Crosslinkable Bicontinuous Cubic Assemblies via Mixtures of Gemini Amphiphiles and Butyl Rubber

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**Abstract**

The original document contains color images.
Introduction

Uses of Butyl Rubber (BR) as barrier material fabric

Advantages:

• Low permeability toward organic solvents, and reactive chemicals
• Excellent chemical resistance
• Low cost

Disadvantages:

• Lack of permeability of air and water vapor
  → Development of fatigue and heat stress in wearer
Overview of Lyotropic Liquid Crystals (LLCs)

- LLCs are amphiphilic molecules that can self-assemble into nanoporous structures.
- Multiple phases: hexagonal ($H_i$), lamellar (L), bicontinuous cubic (Q), inverted hexagonal ($H_{II}$), etc.
- Robust nanoscopic architectural material can be obtained upon crosslinking.
- Application: nanoscale reaction, separation, transportation, etc.
Approach: LLCs and BR Composites

Covalent bonding of surfactants

= BR Precursor

Polymerizable group

Head group

= Polymerizable surfactant

Self assemble

uv

Polymerized surfactant

heat

Vulcanized rubber

BR (Cross-linked)

pore
**Prior Work in H‖ Phase of LLC-1 / BR System**

- LLC-1 retains H‖ phase even with BR content as high as 75 wt %.
- Retention of H‖ structure upon photo-initiated radical polymerization.
- Water vapor permeable and chemical agent simulant CEES impermeable.

Done by Dr. Jizhu Jin
Problems in LLC-1/BR Composites

- Requires pore alignment and continuity through material for maximum transportation.
- The acrylate ester tail is not hydrolytically stable.

![Diagram showing water vapor channels and their conditions.](image)
New objective: Bicontinuous Cubic Phases

- Image of polarized light microscopy (PLM): Black (Pseudo isotropic)
- X-Ray diffraction (XRD): D-spacing proceeds in the ratio:
  \[ 1 : 1/2^{1/2} : 1/3^{1/2} : 1/4^{1/2} : 1/5^{1/2} : 1/6^{1/2} : 1/7^{1/2} : 1/8^{1/2} \ldots \]

Advantage:

3-dimensional network of pores: eliminate the alignment problem

Prior Work on Bicontinuous Cubic Phase LLC Monomers

Disadvantage:

- Brittle after cross-linking in pure form

> Difficult to make barrier material

Research Objectives

- Characterize composition and temperature ranges of LLC BR mixtures and specifically identify the bicontinuous cubic phase region

- Produce films of “breathable” cubic phase LLC- BR composites

- Characterize and optimize the polymerization of the surfactants and the vulcanization of the BR.

- Test the films for permeation of water vapor and rejection of chemical agent stimulants.
Blending and copolymerizing of Gemini Monomers with BR

**Blending Procedure**

- LLCs and H₂O were mixed in a glass vial and centrifuged three times (3800 RPM, 15 min.).

- Add the LLC mixture obtained in the above step with BR precursor solution (10 wt. % in hexane) and then mix/centrifuge three times (3800 RPM, 15 min.).

- Equilibrate above mixture for at least 16 hours at room temperature for testing.
**Characterization of Cubic Phase**

- **Proof-of-concept** for blending LLC with BR precursor with retention of cubic structure.
Preliminary Phase Diagram of LLC - BR Composites

Q: Cubic; H: Hexagonal; L: Lamellar; M: Mixture; Other regions are unidentified.

- Cubic phase can be made at high temperature.
Polymerization of the Cubic phase LLC-BR composites

- Retention of cubic phase upon radical polymerization
- The polymerized material is flexible.
- Degree of polymerization is to be done by IR.
Processing to Make Membranes

- Solvent casting – no retention of cubic phase after solvent evaporation

- New method: **Pressing**

  - The LLC-BR precursor gel is put between two Mylar sheets and pressed by hydraulic press at room temperature
  - Heat up to 75±10°C to form the desired cubic phase
  - Cross-link to lock the structure

- LLC-BR cubic phase can be formed as supported film for barrier application.

XRD of above thin film

- 30.0Å (1/6½)
- 25.3Å (1/8½)
- 18.8Å (1/16½)

69.5% LLC-2 27.0% H₂O 3.5% BR
Summary and Future Work

Summary

• Bicontinuous cubic phase was made by blending and copolymerizing LLC surfactants and commercial BR.

• The material can be precessed and applied as thin films for barrier materials.

Future Work

• Explore better methods to make supported thin film

• Test mechanical properties of breathable cubic LLC-BR composites

• Test the permeation of Water vapor and chemical agent simulants with TDA Research
• Professor Doug Gin

• Dr. Jizhu Jin - Gin group

• Dr. Brian J. Elliott - TDA Research, Inc.

• ARO Funding(grant #:DAAD19-02-C-0018)