Swelling and softening of lithium-ion battery separators in electrolyte solvents

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HIGHLIGHTS

- We perform compressive tests of polypropylene battery separator in different solvents.
- Some electrolyte solvents (DMC, DEC, Ethyl Acetate) cause softening and swelling of the separator.
- The separator mechanical properties reduction is due to the polymer-solvent interactions.
- We show that Hildebrand and FH parameters can be used to identify stable separator/solvent pairs.

GRAPHICAL ABSTRACT
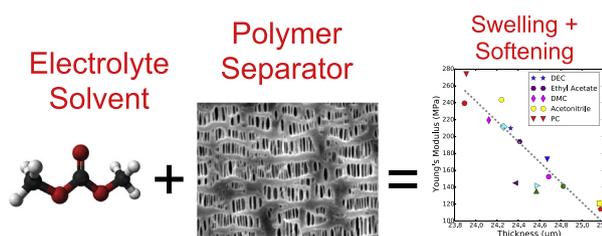
ABSTRACT

The mechanical stability of inactive polymeric components (e.g. separator and binder) can play an important role in the long term performance of lithium-ion batteries. Here we investigate the effects of electrolyte solvents on the mechanical properties of a polypropylene battery separator through experimental measurements of thickness and elastic modulus of separator samples immersed in different solvent environments. We find that certain electrolyte solvents such as dimethyl carbonate, diethyl carbonate, and ethyl acetate cause noticeable softening of the separator. However, in other solvent environments such as propylene carbonate and acetonitrile, the separator retains the mechanical properties of a dry material. We show that the mechanical property reduction can be attributed to polymer swelling and explain these observations in the context of the Hildebrand solubility and Flory—Huggins interaction parameters. The solubility/interaction parameter analysis provides a straightforward method for predicting the *in situ* mechanical behavior of polymer separators in solvent environments. The relationships discussed herein can be used to screen and identify mechanically-stable polymer and electrolyte solvent pairs for use in lithium-ion batteries designed for long life.

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1. Introduction

The separator is a porous polymer membrane that electronically isolates a battery cell's positive and negative electrodes while allowing ion transport between them [1–3]. The mechanical stability of this membrane is critical to battery cell operation, as

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mechanical failure of the membrane can cause catastrophic failure of the battery through an internal short circuit [4–7]. More recently, mechanical stability of the separator has been shown to be important in the context of battery aging, whereby deformation and subsequent pore-closure in the separator leads to accelerated degradation [8–11]. This deformation proceeds due to compressive mechanical stresses that accumulate as a result of the swelling of battery electrodes that occurs during battery operation [10,12,13], and is expected to be more severe in next generation systems employing high expansion, high capacity electrode materials [14–16]. Consequently, there has been much work in developing new separator membranes with enhanced properties [17,18] as well as in characterizing and understanding the mechanical properties of separator membranes [19–25].

Much of the recent work on separator mechanical properties shows substantial weakening upon immersion in typical electrolyte environments compared with the mechanical properties of a dry separator membrane [20–24]. These studies show reductions in elastic modulus, creep modulus, and yield strength, both in tension and compression. Despite the importance of the electrolyte environment in dictating *in situ* mechanical properties, the only investigation into the physical origins of this softening phenomenon is a modeling treatment by Yan et al. [24]. In Ref. [24], Yan et al. attribute the reduction in mechanical properties to softening resulting from solvent penetration into the polymer host based on the results of molecular dynamics simulations of polypropylene in dimethyl carbonate (DMC). In this present work, we experimentally investigate these phenomena by measuring the thickness and mechanical properties of the separator in a wide range of solvent environments to determine swelling and softening. We then use these experimental measurements to show that the reduction in mechanical properties can be explained in the context of the commonly-used Hildebrand solubility and Flory–Huggins interaction parameters, which provides a straightforward means of quantifying and predicting the solvent-polymer interactions associated with polymer swelling [26–28].

The ability to predict the *in situ* mechanical behavior of these separator membranes is useful for both understanding and simulating the mechanical behavior of current lithium-ion batteries as well as for developing advanced materials for future lithium-ion batteries. In particular, there is much recent interest in exploring the use of new electrolyte solvents (e.g. ethyl acetate and acetonitrile [29–31]), new separator materials [17], and new binders [32–34]. The results described herein contribute to these development efforts by providing an easy method for identifying promising pairs of electrolyte solvents and polymer components with respect to mechanical stability. It is anticipated that the consideration of both chemical and mechanical compatibility of the electrolyte, separator, and binders in the design of advanced batteries will result in better batteries with greater durability.

2. Material and methods

The separator considered in this work is Celgard 3501, which is a porous monolayer dry-stretched membrane made from semi-crystalline polypropylene (PP). All compressive mechanical tests are performed using an Instron electromechanical universal testing machine (model 5969) fitted with a 5 kN load cell and spherically-seated platens for good alignment. Due to the small thickness of the separator (nominally 25 μm), the tests are performed using a stack of 32 layers of separator with a diameter of 0.953 cm. More details on the sample preparation and the testing procedure can be found in our previous work [22]. All tests are carried out at the constant strain rate of 10^{-3} s^{-1}, such that the poromechanical effects causing apparent stiffening of the sample are weak [23]. All tests were repeated five times.

All tests are carried out at room temperature in either air ("dry") or immersed in a liquid solvent ("wet"). Following Ref. [20] for the wet tests, samples are immersed in solvent for at least 20 min prior to testing to ensure complete wetting. It is verified that longer wetting times do not alter the measured mechanical properties. The solvents used for testing are summarized in Table 1. In addition to battery electrolyte solvents DMC, diethyl carbonate (DEC), propylene carbonate (PC), acetonitrile, and ethyl acetate, we test a number of other organic solvents of different quality with respect to PP. The quality of solvent is quantified via the single-component Hildebrand solubility parameter δ [26] and Flory–Huggins parameter χ [27,28] for PP-solvent interactions. The δ values are obtained from Refs. [35,36], while the χ values are calculated as described below.

To calculate the Flory–Huggins interaction parameters for the polymer-solvent pairs, we use the UNIFAC-FV model [37] for calculations of activities. This model is based on representation of both solvent and polymer molecules as a set of relatively simple functional groups with well-determined parameters. The free-volume (FV) correction is essential for polymers, and it is taken into account as an additional correction term in the free energy.

First we calculate the solvent activity a_1 for different values of mass fraction w_1 of solvent in the polymer-solvent mixture. We use the range 10^{-5} to 10^{-1}, which is relevant to the polymer swelling as opposed to total dissolution. We present the calculated data for a_1 as a function of w_1 as a dependence of $\ln(a_1/w_1)$ on $\ln(w_1)$, so that it can be easily fit to the Flory–Huggins equation [27] using the standard least squares algorithm. The result of the fitting gives the Flory–Huggins interaction parameter χ.

The UNIFAC-FV calculations are done assuming an amorphous PP density of 0.866 g/cm^3 and using standard UNIFAC parameters for most of the functional groups [38]. More recent data is used for the carbonate group parameters [39]; the propylene carbonate molecule is treated as a single group following Ref. [40]. We validate our procedure for calculation of the Flory–Huggins parameter on several PP-solvent systems, for which the values of χ are given in the literature [35], namely benzene, acetone, and 1-pentanone dissolved in PP at room and elevated temperatures. The calculated values of χ show good agreement with established literature values [35]. Note that hypothetically it is also possible to calculate χ based on δ, but this approach often gives poor agreement with the experiment for polymer solutions [41], which we find to be the case for separator system in this work as well.

Table 1
Solvents discussed in the current work, their Hildebrand parameters, and Flory–Huggins parameters for PP-solvent pairs. All δ values are taken from Ref. [35], except for the value for perfluorooctane, which was estimated based on the values for perfluoroheptane and perfluorononane [36]. All χ values are calculated by UNIFAC-FV at the temperature 293.15 K as described in the text.

Solvent	δ (MPa$^{1/2}$)	χ (PP-solvent)
Perfluorooctane (PFO)	11.7	2.9
Decane	13.5	0.165
n-Pentane	14.3	0.48
Hexane	14.9	0.395
n-Heptane	15.1	0.32
Octane	15.6	0.25
Cyclohexane	16.8	0.055
Cyclopentane	17.8	0.135
Diethyl carbonate (DEC)	18	1.77
Toluene	18.2	0.24
Ethyl acetate	18.6	1.04
Acetone	20.3	1.93
Dimethyl carbonate (DMC)	20.3	2.1
Acetonitrile	24.3	3.5
Propylene carbonate (PC)	27.2	3.7

3. Results and discussion

3.1. Experimental characterization of swelling and softening

Typical compressive stress–strain curves for the separator samples in the dry conditions and immersed in different electrolyte solvent environments are shown in Fig. 1. From these curves, one can qualitatively see the effects of the *in situ* solvent environment on the mechanical properties of the separator. Separator samples immersed in DMC and DEC show lower stress values for a given amount of strain compared to the dry separator. This is attributed to a polymer swelling phenomenon in which interactions between the solvent and polymer material reduce the mechanical properties. It can be seen that these interactions are reduced for the separators immersed in acetonitrile and PC. For acetonitrile the mechanical properties of wet separators are similar to those of the dry one. The PC-immersed sample shows even higher stresses for a given strain than the dry sample, which is attributed to the poroelastic effects discussed in our prior works [22,23]. Poroelastic effects are more pronounced for PC than the other solvents because of its higher viscosity.

To quantify the effects of softening and swelling due to the solvent-polymer interactions, we focus on two properties: effective modulus and thickness. The effective modulus is used to measure the effects of the solvent-polymer interactions on mechanical properties, and thickness is used to measure the degree of polymer swelling arising from these interactions. Following Ref. [22], we define the effective modulus as the maximum slope of the stress–strain curve, which generally corresponds to ~2–3% strain. We define thickness as the average thickness of a single separator membrane in the 32 layer sample stack at a compressive stress of 0.5 MPa. This thickness measurement is determined by dividing the measured platen separation distance of the compression testing machine by 32.

Fig. 2 shows the effective modulus and thickness of separator samples immersed in 15 different solvents from Table 1. The selected solvents span a wide range of δ and χ values, which allows obtaining physical insight into the observed swelling and softening phenomena. It can be seen that the selected solvents produce a wide range in the strength of solvent-polymer interactions such that the measured effective modulus is reduced from 263 MPa in the dry condition to 114 MPa for the cyclopentane-immersed
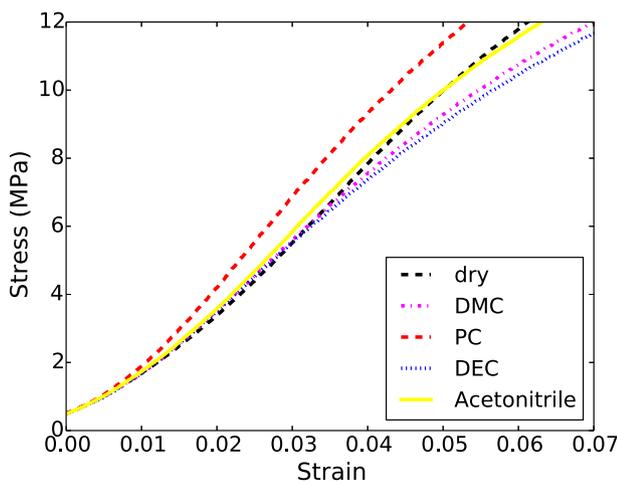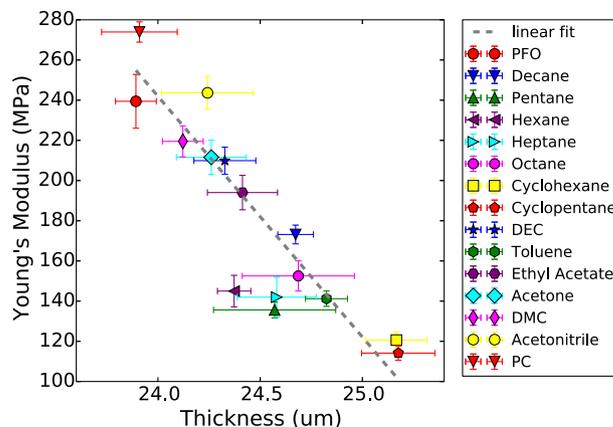

Fig. 2. Young's modulus for separator samples immersed in different solvents as a function of separator thickness. The more swollen samples have lower Young's moduli. Hereinafter, the error bars are estimated from five repeated measurements.

sample. Note that as discussed previously, the PC-immersed sample exhibits a modulus higher than the dry sample due to its high viscosity which causes noticeable apparent poroelastic stiffening.

The variation in effective modulus with solvent immersion corresponds to a proportional variation in thickness such that a linear correlation between modulus and thickness emerges for the different solvents, as seen in Fig. 2. It can be seen that the solvents that produce the largest reduction in mechanical properties (cyclohexane and cyclopentane), also produce the greatest degree of swelling as measured by thickness increase. Our results experimentally support previous *in silico* observations of separator softening due to penetration of DMC solvent molecules into the polypropylene host [24]. This coupling between swelling and softening occurs when interactions between the solvent and polymer molecules are energetically favorable, such that the solvent molecules penetrate between the polymer chains, causing the increase of the polymer volume (swelling). This swelling enhances the mobility of the polymer chains which results in a reduction of mechanical properties [42].

3.2. Predicting swelling using solubility parameters

The correlation between swelling and softening in this system suggests that the reduction in mechanical properties of battery separator membranes due to solvent immersion can be understood and predicted in the context of solubility parameters, which predict solvent-polymer interactions based on energetic considerations. To this end, we analyze the swelling and softening data from Fig. 2 in terms of the Hildebrand parameter δ [26] and the Flory–Huggins parameter χ [27,28], the two most common quantitative criteria for characterizing solvent compatibility. The use of solubility parameters to predict the interactions in different solvent-polymer systems is attractive because it offers a straightforward and easy framework for analysis. This is a distinct advantage to other methods such as molecular dynamics simulation, which comes with the tradeoff of significantly higher complexity and cost for more detailed physical insight. The use of both the δ and χ parameters each have their own advantages, and we will discuss each one as it pertains to separator swelling individually.

3.2.1. Hildebrand parameter

The Hildebrand solubility parameter δ is defined as the square root of the cohesion energy per unit volume:

Fig. 1. Stress–strain curves for separator samples compressed at a strain rate of $10^{-3}\,s^{-1}$ in different environments: in air and in four electrolyte solvents, DMC, PC, DEC and acetonitrile.

$$\delta = \left(\frac{\Delta E_{\mathrm{v}}}{V_{\mathrm{m}}}\right)^{1/2}. \tag{1}$$

For a non-polymer, ΔE_{v} is the molar energy change upon isothermal vaporization of the saturated liquid to the ideal gas state and V_{m} is the molar volume. Note that δ is a single-component property; δ is typically low for non-polar liquids and high for associating liquids such as water or ethylene glycol. Generally, the lower the difference in solubility parameters between a pair of liquids, the more favorable are the interactions between them, which, in our case, means stronger swelling. The Hildebrand solubility parameters for the solvents discussed in the current work are summarized in Table 1.

The determination of the Hildebrand parameter for a solid polymer is less straightforward. For the case of polypropylene (the polymer comprising the battery separator studied in this work), reported Hildebrand values vary between 17.49 and 19.2 MPa$^{1/2}$ depending on microstructure [35]. It is not obvious which value should describe the battery separator, as separators in general have unique structures owing to their intricate manufacturing process. For example, the dry stretch process used to produce the Celgard membrane studied in this work starts with an anisotropic lamellar structure which is then stretched to form alternating regions of crystalline pore walls and interconnecting amorphous fibrils [43–45].

Unlike the Hildebrand parameters for solvents, which can be determined directly from experimental measurements of latent heat of evaporation, the Hildebrand parameter for polymers cannot be directly measured. Instead, it is common to use indirect experimental determination techniques such as solvent-screening, in which a polymer of unknown δ_p is immersed in a set of solvents with known δ_s values to determine δ_p. In this procedure, δ_p is assumed equal to δ_s for the solvent which shows the strongest effects on the separator properties [35]. The compressive testing performed in the current work can therefore be regarded as a solvent screening procedure for determining of the Hildebrand solubility parameter for PP Celgard separators. Since cyclopentane shows the most pronounced softening among the considered solvents, we can estimate the δ for PP separator to be that of cyclopentane, 17.8 MPa$^{1/2}$. This value is consistent with the literature values for isotactic PP [35].

The effective modulus and layer thickness of separators in Table 1 solvent environments is plotted as a function of solvent Hildebrand parameter in Fig. 3. This plot shows that the observed reduction in mechanical properties can indeed be understood in the context of Hildebrand parameter, which shows increasing effective moduli values for solvents with Hildebrand parameters outside the vicinity of $\delta = 17.8$ MPa$^{1/2}$ of the polypropylene separator. Our results show that observations of reduced mechanical properties in DMC, DEC, and ethyl acetate, but not in PC and acetonitrile is predicted based on the Hildebrand parameter analysis; the former group of solvents has Hildebrand parameters much closer to that of the polypropylene separator than the latter group of solvents.

Based on this analysis, we should expect that ethylene carbonate ($\delta = 30.1$ MPa$^{1/2}$) will not cause noticeable softening of the separator. Although not tested in this work (EC is solid at room temperature), results of Sheidaei et al. [20] show that softening of the separator in pure DMC is more pronounced than in 1:1 EC/DMC mixture, which is in line with our conclusions. Based on the data for Hildebrand parameters for various electrolyte solvents, the best performance in terms of mechanical stability is expected from EC/PC mixtures. Another good candidate is acetonitrile, which has been recently demonstrated to be suitable for use in battery
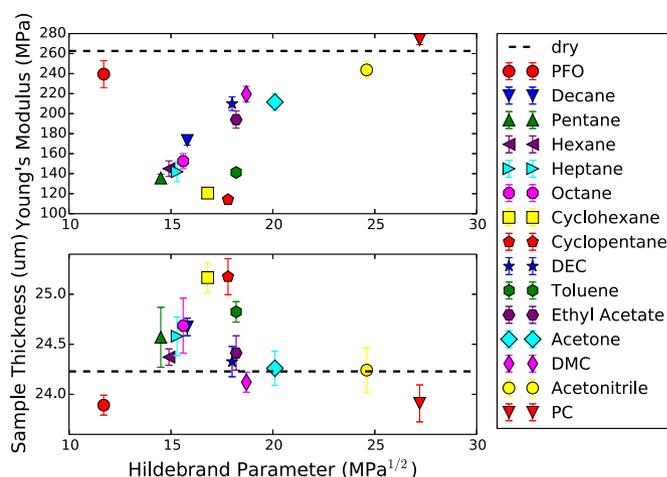

Fig. 3. Experimentally measured mechanical properties as functions of Hildebrand solubility parameter of solvents. (Top) Effective Young's modulus of separator samples compressed at a strain rate of 10^{-3} s^{-1} in different environments. (Bottom) The thickness of separator immersed in different solvents (at compressive stress 0.5 MPa).

electrolytes under certain conditions [31].

Our results are applicable for all types of polymer separators, be they prepared by dry technique (like the one studied here) or wet technique. For example, based on the literature data for the Hildebrand solubility parameter for polyethylene (PE), which is in the range of 15.8–18.4 MPa$^{1/2}$ [35], it should swell in DMC. Therefore, one can expect softening and swelling of all the three layers of the widely used tri-layer PP-PE-PP separators. Indeed, recent mechanical testing of tri-layered Celgard C480 separators shows that its Young's modulus noticeably decreases when the separator is immersed in DMC [21].

3.2.2. Flory–Huggins parameter

The above analysis shows that the Hildebrand parameter can qualitatively predict the degree of softening/swelling between different solvent-polymer pairs. However, the correlations observed for solvents with δ values lower than that of the separator are different than those observed for solvents with δ values higher than that of the separator. This can be seen in Fig. 3, which shows a steeper negative slope approaching the minimum from lower δ, and a shallower positive slope approaching the minimum from higher δ. This discrepancy is because the Hildebrand parameter was introduced for describing non-polar liquids, and consequently polar solvents (which are associated with high δ) are not as well-described as non-polar solvents (which are associated with low δ). Additionally, δ is a single-component property, and therefore lacks the detail required to more accurately predict interactions for specific polymer-solvent systems (see e.g. Ref. [41]). To improve the fidelity of the correlation between measured properties and polymer-solvent interaction parameters, we also analyze the data in the context of the Flory–Huggins interaction parameter.

The Flory–Huggins parameter χ in general provides a better description of the interactions between a given solvent-polymer pair compared with the Hildebrand parameter. This is because the Flory–Huggins parameter is specific to a particular binary system and is based on experimental thermodynamic properties of relevant solutions, whereas the Hildebrand parameter is calculated individually for each component based on cohesion energy. The Flory–Huggins parameter also incorporates entropic interactions between the two components in addition to the enthalpic contributions measured by the Hildebrand parameter. In principle, it is possible to estimate the Flory–Huggins parameter for a given

system based on each component's Hildebrand parameter, but in practice this often leads to poor agreement with experiments. Thus, in this work we calculate the Flory–Huggins parameter using the UNIFAC-FV model described in Section 2, which is a more accurate way than the estimates based on the Hildebrand solubility parameters.

The separator modulus in different solvent environments as a function of Flory–Huggins parameter is plotted in Fig. 4. Note that a similar plot could be made for thickness, as thickness and modulus are linearly correlated as shown in Fig. 2. Fig. 4 shows that the Flory–Huggins parameter serves as a better predictor of the experimentally measured softening phenomena, showing a monotonic linear relationship over the majority of the calculated parameters ($\chi > 0.5$). The solvents in this range of Flory–Huggins parameters are generally polar solvents, which is of particular interest with respect to battery electrolyte solvent applications. The correlation of mechanical properties with Flory–Huggins parameter is also more robust than the correlation with Hildebrand parameter, such that uncertainty in the Flory–Huggins parameter leads to a smaller uncertainty in expected mechanical properties than does uncertainty in the Hildebrand parameter. It should be noted that the increase in fidelity obtained by using the Flory–Huggins parameter to predict solvent interactions with the separator comes with the tradeoff that the Flory–Huggins parameter is more difficult to calculate and not always readily available for the solvent-polymer system of interest.

4. Conclusions

In this work we investigate the effects of solvent environment on the mechanical properties of a polypropylene separator through mechanical tests under a range of solvent environments. Our results show a correlation between swelling and softening by experimentally demonstrating that the reduction in *in situ* mechanical properties of separators immersed in electrolyte solutions is due to polymer swelling, which agrees with the predictions of molecular dynamics simulations [24]. We then show that these observed effects can be predicted using a straightforward analysis based of the Hildebrand solubility or Flory–Huggins interaction parameters associated with the solvent-polymer system of interest. The Flory–Huggins analysis has the advantage of a more robust correlation between properties and parameter whereas the Hildebrand analysis has the advantage of simplicity.

The conclusions of this work provide a better understanding of the interactions between electrolyte solvents and polymer components (e.g. separator and binder) and their effects on mechanical properties in battery systems. The solubility parameter analyses described herein show that these interactions can be easily predicted, allowing for the rational design of battery systems with combinations of electrolyte and polymer components that are expected to exhibit higher mechanical stability. Because the mechanical stability of the separator and binder in a battery cell is important with respect to long term operation, it is expected that this work will contribute to the development of future longer-life batteries.

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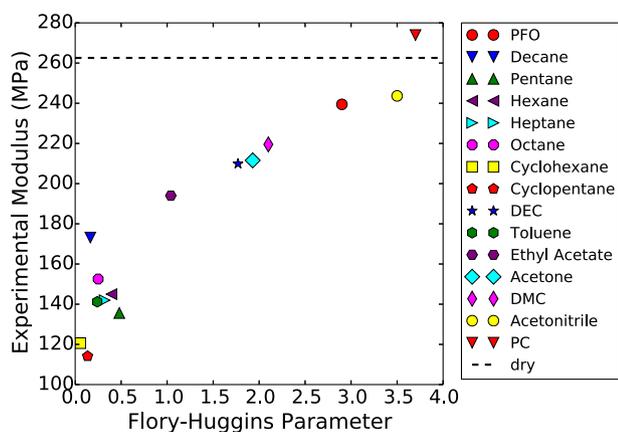

Fig. 4. Effective Young's modulus of separator samples compressed at a strain rate of $10^{-3}\,\text{s}^{-1}$ in different environments as a function of the Flory–Huggins parameter for the PP-solvent system.

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