

Diluent selection for Nylon 11 and Nylon 12 thermally induced phase separation systems

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ABSTRACT: Nylon 11 and Nylon 12 are commercially important polymers due to their unique combination of mechanical strength, chemical resistance, and processability. Products have been prepared from these polymers via thermally induced phase separation (TIPS) for many years. Nevertheless, known diluents for Nylon 11 and 12 pose specific processing problems, and it would be desirable to find a diluent that allows low processing temperatures, has a high flash point, is inexpensive, and exhibits low toxicity. This work investigated a variety of alternative diluents not previously documented in the literature. A fundamental study was also performed to determine which factors are important in selecting a diluent for preparing Nylon liquid–liquid TIPS membranes. The information gathered in this study, including phase diagrams for all feasible systems investigated, will be important in shaping future formulation work for Nylon use in microporous membranes. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43237.

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INTRODUCTION

Microporous polymeric membranes are made using a variety of methods, including diffusion induced phase separation (DIPS) or phase inversion,¹ track etching,² and thermally induced phase separation (TIPS).^{3–5} Of particular interest to this work are TIPS membranes, due to their more uniform structure and solidification profile compared to DIPS membranes, and extensive information has been published on TIPS processing of dozens of polymers, including polyolefins,⁵ poly(vinylidene fluoride),^{6–8} polystyrene,⁹ and poly(methyl methacrylate),¹⁰ to name a few. For this work, the polymers of interest, Nylon 11 and Nylon 12, were more amenable to processing by TIPS than by DIPS.

Thermally induced phase separation involves mixing a polymer with a high boiling point diluent, which acts as a good solvent at high temperatures and a poor solvent at lower temperatures. The polymer and diluent are mixed at a high temperature until a homogeneous solution is formed. This solution is then cooled to induce phase separation. Of particular interest to this work is the cellular structure produced by a liquid–liquid (L–L) TIPS process. During cooling of a L–L TIPS system, the solution becomes thermodynamically unstable and separates into polymer-lean droplets within a continuous, polymer-rich, fluid matrix. This point is known as a cloud point, since the difference in the refractive indices of the two phases typically causes the system to appear cloudy. These droplets can coarsen over

time until the system is cooled below its crystallization temperature, which locks in the prevailing morphology. Upon removal of the diluent by a low boiling point extractant, the resulting membrane can be dried, leaving interconnected voids.⁵ In contrast, a solid–liquid (S–L) TIPS system consists of areas of solid polymer that form and grow within a polymer-lean solution upon cooling.⁴

A rough rule of thumb for selecting an appropriate diluent for use with a specific polymer involves matching the Hildebrand solubility parameter, δ_p , or its constituents, the Hansen solubility parameters, for the polymer and diluent.¹¹ These parameters are calculated based on dispersive (δ_d), polar (δ_p), and hydrogen bonding (δ_h) interactions.

$$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2 \right)^{1/2} \quad (1)$$

Nonpolar compounds, such as mineral oil have low Hildebrand parameters, while highly polar, hydrogen bonding compounds, such as glycerol have high Hildebrand parameters.

These parameters can be determined experimentally and data is available in the literature for many common solvents and polymers. It is difficult to predict Hildebrand parameters by calculation, although various methods have been described for their estimation. In particular, the relative magnitude of polar and

Table I. Nylon Properties

| Polymer | Moisture uptake at saturation (wt %) | Melting point (°C) | Tensile strength (MPa) |
|-----------|--------------------------------------|-----------------------|------------------------|
| Nylon 6,6 | 8.0 ¹⁶ | 250–260 ¹⁶ | 80–85 ¹⁷ |
| Nylon 11 | 2.5 ¹⁸ | 198 ¹⁸ | 47 ¹⁸ |
| Nylon 12 | 1.4 ¹⁹ | 178 ¹⁹ | 35–55 ¹⁹ |

hydrogen bonding effects are hard to predict because they depend strongly on the particular system in question. This is illustrated by the fact that cohesive energy density calculations, which are important factors in these predictions, vary greatly from method to method, even for a particular functional group.¹² Furthermore, when calculating the hydrogen bonding solubility parameter for large molecules such as poly(ethylene glycol) (PEG) with relatively small hydrogen bonding contributions, those same cohesive energy density calculations become even less accurate.¹³

Assuming the values are accurate, the difference between the Hildebrand parameters of the polymer and diluent for a liquid–liquid TIPS system is usually in the range of 1–3 MPa^{1/2}. If the solubility parameters are too close, the diluent can be a solvent for the polymer, dissolving it even at room temperature, or a solid–liquid diluent, dissolving it at high temperature, but lacking the thermodynamic instability required to form a liquid–liquid system at lower temperature. Conversely, if the difference in solubility parameters is too large, the required processing temperature may become very high. Other considerations, such as hydrogen bonding capabilities are also important to note when selecting a diluent, as large differences in this property can prevent dissolution even at high temperature. For example, although the solubility parameters appear appropriate, poly(ethylene glycol) will not dissolve polyolefins, even at high temperatures, because of the significant differences in their polarities, and hydrogen bonding tendencies.

Another widely used tool is the Flory–Huggins interaction parameter for a polymer–diluent pair, which can be calculated from the Hansen solubility parameters. In general, a high interaction parameter between polymer and diluent leads to a liquid–liquid TIPS system, whereas a low interaction parameter leads to a solid–liquid TIPS system.⁴ Since the Hansen parameters, like the Hildebrand parameters, are difficult to calculate accurately without experimental data, the Flory–Huggins interaction parameters should be treated with similar caution.

POLYMER AND DILUENT SELECTION

Candidate polymers were selected based on certain desirable characteristics:

1. Low melting point, which will help to keep the required processing temperature low;
2. High strength, which will improve the processability and durability of the final membrane;

3. Compatibility with low toxicity diluents, which will reduce waste treatment costs and improve process safety;
4. Low cost;
5. Hydrophilicity (specific to this investigation);
6. Low water uptake (specific to this investigation).

One group of candidate polymers meeting the above criteria are the Nylon or polyamide resins. Nylon 6, which is polymerized from caprolactam, has 6 carbon atoms in its repeat unit and is quite polar, while Nylon 11, made from undecanolactam, and Nylon 12, made from lauro lactam, have 11 and 12 carbon atoms, respectively, in their repeat units. Other hydrophilic polyamides, such as Nylon 6,6, are low in cost and have high strength, but also exhibit high melting points due to their extensive interchain hydrogen bonding. Josefiak and Wechs described TIPS materials made with Nylon 6,6, but they reduced the crystallinity by using copolymers of Nylon 6,6 and Nylon 6 to process at reasonably low temperatures.¹⁴ Shalaby and Roweton showed that tetramethylene sulfone and salicylic acid could be used to make TIPS structures with Nylon 6, but required processing temperatures of 230–250°C.¹⁵ Furthermore, Nylon 6,6 is known for its tendency to absorb and retain water (see Table I), which is undesirable for a process where the final product would likely be dried and later rewetted. Nylon 11 and Nylon 12, on the other hand, combine reasonable hydrophilicity with low melting points and reasonable strength, while absorbing considerably less water than Nylon 6,6.

The TIPS process is preferred for use with Nylon 11 and 12 in order to avoid the need for toxic solvents, such as *m*-cresol, formic acid, or fluorinated alcohols that might be required for a DIPS process.^{20,21} Potential diluents were selected in this work based on the following properties:

1. High flash point (at least 5°C above the necessary processing temperature);
2. Low toxicity, both for process safety and residual solvent content in the finished membrane;
3. Reasonable water solubility;
4. Low cost;
5. Low processing temperature when used with Nylon 11 or Nylon 12;
6. Liquid–liquid TIPS behavior in the range of 30–40 wt % polymer, which is anticipated to provide a combination of high porosity and a high enough melt viscosity for the preparation of tubular and other extruded structures.

Previously published diluents for Nylon 11 and Nylon 12 include poly(ethylene glycol) (PEG) of various molecular weights.^{6,7} Cha *et al.*⁶ showed that PEG with molecular weights of 200, 400, and 600 g mol⁻¹ produced liquid–liquid TIPS systems, and that increasing the PEG molecular weight led to increasing cloud point temperatures. This is due in part to an increase in enthalpy of the system, which is evident in the increasing Hildebrand solubility parameter difference between PEG and Nylon with increasing PEG molecular weight. The decrease in the entropy of the system accompanying mixing is also important, and these combined effects increase the system's total free energy, causing instability at higher temperatures.

Table II. Diluent Candidates for Nylon 11 and Nylon 12

| Compound | Hildebrand solubility parameter (MPa ^{1/2}) | Calculated Hildebrand solubility parameter (MPa ^{1/2}) | | |
|-------------------------------|---|--|--------|------|
| | | van Krevelen | Fedors | |
| Polymers | Nylon 6,6 | 22.9 ²³ | 29.9 | 25.4 |
| | Nylon 6 | ~23 | 29.9 | 25.4 |
| | Nylon 11 | ~21 | 24.0 | 22.0 |
| | Nylon 12 | ~21 | 23.4 | 21.7 |
| Previously published diluents | PEG200 ^{6,7} | 20.3 ²³ | 27.2 | 23.7 |
| | PEG300 | ~19–20 | 25.8 | 22.4 |
| | PEG400 ^{6,7} | ~19–20 | 25.2 | 21.6 |
| | Propylene carbonate ³ | 27.2 ¹² | 22.8 | 20.8 |
| | Ethylene carbonate ³ | 30.1 ¹² | 24.5 | 22.5 |
| | Tetramethylene sulfone ³ | 27.4 ¹² | - | - |
| Experimental diluents | Glycerol propoxylate 260 | ~19–21 | 27.5 | 23.7 |
| | Triacetin | ~19.4 ⁶ | 18.8 | 20.9 |
| | Diacetin | 23.5 ⁶ | 22.5 | 23.4 |
| | Triethanolamine (TEA) | ~35 ⁶ | 29.1 | 25.9 |
| | Triisopropanolamine (TIPA) | ~30–35 | 25.9 | 23.5 |
| | VORANOL™ RA 500 | ~30–35 | 22.5 | 20.0 |
| | VORANOL RA 640 | ~30–35 | 23.2 | 20.9 |
| | VORANOL RA 800 | ~30–35 | 24.9 | 22.8 |

Table II lists other possible potential diluents for Nylon 11 and 12. A variety of known diluents exist, but do not conform to the list of diluent selection criteria. For example, two diluents suggested by Castro³—ethylene carbonate and tetramethylene sulfone—both fail to meet the toxicity requirement. Propylene carbonate, also suggested by Castro, has a very low flash point of 132°C, and although was not studied in this work, it is unlikely to dissolve Nylon 11 or Nylon 12 at desired temperatures. Due to its low cost, PEG is an ideal candidate; however, PEGs with molecular weights higher than ~400 g mol⁻¹ require processing temperatures that are too high for consideration, and are therefore not listed.⁷ The experimental diluents listed in Table II were selected to produce lower cloud point systems, either neat or in combination with PEG. Experimentally derived solubility parameters could not be found for some of the diluents in Table II and are denoted as approximations.

Table II also lists solubility parameters calculated first with van Krevelen's group molar attraction constants and also with cohesive energy densities determined by Fedors.^{12,22} The differences between the two calculated values for a given polymer repeat unit or solvent illustrate the difficulty associated with using these group contribution methods to predict TIPS behavior. The discrepancies between the experimental values and the calculated values provide further evidence of this difficulty, particularly involving compounds with hydrogen bonding capabilities.

While values for the Hildebrand solubility parameters for Nylon 11 and Nylon 12 have not been determined experimentally, it can be inferred from literature data and the parameters for the known

diluents in Table II that they should be slightly higher than PEG200 on the solubility parameter scale, at approximately 21 MPa^{1/2}.

The goal of this work was to develop a polymer–diluent system for forming TIPS membranes that meet the above set of polymer and diluent selection criteria defining microporous membranes useful for water purification. Furthermore, a method of diluent selection in strongly hydrogen-bonded systems is presented to aid in future development efforts.

EXPERIMENTAL

Materials

Glycerol propoxylate (MW ~260 g mol⁻¹), PEG200, PEG300, triethanolamine, triisopropanolamine, triacetin, and diacetin were all obtained from Aldrich and used as received. CARBO-WAX™ 400 (PEG400) and the ethylenediamine propoxylate tetrols (VORANOL™ RA 500, VORANOL RA 640, and VORANOL RA 800) are all products of the Dow Chemical Company and were obtained from this source.

Four different polymer samples were used in this study. Low molecular weight Nylon 11 and Nylon 12 resins were purchased from Aldrich. In the course of this work, higher viscosity solutions proved more valuable. Therefore, a higher molecular weight Nylon 11 resin was obtained from Arkema (Rilsan BESNO), and a higher molecular weight Nylon 12 resin was obtained from Evonik (Vestamid 1940) for the final experiments.

Measurements

Samples for cloud point measurement were prepared by heating polymer–diluent mixtures in 2 mL glass vials with aluminum

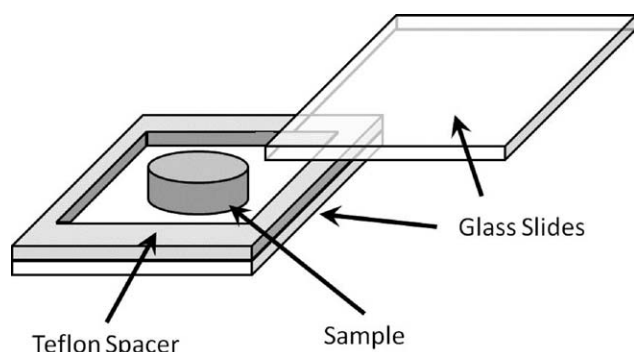


Figure 1. Sample arrangement for cloud point measurement.

caps fitted with PTFE septa and manually crimp-sealed. A small stainless steel stirring rod was added to each vial to enhance mixing via manual agitation with a rare-earth magnet. Samples were heated to 200°C for 8–12 h in a convection oven and agitated periodically to homogenize the mixtures. Once fully mixed, the samples were cooled in ice water and brought back to room temperature before being removed from the vials. A small portion of each sample was placed between two Fisherbrand borosilicate glass microscope cover slips with a greased 0.1 mm thick PTFE spacer. This assembly (shown in Figure 1) was placed on a Linkam TMHS600 hot stage connected to a Linkam TS94 temperature controller. Cloud point measurements were typically made with the naked eye while cooling at 10°C min⁻¹.

In most cases, the same samples used for cloud point measurement were also used for crystallization point measurement, since the clouded samples had limited opacity. This made it easy to witness the onset of crystallization with further cooling. For phase diagrams with triethanolamine; however, which exhibits only a small difference in refractive index between the polymer-rich and polymer-lean phases, the liquid–liquid phase transition was observed using an optical microscope.

Diluent viscosities were measured using a Brookfield RVT viscometer at 25°C. A #4 spindle was used for each sample at a rotational speed of 5 rpm.

Scanning electron microscope (SEM) imaging was performed with a JEOL JSM-7500F field emission microscope. Samples were first extracted in isopropanol for 24 h, then dried, and sputter coated with gold prior to imaging. Compression molded samples for imaging were cooled in ice water, but were somewhat insulated by the glass slides. Furthermore, in the process of heating the samples, diluent blooming occurred to a significant extent, causing an increase in apparent polymer concentration as the glass was wetted disproportionately by diluent drawn from the solution. As a result, many of the images intended to prove the occurrence of L–L TIPS show many cells of a lighter shade not containing pores, indicating poorly connected cellular structures. However, this should not be taken as an indication of the degree of connectivity in a continuous formation process where a direct aqueous quench would result in faster cooling rates and diluent blooming would be eliminated.

RESULTS AND DISCUSSION

The method of diluent selection for the two polymers studied began with an investigation of the PEG systems described in the literature. Then approximate solubility characteristics for ideal candidates were deduced and available diluents possessing those characteristics and meeting the six criteria for diluent selection described earlier were selected for testing.

Nylon with PEG

Literature data show that various polyethylene glycols are capable of forming L–L TIPS structures with Nylon 11, Nylon 12, and Nylon 6,6. In particular, PEG400 has been shown to yield L–L TIPS structures for all three polymers, but with cloud points well above 200°C for most polymer concentrations.⁷ These high temperature requirements make PEG400 a less desirable diluent.

PEG200 and PEG300, on the other hand, result in much lower cloud points, as shown in Figures 2 and 3. These phase diagrams show that as the molecular weight of PEG decreases, the cloud point curves for both Nylon 11 and Nylon 12 also decrease in temperature. This appears to be the result of the

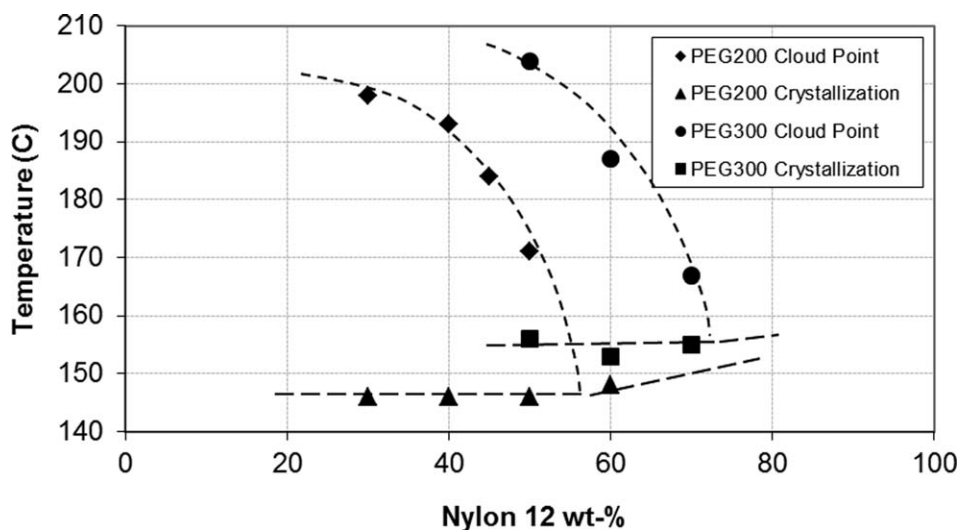


Figure 2. Phase diagrams for Nylon 12 in PEG200 and PEG 300, cooled at 10°C min⁻¹.

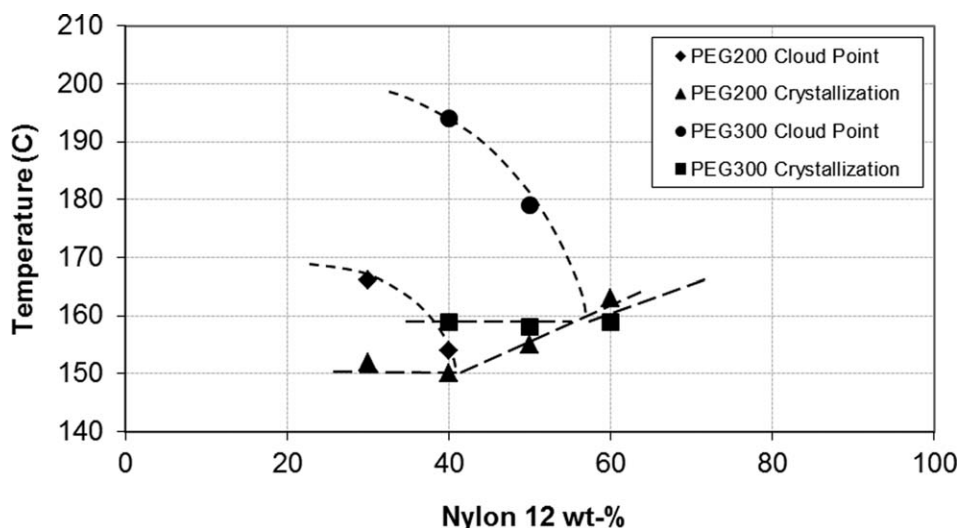


Figure 3. Phase diagrams for Nylon 11 in PEG200 and PEG300, cooled at $10^{\circ}\text{C min}^{-1}$.

diluent solubility parameter becoming increasingly similar to those of Nylon 11 and Nylon 12 as well as improved stability at lower temperatures resulting from an increase in entropy with decreasing molecular weight. With improved solubility in the diluent, the polyamide is stable in solution down to lower temperatures, yielding lower L–L phase separation temperatures. Furthermore, these phase diagrams show that Nylon 11 has a more favorable interaction with PEG200 and PEG300 than Nylon 12, resulting in lower L–L phase transitions. Many of these formulations result in typical L–L structures as shown, for example, in Figure 4. It is important to note that the crystallization curves at concentrations above each monotectic point were extrapolated to the same point at 100% polymer for each data set based on the line extending from the Nylon 12–PEG200 monotectic point and the single measured crystallization point at 60 wt % polymer.

From this information, it is clear that PEG300 fulfills the six diluent selection criteria when applied to Nylon 11. PEG200 fails to meet the sixth criterion of L–L TIPS behavior, because its cloud point is so close to the monotectic temperature that small variations in polymer concentration could result in S–L TIPS behavior. For Nylon 12, PEG200 appears to be a reasonable choice; however, subsequent work with glycerol propoxylate suggests that diluent to be even more desirable.

Nylon with Glycerol Propoxylate

Similar overall to PEGs, the polypropylene glycols are another class of polyols with lower solubility parameters than the corresponding PEGs due to an additional methyl group on one of the carbons in the repeat unit. Such a diluent would be unlikely to improve the phase behavior with Nylon for the purposes of this study, but it was desired to investigate the effect of a higher solubility parameter diluent similar to PEG. A suitable candidate was glycerol propoxylate (GP), a 3-arm polypropylene glycol molecule formed from a glycerol core, which is more readily available than glycerol ethoxylate. The third hydroxyl group on this molecule was expected to increase the polarity of the diluent, giving it a more favorable interaction with Nylon.

Specifically, a GP with a molecular weight of 260 g mol^{-1} was chosen, and the resulting phase diagrams for GP with Nylon 11 and Nylon 12 are shown in Figure 5. Inspection of these phase diagrams shows that the phase behavior with GP is much like that with PEG. Higher molecular weight GPs (GP 450, and GP 725) were also tested, but these diluents were not fully miscible with Nylon 11 or 12 at temperatures below 220°C . Figures 6 and 7 show the structures resulting from cooling 50 wt % Nylon 12 and Nylon 11 solutions, respectively: Nylon 12 (Figure 6) gives a cellular L–L structure, while Nylon 11 (Figure 7) exhibits a spherulitic S–L structure.

This data, combined with the phase diagrams for PEG200 above, suggests that the rule of thumb described above for using solubility parameters to estimate phase behavior does not accurately reflect the differences between the Nylon 11 and Nylon 12 phase diagrams. Since Nylon 11 has a higher calculated solubility parameter than Nylon 12 (having a shorter nonpolar hydrocarbon chain in each repeat unit), one would predict that

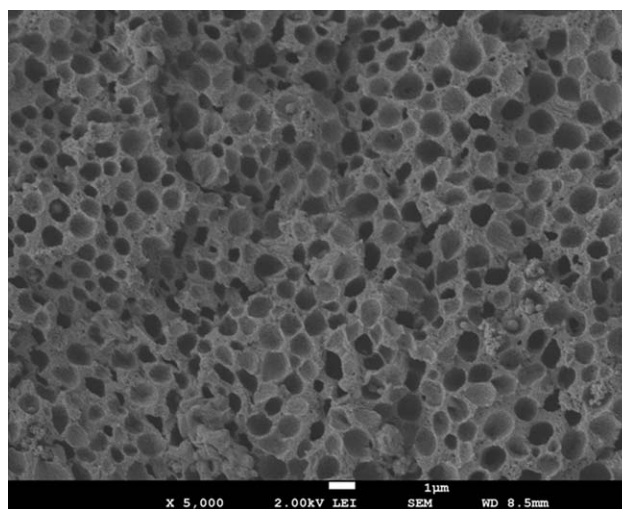


Figure 4. Compression molded membrane made from a 40 wt % solution of Nylon 11 in PEG300, cooled in ice water.

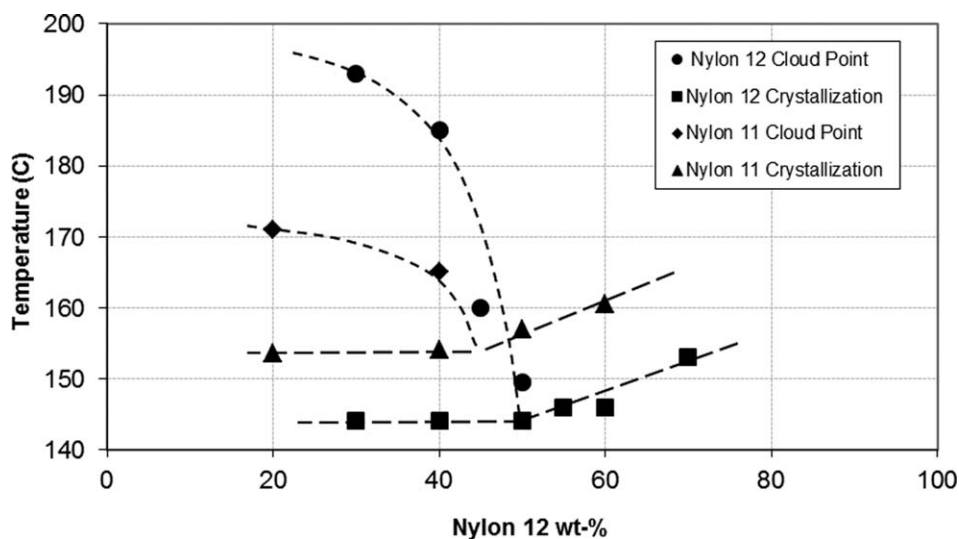


Figure 5. Phase diagrams for Nylon 11 and Nylon 12 in GP260, cooled at $10^{\circ}\text{C min}^{-1}$.

Nylon 12 should have a lower cloud point than Nylon 11 with PEG200, PEG400, and GP 260 as the diluents. While Nylon 6,6 has higher cloud points than Nylon 12 with PEGs, this is likely due to a tendency for Nylon 6,6 to interact more strongly with itself than Nylon 12, reducing the strength of its interactions with PEG and raising the cloud point of those systems. Nylon 11, with a much longer hydrocarbon chain between amide linkages than Nylon 6,6, does not show as much interaction between polymer chains in solution. With its shorter monomer chain length, Nylon 11 is more hydrophilic than Nylon 12, causing it to interact slightly more favorably with polar diluents such as PEG and GP. The experimental data above suggest that PEG polarity effects win out over polymer self-interaction effects for longer Nylon monomer chain lengths.

Again applying the diluent selection criteria, GP260 is a favorable choice for use with Nylon 12. However, since the polymer concentration necessary to achieve the desired viscosity with

Nylon 11 is so close to the monotectic point, GP260 is not a good choice as a diluent for Nylon 11.

Glycerol Acetate Diluents

Two other diluents investigated for dissolution of Nylon 12 were diacetin and triacetin, the diacetate, and triacetate esters of glycerol, respectively. Diacetin was able to dissolve Nylon 12 below 170°C ; however, since that is near the boiling point of diacetin, it would not make a suitable codiluent with for Nylon. Triacetin was found to be immiscible with Nylon 12 below 200°C . Despite this, the authors hypothesized that combining triacetin with PEG200 may result in better solvation of Nylon 12 and lower cloud points despite the fact that triacetin's solubility parameter is lower than that of PEG200. To test this hypothesis, 90:10 and 80:20 mixtures of PEG200 and triacetin were tested as diluent mixtures in formulations containing 30–60 wt % Nylon 12. The results are shown in Figure 8.

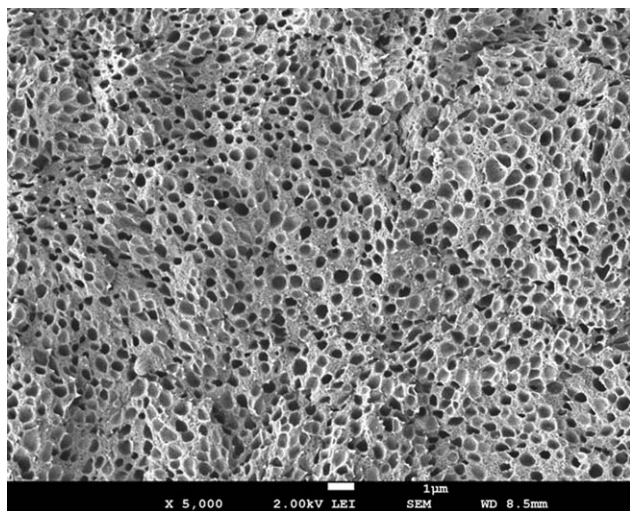


Figure 6. Compression molded membrane made from a 50 wt % solution of Nylon 12 in GP260, cooled in ice water.

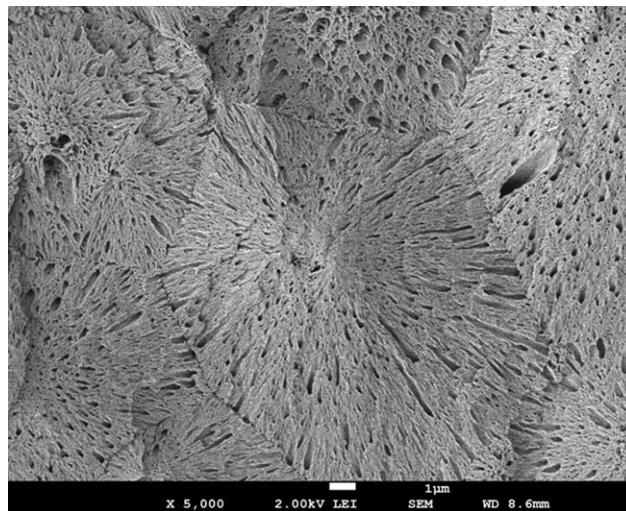


Figure 7. Compression molded membrane made from a 50 wt % solution of Nylon 11 in GP260, cooled in ice water.

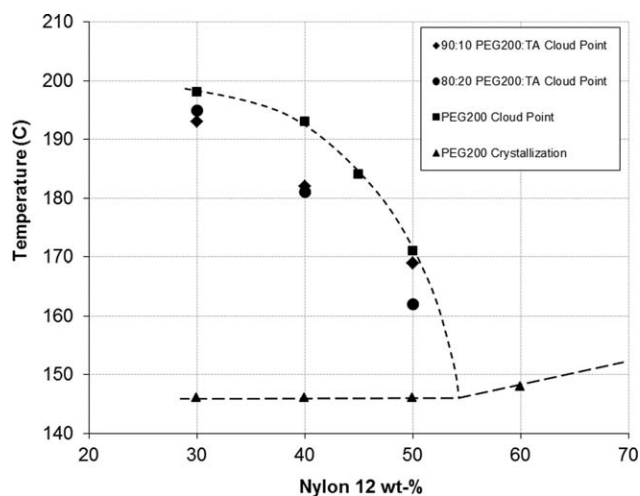


Figure 8. Phase diagram for Nylon 12 in PEG200–triacetin mixtures, cooled at $10^{\circ}\text{C min}^{-1}$.

The 90:10 mixtures of PEG200 and triacetin did reduce the cloud points of 30, 40, and 50 wt % Nylon 12 solutions compared to the same concentrations using pure PEG200, albeit only slightly. This result is interesting in that triacetin, although a poor diluent alone, small additions appear to improve the solvent power of PEG200, suggesting that the esters of the triacetin molecule may help PEG200 to dissolve Nylon 12 by providing a partial negative charge capable of interacting with the amide nitrogen in solution.

The 80:20 mixture of PEG200 and triacetin yielded more interesting results. In the 50 wt % polymer sample, where there was $5\times$ as much polymer as triacetin, the cloud point was reduced even further. However, in the 40 wt % polymer sample, with approximately $3.3\times$ as much polymer as triacetin, the cloud point was unchanged. Finally, in the 30 wt % polymer sample, with $2.1\times$ as much polymer as triacetin, the cloud point

increased. This suggests that there is a limit to the benefit of triacetin, and that above a certain threshold (at polymer : triacetin ratios ranging from 3:1 to 4:1), the triacetin begins to degrade the solvent power of the diluent mixture.

Using triacetin as a diluent for Nylons fails to meet the flash point criterion of diluent selection. Nonetheless, this concept of addressing multiple molecular interactions with multiple diluents at the same time led to the investigation of single amine diluents capable of interacting with both the amide nitrogen and oxygen.

Amine Diluents

Triethanolamine (TEA) was investigated based on anticipated interactions with Nylon 12. It was hypothesized that the hydroxyl groups in triethanolamine would hydrogen bond with the $\text{C}=\text{O}$ and $\text{N}-\text{H}$ of Nylon 12. It was also known that the tertiary amine in TEA would hydrogen bond with the $\text{N}-\text{H}$ of Nylon 12. Still, due to the high solubility parameter of TEA, one might not have predicted Nylon 12 to be soluble in TEA. Experimentally, the system is miscible at high temperatures and can exhibit liquid–liquid phase separation, as shown by the phase diagram in Figure 9 and the SEM photomicrograph in Figure 10. This system illustrates that solubility parameters are based on averaged continuum models, while hydrogen bonding is a specific interaction requiring both energetics of interaction and specific three-dimensional spacing for effective representation.

As seen in Figure 10, the cell size within the Nylon 12–triethanolamine system is large compared to the Nylon 11–PEG300 system and the Nylon 12–GP260 system, as shown in Figures 4 and 6. Cell size measurements are also included in Table III, where the Nylon 12–triethanolamine system is shown to have an average cell size more than twice that of the Nylon 11–PEG300 system and three to ten times that of the other systems pictured. This is due, in large part, to the temperature differences between the cloud point and crystallization curves for each

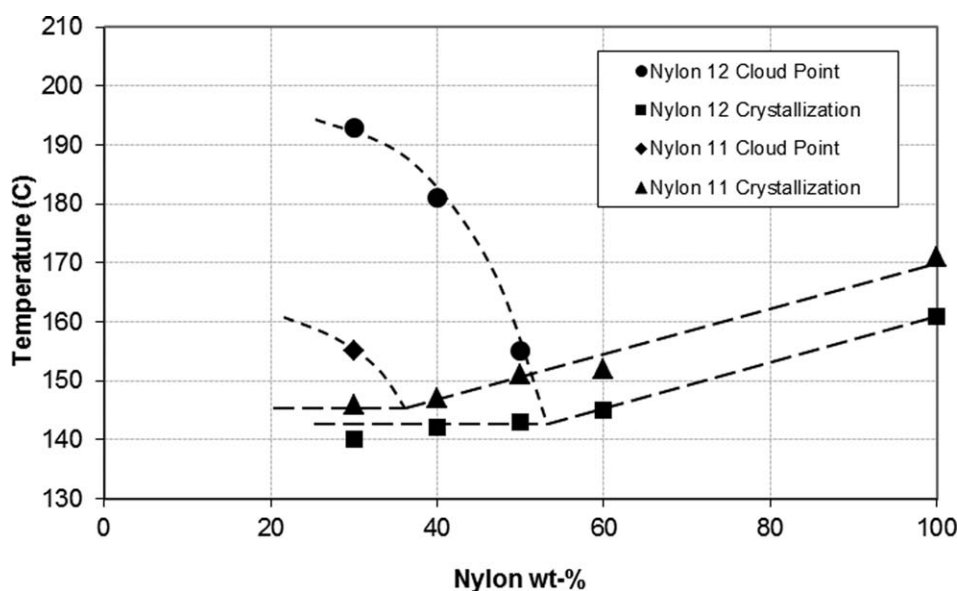


Figure 9. Phase diagrams for Nylon 11 and Nylon 12 in triethanolamine, cooled at $10^{\circ}\text{C min}^{-1}$.

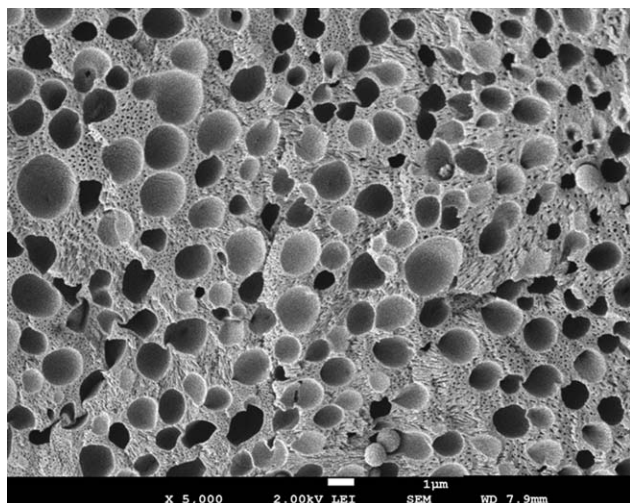


Figure 10. Compression molded membrane prepared from a 40 wt % solution of Nylon 12 in triethanolamine, cooled in ice water.

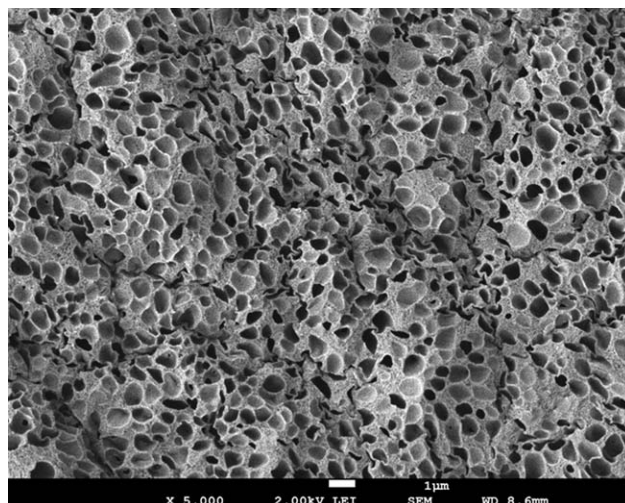


Figure 12. Compression molded membrane made from a 30 wt % solution of Nylon 12 in VORANOL™ RA 640, cooled in ice water.

Table III. Cell Size Measurements for Selected Polymer–Diluent Systems

| Polymer | Polymer concentration (wt %) | Diluent | Average cell size (μm^2) |
|----------|------------------------------|-----------------|---------------------------------------|
| Nylon 11 | 40 | PEG300 | 0.52 ± 0.26 |
| Nylon 12 | 50 | GP260 | 0.11 ± 0.06 |
| Nylon 12 | 40 | TEA | 1.27 ± 0.75 |
| Nylon 12 | 30 | VORANOL™ RA 640 | 0.38 ± 0.18 |

system. At 40 wt % polymer, the Nylon 12–triethanolamine system has a 34°C difference between cloud point and the crystallization temperature, while at the same polymer concentration,

the Nylon 11–PEG300 system has only a 4°C separation, and at 50 wt % polymer, the Nylon 12–GP260 system has a 5°C separation. This simply means that at similar cooling rates, the time available for diluent droplet coalescence becomes very small for the latter two systems relative to the Nylon 12–triethanolamine system, resulting in smaller cell sizes. Other factors such as formulation viscosity and surface tension are also relevant in this comparison, but likely less so.

Due to the promising behavior of triethanolamine, the authors decided to investigate a broader range of tertiary amine diluents to better understand their phase behavior in solutions with Nylon 11 and Nylon 12. Alternative amine diluents tested include triisopropanolamine and a series of high viscosity, ethylenediamine-initiated polyols produced by Dow Chemical: VORANOL™ RA 500, VORANOL RA 640, and VORANOL RA 800. The latter three materials were drawn from Dow's rich

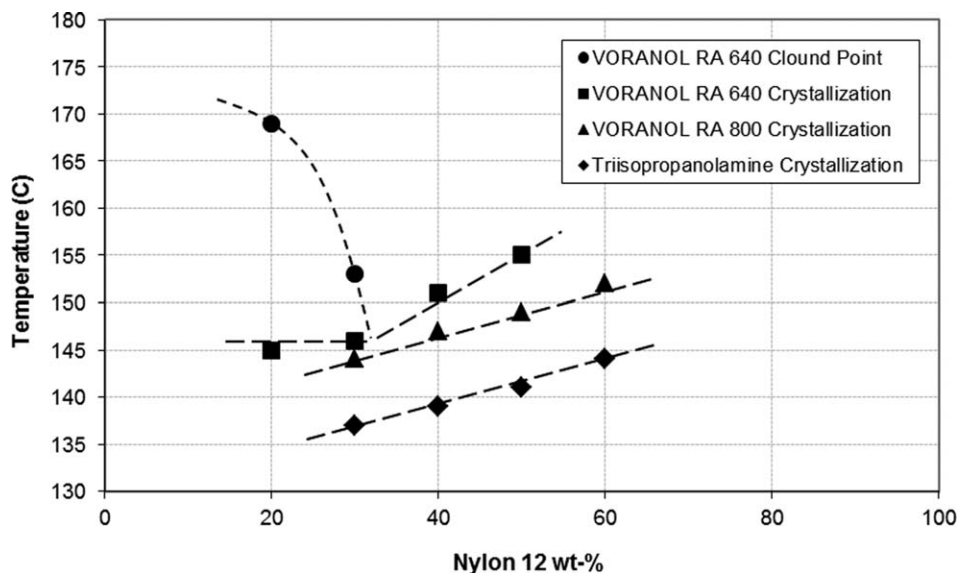


Figure 11. Phase diagrams for Evonik Nylon 12 with VORANOL™ RA 640, VORANOL RA 800, and triisopropanolamine.

Table IV. Comparison of 3- and 4-Arm Polyols

| | Number of hydroxyl groups | Average M.W. (g mol ⁻¹) | Viscosity at 25°C (cp) |
|--------------------------|---------------------------|-------------------------------------|------------------------|
| Glycerol propoxylate 260 | 3 | 260 | 1,400 |
| VORANOL™ RA 500 | 4 | 450 | 9,600 |
| VORANOL RA 640 | 4 | 350 | 35,000 |
| VORANOL RA 800 | 4 | 280 | 30,000 |

polyol portfolio, which is used primarily in the production of polyurethanes, especially for foams in the automotive, insulation, and durable goods markets.

As shown in Figure 11, mixtures of triisopropanolamine with Nylon 12 do not undergo L–L phase separation down to a polymer content of 30% by weight. Triisopropanolamine is therefore not an improvement over triethanolamine when L–L TIPS is desired. It is, however, the strongest S–L TIPS diluent for Nylon found in this work, reducing the Nylon 12 crystallization temperature to below 140°C at a 40 wt % polymer concentration.

Figure 12 shows the structure resulting from ice-water quench of a homogeneous 30 wt % Nylon 12 solution in VORANOL™ RA 640. As shown in Table III, the cell sizes produced are similar to those of the Nylon 11–PEG300 system. Due to the larger difference between cloud point and crystallization temperatures at 30 wt % polymer compared to the 40 wt % Nylon 11–PEG300 system, one might expect the cells to be larger. However, the viscosity of the VORANOL RA 640 diluent is much higher than that of PEG300, the diluent droplets did not grow as quickly as the PEG300 droplets, resulting in smaller cells under similar quenching conditions.

VORANOL™ RA 640 is a 4-arm poly(propylene glycol) tetrol initiated by ethylenediamine with an average molecular weight of 350 g mol⁻¹. Looking at the ratio of hydroxyl groups to molecular weight, one might expect that VORANOL RA 640 would behave quite similarly to glycerol propoxylate 260, which has the same ratio. However, the phase diagram for the Nylon 12–VORANOL RA 640 system has a much lower binodal curve than the Nylon 12–glycerol propoxylate 260 system. The difference is so large that the liquid–liquid behavior seen at 40 and 50 wt % polymer with glycerol propoxylate is not observed at all when using VORANOL RA 640 (see Figure 11). This can be explained by comparing this system to the Nylon 12–triethanolamine system. Triethanolamine has such a high ratio of hydroxyls to molecular weight that one would expect it to be far too polar to dissolve Nylon. However, the tertiary amine interacts so favorably with Nylon that TEA does dissolve Nylon at high temperatures. The same interaction effect for the two tertiary amines of VORANOL RA 640 helps to solvate the Nylon better at lower temperatures, thereby depressing the binodal curve.

The molecular weights and number of hydroxyl groups for the 3- and 4-arm polyols used in this study are summarized in Table IV. VORANOL™ RA 800, with a lower molecular weight than VORANOL RA 640, exhibits no cloud point in mixtures with Nylon 12 down to 30% polymer, due to its higher ratio of solvating hydroxyls to molecular weight. The same principle, dilution of the active end groups as the molecular weight increases, also explains the change in the solvent quality of polyethylene glycol for Nylon in going from PEG200 to PEG400. The opposite effect is seen when using VORANOL™ RA 500, which has a higher molecular weight than VORANOL RA 640, but the same number of hydroxyls per molecule. For samples containing 50 wt % or less of polymer, neither Nylon 11 nor Nylon 12 would fully dissolve in VORANOL RA 500, although mixtures of RA 500 with RA800 can be used to obtain intermediate phase separation temperatures between those of the individual diluents.

When used with Nylon 12, VORANOL™ RA 640 meets all six selection criteria, making it an excellent choice of diluent. Furthermore, its high viscosity compared to the other available diluents makes it particularly valuable in extrusion applications.

CONCLUSIONS

A variety of polymer–diluent formulations for Nylon 11 and Nylon 12 were investigated in this study. Beginning with known diluents, adjustments in the target solubility parameter and selection for specific molecular interactions led to a set of suitable diluent candidates. In performing this work, the authors concluded that for the Nylons studied, just using solubility parameters to select diluents is insufficient due to the importance of hydrogen bonding in the solvation of the Nylon's amide groups. This method can be applied to other polymers, reducing the time to develop new systems, or enabling the identification of new diluents that might not be predicted through traditional methods.

Based on the diluent selection criteria and the experimental results from this study, the authors determined that the best diluents for preparing microporous TIPS articles with Nylon 12 were glycerol propoxylate 260 and VORANOL RA 640. For Nylon 11, PEG300 appeared to perform best. Overall, these systems showed the most favorable combination of low toxicity, high flash point, and low cloud point while still yielding the desired L–L TIPS structures in the polymer concentration range pertinent to this study.

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