



Review Paper

Recent Progress on Improving the Sustainability of Membrane Fabrication

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Article info

Received 2019-04-19

Revised 2019-07-11

Accepted 2019-07-15

Available online 2019-07-15

Keywords

Membrane

Green

Sustainability

Phase inversion

Membrane wastewater

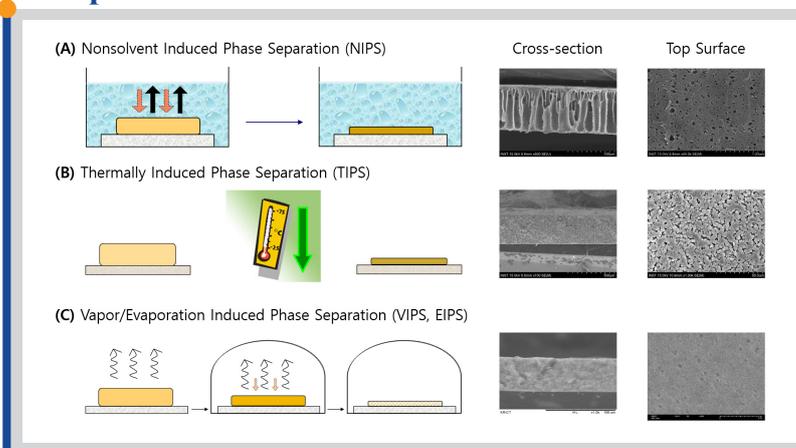
Highlights

- Evaluate current status on the sustainability of membrane fabrication process
- Discuss current research trends on improving the sustainability of membrane fabrication process
- Suggest future research directions on how to go from here

Abstract

Although the membrane process is recognized as a green technology and is considered as a key player in the process intensification movement, it is not widely known that the fabrication of membrane itself generates significant amount of waste. With the growing membrane market, more efforts must be placed on improving the sustainability of membrane fabrication such as replacing toxic organic solvents, minimizing mass intensity of fabrication process, and treating solvent-contaminated membrane wastewater. In this review, recent progresses on improving the sustainability of membrane fabrication have been discussed. In particular, recently-identified green solvents have been compiled, as well as novel methods to apply green solvents to fabricate high performance membranes. In addition, process intensification to minimize solvent waste, and to treat solvent-contaminated wastewater from membrane fabrication process, have been discussed.

Graphical abstract



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1. Introduction: principles and sustainability of phase inversion method

The membrane market is expanding in all fronts including water treatment, gas separation, healthcare, bioprocess, and solvent separation applications [1].

Among the markets, ultrafiltration and microfiltration membranes currently account for near 50% [2], and essentially all of these membranes are fabricated via the well-known phase inversion method.

The phase inversion method was first reported back in 1960 by Loeb and

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DOI: 10.22079/JMSR.2019.106501.1260

Sourirajan [3]. Since then, a significant progress has been made and it is now safe to claim that we have a deep understanding of phase inversion process in terms of solution thermodynamics and kinetics [4]. More specifically, it is now possible to accurately control the membrane pore sizes depending on the applications, as well as overall morphology, pore connectivity and presence of macrovoids [5].

There are different types of phase inversion methods (see Figure 1), and the main ones include nonsolvent-induced phase separation (NIPS), thermally-induced phase separation (TIPS), vapor-induced phase separation (VIPS), and evaporation-induced phase separation (EIPS). Despite the difference in the names, the principle behind each method is essentially the same. Among the methods, NIPS technique most commonly used due to its versatility, closely followed by the TIPS technique. VIPS and EIPS techniques are now gaining more attention, but most industrial membranes are prepared by either NIPS or TIPS. It is also worthwhile to note that VIPS and EIPS sometimes precede NIPS or TIPS in some reported works [6].

In thermodynamic perspectives, the first step of phase inversion method is to prepare a stable homogeneous solution by dissolving a polymer in an organic solvent, commonly referred to as a dope solution. The prepared dope solution is then cast into a thin film using a casting knife either onto a glass plate or a nonwoven support (sometimes a slot die is used instead of a casting knife). The cast film (still in solution state) is then placed in thermodynamically unstable environment, and it spontaneously phase separates (and/or solidifies) to lower its Gibbs free energy. It is important to clearly distinguish the phase separation and solidification. Roughly speaking, the phase separation precedes the solidification. In the case of NIPS (see Figure 1a), the solution is exposed to a non-solvent (often water) [7]. In the case of TIPS, the solution is quenched (or cooled) to a point where the solution is no longer stable in solution form [8]. In the case of VIPS/EIPS, the solution is exposed to a humid environment and vapor adsorbs onto the film while the solvent slowly evaporates away [5].

In kinetic perspectives, once the solution is no longer stable, the rate at which the solution phase separates (into polymer-rich and polymer-poor phase) and the rate of solidification determines the final membrane morphology, *i.e.* pore size, pore connectivity, presence of macrovoids [5]. A heuristic optimization process is generally required to fine tune the membrane morphology and performance, but a competent membrane researcher can obtain the desired membrane pore size after several trials-and-errors.

Now that the membrane community has a deep understanding of the phase inversion principles and mechanisms, researchers have begun to assess the overall sustainability of membrane processes in general [9]. Mainly, one of the key bottlenecks in the phase inversion method is that a toxic solvent is almost always required to dissolve a polymer of interest and form a stable dope solution. Some of the main solvents and polymers have been used for membrane fabrication via NIPS are compiled in Figure 2.

It can be seen, as expected, that PVDF (polyvinylidene fluoride), PES (polyethersulfone), PSU (polysulfone) are some of the most commonly used polymers in literature, as these polymers are mainly used for MF and UF applications and it is important to note that the solvents used to prepare the membranes are harsh polar aprotic solvents like NMP (*N*-methylpyrrolidone), DMAc (dimethylacetamide) and DMF (dimethylformamide). These solvents, which are highly toxic and more importantly, are strictly regulated in industry. In fact, the regulation is becoming ever more stringent with time. For instance, these toxic solvents are on the watch-list of European Chemicals Agency (EACH) and soon to be banned for large-scale manufacturing processes [10]. Hence, not only for environmental reasons, the membrane community must actively seek suitable solvent alternatives that can be used in industrial-scale [11].

Another disadvantage of the phase inversion method, particularly for NIPS (most commonly used), is that it generates significant amount of solvent-contaminated wastewater (see Figure 3). It has been estimated that more than 50 billion liters of wastewater are discharged from the membrane manufacturing industry every year [12]. And these wastewaters unfortunately are above the threshold level for discharge, and hence must be treated on-site or off-site prior to disposal.

According to a survey that we carried out in 2016 [12], sadly, approximately 70 per cent of membrane fabrication industries flushed it down the sink without any treatment or diluted it with excess water to lower the solvent concentration below the threshold level. Wastewater dilution used to be a common method to meet the regulation requirements in chemical industries but now environmental agencies are putting a cap on the maximum water usage, preventing this loop-hole. It is worth noting that the solvent concentrations in membrane wastewater is relatively low and mild, and can easily be treated if an appropriate solution is suggested (discussed in subsequent sections).

Hence it is clear that for sustaining the growth of membrane industry, it is urgent to improve the sustainability of membrane fabrication process. The scope of “sustainability” is very wide and can be vague, but researchers must work on all possible fronts to improve the sustainability and green-ness of membrane technology [13]. Generally, a green solvent should be safe, non-toxic to both health and environment, biodegradable, and preferably bio-derived, yet must perform as well as the conventional solvents. A green membrane process should exhibit low mass intensity (mass of reagent per mass of product), highly energy efficient, and generate minimal waste low toxicity. In this review, three main points that researchers are currently working on them have been discussed: (1) Searching for alternative green solvents, (2) minimizing mass intensity of membrane fabrication process, and (3) treating solvent-contaminated wastewater in economically feasible ways.

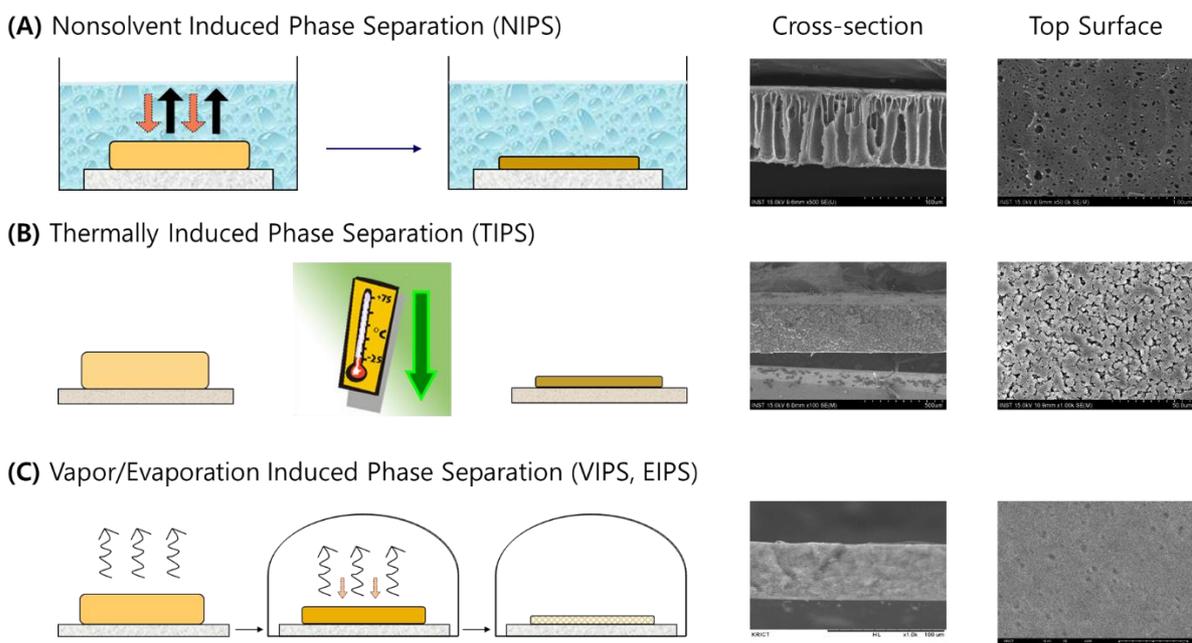


Fig. 1. Various methods for phase inversion: (A) phase inversion using a non-solvent (NIPS) (reprinted with permission from [7]), (B) phase inversion by inducing thermal gradient (TIPS) (reprinted with permission from [8]) and (C) phase inversion via vapor adsorption (VIPS) (reprinted with permission from [5]).

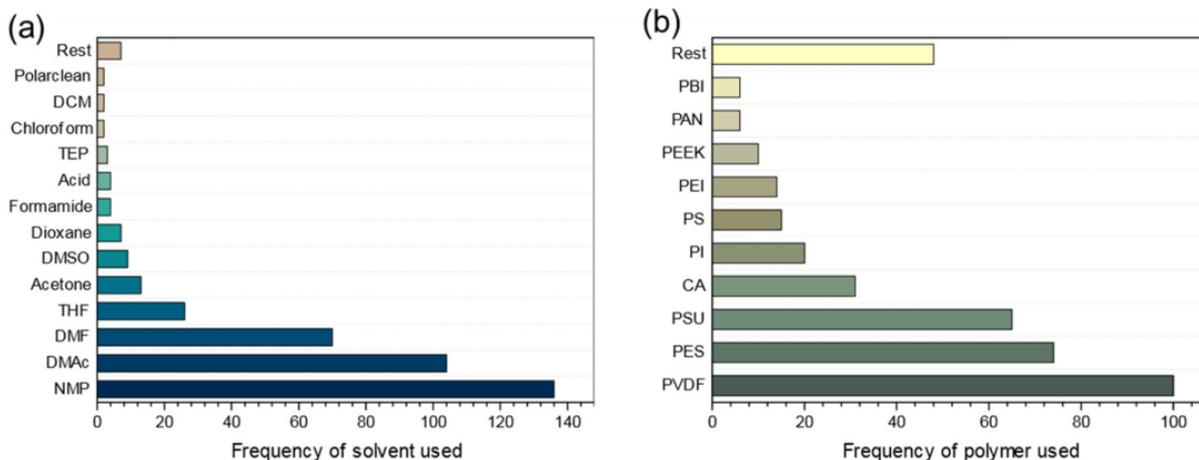


Fig. 2. Results of a literature survey documenting frequency of use: (a) solvents and (b) polymers used for NIPS membrane preparation over the past five years (reprinted with permission from [11]).

2. Search for alternative solvents - why TIPS is gaining momentum

The first step or criteria in all phases of inversion process is preparing a thermodynamically stable dope solution. Most of the membrane polymers shown in Figure 2 generally show little or no solvation properties in most solvents except harsh polar aprotic solvents. In other words, the main reason that toxic polar aprotic solvents are used for membrane fabrication is that they are good solvents to solvate polymers at ambient temperature.

There has been an active search to replace these toxic solvents that can solvate polymers at ambient temperature with little or no success [11]. A notable exception recently identified to be a promising NIPS solvent is Cyrene [14, 15]. Expectedly, the number of possible options expands at higher temperature, as the polymer solubility increases with temperature. This is the precise reason why most of the green alternatives now being identified and reported are for TIPS, which has been recently reviewed [4,16]. Some of the identified TIPS solvents are ATBC [8], TEGDA [17], TEP [6], DMSO₂ [18], sulfolane [19]. It is rather unfortunate that even with many possible options, most of the TIPS solvents employed in practice now are toxic chemicals like phthalates, due to availability, efficacy, and cost. For instance, battery separators are made from polyolefin (polyethylene and polypropylene) via TIPS and phthalates are employed as solvents (or diluents) in most cases.

Nevertheless, there has been a growing number of publications that studied possible green solvent alternatives for TIPS [4,20], which is promising. Some of the recent identified green solvents are summarized in Figure 4.

These three solvents in Figure 4 were reported by Drioli and Lee et al. from Hanyang University [7,8,17]. Each solvent meets the necessary requirements to be a TIPS solvent such as high boiling temperature, low molecular weight, decent solvation of polymers at high temperature, and most importantly environmentally sustainable. An important aspect here is that the performance of membranes prepared by these green solvents is quite competitive to even superior than previously reported membranes.

One of the features of the TIPS method is that the membrane pores are induced by removing thermal energy from the dope solution, and since heat transfer is approximately an order of magnitude faster than mass transfer (NIPS), a more uniform formation of pores is possible, and a very narrow pore size distribution can be obtained, as shown in Figure 5(a).

It can also be confirmed from the data in Figure 5(b) that green alternative solvents can be used to fabricate membranes with competitive performance in the microfiltration range. However, the TIPS method is not suitable to fabricate membranes with pore size less than 50 nm, and hence was difficult to meet the requirements of the growing ultrafiltration and nanofiltration market.

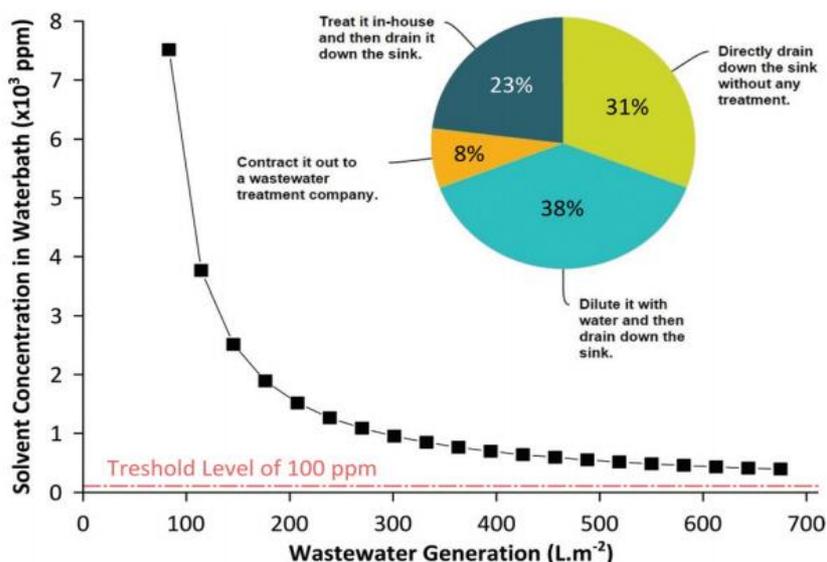


Fig. 3. Concentration of solvent in the wastewater after a phase inversion process. The allowable organic solute concentration is below 100 ppm (in Korea), which is exceeded in typical membrane fabrication process, hence an appropriate treatment prior to disposal or reuse is required. The pie chart describes the current practice among membrane manufacturing companies on disposal of their coagulation bath wastewater (reprinted with permission from [12]).

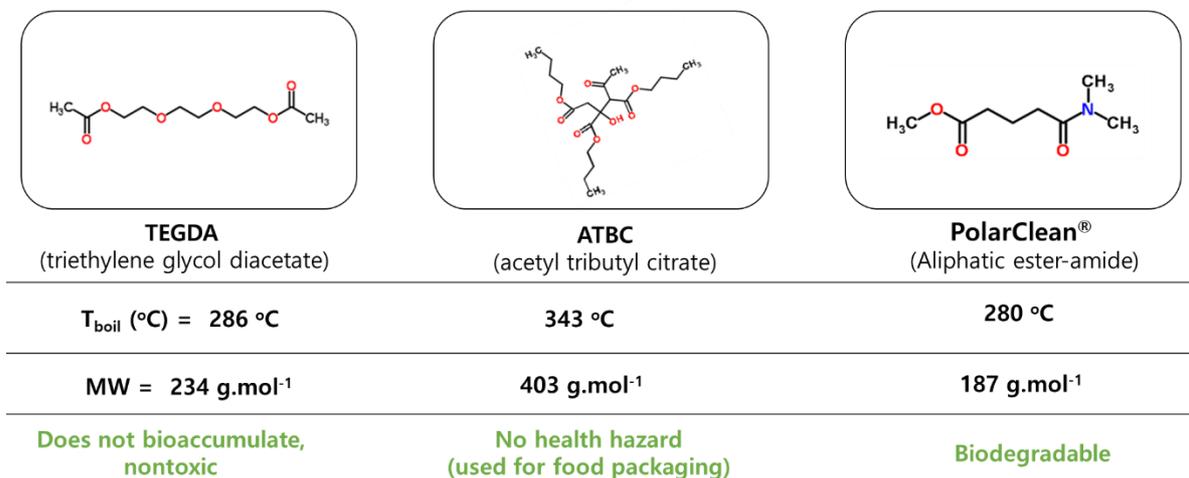


Fig. 4. Recently-identified green alternative for TIPS.

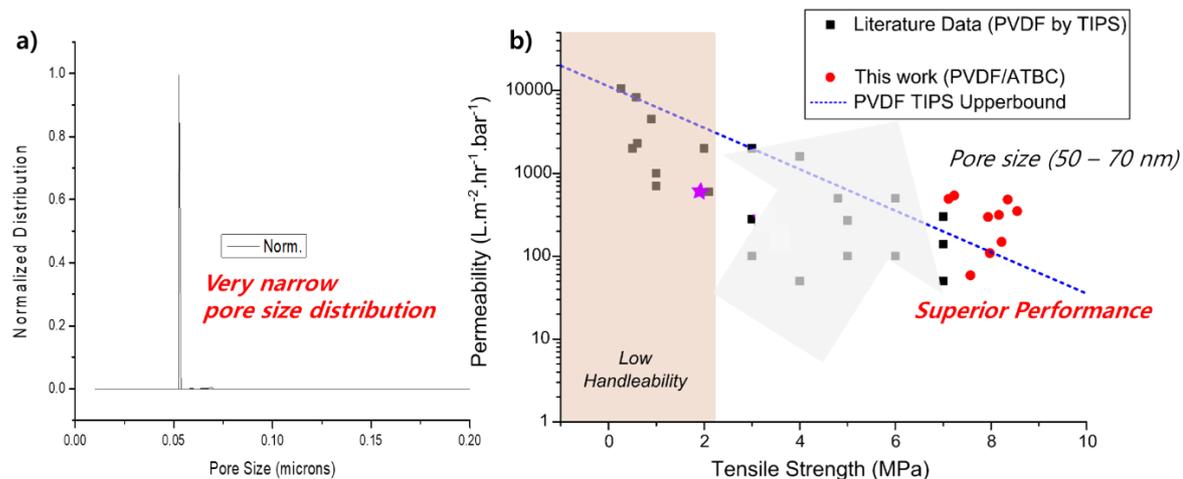


Fig. 5. PVDF membranes fabricated via TIPS using ATBC green solvent (a) pore size (b) performance (reprinted with permission from [8]).

One of the features of the TIPS method is that the membrane pores are induced by removing thermal energy from the dope solution, and since heat transfer is approximately an order of magnitude faster than mass transfer (NIPS), a more uniform formation of pores is possible, and a very narrow pore size distribution can be obtained, as shown in Figure 5(a).

It can also be confirmed from the data in Figure 5(b) that green alternative solvents can be used to fabricate membranes with competitive performance in the microfiltration range. However, the TIPS method is not suitable to fabricate membranes with pore size less than 50 nm, and hence was difficult to meet the requirements of the growing ultrafiltration and nanofiltration market.

3. N-TIPS (Nonsolvent and thermally induced phase separation) method

Recently, N-TIPS method has been reported that combines the advantages of NIPS and TIPS. The concept of N-TIPS was first reported by Matsuyama et al. back in 2002 [21], when solvent-nonsolvent exchange was observed on the surface during TIPS. Although a quenching drum is generally used to fabricate flat-sheet membranes via TIPS, water is an excellent quench

bath to fabricate hollow fibers via TIPS. One can appreciate that when a TIPS solvent has miscibility with water, NIPS effect can occur on the surface (dope-water interface). Notably, as heat transfer rate is much faster than solvent-nonsolvent exchange rate, the effect of NIPS mostly remains on the surface.

The phase diagram of N-TIPS can be illustrated by appending a temperature axis (see Figure 6) on a typical NIPS ternary diagram. Hence, the dope composition follows a path in 3-dimension, with simultaneous effects from TIPS and NIPS. A notable N-TIPS solvent recently identified is called Rhodiasolv PolarClean [7, 22, 23]. But since most solvents exhibit at least a small miscibility with water, N-TIPS effect is fairly common when water is used as a quenching bath, albeit rarely reported. Nevertheless, when carefully optimized, the surface pore size can be controlled down to the ultrafiltration range (3~50 nm), and possibly down to the nanofiltration level (0.5~3 nm). Therefore, the concept of N-TIPS may open new doors to apply green alternatives to fabricate ultrafiltration and nanofiltration membranes. In fact, the N-TIPS method is currently used to fabricate membranes for blood oxygenation applications using polymethylpentene (PMP). PMP polymer has limited solubility in most solvents and can only be fabricated into membranes via TIPS. However, interestingly, these membranes exhibit a dense skin layer,

indicating that it was fabricated by N-TIPS method.

It is worth noting that it is difficult to fabricate dense membranes with semi-crystalline polymers (PVDF and PP as main examples), as grain boundaries act as defects when trying to make dense or nanofiltration membranes. However, some semi-crystalline polymers with low crystallinity due to side chains, such as PVDF-co-HFP and PMP, can be processed to exhibit a skin layer.

On the other hand, there can be a case where a potential green alternative has a high miscibility with water, but no NIPS effect is desired. In such case, a novel solution to apply a triple spinneret was proposed by Jung et al. [24] and Jeon et al. [25], as shown in Figure 7.

The principle behind using a triple spinneret is to employ a transient coating layer between the dope solution and water quenching bath to temporarily inhibit the NIPS effect, and only allow heat transfer (TIPS) to proceed during the first few seconds (or minutes) of phase inversion, as illustrated in Figure 8. It can be seen that without a transient coating layer, a dense skin was observed on the surface, indicating that a rapid solvent outflow had occurred. On the other hand, when a hydrophobic transient coating layer (e.g. ATBC and DBP, not miscible with water) was introduced using a triple spinneret, a complete TIPS surface morphology was observed. The data clearly indicates that a transient coating layer prevents NIPS effect

on the surface, and the surface pore size can be controlled within the MF range. Interestingly, an intermediate result was obtained when a water-miscible solvent (e.g. NMP) was employed as a coating layer. Hence, this novel method effectively provides membrane researchers with a unique tool to control both the NIPS effect during a N-TIPS process and the pore size from MF down to NF range.

4. Reverse-engineering a new green solvent with solubility parameter approach

One of the essential tools in searching for green alternative solvents is the solubility parameter, more specifically, Hansen solubility parameter (HSP) [26]. Contrary to the Hildebrand solubility parameter (researchers need to refrain from using Hildebrand), Hansen solubility parameter can better describe solution thermodynamics using three discrete terms: polar term, dispersion term, and hydrogen bonding term. The thermodynamic aspects of membrane fabrication using HSP has been recently compiled and reviewed [4]. The HSP distance between a solvent and a polymer, also called Ra, is a useful parameter to estimate the applicability of a solvent (see Figure 9).

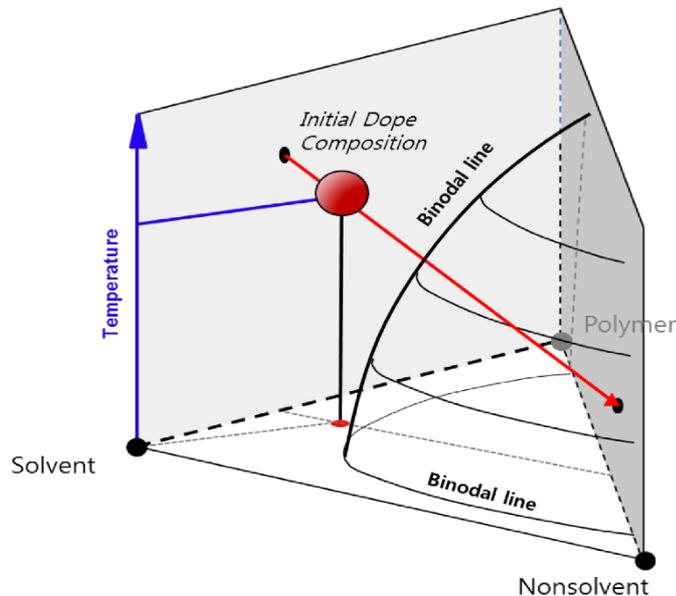


Fig. 6. N-TIPS phase diagram showing a path of a dope solution (reprinted with permission from [4]).

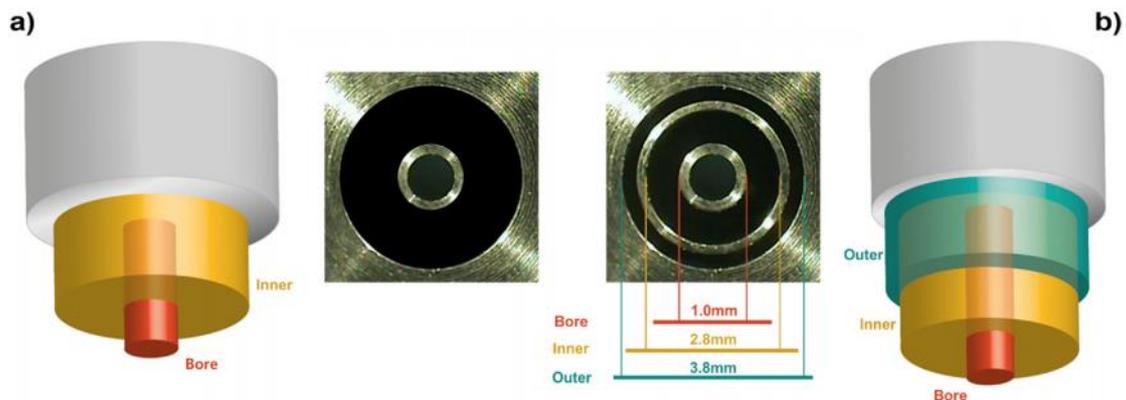


Fig. 7. Schematic of a triple spinneret to control NIPS during N-TIPS (reprinted with permission from [24]).

The requirements for TIPS and NIPS solvent are different. For instance, a stronger solvent is required for NIPS, whereas a relatively weak solvent at ambient temperature is required for TIPS. In other words, a lower Ra value is required for NIPS solvent. Based on the data we have collected in the past years, several trends can be obtained. First, having a dimethylamide functional group seems to enhance the solvation of polymers. For example, PolarClean has a dimethylamide functional group similar to DMF and DMAc, and has recently been applied to NIPS [11]. Secondly, water miscible solvent generally exhibits stronger interaction with membrane polymers (lower Ra). Thirdly, there is yet no clear relationship between green-ness and chemical functional groups. As membrane researchers search for more alternative solvents, we expect the data will continue to be accumulated. Furthermore, with more data, we will be able to reverse-engineer a solvent molecule that exhibits desired properties. However, there are still many hurdles to be overcome, such as absence of a clear guideline for green solvent, and absence of comparable dataset. A helpful guideline suggested by the GSK company could be used as a starting point [27]. In addition, membrane researchers must evaluate the solvents from membrane perspectives (*e.g.* recyclability, biodegradability, toxicity, etc.).

5. Minimizing mass intensity of membrane fabrication process

Another route to improve the sustainability of membrane fabrication process, just as important, is to lower its excessive mass intensity. Mass intensity (MI) is defined as the amount of spent reagent per mass of product.

An interesting work by Kim et al. [28] calculated the mass intensity for fabrication of organic solvent nanofiltration (OSN) membranes. As it can be seen in Figure 10(a), majority of the waste (> 95 wt.%) is the solvent-contaminated wastewater used as a coagulation bath. Kim et al. [28] proposed to utilize spray-coating technique to eliminate the need for coagulation bath and lower the waste generation drastically. The proposed method can be considered as EIPS, and phase inversion proceeds by evaporating off the solvent from the dope solution, inducing polymer solidification.

As discussed previously, VIPS and EIPS are slowly gaining more attention for couple of reasons. First, VIPS and EIPS proceed slower than that of NIPS and TIPS, and hence allows longer phase separation period. Such feature gives more control of the membrane morphology, and an ideal bicontinuous structure with high pore connectivity (higher permeability) can be obtained, as shown in recent works by Figoli et al. [6,29]. Secondly, and perhaps more importantly, VIPS and EIPS generate significantly less waste compared to that of NIPS and TIPS. As shown in Figure 10, the proposed method by Kim et al. can fabricate the same amount of membrane with much lower waste in much shorter time. This technique is applicable to fabricate NF and dense membranes. It is worth noting that the electrospinning method [30] is also becoming a promising option to fabricate MF membranes with much lower mass intensity, as low as the spray-coating technique. However, the overall productivity and throughput is very low (comparatively) at the same capital cost investment. Nevertheless, as shown in the work of Kim et al., [12] key environmental indicators such as waste generation, processing time, and CO₂ emissions all favor the spray-coating (or electrospinning) over NIPS and TIPS methods.

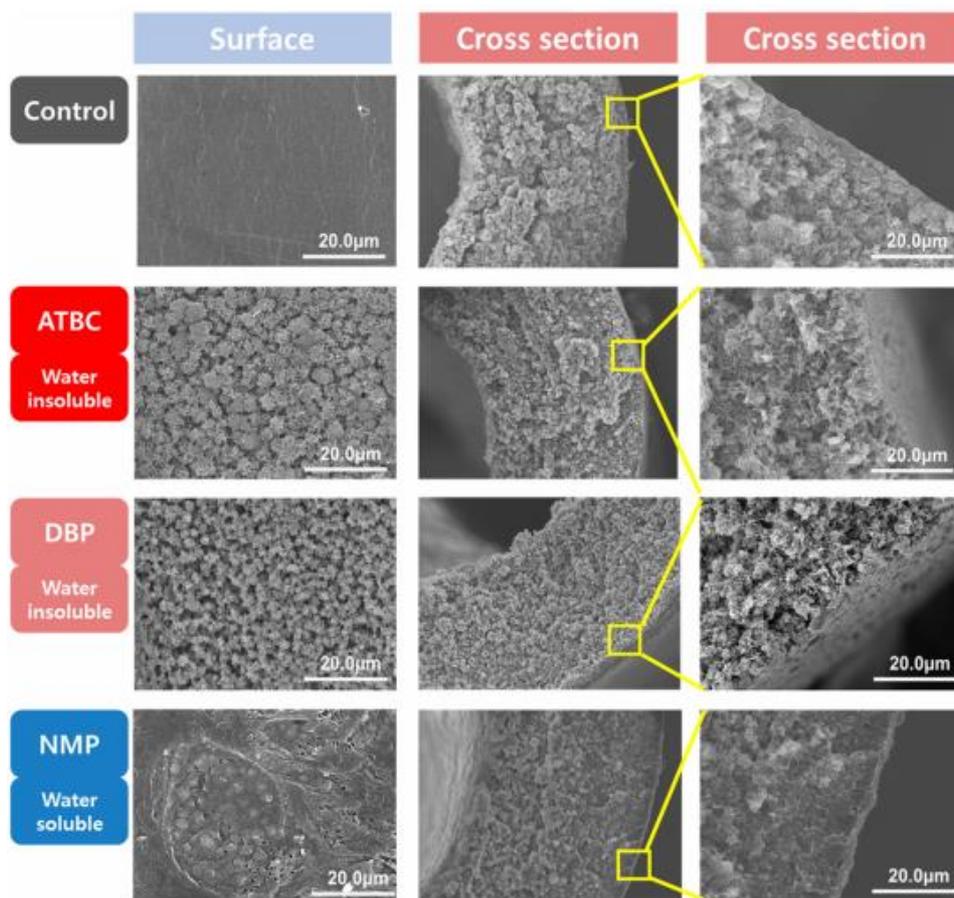


Fig. 8. PVDF hollow fiber fabricated with water-miscible PolarClean solvent using a triple spinneret via N-TIPS method (reprinted with permission from [24]).

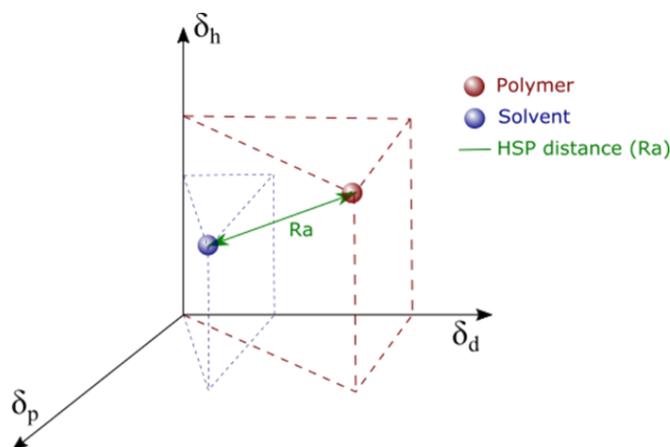


Fig. 9. Hansen solubility parameter distance (R_a) between a polymer and a solvent (reprinted with permission from [4]).

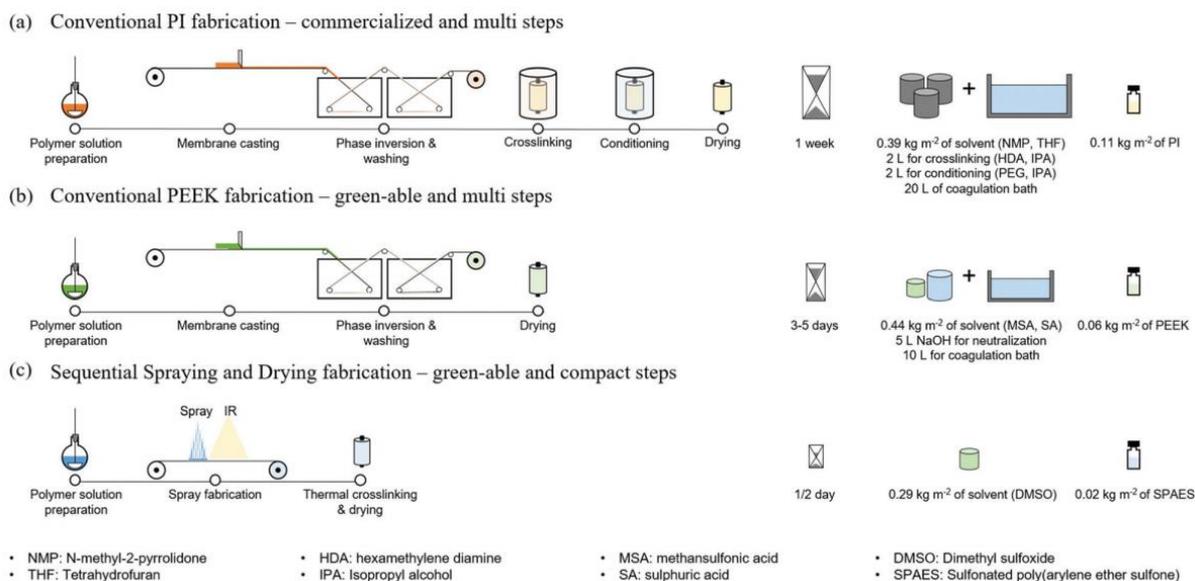


Fig. 10. Comparison of membrane fabrication protocols : (a) fabrication of crosslinked polyimide membranes by casting, NIPS, crosslinking, followed by conditioning steps, (b) fabrication of PEEK membranes using acidic solvents, (c) fabrication of membranes via sequential spraying and drying method. (reprinted with permission from [28]).

6. Sustainable treatment of solvent-contaminated membrane wastewater

Unfortunately, it is unlikely that NIPS and TIPS methods will be replaced by other methods anytime soon. Therefore, one of the most pressing challenges now is to lower the mass intensity of NIPS and TIPS in its current form. As shown in Figure 10 above, the best way to achieve this is to treat the solvent-contaminated wastewater sustainably. It is important to note that the solvent concentration in the wastewater is in the ppm level, and hence relatively low. Several different technologies exist to treat solvent-contaminated wastewater, mainly via biological treatment in wastewater treatment plants. However, an in-situ treatment within the membrane manufacturing plant could improve the overall sustainability. One potential solution may be to apply organophilic pervaporation to selectively permeate the solvent [31,32]. Another solution could be to apply adsorption technologies like molecularly-imprinted polymers (MIP) to selectively capture solvent molecules within wastewater [12].

The application of adsorption to treat membrane wastewater was neatly demonstrated by Szekely et al. [12] Seven different classes of adsorbents – graphene, polymers of intrinsic microporosity (PIM), molecularly imprinted

polymers (MIP), zeolites, metal organic frameworks (MOF), activated carbon (AC), and resins - were evaluated to selectively adsorb NMP and DMF from wastewater. MIP is a particularly interesting technology, as a specific adsorbent can be designed to match the shape of the adsorbate, as in key and lock configuration. Figure 11 shows the adsorption capacity and kinetic profiles of the tested adsorbents. The results show that MIP adsorbents show the highest adsorption capacity, whereas graphene oxide (EGO) and activated carbon (PHO) show the fastest adsorption. It is worth noting that DMF generally shows higher adsorption to most adsorbents compared to NMP, likely due to its unique amide functional group that can interact favorably with the adsorbents.

The unique advantage of MIP adsorbent is that it can be easily regenerated. Hence, a continuous adsorption unit process (50 g of adsorbent) was implemented to purify 12.5 L of membrane wastewater as shown in Figure 12. The system can be automated to treat membrane wastewater in a sustainable way. It was also tested that MIP adsorbent can maintain its full performance up to 10 cycles.

The efficacy of the wastewater treatment and recyclability of the purified water was also tested. It was determined that the membrane fabricated with

NMP-contaminated coagulation bath exhibit lower permeance and higher rejection compared to the membranes cast from fresh water. This expected result is due to the fact that solvent molecules in the water, albeit small, affect the membrane formation kinetics. The important result is that the membrane fabricated with the purified water show almost identical performance to the membranes prepared using fresh water, validating the recyclability of the membrane wastewater.

Figure 13 summarizes the important outcome of the proposed method. It can be seen that the mass intensity of membrane fabrication process can be reduced by near 99% if the proposed wastewater recycling unit with adsorbents is implemented. The proposed unit is simple and can be automated, and can dramatically improve the overall sustainability of the membrane fabrication process. The use of adsorption process also has some disadvantages such as generation of solid waste and the need for regeneration of adsorbents. On the other hand, membrane-based processes such as organophilic pervaporation does not suffer from such disadvantages and could offer more compact and continuous operation if a reliable membrane can be developed.

Apart from the three main points discussed in this review, membrane researchers are also working on different aspects of membrane fabrications. The works by Szekely group to use bio-derived bamboo materials as nonwoven supports [33], use of biophenol coatings to improve the chemical stability of membranes and to fine-tune the selectivity [34,35], and incorporation of 2nd function into the membranes to achieve process intensification [36,37], give a clear direction on how to improve the sustainability of membrane processes.

In order to fully clarify the vague concept of “sustainability” in membrane technology, it is indeed necessary to employ the life cycle assessment (LCA) technique to assess the overall cycle. However, although LCA has been used to analyze membrane processes such as desalination [38-40], an LCA on membrane fabrication has not been carried out yet, likely due to its complexity involving many different chemicals and polymers.

7. Conclusions

In this short review, recent progress for improving the membrane fabrication process was assessed. Although not as widespread as it should be, the notion of unsustainable membrane fabrication mass intensity has been spreading, and the number of research articles on this issue has been rising steadily. Most of the work has been dedicated on replacing the toxic solvent

to prepare a dope solution, explaining the reason why TIPS has been gaining a lot of attention. The concept of N-TIPS to fabricate UF and NF membranes using a green solvent has been discussed, and an interesting means to control the phase separation phenomenon using a triple spinneret was reviewed. With more data on green solvents, it will soon be possible to apply solubility parameter method to reverse-engineer an ideal green solvent. Apart from finding solvent alternatives, recent works for reducing the mass intensity of current phase inversion method were evaluated. Particularly, VIPS/EIPS and electrospinning methods offer significant advantages to prepare high performance membranes with much lower mass intensity. Finally, the use of adsorption technologies to treat the solvent-contaminated wastewater seems to be a suitable solution to drastically lower the mass intensity of current NIPS&TIPS processes.

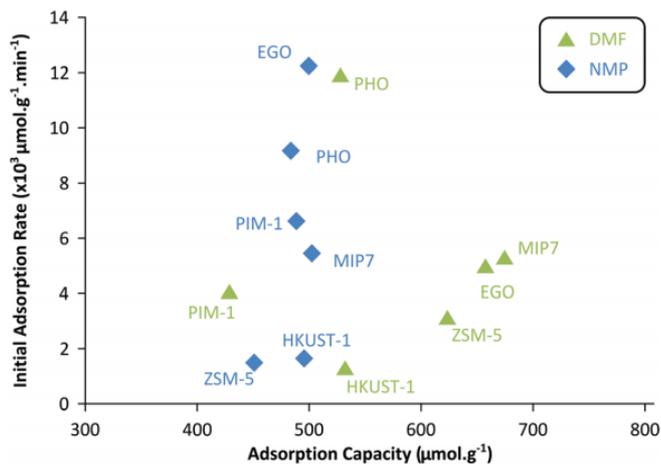


Fig. 11. Adsorption capacity versus initial adsorption rate for the tested adsorbents. (Reprinted with Permission from [12]).

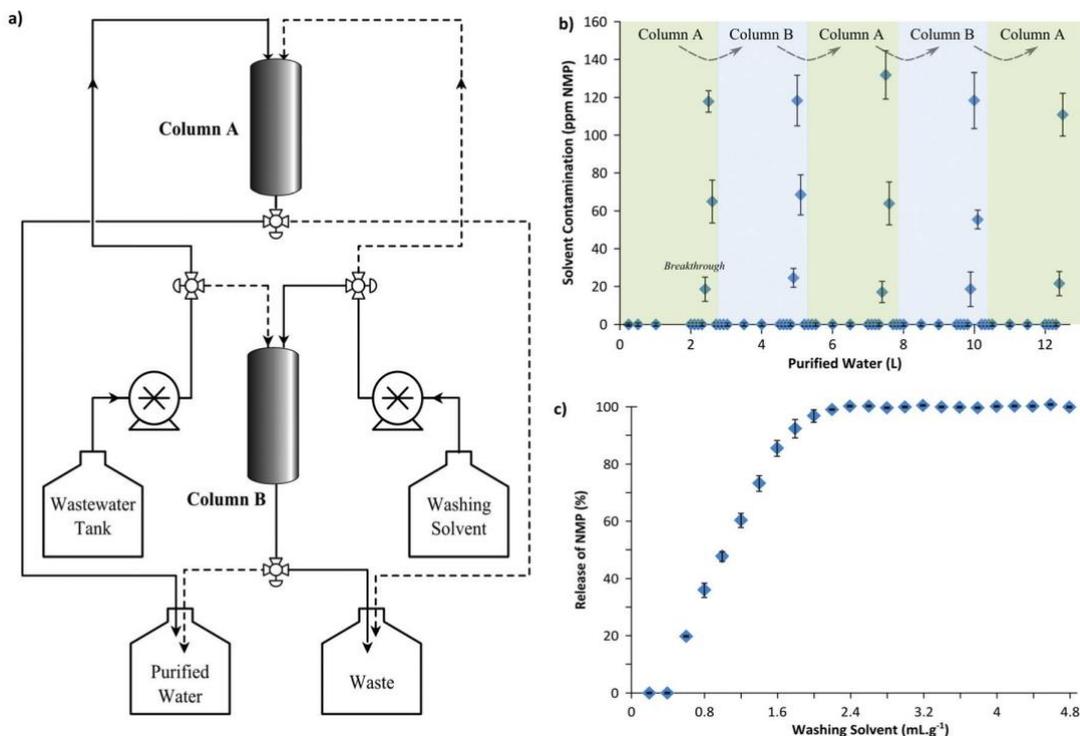


Fig. 12. (a) Continuous adsorption unit process diagram. Two columns were used simultaneously to purify contaminated wastewater while regenerating saturated adsorbent; (b) continuous purification of wastewater from membrane casting; (c) Adsorbent column regeneration profile using a washing solvent (MeOH:water 1:9). (reprinted with permission from [12]).

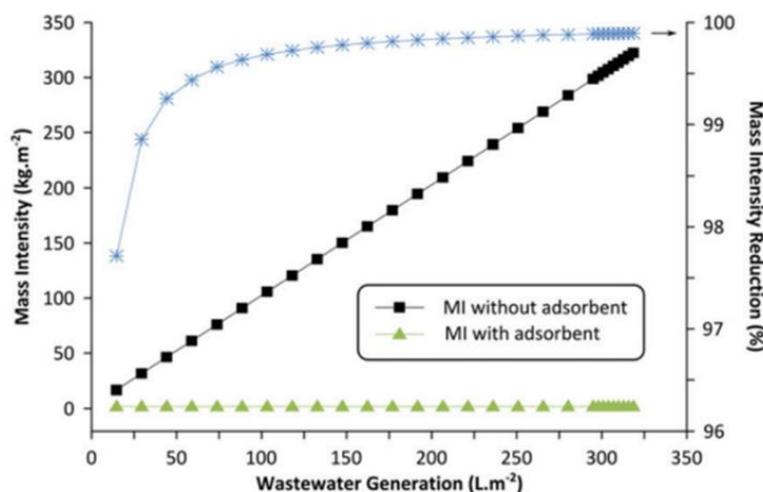


Fig. 13. Mass intensity with and without an adsorption unit: over 99% mass intensity reduction is achieved with adsorption. (reprinted with permission from [12].

Acknowledgements

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 201820101066550 and No.20172010106170)

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