a desired outcome.

Use of HSP values for new applications generally involve matching parameters between two (or more) components in terms of some previously defined radius of interaction. The radius of interaction used for the polymers in this research are based on

the dissolution behavior of these polymers in organic liquid solvents, R_o^{liq} . The direct applicability of this radius for polymer/supercritical fluid interactions is not known, but based on the results of this work, a larger interaction radius (R_o^{SCF}) appears to be available for the prediction of favorable interactions. As with the database generated overtime and as a result of numerous polymer/liquid evaluations for the determination of R_o^{liq} , the creation of a similar database for polymer/supercritical fluid systems, R_o^{SCF} , will be necessary to increase the usability of the model framework developed here.

Chapter 8 serves as a compilation and review between the observed, experimental results, and the effects that would be predicted by the current model. In the first general application, photoresist on silicon wafers, the experimental result was known and the model predicted favorable results for both the experimental conditions – in agreement with experiments. The second general application, polymer film on aluminum drums, an application where the answer was not known, but the polymer was well characterized, the model predictions were consistent with experimental results at different temperatures and pressures.

Results of the research indicate significant promise in the use of supercritical fluids for replacement of organic liquid solvents for polymer coating removal applications. In terms of the goal of reducing the amount of required experimentation, predictive capabilities are attainable for supercritical fluid/polymer systems, where the steps undertaken in this work are carried out and no equipment limitations in terms of temperature or pressure are encountered. Specifically, full characterization of the solvent and polymer in terms of HSP values, and matching these components such that $Ra < R_o^{liq}$, allows the development of a very narrowly defined experimental matrix. This is a

significant improvement over the current trial and error approach, and greatly reduces the required experimentation.

If equipment limitations are a factor, or if reduction of the required temperature and/or pressure is desirable for a particular application, this research demonstrates that the use of cosolvents, specifically cosolvents chosen to target specific interactions (Lewis acid/base) with the polymer, broadens the temperature and pressure range where favorable effects are achievable. A complete understanding of these effects, and a quantitative incorporation of these interactions into the model framework will require further research and is a consideration in Section 9.2

It is highly unlikely that a predictive model will ever be developed that would eliminate all experimentation, simply because of the range of solvents, cosolvents, and polymers that would be encountered in real applications. However, it is entirely possible that the proposed model framework could be expanded and refined to encompass more and more experimental situations, and provide increasing levels of predictive accuracy. To achieve this goal of a comprehensive model, the areas of expertise that would need to be enlisted will be described.

1. Supercritical (and high-pressure) fluids, including the design and operation of high-pressure experimental equipment; solubility parameters, including the development of equipment to make measurements on both fluids and polymers; polymer chemistry, including the measurement of composition (if the polymer is not pure) T_g (and its variation with both T and P), molecular weight, morphology (degree of crystallinity), cross-link density, as well as measurements of thermal expansion coefficient and compressibility, and their temperature and pressure variation (if extensive PVT data

are not available or are not measured). Expertise in polymer equations of state might well be required to either transform the measured PVT into a form amenable to automation, or to make use of data available for a similar polymer.

2. Organic chemistry, to understand the behavior of conventional liquid solvents, as well as the behavior of solvent mixtures, and perhaps the synthesis of new solvents, tailored to specific situations.
3. Thermodynamics, including the measurement of PVT data over a useful range of T and P, and the determination or development of methods to predict physical parameters such as thermal expansion coefficient and compressibility, as well as their temperature and pressure variation, especially for those compounds intended as the minority component of a supercritical solvent.

It will also be necessary to generate vapor-liquid equilibrium measurements for binary (or higher-order) solvent-cosolvent systems in which published data are not available.

Phase equilibria models, including VLE models, will have to be brought to bear which can accommodate the behavior of complex, possibly multicomponent, liquid-liquid and liquid-polymer systems. This would most certainly include models for describing phase equilibria behavior of polymers exposed to supercritical fluids, such as swelling, solvent sorption, and glass transition depression.

All of these areas have been touched on in the basic model developed in this work. It remains only to incorporate these improvements. This will be discussed as future work.

9.2 Suggestions for Future Work

The development of HSP values for CO₂ was initiated with total solubility parameter values determined using fundamental thermodynamics and a CO₂ EOS. The use of a more accurate CO₂ EOS, such as that given by the IUPAC⁵⁸², may be available and an area of future research may explore this issue in greater detail. However, the methodology developed in this work is not limited to, nor is it specific to, CO₂. Therefore, depending on the particular application, solvent selection can include a range of fluids for which the same framework considered here can be used. Appendix D contains an alternative EOS reference for CO₂, as well as EOS references for other fluids which might see use as a supercritical fluid solvent: argon, nitrogen, water, ammonia, and toluene.

The use of thermodynamics for the development of solubility parameter values for a given fluid, however, requires consideration in the applicability of equating internal pressure to cohesive energy density. As noted in Chapter 4, these two quantities are fundamentally different, especially for highly polar fluids or molecules which exhibit specific interactions. Therefore, future work should include research into a means of either evaluating directly through a correlation with other properties the ratio of internal pressure to cohesive energy density (n). A proposed concept is a relationship correlating n with a fluid's dielectric constant.

For the determination of the CO₂ HSP values an extensive evaluation of CO₂ gas solubility was conducted (Appendix B, Table B-3) and from this one set of HSP values was derived. Two comments are worth noting in this determination. First is the method used for optimizing the data set. More sophisticated optimization techniques are, of

course, available, however the focus of this work was to illustrate the idea of the determination of a set of HSP's using solubility data. If additional experimentation data were made available on the solubility of CO₂ in a wider range of solvents for which the CO₂ solubility were high, such improved optimization techniques would be worth pursuing. A more difficult, although perhaps more interesting issue is the implicit assumption of equating the HSP value to that of the solvent in which it is found to have the greatest solubility, and whether there is such a thing as a perfect solvent for CO₂. In a "perfect" solvent, the solvent/solvent forces and solute/solute forces must be of similar type and magnitude if solvent/solute interactions are just as likely to occur as the self-associations, in essence an ideal mixture. And yet HSP's do not necessarily represent all the subtleties of intermolecular interactions, they are instead a generalized tool whose use has been promoted by their balance between accuracy and simplicity. Solvents, therefore, which exactly match the HSP's of CO₂, may not even then represent all of the intermolecular interactions of that compound! These theories could be pursued with research directed towards building or manufacturing "perfect" or "ideal" solvents, and subsequently polymers as well, to develop compounds which result in HSP values (or some other quantification of intermolecular interactions) for CO₂.

Another key in the applicability of this research is characterization of polymers to be processed by a solvent. This is because while the prediction of favorable or unfavorable interactions with CO₂ can be initiated from an analysis of the polymer chemical structure, including type and location of functional groups, the polymer's behavior following the sorption of CO₂ is difficult to predict. As exhibited in two of the polymers studied in this work, PMMA and PC, very different behavior can occur as a

result of changes in temperature and pressure during CO₂ sorption. From the literature, it was observed that PMMA initially solubilizes a large amount of CO₂, resulting in considerable swellings and significant depressions in T_g. However this behavior changes with increasing temperature, where PMMA sorption of CO₂ decreases, a behavior characteristic of systems possessing a lower critical solution temperature. Alternatively, PC sorption of CO₂ increases with increasing temperature, a behavior of systems possessing an upper critical solution temperature. Further understanding in these opposite behaviors is necessary, and the contribution of collaborative efforts with a polymer scientist would be extremely valuable in continuing this work.

The need for a model to describe polymer sorption behavior was circumvented by the use of experimental sorption data available in the literature. An improvement in this approach however, would be the use of models which can be used to describe equilibrium behavior of polymer phases exposed to gases, such as swelling, solvent sorption, and glass-transition temperature depression for glassy and rubbery polymers. Models for polymer phase equilibrium calculations fall into two general areas; lattice theories and cubic EOS's.

Lattice theories have been developed from the quasicrystalline nature of polymers. For although polymers are considered liquid like when in a rubbery state, each molecule also tends to stay in a small region, a more or less fixed position in space, about which it vibrates back and forth. The quasicrystalline picture of the liquid state supposes molecules to sit in a regular array in space, called a lattice, and therefore theories of polymers and polymer mixtures are called lattice theories.⁵⁸³ One of the best known attempts to formulate a model for these systems was the Flory-Huggins lattice model.⁵⁸⁴

Other lattice theories evolved out of this work, including the Sanchez-Lacombe EOS^{585,586} and the Panayioutou-Vera EOS.^{587,588} Alternatively, polymer/fluid systems are also modeled with cubic EOS's. Two references for this type of approach include: (1) a modification of the SRK EOS,⁵⁸⁹ and (2) a modification of the PR EOS.⁵⁹⁰

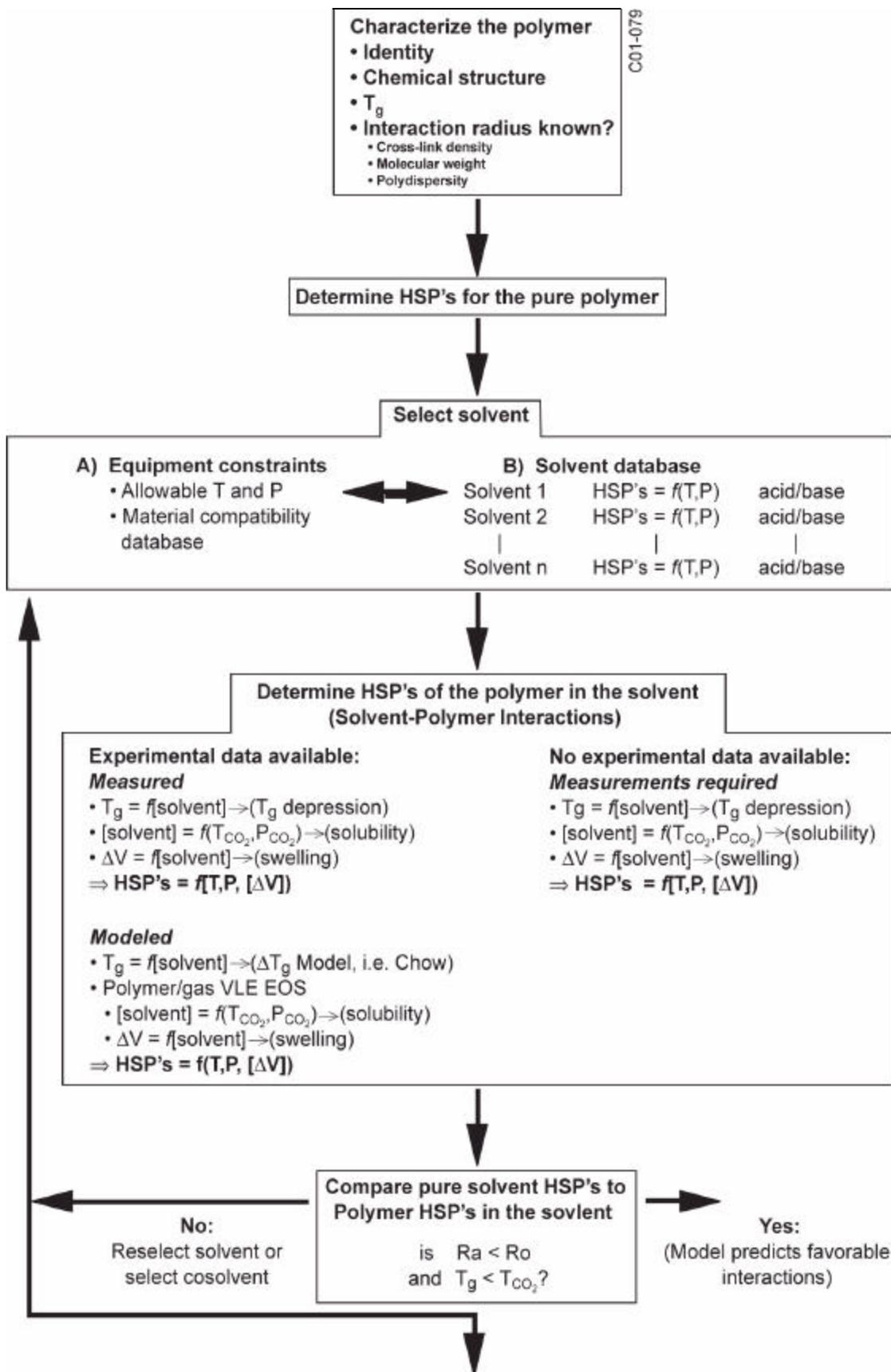
A suggestion in future work would incorporate these theoretical methods, to develop a larger polymer/SCF database. This will quickly expand the polymer/solvent systems which can be evaluated and greatly enhance the models usability. The successful incorporation of modeled data can potentially include EOS for all the systems evaluated. Such systems would include: (1) Pure Fluids (either liquid or gas) EOS, such as the Huang EOS used in this work or those referenced in appendix D; (2) Vapor/Liquid Equilibria for supercritical fluid/cosolvent mixtures such as the Redlich-Kwong EOS, the Soave-Redlich-Kwong EOS, or the Peng-Robinson EOS, with appropriate mixing rules; (3) Pure polymer EOS as outlined in Section 5.5.1; and (4) Polymer/Fluid Equilibria, discussed above.

Systems that are not suited to theoretical modeling must also be addressed. This will require equipment and experimentation techniques capable of generating the data needed to optimize the conditions for the desired effect. Specific measurements required include; polymer glass transition behavior in the SCF or SCF mixture environment, polymer sorption of the SCF or SCF mixture as a function of temperature and pressure, and polymer swelling as a result of solvent sorption as a function of temperature and pressure. Additionally, purpose built equipment, capable of precisely measuring the temperature of the polymer film, as well as the solvent throughout the experiment is essential. This in combination with a visual indication, or some other experimental

evidence of precisely when the polymer coating is removed or effected in a desirable manner, is necessary to accurately develop experimental and ultimately industrial testing. This is also necessary for building a supercritical fluid radius of interaction database.

Where it is necessary to use cosolvents to promote polymer coatings removal, experimental results in Chapter 8 indicate that cosolvents capable of interactions such as hydrogen bonding or Lewis acid/base complexing with the polymer should be considered. However, the ability to predict this type of enhanced interaction was not quantified in this research. Therefore, a suggestion for future research is an incorporation of the cosolvent effect (above the slight increase in the mixture HSP values), into the model framework. Such incorporation might take the shape of a quantified cosolvent “factor”, developed from an expanded cosolvent experimental matrix or investigations into the partitioning of the cosolvent towards the polymer phase. A method currently being used to measure the partitioning of cosolvents is an in-situ Fourier transform IR and UV-vis spectroscopy.⁵⁹¹ This type of data, for inclusion of a more developed model would be useful.

Figure 9-1 illustrates the use of the model framework, for any solvent/cosolvent/polymer system, and briefly touches upon potential areas of future work.



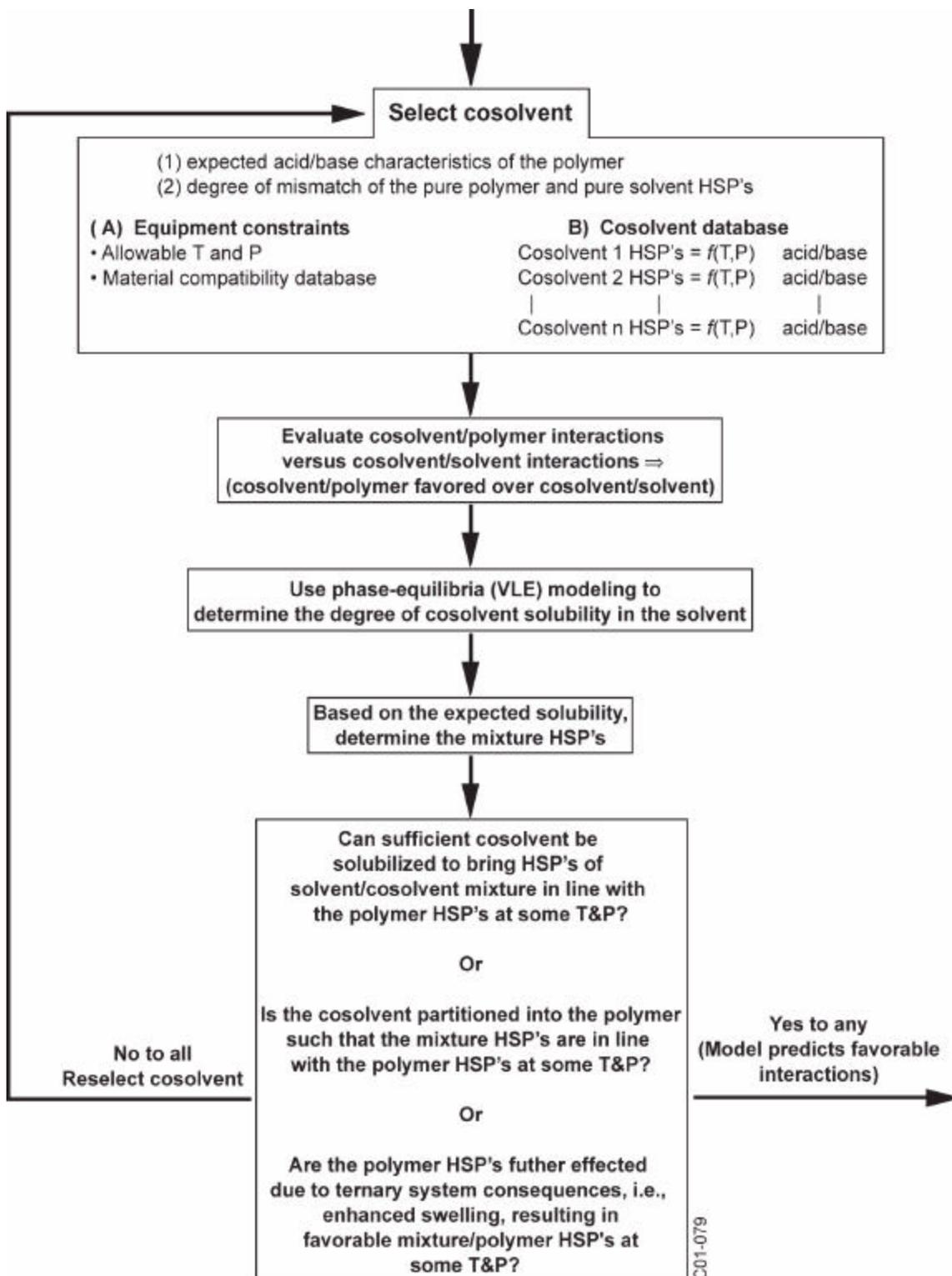


Figure 9-1 Model framework flow diagram.