

CHAPTER II

THEORETICAL AND LITERATURE SURVEY

2.1 Benzoxazine Resin

A new class of phenolic resin, namely polybenzoxazine, was recently developed. Polybenzoxazine has excellent molecular design flexibility that allows the properties of the cured material to be controlled for various applications. This is because polybenzoxazine can be synthesized from a wide selection of raw materials, consisting of phenolic derivatives and primary amines.

Furthermore, polybenzoxazine has many advantageous characteristics, as compared with traditional phenolic resins (Ning and Ishida, 1994; Ishida and Allen, 1996; Ishida, 1996). The interesting properties of benzoxazine resin are shown below:

- No catalyst or curing agent required
- No by-products during cure
- Low melt viscosity
- Near zero mold shrinkage
- Low water absorption
- Excellent electrical properties
- High mechanical integrity
- Self-polymerized upon heating

According to Ishida (1996), synthesis of benzoxazine monomers consists of a few simple steps using the patented solventless synthesis technique. This technique provides almost contaminant-free monomers. Thus, we can omit the purification process, save a production cost, and also decrease pollution from the use of solvent. As benzoxazine resin can be cured through thermally activated ring-opening polymerization without a catalyst, and its mechanical properties can be rapidly developed even at a low crosslinking conversion, polybenzoxazine becomes an excellent candidate resin to replace the traditional reactants for aerogel and foam preparations.

Benzoxazine resin can be classified into a monofunctional and a bifunctional type, depending on the type of phenol used, as shown in Figures 2.1 and 2.2.

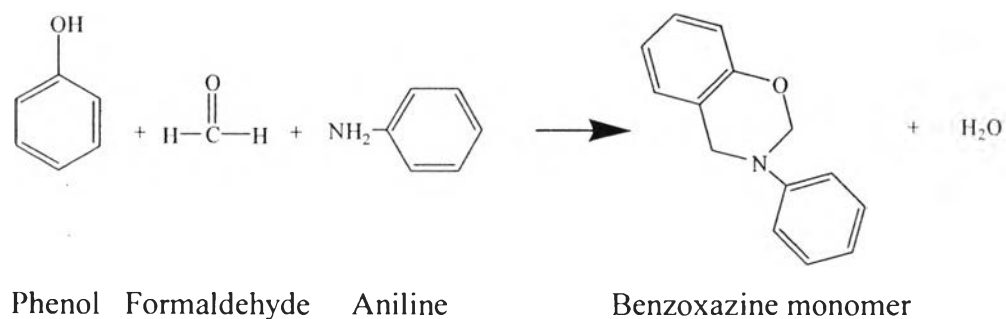


Figure 2.1 Monofunctional benzoxazine monomer synthesis.

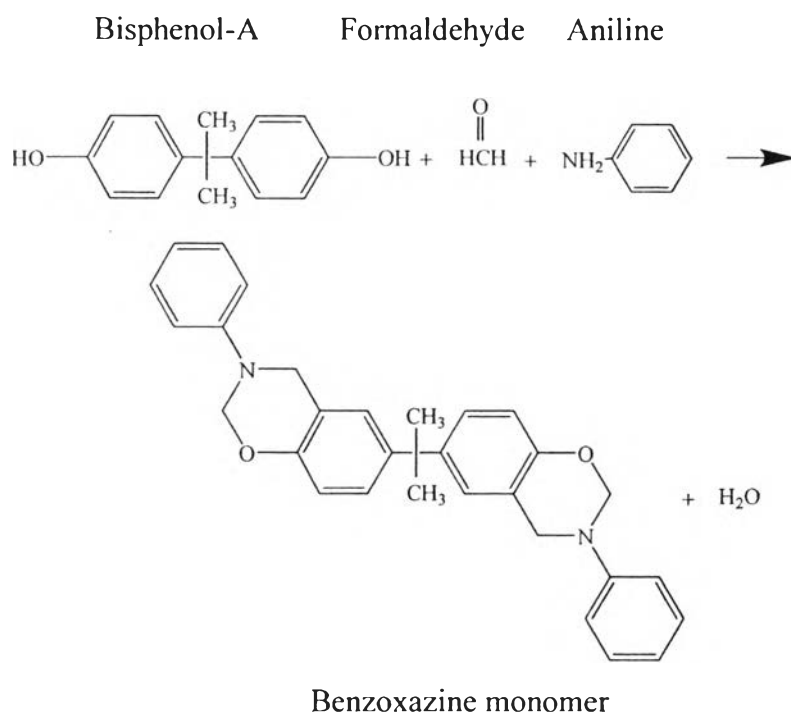


Figure 2.2 Bifunctional benzoxazine monomer synthesis.

2.2 Porous Materials

As defined by Ishizaki *et al.* (1998), porous materials are any solid materials containing pores, which generally have pore volume fraction in the range between 0.2-0.95. Porous materials have been used in a wide range of applications from daily utilizations, such as purifying drinking water, to aero space applications, such as dust capturing in outer space. According to the IUPAC classification, porous materials have been regularly categorized into three groups based on predominant pore size, as follows.

- Microporous materials: porous materials having pore with internal width less than 2 nm
- Mesoporous materials: porous materials having pore with internal width between 2 and 50 nm
- Macroporous materials: porous materials having pore with internal width greater than 50 nm

Nowadays, the term “nanoporous materials” is widely used for both micro- and mesoporous materials.

The pore presenting in the porous materials can also be classified into two types on a basis of pore morphology, which are opened and closed pores. The opened pore is the pore that connects to the outside of the materials. On the other hand, the closed pore is the pore isolated from the outside and may contain fluid inside the pore.

According to the objectives of this study, there are two types of porous materials studied, i.e. aerogel and foam.

2.3 Introduction to Aerogel

Aerogel is a nanostructure material with very high porosity (Fricke and Emmerling, 1998; Lorjai *et al.*, 2009). The aerogel is mostly derived from sol-gel process, in which the liquid component in the gel is replaced with gas. The output of this process is a low-density solid with several remarkable properties, such as very light weight, high porosity, high surface area, and excellent thermal insulation. In the

first step of traditional aerogel synthesis, hydrogel, three-dimensional polymer networks swollen in medium fluid, is prepared via sol-gel process. Then, the hydrogel is dried to remove the liquid in its structure by several methods, resulting in porous structure materials called aerogels (Lorjai *et al.*, 2009; Pekala, 1989; Qin and Guo, 2001). The traditional process of aerogel preparation requires approximately 2 weeks. Recently, many attempts have been made to shorten the process, such as using alcohol-sol-gel polymerization and drying with supercritical acetone to avoid the solvent exchanging period (Qin and Guo, 2001).

2.3.1 Types of Aerogel

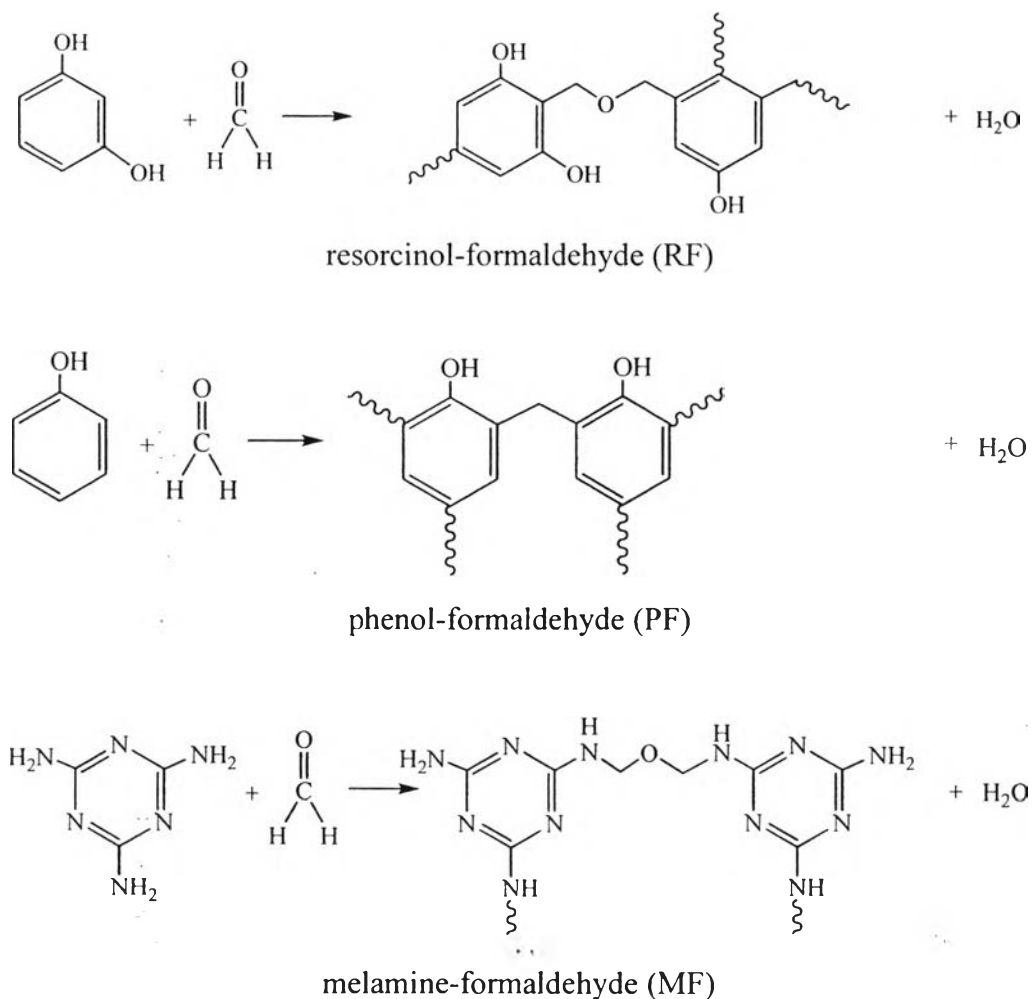
Generally, aerogel has been classified into 4 different types based on its chemical component (Chattrabhuti, 2008; Chantarasataporn, 2008).

a) Inorganic Aerogel

Inorganic aerogel is classified as an aerogel derived by using inorganic substrate as a precursor. Inorganic aerogel is usually derived from a sol-gel process by using metallic salts as precursors. As generally used in the process, the metal salts MX_n compose of metal M which is bounded to number n of anions X. In the sol-gel process, these precursors act as solvated cations $M[H_2O]_n^{Z+}$. The reactions to form sol particle and gel comprise of hydrolysis reaction which H_2O will be replaced by OH group along with a loss of proton and condensation reaction, leading to the construction of M-O-M with elimination of water molecule.

b) Organic Aerogel

In this type of aerogel, various types of organic precursors have been generally used. The precursors form organic polymer networks with strong covalent bonds. The favorite organic precursors for the organic aerogel are resorcinol-formaldehyde (RF), phenol-formaldehyde (PF) and, melamine-formaldehyde (MF). The polymerization reactions between resorcinol, phenol, or melamine and formaldehyde are classified as condensation reactions. The reactions are mostly in aqueous phase with basic catalysts, such as sodium hydroxide and sodium hydrogen carbonate. The polycondensation reactions of those well-liked precursors are shown in scheme 2.1.



Scheme 2.1 Polycondensation reactions of well-liked precursors.

c) Carbon Aerogel

Carbon aerogel was discovered by Pekala *et al.* at the beginning of the 1990s from the pyrolysis of resorcinol-formaldehyde (RF) aerogels (Pekala, 1995), see Figure 2.3. Carbon aerogels are commonly obtained by pyrolysis of organic aerogels mostly synthesized via the sol-gel process of phenol compounds and formaldehyde by using base as catalyst. When the resulting organic hydrogels is dried and all solvent is extracted, the carbon aerogels can be derived via the pyrolysis of the organic precursors in an inert atmosphere (Jimenez, 2006). The pyrolysis is performed at high temperature, usually between 800–1000 °C, with the final carbon

aerogels being around 95% pure carbon. As observed from many studies (Wu and Fu, 2005; Tamon *et al.*, 1998; Shen *et al.*, 2005), the pyrolysis leads to the formation of microporosity and impairs the mesopore and macropore structures of the starting organic aerogels, which most likely are due to the shrinkage during the pyrolysis.

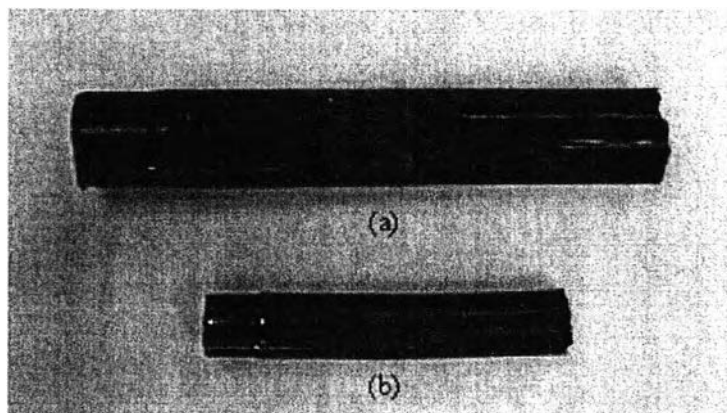


Figure 2.3 (a) Resorcinol-formaldehyde aerogel and (b) resorcinol-formaldehyde based carbon aerogel.

d) Clay Aerogel

As described above, most aerogels are derived from chemical condensation reactions of their substances while the other types of aerogels, as clay aerogel, are derived from a solution of montmorillonite clay and water without any condensation reactions. Clay aerogel is formed by physical/electrostatic interaction between clay particles (Bandi and Schiraldi, 2006). As reported by Bandi and Schiraldi (2006), clay aerogels were produced by blending clay with water. Then, the mixture was sheared at very high speed to obtain clay gel. Finally, the resulting gel was freeze-dried at $-35\text{ }^{\circ}\text{C}$, and the ice was sublimed under vacuum to generate the clay aerogel.

2.3.2 Organic and Carbon Aerogel Background

As mentioned earlier, the organic and carbon aerogel processing normally use phenol compounds and formaldehyde as precursors. As observed from many studies, there are many synthesis parameters affecting properties of the

resulting aerogel, such as concentration of precursor solution, type of solvent, phenol to formaldehyde ratio, catalyst content, and gelation time (Qin and Guo, 2001; Wu and Fu, 2005-2006). Physical properties of carbon aerogels derived from various organic precursors are summarized in Table 2.1. However, in all recent synthesis methods, catalyst for pre-polymerization is still required.

Table 2.1 Summarized physical properties of carbon aerogels derived from various organic precursors (Wu and Fu, 2005-2006)

Sample	Density (kg/m ³)	S _{mic} (m ² /g)	S _{mes} (m ² /g)	V _{mic} (cm ³ /g)	V _{mes} (cm ³ /g)	V _{mic} / V _{mes}	S _{mic} / S _{mes}
PF aerogel ² , PF = 40wt%,NaOH/P = 3 wt%	310	297	325	0.14	1.01	0.14	0.91
PF aerogel ² , PF = 50wt%,HCl /P = 1.5	320	229	297	0.11	0.71	0.15	0.77
RF aerogel ¹ , Rf = 30wt%,R/F = 0.4	330	326	511	0.15	1.33	0.11	0.64
RF aerogel ¹ , Rf = 40wt%,R/F = 0.33	500	304	528	0.14	1.09	0.13	0.58
PF aerogel ² , PF = 60wt%,HCl /P = 3	510	359	206	0.17	0.67	0.25	1.74
PF aerogel ² , PF = 40wt%,NaOH/P = 3 wt%	590	296	334	0.14	0.74	0.19	0.89
PF aerogel ² , PF = 70wt%,HCl /P = 3	640	326	192	0.15	0.51	0.29	1.69

RF aerogel¹ represents carbon aerogel from Resorcinol-Formaldehyde

PF aerogel² represents carbon aerogel from Phenol-Furfural

Li and Guo (2000) successfully prepared very low-density organic and carbon aerogels from a cresol/formaldehyde mixture. The densities of the organic and carbon aerogels were 60 and 90 kg/m³, respectively. The surface area of the resulting carbon aerogel was 508 g/cm².

In order to obtain more practical process for carbon aerogel synthesis, resorcinol-formaldehyde (RF) organic aerogel was prepared with very high

resorcinol to catalyst molar ratio and was dried under ambient conditions. Then, the carbon aerogel was gained after pyrolysis of the obtained organic aerogel. The physical properties of the resulting carbon aerogel are shown in Table 2.2.

Table 2.2 Physical properties of carbon aerogels derived from resorcinol-formaldehyde (RF) via ambient drying method (Shen *et al.*, 2005)

Sample	R/C ratio	RF mass concentration (%wt)	Density (kg/m ³)	Specific surface area (m ² /g)	Average pore diameter (nm)
Carbon aerogel	500	30	320	303	4.6
Carbon aerogel	1000	30	514	487	4.5
Carbon aerogel	1500	30	340	521	3.5
Carbon aerogel	1500	40	576	606	5.1

R/C ratio represents resorcinol to catalyst ratio

As described by Li *et al.* (2001), the porosity in organic and carbon aerogels resulted from two primary causes. The first cause was the entanglements and connections of particles produced during the sol-gel process. The second cause was the evaporation of a great amount of small molecular species during the pyrolysis, which produced a new porosity in the aerogel structures.

Not only thermosetting plastics, but thermoplastics have also been used as aerogel precursors. As seen in Figure 2.4, polyurethane-based organic aerogels were synthesized by Biesmans *et al.* (1998). The volume of the open pores of the resulting polyurethane-based organic aerogel was 4.15 cm³/g; nevertheless, the aerogel nearly loosed all of its pore volume after the carbonization (0.27cm³/g).

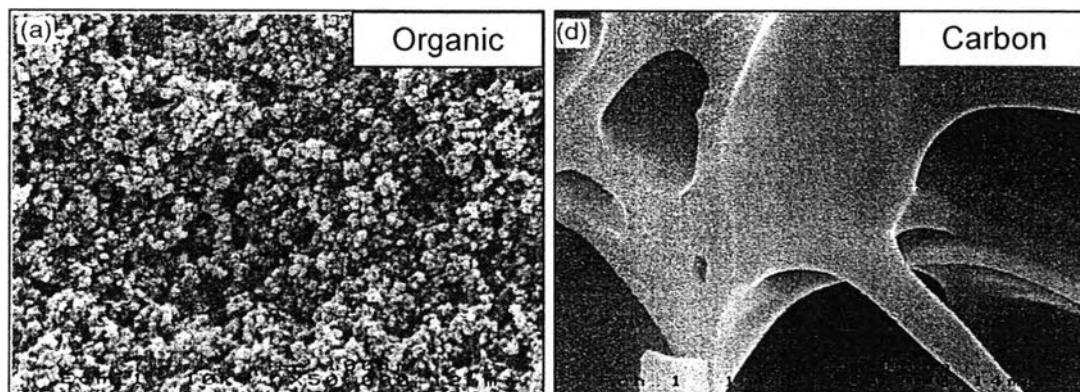


Figure 2.4 SEM photographs of polyurethane-based organic and carbon aerogels.

2.4 Introduction to Polymeric Foam

Polymeric foam is a two-phase material, consisting of gas dispersed in a continuous polymer matrix. The polymer matrix may be more than one solid phase present, as in the case of polymer blend or polymer alloy. Furthermore, other solid phase may be added in the form of filler, e.g. fiber, wood, talc, etc. The foam can be normally classified in term of cellular morphology and mechanical behavior (Pentrakoon, 2005). According to cellular morphology, polymeric foam can be classified into two types, i.e. opened and closed cell foams. In case of the opened cell foam, the void within the foam coalesces, so polymeric and gas phases become continuous. As a result, by the influence of some driving force, the gas can flow throughout the foam. In addition, the opened cell foam is generally formed via low pressure foaming condition. On the other side, the gas phase is dispersed as bubbles within the closed cell foam. As stated by Pentrakoon (2005), the closed cell foam is generally formed via high pressure foaming condition. The schemes of ideal opened and closed cell foams are illustrated in Figure 2.5.

With respect to the mechanical behavior, the polymeric foam can be divided into two general classes.

a) Rigid Foam

In this class, the polymer matrix is in crystalline state for crystalline polymer, or below glass transition temperature (T_g) for amorphous polymer. The

compressive strength of the rigid foam is usually reported at a relatively low deformation (5-10% strain). Typical examples include most polyolefin foams, polystyrene foam, and phenolic foams.

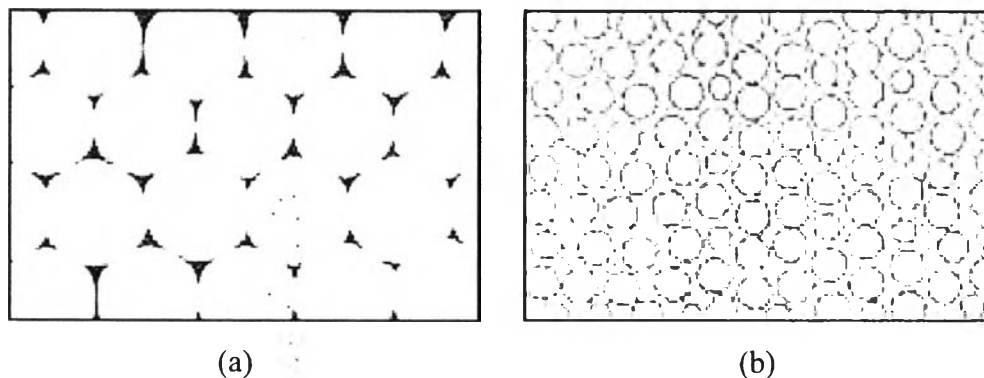


Figure 2.5 Idealized representation of (a) opened cell foam structure and (b) closed cell foam structure.

b) Flexible Foam

The polymer matrix of the flexible foam is always above its glass transition temperature. As a nature of the flexible foam, the compressive strength of the foam is usually reported at a load-deflection curve up to 75% strain. Typical examples include polyurethane foam and rubber foam.

2.4.1 Polymeric Foam Technology

According to the manufacturing process for creating foams, there are three different foam formation methodologies, i.e. reactive foaming, soluble foaming, and quenching foaming (Lee *et al.*, 2007).

a) Reactive foaming is the most popular method used in the polymeric foam industry today. According to the process, the final foam products are yielded from a chemical reaction of a foaming agent that generates a certain amount of gases, which inflates newly polymerized or molten polymer matrixes. After cooling, the polymeric foam products are ultimately obtained.

b) Soluble foaming is another well-developed technology. This process involves in the dissolution of a physical blowing agent in the polymeric melt

or in the newly polymerized polymer matrix. Then, the gases are produced as a result of physical processes, such as evaporation, reduced pressure, or elevated temperature, to expand the polymer matrix.

c) Another foaming technology is solution quenching (Figure 2.6). It was originated from aerogel methodology, which involves in using compatible solvent to dissolve or expand the polymer matrix. Then the solvent is replaced with gases by several techniques, yielding the polymeric foam.

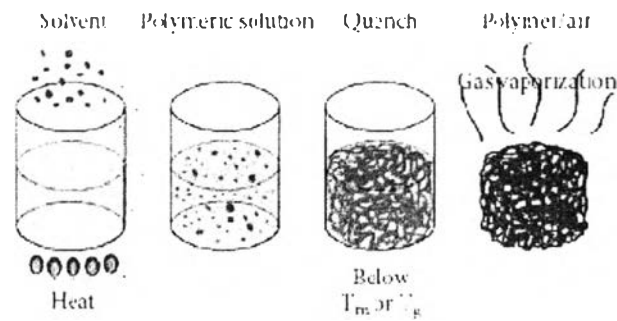


Figure 2.6 Solution quenching foaming method.

2.4.2 Polybenzoxazine Foam Background

From all former researches, the synthetic polybenzoxazine foam was prepared mostly via the resin/glass microballoon composite fabrication technique, which required a high glass microballoon volume fraction (Kumar *et al.*, 2008). Kumar *et al.* (2008) found that the strength of their resulting polybenzoxazine foam increased as the foam density increased and the specific tensile and the compressive strength were optimized at 40 wt% (68 vol%) of the glass microballoon (Figure 2.7).

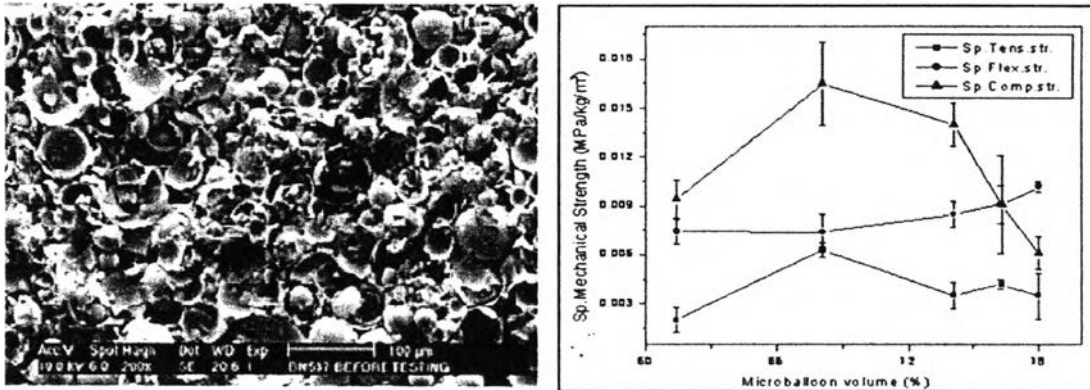


Figure 2.7 SEM photograph of polybenzoxazine foam and its specific properties.

Polybenzoxazine filled with glass microballoon and chopped glass fibers was also prepared and studied by Kumar *et al.* (2008). From the dynamic mechanical analysis, it revealed that the thermodynamic mechanical properties of the foam could be enhanced by introduction of glass reinforcing fiber (Figure 2.8).

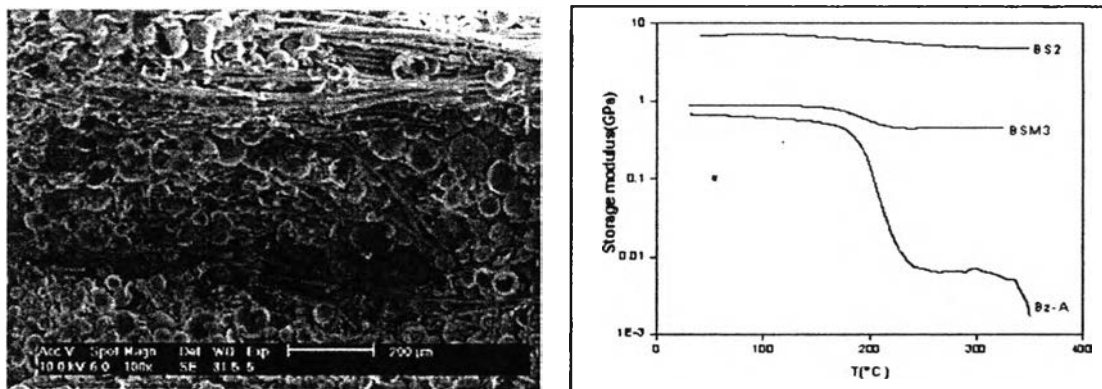


Figure 2.8 SEM photograph of glass fiber reinforced polybenzoxazine foam and its specific properties.

2.5 Objectives

The aim of this work is thus to find the most appropriate synthesis method of a novel type porous phenolic resin by using polybenzoxazine as a precursor and to transform the porous resin into carbon form. As it is a question to us that how the

porous polybenzoxazine shows superior thermal degradation stability to the related bulk polybenzoxazine, the difference between the thermal degradation behaviors of the bulk polybenzoxazine and the porous polybenzoxazine was investigated in this study. This work is also extended to study the properties of the obtained porous polybenzoxazine, and the corresponding carbon materials.