Recent Advances of Benzoxazine Precursors for Multidisciplinary applications in Petroleum and Chemical Engineering

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Abstract

Polybenzoxazine is a new class of thermosetting polymers that have gained a great interest in many applications. The extraordinary flexibility in molecular design of polybenzoxazines allows the synthesis of benzoxazine precursors in different functionalities. The presence of suitable reactive groups into benzoxazine monomers leads to widening the applications of benzoxazine resins. In addition, the supramolecular structure of benzoxazine monomers and their unique properties provide the benzoxazine field a potential candidate for engineering applications including enhanced oil recovery, adsorption, coatings, and membrane processes. This review highlights the recent advancements of benzoxazine precursors for multidisciplinary engineering applications and the role of benzoxazine functionalities for the desired application field.

Keywords: Polybenzoxazine; chemical; petroleum; gas; applications.

1. Introduction

Thermosetting polymers are considered as an important class of materials for many applications. The potential applications originate from their network structures. The structures are responsible for dimensional stability, chemical resistance, and improved thermal and physical properties. In general, the structure of the thermosetting polymers consists of long macromolecular chains crosslinked with each other by chemical or physical bonds to form three-dimensional network. Different methods have been reported for the polymerization process including heat, chemical reaction, or irradiation [1-3]. Benzoxazine resins commonly known as polybenzoxazines are a recently developed class of thermosetting polymers that belongs to the addition polymerized phenolics family. Although the history of benzoxazine dates back to 1944 when Holly and Cope developed a small molecular weight benzoxazine [4], the first study for the synthesis and properties of crosslinked polybenzoxazines and their properties was reported in 1994 by Ning and Ishida [5]. From then on, many articles have been published on the development of polybenzoxazines [6, 7] and recently a handbook of benzoxazine resins covered most of up-to-date researches in polybenzoxazine area was edited by Ishida and Agag [8]. Benzoxazine monomers are synthesized via the Mannich condensation reaction of a primary amine, phenol, and formaldehyde. The polymer is then undergo polymerization when subjected to high temperatures through cationic ring opening polymerization mechanism without any added initiators, catalysts, or by-product formation as shown in Figure 1.1.

At the discovery of polybenzoxazine, it was proposed to be a replacing material for the traditional phenolic resins, as the polymerization through ring-opening approach eliminated almost all the short-
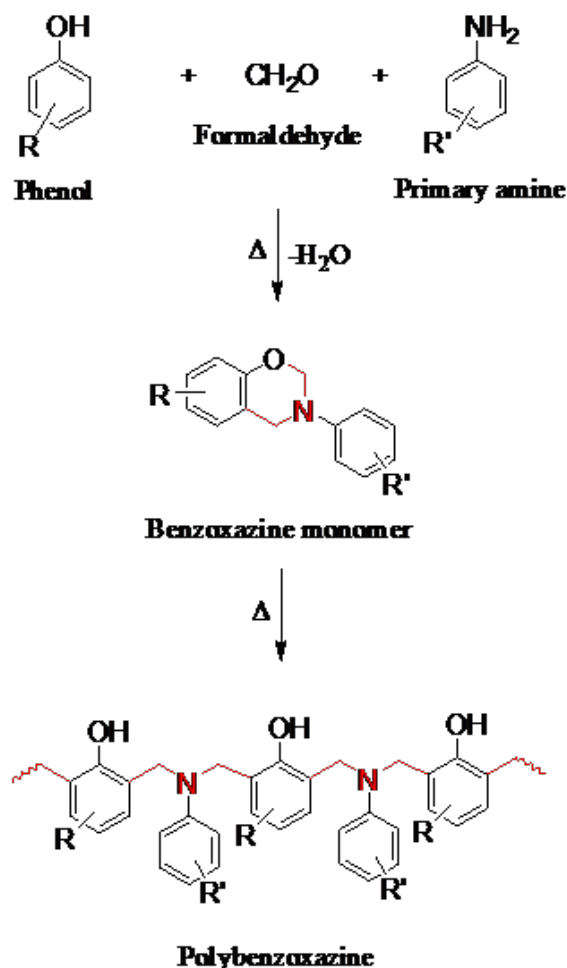
Figure 1.1: Condensation reaction of primary amine, phenol and formaldehyde to form benzoxazine monomer. The polymer is then undergoes polymerization when subjected to high temperatures.

comings associated with the polymerization through condensation reactions. Several studies showed that polybenzoxazines feature a wide range of properties that enable their use in many demanding applications. The diversity of their applications comes from the extremely flexible molecular design, near zero shrinkage upon polymerization and excellent thermal and mechanical properties [9].

These days, polybenzoxazine is not considered as a replacement material for the traditional phenolic resins, but as a class of materials with properties far beyond those materials. The polymer can be applied to areas where phenolics, epoxies, polyesters, vinylesters, bismaleimides, cyanate es-

ters, and polyimides are used. The remarkable flexibility in molecular design of monomers allows the entire range from inexpensive to high performance materials to be synthesized. Therefore, polybenzoxazines have been considered in many potential application areas include coatings and adhesives, gas adsorption, aerospace and automobile materials, electronic packaging materials, polymeric surfactants, and matrices for composite materials. For example, the high performance mechanical and physical properties with T_g of about 350 °C, make them a good choice for aerospace applications. This considers benzoxazine resins as an alternative to the traditional epoxy chemistry that has served the aerospace industry for decades.

Furthermore, the combination of some physical and mechanical properties (e.g. low water absorption, low coefficient of thermal expansion, low dielectric constants ($\varepsilon = 2.7$) and loss factor (better than 0.01)), offer the benzoxazine to be a good candidate for electronic packaging materials. These values favorably compare with many polymers that are considered low dielectric constant polymers [10]. In addition, the low viscosity, easy processability and no volatile formation properties in a combination with excellent mechanical properties make the polymer very attractive for composite material manufacturing. Another property of the benzoxazine polymers is having both acidic and basic nature which offers wide applicability as adhesives for both basic and acidic surfaces due to acid-base interactions [11]. This phenomenon can help effectively both acidic and basic fillers to be interacted with benzoxazine resins. In this review article, the strategies for the preparation and the structure–property relationships of some of different benzoxazine precursors used for these applications are highlighted.

2. Coating and Adhesives

Polymers are considered the best choice as coating material. Materials that have a low surface energy attracted significant attention due to their practical applications. Most of the low surface energy polymeric materials that have been developed were based on flurorine- or silicon-containing polymers. Both poly(tetrafluoroethylene) (PTFE) and poly(dimethylsiloxane) (PDMS) are well-known materials that possess low surface free energies. PTFE is considered as the benchmark of lower surface free energy material. However, PTFE and many fluorinated polymers have some limited application such

26

as high cost and poor processability.

Polybenzoxazines have been reported as low surface free energy materials with a wide range of interesting features including near-zero volumetric change upon polymerization, good UV and chemical resistance, and higher glass-transition temperature. In this context, these remarkable properties of polybenzoxazines suggest their use among other polymers in coating and adhesive applications.

Steel is an important part for applications in highways, bridges, buildings, oil and gas, and chemical processing systems. Mild steels are selected for construction because of their mechanical properties whereas stainless steels are widely used in industry due to their resistance against some corrosion phenomena and their low price. However, stainless steels cannot meet the requirements of corrosion resistance under certain conditions, which results in the application of coatings on steel surface as a cost effective way to inhibit the process of corrosion. There are few reports on polybenzoxazines associated with corrosion-inhibiting coating. In general, silane-functional benzoxazine [12-14] can be used as an anticorrosive coating material with superior adhesion. In addition, a fluorinated silane-functional benzoxazine, which can bond to the substrate through the Si–O–Si linkage, was also reported [15] as shown in Figure 2.1. The films prepared from these polymers exhibited surface free energy of about 15 mJ/m^2, which is much lower than that of pure Teflon of 21 mJ/m^2.
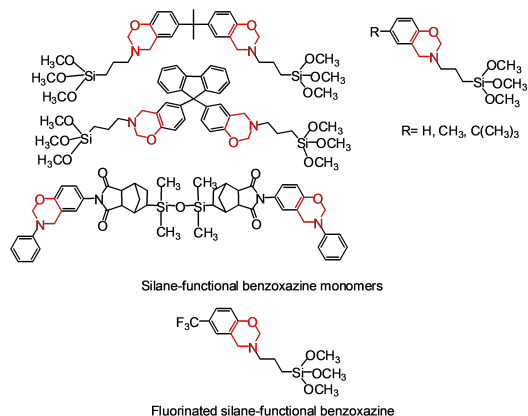

Figure 2.1: Silane functional benzoxazine (top) and fluorinated silane functional benzoxazine (bottom) monomers.

Carbon/carbon composites are other attractive materials for industry. Their properties include good electrical conductivity, fire retardant characteristics, resistance to erosion and most importantly exceptional thermal stability. However, unprotected carbon/carbon composites suffer from thermo-oxidative degradation and the brittleness of the carbon matrix leads to matrix cracking. The cracks penetrate deep into the core of the material, leading to accelerated thermo-oxidative decomposition beyond the surface degradation. For these reasons, oxidative protection method is required especially at high temperatures. Among these methods is the use of polybenzoxazine coating technology. Jin and Ishida reported the preparation of main-chain type, oligomeric benzoxazine as a highly thermo-oxidative matrix material as shown in Figure 2.2 [16]. In this coating technology, octasilane polyhedral oligomeric silsesquioxane and glass sphere are incorporated to form an effective oxidation protective coating for the carbon/carbon composites.
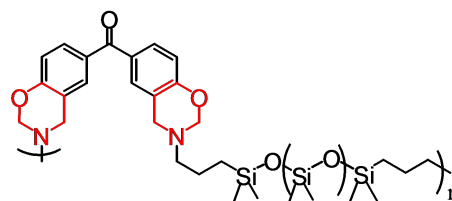

Figure 2.2: Main-chain type oligomeric benzoxazine.

The film adhesion to the glass substrate is another issue that needs to be addressed. Raza *et al.* [17] synthesized a benzoxazine monomer with comparable low surface free energy, which can incorporate SiO$_2$ nanoparticles with high adhesion to the substrate. The fabrication of the films on the glass substrate was applied by in-situ polymerization of fluorinated polybenzoxazine. In this process, the fluorinated benzoxazine monomer was used as a starting monomer with outwardly projected drooping aliphatic hydrocarbon chains that could directly form a hydrophobic cross-linked thermosetting polymer incorporated with SiO$_2$ nanoparticles through in situ polymerization as shown in Figure 2.3. The system showed water contact angle of as high as 150°.

Lastly, it should be noticed that many polymer substrates such as polycarbonate, poly(4-vinyl pyridine), poly(4-vinyl phenol) and similar polymers can be coated by the modified polybenzoxazine in
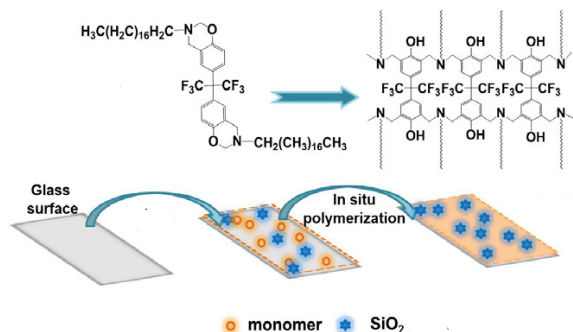
Figure 2.3: The strategy using the in situ polymerization approach for fluorinated benzoxazine/ SiO$_2$ nanoparticles coated on the glass surfaces.

order to possess low surface energy. The investigation is still in progress for other substrates to be coated using polybenzoxazine technology.

3. Electronic Area

In general, low dielectric constant materials ($k < 3$) have applications in higher performance integrated-circuit (IC) devices. In addition, the low dielectric constant materials are required to decrease the relative capacitance (RC) delay, power consumption and cross-talk noise. These demands have resulted in an intense increase in research towards the exploration and applicability of polymers and nanoporous materials. Various polymers have been employed as potentially low k materials in advanced IC chips. Among these materials are polybenzoxazines. The study of polybenzoxazines showed some excellent electrical properties due to their low water content. Even though polybenzoxazine has high concentration of polar groups, the formation of intramolecular six-membered hydrogen bonding counteract the polar OH and N atoms and thus leads the polymer to show low dielectric constant. In addition, the hydrogen-bonding networks also increases the rigidity of the polymer chain and lower dissipation factor, tan δ. There have been several approaches made to reduce the dielectric constant of polybenzoxazine. Among these approaches is the incorporation of a fluorinated substituent into polybenzoxazine [18-20]. Fluorine containing benzoxazine monomer was prepared as depicted in Figure 3.1. The study showed that fluorine containing polybenzoxazines exhibits dielectric constant as low as 2.36. On another hand, polybenzoxazines are also found to be ideal matrices for high dielectric

constant nanocomposites. For example, the blend prepared by extracting polycaprolactone from polybenzoxazine/polycaprolactone showed dielectric constant as low as 1.95 due to the increased void content as illustrated in Figure 3.2 [21]. POSS-poly benzoxazine nanocomposites and the introduction of an air gap into the interconnected structures produces materials with low dielectric constant. Benzoxazine functionalized mesoporous SBA-15 filled polybenzoxazine nanocomposites exhibited dielectric constant as low as 1.75 [22].

These promised results open the field for polybenzoxazine as a good candidate for electronic packaging materials.
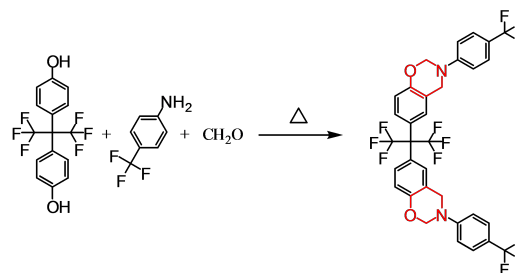

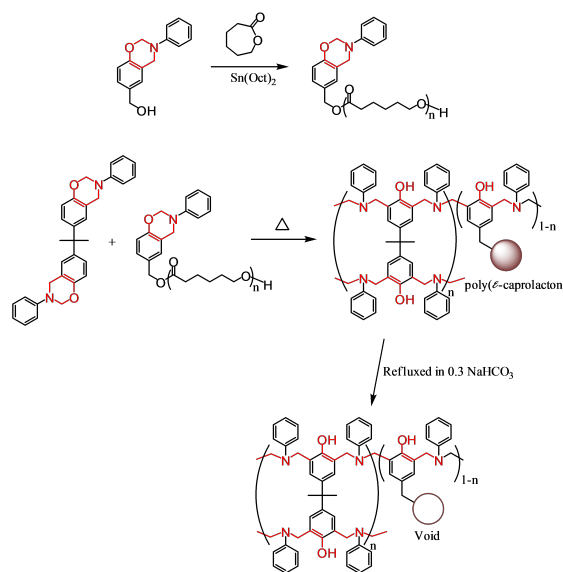**Figure 3.1:** Preparation of fluorine atoms-containing benzoxazine monomer.

Figure 3.2: Preparation of nanoporous based polybenzoxazine by extracting polycaprolactone from polybenzoxazine/polycaprolactone.

Katanyoota *et al.* [23] prepared two types of poly-

benzoxazines carbon aerogel derived from two different amines (aniline and triethylenetetramine) abbreviated as BA-a and BA-teta as shown in Figure 3.3. The surface area of carbon aerogels from BA-a and BA-teta was 391 and 368 m^2/g, respectively. The study showed that pore size of each carbon aerogel was in the range of 2–5 nm, which is a suitable pore size for use as electrodes in electrochemical applications. The specific capacitance of BA-teta and BA-a was 55.78 and 20.53 F/g, respectively, which is considered as good performance for supercapacitor applications. The study also proposes a method to reduce the production cost of carbon aerogels by using an ambient drying process, to prepare carbon aerogels from benzoxazine precursors.
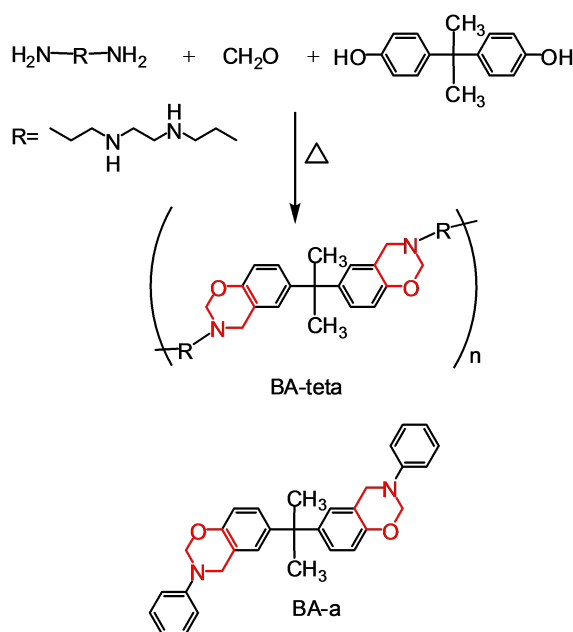

Figure 3.3: Preparation of benzoxazine precursors based on aniline (BA-a) and triethylenetetramine (BA-teta).

Hao *et al.* [24] prepared sandwich-type microporous hybrid carbon nanosheets as an electrode material for supercapacitors. These advanced materials consisting of graphene and microporous carbon layers which fabricated using graphene oxides as shape-directing agent. In this study, the in-situ formed poly(benzoxazine-co-resol) was used as carbon porous matrials. The obtained material has a high density of accessible micropores that reside in the porous carbon with controlled thickness of 17

nm, a high surface area of 1293 m^2/g and a narrow pore size distribution of ca. 0.8 nm. These properties allow rapid diffusion and high loading of charged ions, which outperform the diffusion rate in bulk carbon and are highly efficient for an increased double-layer capacitance. The best practice two-electrode test demonstrates that this materials show a gravimetric capacitance of high up to 103 F/g and a good energy density of ca. 22.4 Wh/kg at a high current density of 5 A/g.

4. High Surface Area Technology

Nanostructure materials have in general high surface area and consequently are used for diverse applications. Commonly, the structure can be attained by two methods. The first method is by fabricating small particles or clusters where the surface to volume ratio of each particle is high. Materials such as highly dispersed supported metal catalysts and gas phase clusters fall into this category. The second method is by creating materials where the void surface area (pores) is high compared to the amount of bulk support material. Materials with microporous (nanometer-pored) materials such as zeolites, high surface area inorganic oxides, porous carbons, and amorphous silicas fall into this category. In this section, emphasis is directed toward the technologies and related applications.

Gas separation represents a major challenge in a time of concerns for growing air pollution based on the emission of toxic and greenhouse gases from power generation and industry. In particular, carbon dioxide (CO_2) is one of the primary greenhouse gases that have been suggested to contribute significantly to global climate change [25]. Various technologies are available for reducing CO_2 emission from flue gas into the atmosphere and have been employed in recent years. Among the available CO_2 separation and capture technologies are cryogenic distillation, membrane separation, absorption with liquid amines, and adsorption with solid sorbents [26-29]. In addition, complementary strategies of utilizing CO_2 as a chemical feedstock in reactive processes that provide carbon-rich useful materials, such as fuels, hydrocarbons, and polymers, have been suggested [30-31]. Adsorption techniques using porous solids are effective alternatives to the currently most commonly used amine absorption processes for CO_2 capture due to low cost-effectiveness, greater adsorption capacity, ease of handling, reduction of environmental impact, and

high selectivity [32]. Consequently, porous carbon adsorbents with high nitrogen content and controllable properties have been directly developed from nitrogen-containing polymers. However, their use in a wide range of applications for gas treatment is restricted due to their higher cost and due to the environmental impacts of their reagents [33].

Polybenzoxazine based porous solids have recently been investigated and the chemistry of benzoxazine provides significant features for excellent porous carbons due to self cross linking via ring opening polymerization and molecular structure flexibility towards other desirable functional moieties. Recently, performance of benzoxazine-co-resol based carbons for CO_2 capture has been reported. The carbons showed mesoporous and microporous material with superior CO_2 adsorption, as well as strong mechanical integrity (16 MPa) due to cross-linking affinity of polybenzoxazine [34].

Recently, Alhwaige *et al.* [35] developed biobased chitosan-polybenzoxazine aerogels for CO_2 adsorbing applications. They used Montmorillonite for reinforcing the aerogel. The nanocomposite aerogels were synthesized using the freeze-drying technique followed by carbonization at 800 °C. They found that polybenzoxazine improves the structural stability of the aerogel and assist removing CO_2 even at high pressure. In addition, the structure exhibits mesoporous materials with pore sizes in the range of 2–7 nm and high BET surface area. The nanocomposite showed high CO_2 adsorption capacity at ambient conditions and excellent CO_2 adsorption–desorption reversible performance with a maximum of 5.72 mmol/g.

Polybenzoxazine aerogel was also used for the removal of heavy metals from model wastewater. Chaisuwan *et al.* [36] showed that polybenzoxazine aerogel as a chelating polymer exhibits the removal of metal ions in the following order: $Sn^{2+} > Cu^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+} > Cr^{2+}$ as shown in Figure 4.1. Additionally, the amount of metal ions removed depended on the amount of absorbent and sorption time. Furthermore, the desorption process was shown to be a function of pH, type of solution, and temperature.

Carbon foam is a porous carbon material with low density, high applicable temperature (up to 3000 °C in an inert atmosphere), high modulus and strength, large surface area, and controllable thermal and electrical conductivity depending on the degree of graphitization. This material is used for many applications such as high temperature thermal insu-
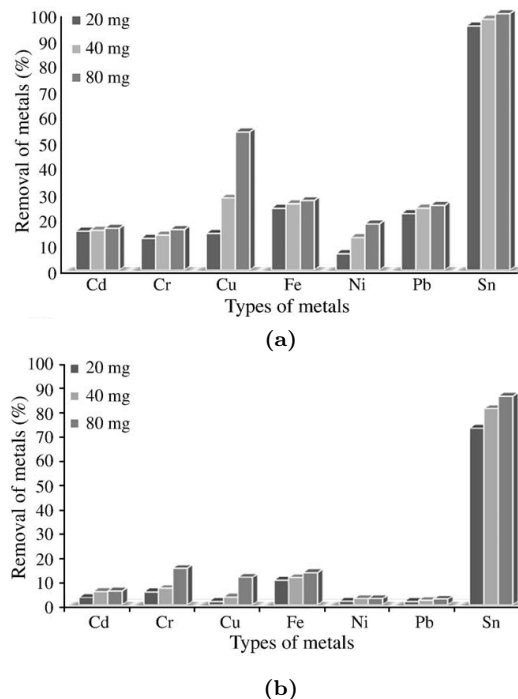

(a)

(b)

Figure 4.1: Adsorption of metal ions in single-metal solutions (A) and mixed-metal solutions (B) at various weights of polybenzoxazine aerogel [36].

lation, lightweight structural parts, catalyst support, radar absorbing material, electrodes for energy storage, and filters for high temperature or corrosive chemicals [37]. Generally, carbon foam is made via the carbonization of polymeric foams. Polyurethane, polystyrene, and polyethylene foam are the most popular polymeric foams used in carbon foam production because they have low thermal conductivity and good mechanical strength. Although the foams produced from these polymers have good mechanical and thermal properties, they are easily burned, so they are not appropriate for use in particular applications where fire resistance is required. Among the inexpensive commercial polymeric foams, phenolic foam is the preferred material and in this context polybenzoxazine foam can be used when fire resistance is critical. Polybenzoxazine foams have been prepared using azodicarbonamide as a foaming agent.

The produced foams showed a density in the range of 273–407 kg/m^3 as shown in Figure 4.2, and a compressive strength and a compressive modulus in the range of 5.2–12.4 MPa and 268–681 MPa, respectively [38]. The polybenzoxazine foam was transformed into carbon foam by carbonization at
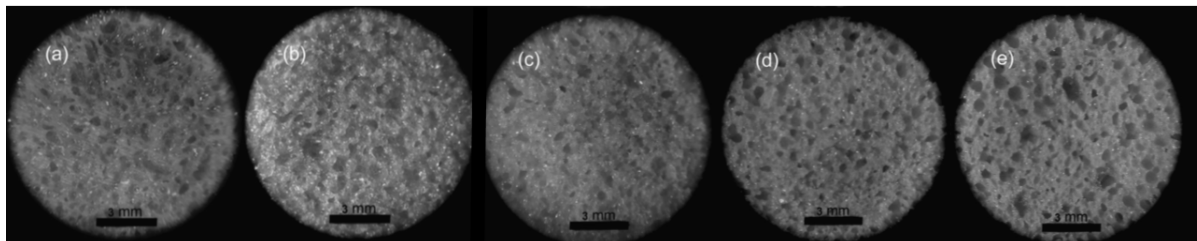
Figure 4.2: Microscope images of polybenzoxazine foams at several densities (a) 407 kg/m^3, (b) 378 kg/m^3, (c) 339 kg/m^3, (d) 306 kg/m^3, and (e) 273 kg/m^3. [38]

800 °C under an inert atmosphere.

Membrane is another effective area of polybenzoxazine applications, especially in ethanol-water separation [39] as shown in Figure 5.1. Nitrogen-containing macrocycles, such as azacalixarene, have been actively studied in the area of selective adsorption of ions. The repeating structure of macrocycles is similar to the chemical repeat unit of polybenzoxazines. Chirachanchai *et al.* [40] studied the use of benzoxazine as a precursor to synthesize these nitrogen- containing macrocycles and found that some of the reactions yielding as high as 80-85%.

## 5. Colloid and Interface Science

Polymeric surfactants attracted considerable attention for applications such as personal care product and stabilization of emulsions and suspensions as in enhanced oil recovery. The properties of polymeric surfactants originate from the formation of aggregates through the association of the hydrophobic alkyl chains in aqueous solution, within a narrow concentration range. The aggregates are called micelles, and the narrow concentration range above which micelles are formed in the solutions is called the critical micelle concentration (cmc).

Polymerizable nonionic benzoxazine surfactants have been reported [42]. The surfactants are suited to stabilize water-based carbon fiber sizing dispersions where in the emulsion, the hydrophobic benzoxazine moiety is oriented towards the inside of the benzoxazine droplets and the hydrophilic polymer chains, *e.g.*, polyethyleneoxide, reach into the aqueous surrounding, and provide steric stabilization. Similar to the commercially available surfactants, benzoxazine surfactants can copolymerize with any emulsified benzoxazine-based formulation. There still some issues that need to be controlled such as reduced adhesive bond strength due to a preferentially interfacial adsorption of the surface active ingredients and surfactant aggregation.
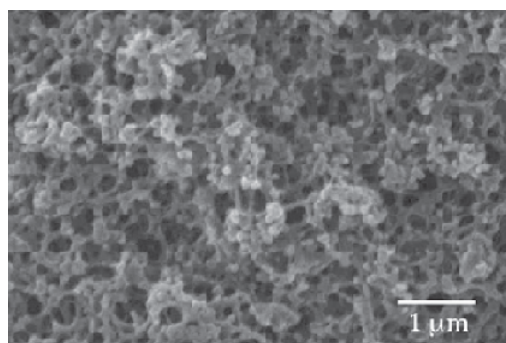
(a)
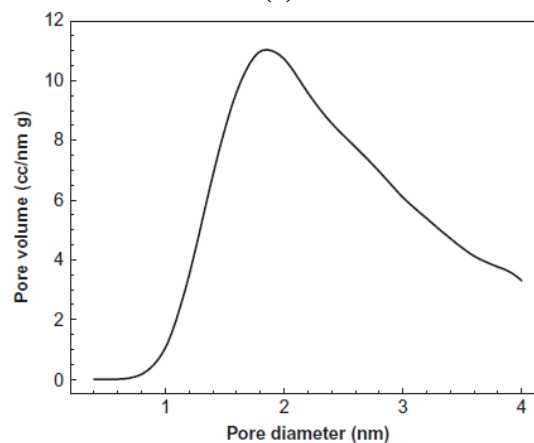
(b)

Figure 5.1: SEM photomirograph of the polybenzoxazine-based aerogel showing nanometer sized voids (top) and Pore size distribution of the polybenzoxazine aerogel of the same figure (bottom).
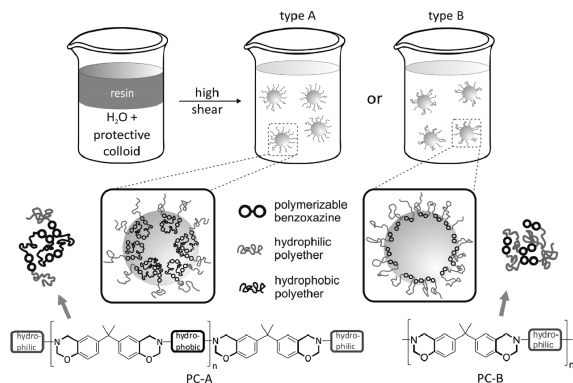
Figure 5.2: Preparation principle of benzoxazine miniemulsions stabilized by two different benzoxazine-based protective colloids [41].

Anionic polymeric surfactants were also prepared using polymerizing benzoxazine monomers [43] as shown in Figure 5.3. The monomers were synthesized by reacting an aliphatic amine of variable chain length (C_8, C_{10} and C_{12}), with 4-hydroxybenzoic acid and paraformaldehyde. The tensiometry results indicate that the adsorption at the air/water interface is similar for the prepared surfactant whereas increasing the alkyl chain length from C_8 to C_{12} does not affect the surface tension at the critical micelle concentration.

The fully atomistic molecular dynamic simulations show that the molecular size and concentration play important roles in micellar morphology. The micellar morphology is spherical at low concentrations, but undergoes a transition to cylindrical shape as the concentration increases [44].
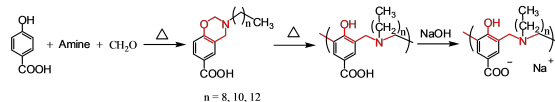

Figure 5.3: Preparation of anionic polymeric surfactants based on polybenzoxazines.

6. Conclusion

In this review, the proposed applications of polybenzoxazine especially in the chemical and oil industry were addressed. Though benzoxazine-based materials possess several advantages, their possible applications have not yet become very attractive to the industries. Future direction of research should focus in this area.

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