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14. ABSTRACT

A highly breathable barrier film was developed during the course of this ARO-funded project. The development of a novel polymer material based on a diol-functionalized room-temperature ionic liquid (RTIL) monomer led to fabrication of membranes, which were tested for their ability to transport water and the CWA stimulant CEES, both in the vapor phase. The neat diol-RTIL polymer was highly breathable with respect to water vapor but also allowed CEES vapor to penetrate. By incorporating amines and zeolites to make composite materials, the resulting membranes effectively blocked CEES while still transporting water at a flux rate above DoD specifications. We are continuing aspects of this work with partial support from a separate DTRA grant. We are currently optimizing the membrane performance and working to determine the mechanism of CEES blockage.

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Final Report

Novel Nanocomposite Structures as Active and Passive Barrier Materials: CBT
Project # ARO AB07CBT010

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Abstract

A highly breathable barrier film was developed during the course of this ARO-funded project. The development of a novel polymer material based on a diol-functionalized room-temperature ionic liquid (RTIL) monomer led to fabrication of membranes, which were tested for their ability to transport water and the CWA stimulant CEES, both in the vapor phase. The neat diol-RTIL polymer was highly breathable with respect to water vapor but also allowed CEES vapor to penetrate. By incorporating amines and zeolites to make composite materials, the resulting membranes effectively blocked CEES while still transporting water at a flux rate above DoD specifications. We are continuing aspects of this work with partial support from a separate DTRA grant. We are currently optimizing the membrane performance and working to determine the mechanism of CEES blockage.

Objectives

The objective of this project was to develop a barrier film material that blocked penetration of chemical warfare agents (CWAs) in the vapor phase while being highly breathable to water vapor. This material would protect personnel while reducing the thermal burden typically associated with such protective garments. The ideal material would have a water vapor flux of at least 1.5 kg m^{-2} day^{-1} and exhibit complete rejection of CWA stimulant vapor.

Technical Report

A polymerizable room-temperature ionic liquid (**4**, Figure 1) was chosen as the starting material for making poly(RTIL) ionic polymers, which are the main components of these thin film barrier materials. Previous work in our labs involving poly(RTILs) as membranes for light gas separations (i.e., CO_2, N_2, CH_4) gave remarkable permeability and selectivity values.[1] Because of these unique properties, the poly(RTIL) scaffold was a logical choice for a base material that could selectively block CWAs while transporting water vapor.

RTILs are a unique class of materials with interesting physical and chemical properties. They are ionic in nature, yet contain organic functionality, which makes structural manipulation feasible. For example, the common RTIL [Hmim][Tf_2N] (**1**, Figure 1) can be derivatized via organic synthesis to prepare a poly(RTIL) analog (**2** or **3**). By combining the poly(RTIL) monomer (**2**) and a radical photoinitiator and exposing to UV light, a polymerization reaction occurs resulting in a poly(RTIL) (**4**). By varying the conditions of the polymerization process we can obtain many types of polymeric material. In this work, the polymerization was carried out between glass plates to produce thin film materials (~150 μm thickness). A support material was also employed during this process to impart mechanical stability to the film which simplifies handing and testing of the membrane.

Figure 1: Structures of common RTILs and poly(RTILs)

Attempts to produce breathable barrier films from poly(RTILs) containing pendant alkyl groups such as [Hvim][Tf_2N] (**3**, Figure 1) resulted in a membrane that was impermeable to both water vapor and the mustard agent stimulant, CEES. In order to develop a material that was breathable and able to transport water vapor, new poly(RTILs) were investigated with alternate functionalities in place of the alkyl group. Polar organic functional groups were chosen because of their hydrophilic nature.

Figure 2: Structures of diol-functionalized RTILs

While preparing a new class of RTILs with a vicinal diol functional group, some unique phase behavior between the RTIL and water was observed.[2] RTILs bearing the diol group with short alkyl chains on the cation (**5** and **6**, Figure 2) were completely miscible with mater. When the alkyl chain was extended (**7-10**), the RTILs became hydrophobic and formed a separate phase when mixed with water. This interaction with water was noteworthy and prompted the synthesis of a polymerizable diol-functionalized RTIL.

We initially chose to prepare a RTIL monomer containing a styrene polymerizable group because much of prior work in our labs with poly(RTIL) membranes employed the same moiety. To prepare the styrene poly(RTIL) monomer (**12,** Scheme 1), imidazole was alkylated to give compound **11**, which was then quaternized and ion exchanged to give the monomer (**12**) in 13% overall yield. The monomer (**12**) was highly viscous, which made it difficult to work with, and easily auto-polymerized in the presence of heat or light. The small amount of material that we were able to isolate and process into a thin film showed high water vapor flux in preliminary testing.

Scheme 1

Because of the low yielding synthesis and difficulty handling the styrene monomer, we sought to develop an alternate monomer that contained a more robust polymerizable group.[3] We chose to replace the styrene with a more stable vinyl group. The synthesis of the vinyl poly(RTIL) monomer (**14**, Scheme 2) began with commercially available vinylimidazole, which was then quaternized and ion exchanged over two steps in 80% yield. Not only could this material be produced quicker and more efficiently, but the resulting product (**14**) was less viscous than the styrene analog and not prone to auto-polymerization problems. The synthesis is scalable to several hundred grams and employs inexpensive reagents and gives a relatively pure crude product. Further purification by a simple chromatographic method results in a monomer with over 98% purity.

Scheme 2

The diol-functionalized RTIL monomer was processed into supported poly(diol-RTIL) (**15**, Scheme 3) thin films by photopolymerizing the diol-RTIL monomer **14** between glass plates on a Supor (polysulfone) support. The resulting films ranged in thickness from 140-160 µm. The films were tested in our labs for their ability to transport water and compared to commercial breathable polymers (Figure 3). Our material was quite breathable but did not perform as well as the commercial polymers. Both ePTFE and Omniflex are porous materials that transport water by allowing it to pass through microscopic pores, which preclude them from acting as barrier materials. Nafion is a breathable polymer with barrier properties but it is very expensive to produce and must be hydrated in order to efficiently transport water. Although our material's flux is lower, it offers several performance and cost advantages over the industry standards. It is also worth noting that our films are still relatively thick and that flux is inversely proportional to thickness, so processing them into thinner films should result in higher water vapor flux.

Scheme 3

Poly(diol-RTIL) membranes were sent to Phil Gibson at Natick to be tested using his cross-flow apparatus for water and CEES vapor penetration. The results from Natick confirmed that the poly(diol-RTIL) was highly breathable with a water vapor flux of 6.2 kg m^{-2} day^{-1} (4-fold higher than the DoD spec). However, the poly(diol-RTIL) film lacked barrier properties and was completely permeable to CEES vapor.

In an attempt to impart barrier properties to the poly(diol-RTIL) membranes, various reagents were blended into the polymer matrix as composites, or additional functional monomers were reacted with monomer **14** to form copolymers. The reagents were added to react with or bind to the CWA and render it inactive. A number of reagents were screened and it was found that those containing a base (*i.e.* amine or zeolite) were effective at blocking CEES penetration. By combining these basic reagents with the poly(diol-RTIL) a breathable barrier material that blocks CEES was obtained.

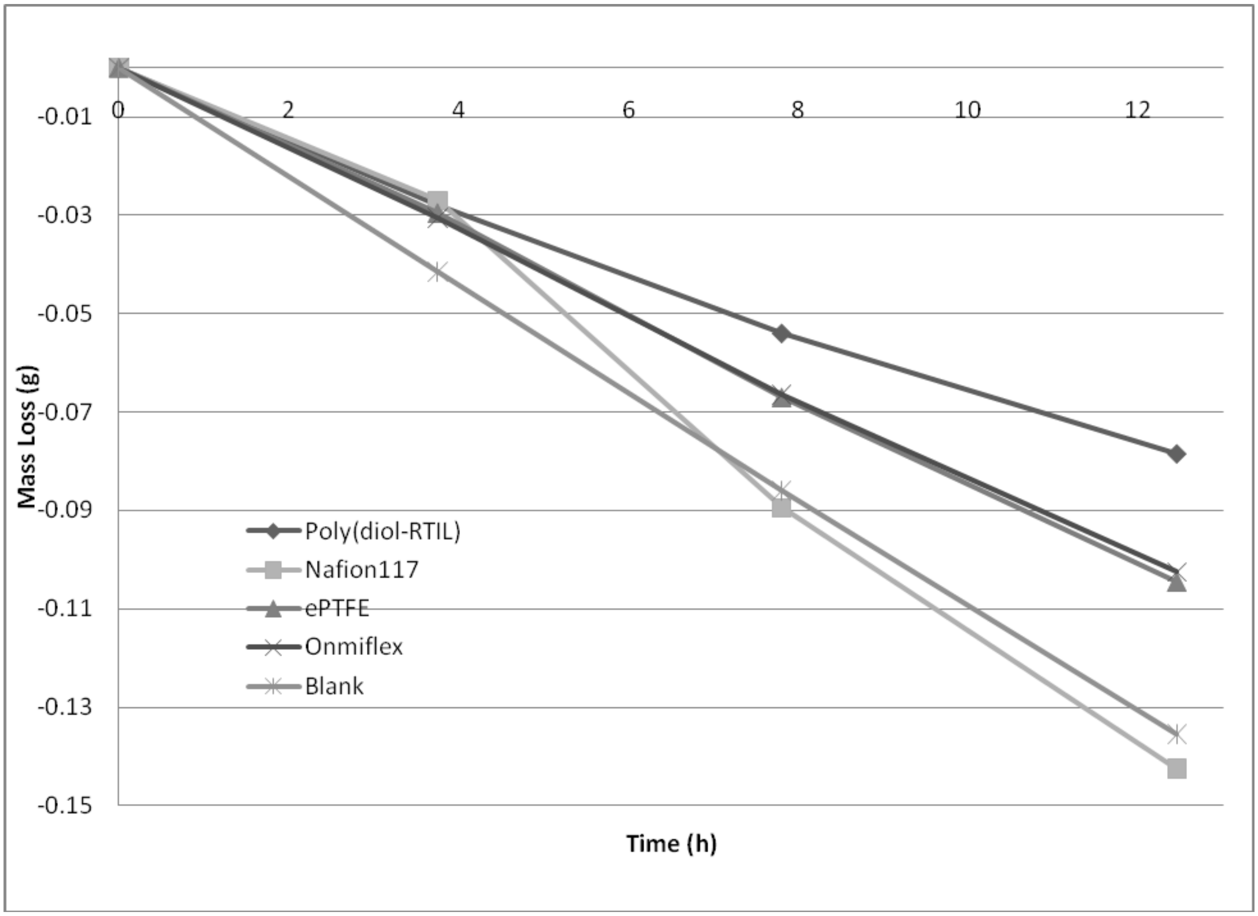

Figure 3: Representative water vapor transport test plot. Data points are the average of three independent sample runs performed in the same round of testing.

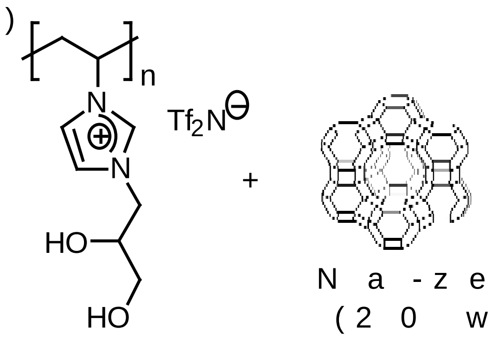

Figure 4: Structures of composite and copolymer materials that transported water and blocked CEES.

Results from the water and CEES vapor penetration testing done at Natick are shown in Table 1. The poly(diol-RTIL) membrane showed a high rate of water flux but also allowed CEES to pass through freely. By adding amines as either a composite or copolymer (Figure 4), the resulting membranes rejected CEES vapor completely but still transported water vapor well above the DoD requirement, even as relatively thick 150 µm films. The composite material showed a higher water flux which was also observed for composite membranes in light gas separations in our lab.[4] The zeolite-poly(diol-RTIL) composite membrane, containing 20 wt% sodium-Y zeolite, also showed a high water vapor flux while rejecting CEES completely.

Membrane	**Type**	**Water Flux (g·m^{-2}·day^{-1})**	**CEES Penetration (%)**
Poly(diol-RTIL)	Polymer	6200	100
Poly(diol-vinylimidazole)	Copolymer	2390	0
Poly(diol-RTIL)/TMHDA	Composite	3770	0
Poly(diol-RTIL)/Na-zeolite Y	Composite	2870	0

Table 1: Results for water and CEES vapor penetration provided by Dr. Phil Gibson from Natick.

The ability of the poly(diol-RTIL)-amine composite membranes to block CEES penetration is thought to involve nucelophilic attack of the amine on the chloride of CEES (Scheme 4). The nucleophilic nitrogen atom on the amine forms a covalent bond with CEES and binds it to the polymer back bone. This reaction is rapid and irreversible. The mechanism for the blockage of CEES by the poly(diol-RTIL)-zeoloite composite material is unknown at this point.

Scheme 4

Our labs recently received additional funding from DTRA to continue investigating aspects of this very promising selective barrier film work, even after the completion of this ARO CBT grant. We are currently developing the next generation of poly(diol-RTIL) composite barrier materials by varying the loading of the basic reagents and screening for the most reactive and high capacity additives. We are also using a number of techniques (IR, NMR, SEM, combustion analysis) to determine the mechanism of CEES rejection and the kinetics of CEES degradation in RTILs.

Publications, Presentations and Intellectual Property Generated

Publications:

1. LaFrate, A. L.; Bara, J. E., Gin, D. L. & Noble, R. D. *Ind. Eng. Chem. Res.* **2009**, *48*, 8757-8759. **(Diol RTIL)**
2. Hudiono, Y.C.; Carlisle, T.K., Bara, J.E., Zhang, Y., Gin, D.L., Noble, R.D *J. Membr. Sci.* **2010**, 350. **(Zeolite-RTIL-Poly(RTIL) Composite Membranes)**
3. LaFrate, A. L.; Gin, D. L. & Noble, R. D. *Ind. Eng. Chem. Res.* 2010, ASAP Article **(Poly(Diol-RTIL))**
4. Hudiono, Y.C.; Carlisle, T.K., LaFrate, A.L., Gin, D.L., Noble, R.D. *J. Membr. Sci*. to be submitted Summer 2010 **(Zeolite-poly(RTIL) Composites)**
5. LaFrate, A. L., Hudiono, Y. C., Gibson, P.; Gin, D. L., Noble, R. D. *Advanced Materials* to be submitted Fall 2010 **(Poly(Diol-RTIL)-Amine/Zeolite composite barrier films)**

Patent applications:

1. Diol-RTILs and poly(diol-RTIL): Spring 2009
2. Poly(diol-RTIL) – amine/zeolite composites: Spring 2010
3. Zeolite-RTIL-Poly(RTIL) Mixed Matrix Membranes: Summer 2010

Presentations

1. LaFrate, A. L. *Novel Nanocomposite Structures as Active and Passive Barrier Materials* Presented at DTRA/JSTO CBD PHM S&T Review for Protective Clothing/Fabrics, Washington D.C., April **2009**.

2. Hudiono,Y.C., LaFrate, A.L., Gin, D.L., Noble, R.D., *Polymerizable Room Temperature Ionic Liquid – Zeolite Composite Membrane for Barrier Materials*, 2009 NAMS Meeting, Washington, D.C., July 18 – 22, **2009.**
3. Hudiono, Y.C., Carlisle, T.K., Bara, J.E., LaFrate, A. L., Gin, D.L., Noble, R.D., *CO2 Separations Using Room Temperature Ionic Liquid-Inorganic Nanoparticle Based Membranes*, 2009 AIChE Annual Meeting, Nashville, TN, November 8-13, **2009**
4. Hudiono, Y.C., LaFrate, A.L., Gin, D.L., Noble, R.D., *Newly Developed Composite Membranes Based on Room Temperature Ionic Liquid For Barrier Films*, 2009 Chemical and Biological Defense Science and Technology, Dallas, TX, November 16-20, **2009.**
5. LaFrate, A. L.; Carlisle, T. K.; Noble, R. D.; Gin, D. L. *Development of Barrier Film Materials Using Imidazolium Polymers,* Poster Presented at CBD Conference, Dallas, TX, November **2009**.
6. LaFrate, A. L.; Noble, R. D.; Gin, D. L. *Vinyl-substituted polymerizable room-temperature ionic liquids: Synthesis, polymerization, and properties*, poster presented at the 239th American Chemical Society National Meeting, San Francisco, CA, March 23, **2010**.
7. Hudiono, Y.C., Carlisle, T.K., Bara, J.E., Zhang, Y., Gin, D.L., Noble, R.D., *Novel Mixed Matrix Membrane Based on Ionic Liquid Improves CO2 Separation*, NAMS Meeting, Charleston, SC, June 20-24, **2010**

References

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[1] Carlisle, T. K.; Bara, J. E.; Gabriel, C. J.; Noble, R. D.; Gin, D. L. Interpretation of CO_2 Solubility and Selectivity in Nitrile-Functionalized Room-Temperature Ionic Liquids Using a Group Contribution Approach. *Ind. Eng. Chem. Res.,* **2008**, *47*, 7005–7012.

[2] LaFrate, A. L., Bara, J. E.; Noble, R. D.; Gin, D. L. Diol-Functionalized Imidazolium-Based Room-Temperature Ionic Liquids with Bis(trifluoromethanesulfonimide) Anions that Exhibit Variable Water Miscibility. *Ind. Eng. Chem. Res.,* **2009**, *48*, 8757-8759.

[3] LaFrate, Andrew L.; Gin, Douglas, L. and Noble, Richard D. *High Water Vapor Flux Membranes Based on Novel Diol-Imidazolium Polymers. Industrial and Engineering Chemistry Research*, **2010**, in press.

[4] Bara, J. E.; Hatakeyama, E. S.; Gin, D. L.; Noble, R. D**.** Improving CO2 Permeability in Polymerized Room-Temperature Ionic Liquid Gas Separation Membranes Through the Formation of a Solid Composite with a Room-Temperature Ionic Liquid. *Polym. Adv. Technol.,* **2007**, *19*, 1415-1420.