

CHAPTER VI
PREPARATION OF POLYBENZOXAZINE FOAM AND ITS
TRANSFORMATION TO CARBON FOAM

6.1 Abstract

An organic foam derived from a new type of phenolic resin, namely polybenzoxazine, was successfully prepared with a noncomplex and economical foaming method by using azodicarbonamide (AZD) as a foaming agent. The influence of foam density on the physical and mechanical properties of the foams was studied. All resulting polybenzoxazine foams and carbon foams exhibit a tailorable uniform microstructure. Polybenzoxazine foams showed a density in the range of 273–407 kg/m³, and a compressive strength and a compressive modulus in the range of 5.2–12.4MPa and 268–681MPa, respectively. The foam density not only affects the physical and mechanical properties, but also affects the deformation response of the foam. In addition, the polybenzoxazine foam was further transformed into carbon foam by carbonization at 800 °C under an inert atmosphere, and its properties were examined.

(Key-words: Benzoxazine; Benzoxazine foam; Carbon foam)

6.2 Introduction

Polymeric foam is a two-phase material consisting of gas dispersed in a continuous polymer matrix. This material is important and useful due to its high strength-to-weight ratio. Furthermore, the chemical resistance, cushioning performance, shock absorption, and thermal insulation are also prominent characteristics of this type of material [1]. Polyurethane (PU), polystyrene (PS), and polyethylene (PE) foam are the most popular polymeric foams because they have low thermal conductivity and good mechanical strength. Nevertheless, in applications such as building materials for civil construction, passenger and military aircraft, and naval vessels, the fire resistance properties have to be considered. Although PU, PE, and PS foams 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 when fire resistance is critical. Phenolic foam also has low flammability, a low peak heat release rate (PHRR), no dripping during combustion, and low smoke density; so they are suitable for use in the applications mentioned earlier [2,3].

Carbon foam is a porous carbon material with many advantageous properties such as 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 [4]. There is a wide range of applications for carbon foam, such as in high temperature thermal insulation, as a catalyst support, as electrodes for energy storage, as lightweight structural parts, as radar absorbing material, as conductive heat sinks, and as filters for high temperature or corrosive chemicals [4, 5]. The precursors widely used to produce carbon foam include coal, pitch, olive stones, polyimide, and thermosetting polymer [4, 6]. Nevertheless, the most effortlessly produced carbon foam is made via the carbonization of polymeric foams. The polymeric foams usually used in carbon foam production are phenol formaldehyde, resorcinol formaldehyde, polyurethane, furfural resin, poly (vinylidene chloride), and polyacrylonitrile. With this synthesis

route, the resulting carbon foams exhibit a uniform cell size and an admissible mechanical strength [5].

This study deals with a new type of phenolic foam derived from polybenzoxazine and carbon foam produced via the carbonization of this polymeric foam. Polybenzoxazine is a newly developed class of phenolic resins derived from ring-opening polymerization. Polybenzoxazine can overcome the drawbacks of conventional phenolic resin synthesis by eliminating the release of any byproducts during the curing reactions, the need for strong acids as catalysts, and for toxic raw materials. Furthermore, polybenzoxazine has many advantageous characteristics compared with the traditional phenolic resin, such as high thermal stability and excellent mechanical properties, easy processibility, low water absorption, and near zero shrinkage after polymerization [7-9]. According to Ishida [10], synthesis of the benzoxazine monomers consists of a few simple steps, using a patented solventless synthesis technique, to obtain a clean precursor, without the need for further monomer purification. Thus, polybenzoxazine is becoming an excellent candidate resin to replace traditional reactants for organic and carbon foam manufacturing. The polybenzoxazine (Ba-A) used in this study is based on bisphenol-A and aniline, which is one of the early polybenzoxazines synthesized [11]. Ba-A can maintain its mechanical integrity until 165 °C, which is its glass transition temperature. The decomposition temperature at 5% weight loss is approximately 370-380 °C and the char yield of the benzoxazine reported at 800 °C is around 30% weight [11]. These characteristics enable Ba-A to be an excellent candidate for phenolic and carbon foams precursors. Over the past few years, there have been many researches involving polybenzoxazine foam. However, in these studies, the synthetic polybenzoxazine foam was prepared totally via the resin/glass microballoon composite fabrication technique, which provides a high glass microballoon volume fraction [12, 13]. For commercialization, simplification of the polybenzoxazine foam production method is necessary. Conventionally, the cellular structured material is produced by introducing a foaming agent to the polymer matrix. There are two common types of foaming agents generally used to expand a polymer, i.e. physical and chemical foaming agents. The physical foaming agents generate gases in a polymer via a physical process, such as evaporation, increasing temperature, or

decreasing pressure, using nitrogen, carbon dioxide, and hydrocarbons [14-16]. The chemical foaming agents provide gases from a chemical reaction resulting from the thermal decomposition of the foaming agent. The advantages of chemical foaming agents are their ease in introducing them into the polymer (such as by hand mixing) and their ease in processing with ordinary equipment [15]. Azodicarbonamide (AZD) is one of the most favored foaming agents, because its decomposition temperature can be adjusted to accommodate the processing of the polymer by using an appropriate activator, such as transition metal salts, polyols, urea, alcohol, amines, and organic acids [15]. In this research, polybenzoxazine foam was prepared with a noncomplex and economical foaming method by using azodicarbonamide (AZD) as a foaming agent; then polybenzoxazine foam was further transformed into carbon foam after carbonization at 800 °C under an inert atmosphere.

6.3 Experimental

6.3.1 Materials

The material used in this research is benzoxazine resin. This benzoxazine resin is based on bisphenol-A, aniline, and formaldehyde. Commercial grade bisphenol-A was supplied by Bayer Thai Co., Ltd. Para-formaldehyde (95%) was purchased from BDH Laboratory Supplies. Aniline (99%) was purchased from Panreac Quimica SA Company, and the azodicarbonamide (Supercell-VR207), used as a foaming agent, was provided by A.F. Supercell Co., Ltd.

6.3.2 Organic and Carbon Foam Preparation

A benzoxazine monomer was synthesized via the solventless process proposed by Ishida *et al.* [10]. Bisphenol-A, aniline, and para-formaldehyde at a 1:2:4 molar ratio were mixed together and heated at 110 °C for 60 min until it became transparent pale yellow. Then, the mixture was left to solidify at room temperature. The acquired monomer was used without further purification. The precursors and the synthesis reaction of polybenzoxazine are shown in Scheme 1. The solidified benzoxazine monomer was ground into a fine powder. After that, azodicarbonamide was added into the monomer powder with different weight ratios

(i.e. 1, 3, 5, 7, and 10 wt%). The mixture was melt-mixed at about 110 °C until a homogeneous mixture was obtained. The molten mixture was transferred to an aluminum mold and heated from 30 to 210 °C using a heating rate of 1 °C/min under atmospheric conditions. The attained product was a cured polybenzoxazine foam, which was ready for further characterizations. In order to prepare the carbon foam, the polybenzoxazine foam was carbonized in a quartz reactor. The carbonization took place in a tube furnace under nitrogen flow at 500 cm³/min, using the following ramp cycle: 30°–250 °C in 60 min, 250°–600 °C in 300 min, 600°–800 °C in 60 min, and holding at 800 °C for 60 min. Then the furnace was cooled to room temperature under nitrogen atmosphere.

6.3.3 Characterization of The Organic and Carbon Foams

The density of the foam samples was determined by weighing the geometrically shaped foam and dividing the weight by the measured volume. The void volume fraction of the polybenzoxazine foam was estimated using ASTM D-2734 [17]. The void volume fraction was calculated by using Eq. (1):

$$\text{Void volume fraction} = \frac{100 \times (q_{\text{theoretical}} - q_{\text{measured}})}{q_{\text{theoretical}}} \quad (1)$$

where $q_{\text{theoretical}}$ is the theoretical density of polybenzoxazine and q_{measured} is the measured density of the resulting foams.

The curing behavior of the benzoxazine and the decomposition temperature range of the foaming agent were investigated by using a PerkinElmer Differential Scanning Calorimeter, DSC 7, analyzer to get useful synthesis parameters for the polybenzoxazine foam. Approximately 5–9mg samples were sealed in aluminum pans and analyzed using the temperature ramp rate of 1 °C/min under nitrogen atmosphere. Cross-sections of the foams were made by cutting perpendicular to the foaming direction around the middle of the mold. The cellular structure of the organic and carbon foams was characterized by using an Olympus SZ-4045-TR optical microscope with 8 times magnification. PerkinElmer's TG/DTA thermo gravimetric analyzer, model SII Diamond, was used to examine the decomposition temperature and char yield of the polybenzoxazine. Approximately

20mg of the polybenzoxazine was heated from 30° to 900 °C using a heating rate of 20 °C/min under nitrogen atmosphere. Using ASTM D 1621 as the standard, an INSTRON universal testing instrument (Model 4502), with a 1kN static load cell, was used to determine the uniaxial compression properties of the organic and carbon foams. Cylindrical specimens were compressed between two parallel steel plates with a crosshead speed of 2.5 mm/min. The compressive modulus was calculated from the steepest slope of the stress–strain curve, and the compressive strength was determined from the fracture failure of the specimens. The X-ray powder diffraction pattern of the carbon foam was obtained using an XRD (Bruker AXS D8 ADVANCE) spectrometer with Cu K α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA to examine the graphitization of the carbon foam after carbonization. The electrical conductivity of carbon foam was measured by the standard four-point probe method with a current of 10 mA.

6.4 Results and Discussion

Several analyzing techniques have been recommended to use for the investigation of the relationship between temperature and any other properties of polymeric materials [18, 19]. In our experiment, curing behavior and the decomposition temperature of the polybenzoxazine foam precursor were obtained by DSC and TGA, respectively. In order to optimize the polybenzoxazine foam fabrication conditions, the polymerization temperature range of the benzoxazine monomer and the decomposition temperature range of the foaming agent had to be investigated by using the DSC. Figure 6.1 shows the DSC thermograms of the benzoxazine monomer, foaming agent, and monomer/foaming agent mixtures with various AZD contents. As seen from the figure, the curing exothermic peak of the benzoxazine monomer is located between 120° and 230 °C, corresponding to its ring-opening polymerization characteristics [20]. According to the thermogram of the foaming agent, the decomposition reaction of the AZD used as a foaming agent in this study exhibited an overall exothermic reaction but including both exothermic and endothermic reactions, which was described as a characteristic of this foaming

agent [14]. The exothermic reaction was found to be in the in temperature range of 170°–210 °C, and the maximum exothermic peak was observed a 198 °C, as seen in the figure. With further rising temperature, a sharp endothermic peak could be observed in the temperature range of 210°–230 °C. Regarding to the decomposition of AZD, several decomposition mechanisms, depending on decomposition environment, have been reported [14-16]. However, CO, CO₂, N₂, NH₃ are the main released gases in all decomposition mechanisms [14-16]. Due to the decomposition temperature of the polybenzoxazine, further discussed, the endothermic decomposition range of the AZD was considered to be outside of the processing window of the polybenzoxazine used in this study. The combined exothermic curing temperature range of benzoxazine and that of the decomposition of AZD in the benzoxazine monomer/foaming agent mixtures with different AZD contents is shown in Figure 6.1. As clearly seen, the exothermic peaks of all the mixtures have the same onset of polymerization exotherm, at approximately 120 °C, which is the same as that of the neat benzoxazine monomer. Upon further consideration, maximum exothermic peaks of the mixtures were observed at 190 °C, which is lower than that of the neat AZD. As previously investigated, the decomposition temperature of AZD can be reduced by using suitable activators (catalysts or kickers), such as transition metal salts (lead, cadmium, and zinc), polyols, urea, alcohol, amines, and organic acids [15, 16]. Since there is a lowering of the maximum exothermic peaks of the mixers, it may be inferred that the benzoxazine might act as a decomposition activator of AZD. On the other hand, due to no observable peak shift of the onset of the curing exothermic peak of benzoxazine in the temperature range between 120 and 230 °C, it could be implied that AZD does not have any effect on the curing reaction of benzoxazine.

For the transformation of polybenzoxazine foam into carbon foam, the thermal degradation of polybenzoxazine had to be investigated. The TG and DTG thermograms of polybenzoxazine under nitrogen atmosphere are presented in Figure 6.2. As shown in the figure, the polybenzoxazine began to decompose into small volatile materials at 250 °C, corresponding to the start of the decrease of its retention weight. Moreover, there are three stages of decomposition observed from this DTG

thermogram. The highest maximum weight loss rate was observed in the temperature range between 250° and 600 °C. The rate became slower after 600 °C and a significant mass loss could not be observed beyond 800 °C. The volatile products emitted during the thermal decomposition processes of aromatic amine-based polybenzoxazines were identified by Kasinee and Ishida [11] using TGA and GC–MS techniques. They found that the decomposition products are a combination of benzene derivatives, amines, phenolic compounds, and Mannich base compounds. In addition, from the thermogram, it could be seen that the degradation temperature at 5% weight loss and the char yield at 800 °C of the synthesized polybenzoxazine was 330 °C and 25 wt% respectively. This degradation behavior is in line with many other related works [21, 22]. According to the polymerization temperature range and the onset of the degradation temperature of polybenzoxazine, as well as the decomposition temperature range of the foaming agent, polybenzoxazine foams were prepared by raising the temperature of the benzoxazine monomer/foaming agent mixtures from room temperature to 210 °C using a heating rate of 1 °C/min, and carbon foams were further obtained by the carbonization of the resulting polybenzoxazine foams with the following three ramp cycles: 30°–250 °C, 250°–600 °C, and 600°–800 °C, which correspond to the degradation behavior of polybenzoxazine, as seen in the TGA thermogram.

Principally, the mechanical and physical properties of foam materials are the most considered parameters in common engineering applications. Figure 6.3 shows the relationship between the measured densities of polybenzoxazine foams and added AZD content. The density reveals an almost linear decreasing trend with increasing AZD content. The decreasing of the foam density corresponds with an increasing amount of the resulting gases developed during the foaming process as the AZD content increases. Figure 6.4 shows the compressive strength of polybenzoxazine foams as a function of foam density. As observed in the figure, the average values of the foam strength continually increased from 5.2 to 12.4 MPa with a density of 273 to 407 kg/m³, respectively. This figure also presents a comparison between the compressive strength of the polybenzoxazine foams prepared in this study and the polybenzoxazine foam synthesized by using the resin/glass microballoon composite

fabrication technique [12]. It can be seen that the strengths of the resulting foams from both synthesizing techniques exhibit a similar trend, in which the strengths increase as the foam density increases. From the data summarized in this figure, it can be deduced that the polybenzoxazine foams derived by using AZD as a foaming agent in this study has a compressive strength significantly higher than that of the foams derived from the resin/glass microballoon composite fabrication method with the same density. In Figure 6.5, the compressive modulus calculated from the stress–strain compression curves was plotted versus the foam density. As shown in the figure, the modulus of the foam increased considerably with the foam density, from 268 to 681 MPa with a density of 273 to 407 kg/m³, respectively. The relationship between the compressive properties and the foam density agrees with many other studies [23-27]. The increasing of the strength and the modulus of the polybenzoxazine foams with increasing foam density corresponds to the calculated void volume fraction values of the foams, shown in Table 6.1. It can be seen that the void volume fraction in the foams decreased with increasing foam density. The increasing of the strength and the modulus of the polymeric foams with decreasing void fraction values certainly complies with the addition rule. This result is analogous to the study of Wouterson *et al.* [17] where the effect of void volume fraction on the mechanical properties of polymeric foam was examined. The cellular structures of the polybenzoxazine and carbon foams were obtained by using 5 times magnification with an optical microscope. Figure 6.6 shows the microscope images of the polybenzoxazine foams with different densities. An examination of the foams revealed well-foamed structure with an orange color. One influence of foam density is that decreasing density of the foam led to an increase of the cell size of the resulting foam. From a detailed observation of the polymer matrix of the foam with very high density, the foams displayed a structure with massive aggregated polymeric cell walls, which can clearly be seen from the foam with a density of 407 kg/m³ (Figure 6.6a). It may further be noticed that the cell wall thickness of the foams decreased with decreased foam density, and they also showed a more uniform cell structure with a larger cell size (Figure 6.6b-e). This result is in line with the study of Chen *et al.* [4], where they observed that the foam density directly relates to the cell wall thickness of the foams.

Figure 6.7 shows the stress–strain responses of the polybenzoxazine foams with various densities. For a comparison of the deformation behavior of all the resulting foams, the samples were compressed beyond their yield points. As previously described, the initial slope and the collapse stress (which represent the modulus and strength of the foams, respectively) systematically increased with increasing foam density. Furthermore, as clearly observed from the stress–strain responses, there were two distinct types of deformation behaviors under the compression loading. The foams with a high density exhibited the conventional brittle fracture without a plateau region beyond their yield points, as clearly seen in the foam with a density of more than 339 kg/m^3 . The rapid drop of compressive strength of the foams represents the fracture failure under compression loading. This result may indicate that the foams would suddenly lose their expected load-carrying capacities after their initial failures occur. On the other hand, the foams with lower density exhibited a more flexible deformation manner. They displayed a plateau region beyond their yield points due to the cell collapse process of the foams under compression loading, which caused the foams to not completely lose their integrity after breakage. The dependence between the stress-strain response and the foam density corresponds to many other related works [23-27]. As described by Zenkert and Burman [23], the variation in deformation behavior is probably due to the difference in the thickness of the cell walls of the resulting foam. A foam with a higher density has thicker cell walls which provide more integrity and resistivity to cell wall buckling than that of a foam with thinner cell walls.

As observed from many other related studies, it is generally well known that the properties of porous materials can be improved after carbonization. In order to observe the property change of the resulting foam after carbonization, the polybenzoxazine having the lowest density was chosen for further examination. Figure 6.8 shows the X-ray diffraction pattern of the carbon foam derived from the polybenzoxazine foam with a density of 273 kg/m^3 . Small broad peaks of the foam could be seen at $2\theta = 23$ and 43 . The d-spacing, calculated by Bragg's equation, corresponds to the interlayer spacing (d_{002}) and the stacking height ($L_{c,002}$) of graphitic carbon material [28-30]. According to this XRD characterization, it can be inferred that the resulting carbon foam prepared in this study was partially

crystalline, but had less crystallinity than graphite. Figure 6.9 is the microscopic image of the resulting carbon foam. When comparing the cellular structures of the precursory polybenzoxazine foam (Figure 6.6e) and the corresponding carbon foam, it can be seen that the carbon foam has a much denser porous structure than the polybenzoxazine precursor, which conforms to its density (Table 6.2). As seen in the table, the density of the carbon foam was greater than that of its precursory polybenzoxazine foam, which could generally be seen in the carbonization of other organic porous materials. This phenomenon was also observed by Wu *et al.* [30] and Shen *et al.* [31] who observed that the density of porous materials increased after carbonization. Figure 6.10a shows the compressive stress–strain curves of the polybenzoxazine foam with a density of 273 kg/m^3 and the corresponding carbon foam. As summarized in the figure, the compressive modulus and the compressive strength of the polybenzoxazine foam were increased approximately 3 and 2 times, respectively after the carbonization. The data from the compression testing of the carbon foams are given in Table 6.2. In order to compare the mechanical properties of the foams with different densities, their specific compressive properties are preferred equitable guidelines. Figure 6.10b is a comparison between the density-normalized compressive stress–strain curves of both polybenzoxazine and the resulting carbon foams. As clearly shown in the figure, the normalized compressive modulus of the carbon foam was still higher than that of the polybenzoxazine foam. Nevertheless, both foams possessed the same normalized yield strength and normalized stress at the plateau region. Moreover, because of carbon foams have been widely used as electrodes, the electrical conductivity of the resulting carbon foam after being carbonized at $800 \text{ }^\circ\text{C}$ was examined (Table 6.2). The measured electrical conductivity of the carbon foam prepared in this study was $0.005 \Omega^{-1} \text{ cm}^{-1}$. Compared to other carbon foam, the electrical conductivities of our resulting carbon foams are in the same range as the carbon foams from the other precursor with the same sintering temperature [5].

6.5 Conclusions

Polybenzoxazine foams and their related carbon foams have been successfully prepared. From the microstructure considerations, it was found that both the resulting polybenzoxazine and carbon foams demonstrated a uniform foamed structure. It was apparent from the stress–strain responses of the polybenzoxazine foams that the compressive stress and compressive modulus of the foam increased with increased density. Moreover, the foam with lower density would display a more flexible deformation manner. After carbonization of the polybenzoxazine foam at 800 °C, partially crystalline carbon foam with superior compressive properties to that of its corresponding polybenzoxazine foam was attained. However, the density-normalized compressive strengths of the polybenzoxazine foam and the corresponding carbon foam were not significantly different.

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6.7 References

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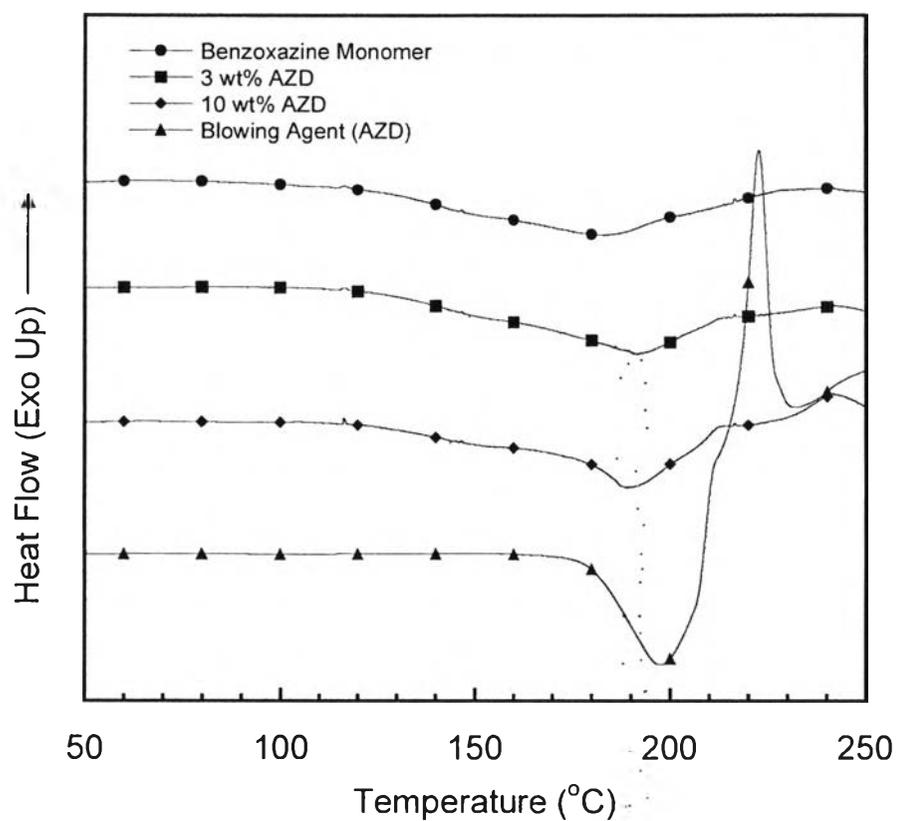


Figure 6.1 DSC thermograms of the benzoxazine monomer, foaming agent, and monomer/foaming agent mixtures with a scanning rate of 1 °C/min.

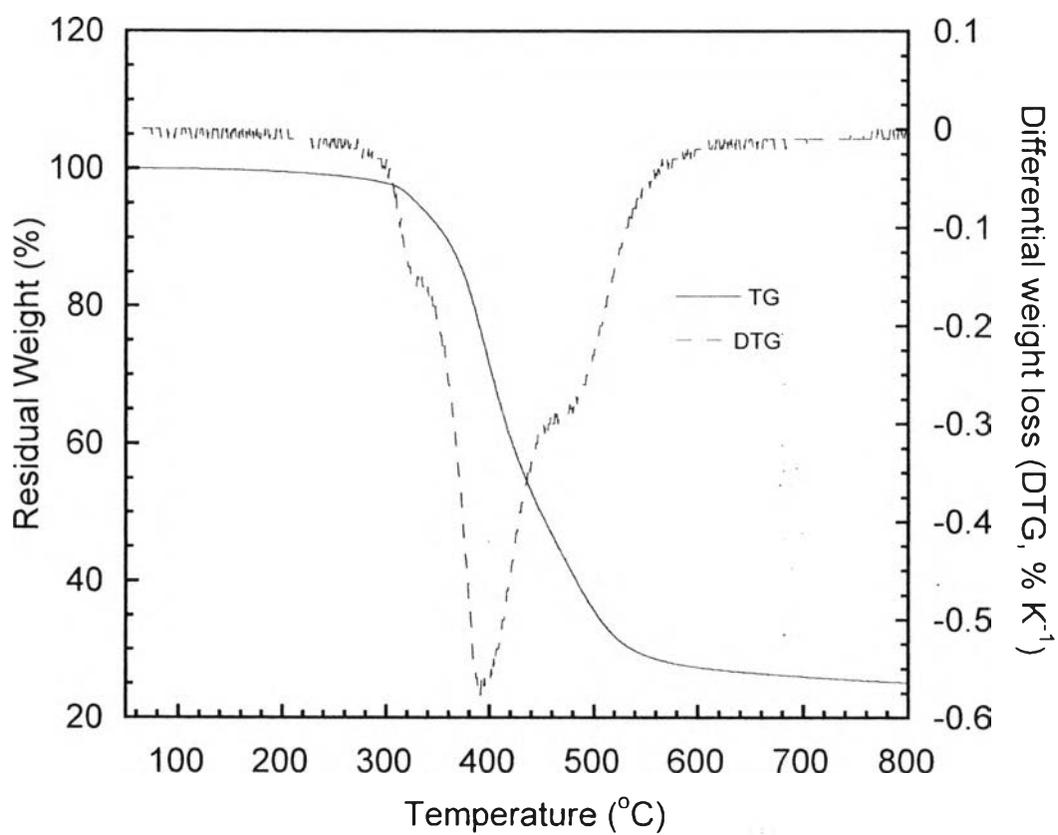


Figure 6.2 TG and DTG analysis of polybenzoxazine.

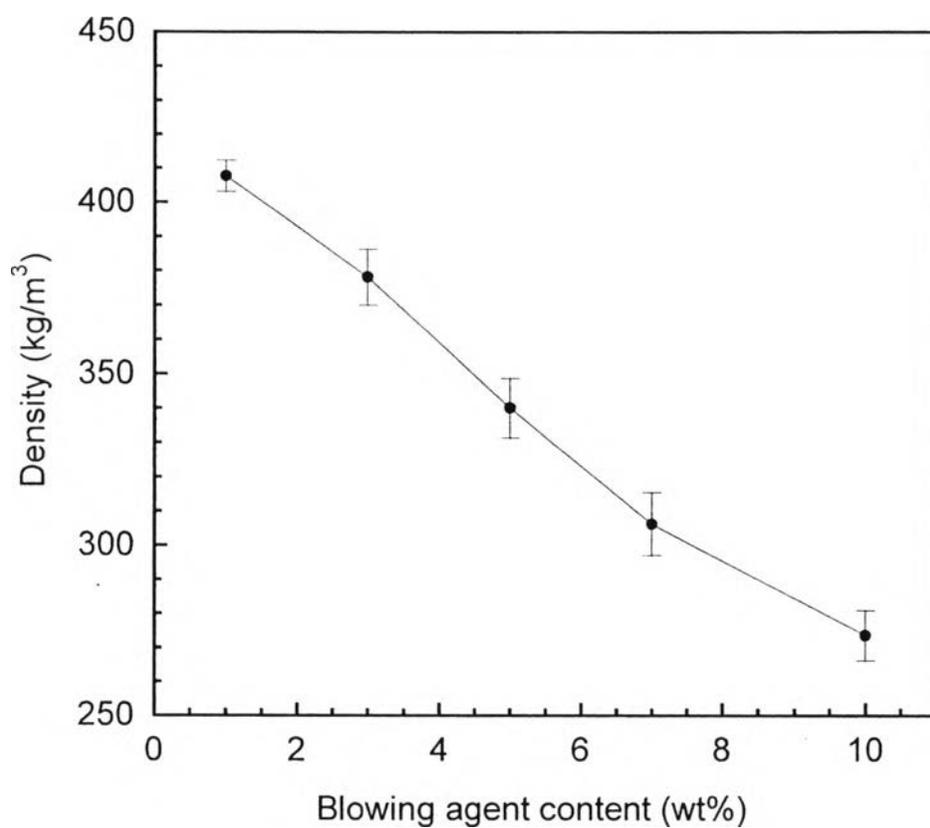


Figure 6.3 Measured densities of polybenzoxazine foams as a function of AZD content.

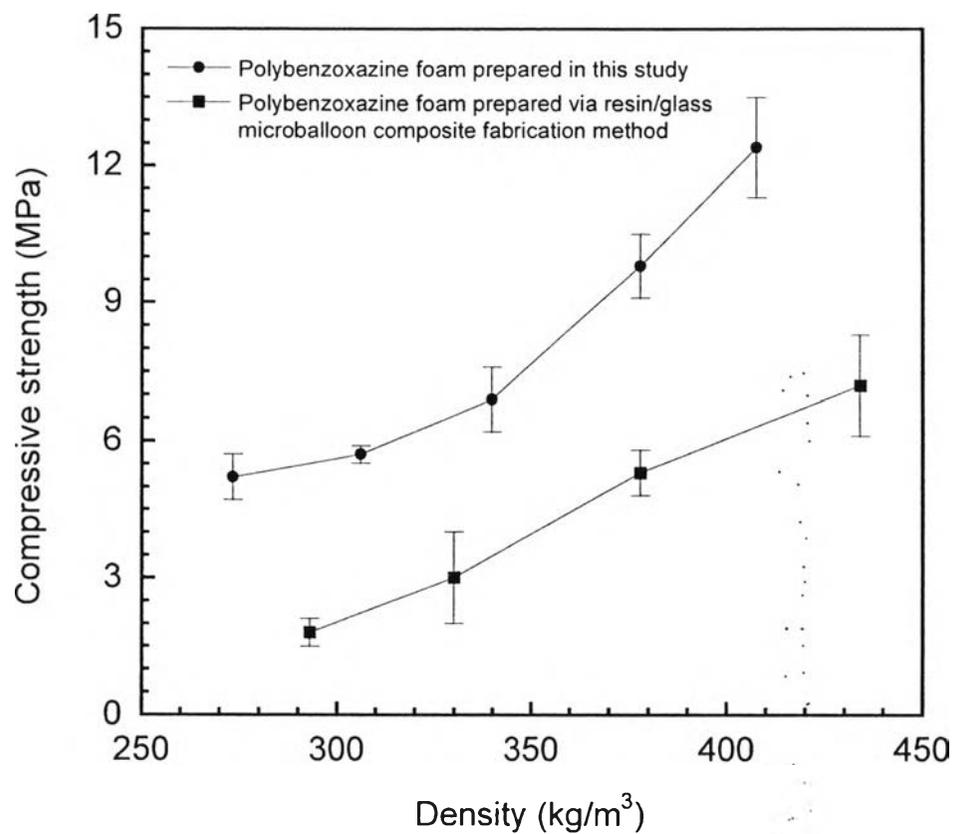


Figure 6.4 Comparison of the compressive strength and the density of polybenzoxazine foam derived from different fabrication techniques [12]. (Note: the compressive strength summarized from [12] was conducted with a crosshead speed of 5mm/min at room temperature, according to ASTM D 790).

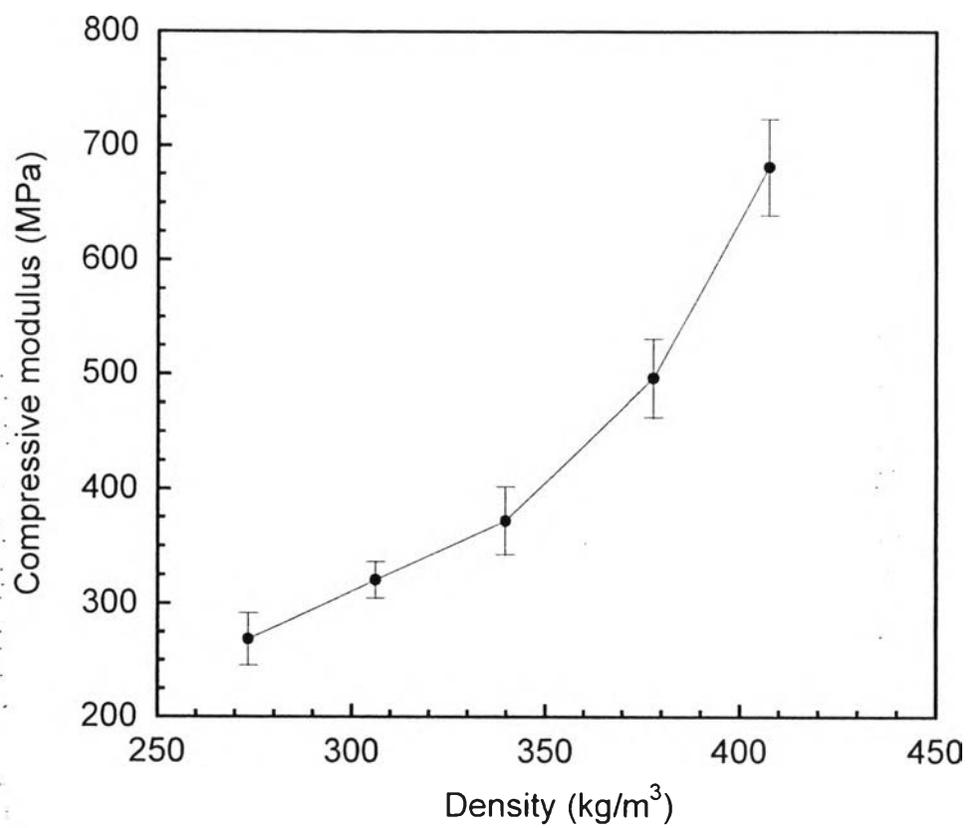


Figure 6.5 Compressive modulus of polybenzoxazine foams as a function of foam density.

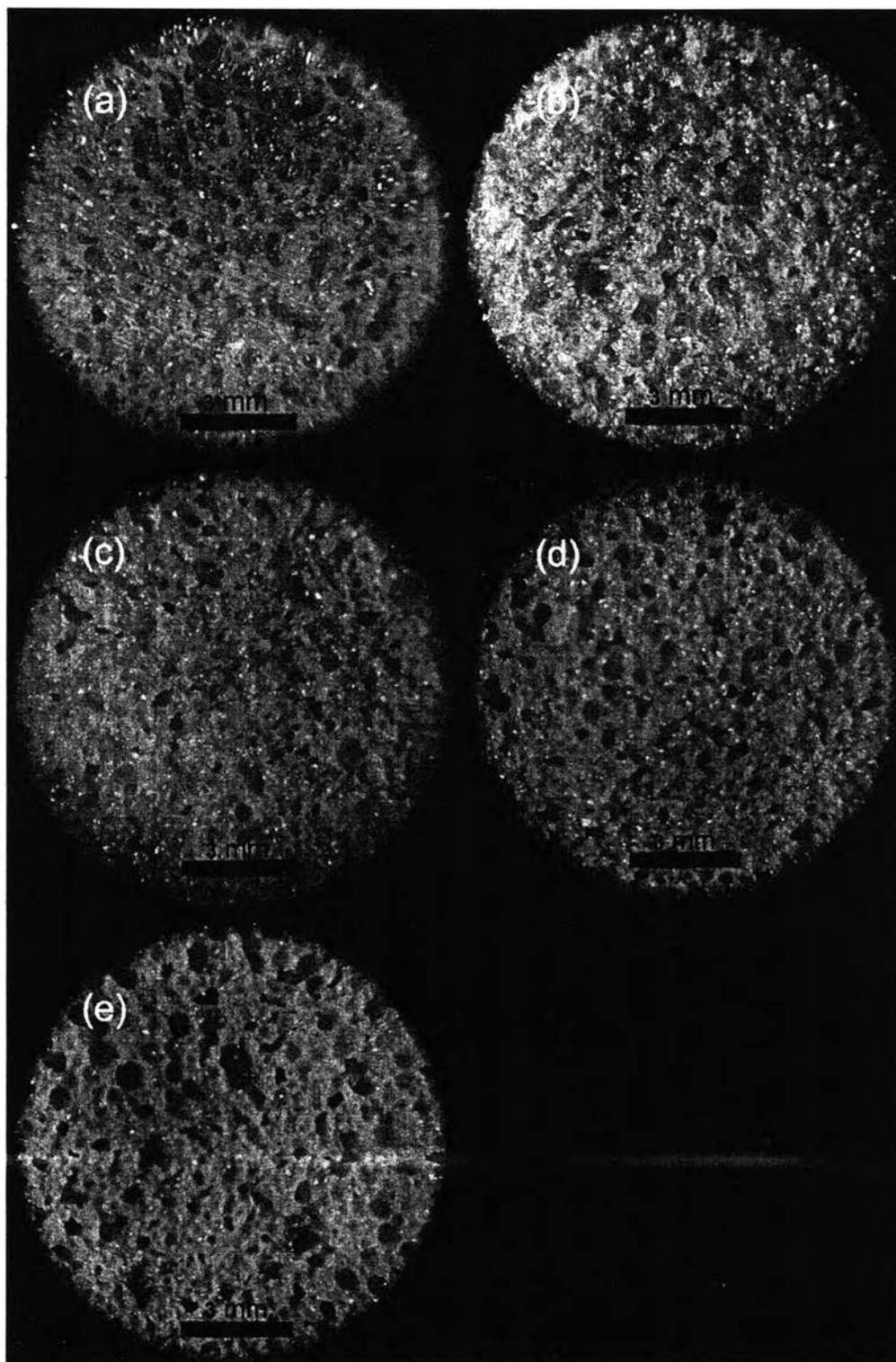


Figure 6.6 Microscope images of polybenzoxazine foams at several densities (a) 407 kg/m^3 , (b) 378 kg/m^3 , (c) 339 kg/m^3 , (d) 306 kg/m^3 , and (e) 273 kg/m^3 .

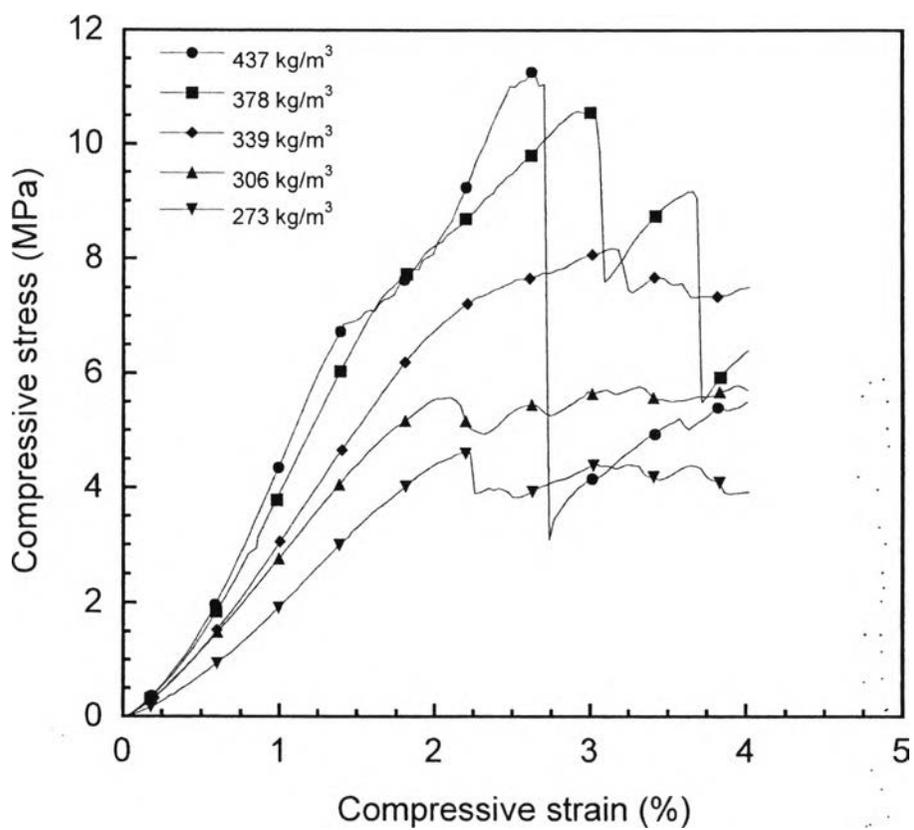


Figure 6.7 Compressive stress–strain curves of polybenzoxazine foam with various densities at a strain rate of 2.5 mm/min.

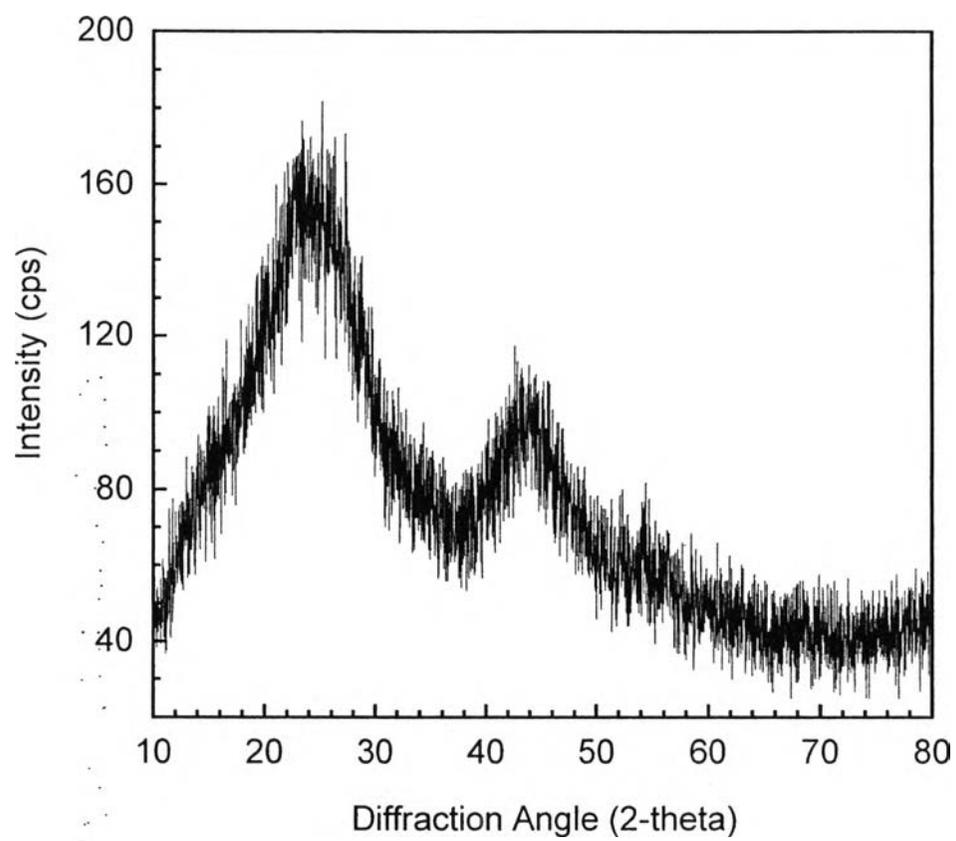


Figure 6.8 XRD pattern of polybenzoxazine-based carbon foam.

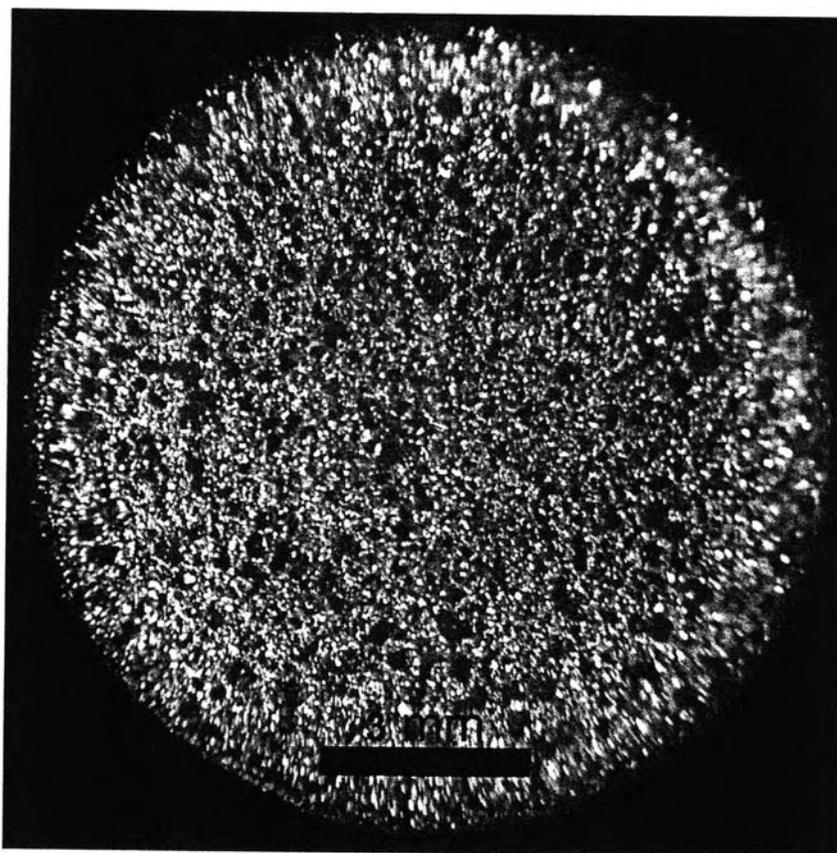


Figure 6.9 Microscopic image of the resulting carbon foam.

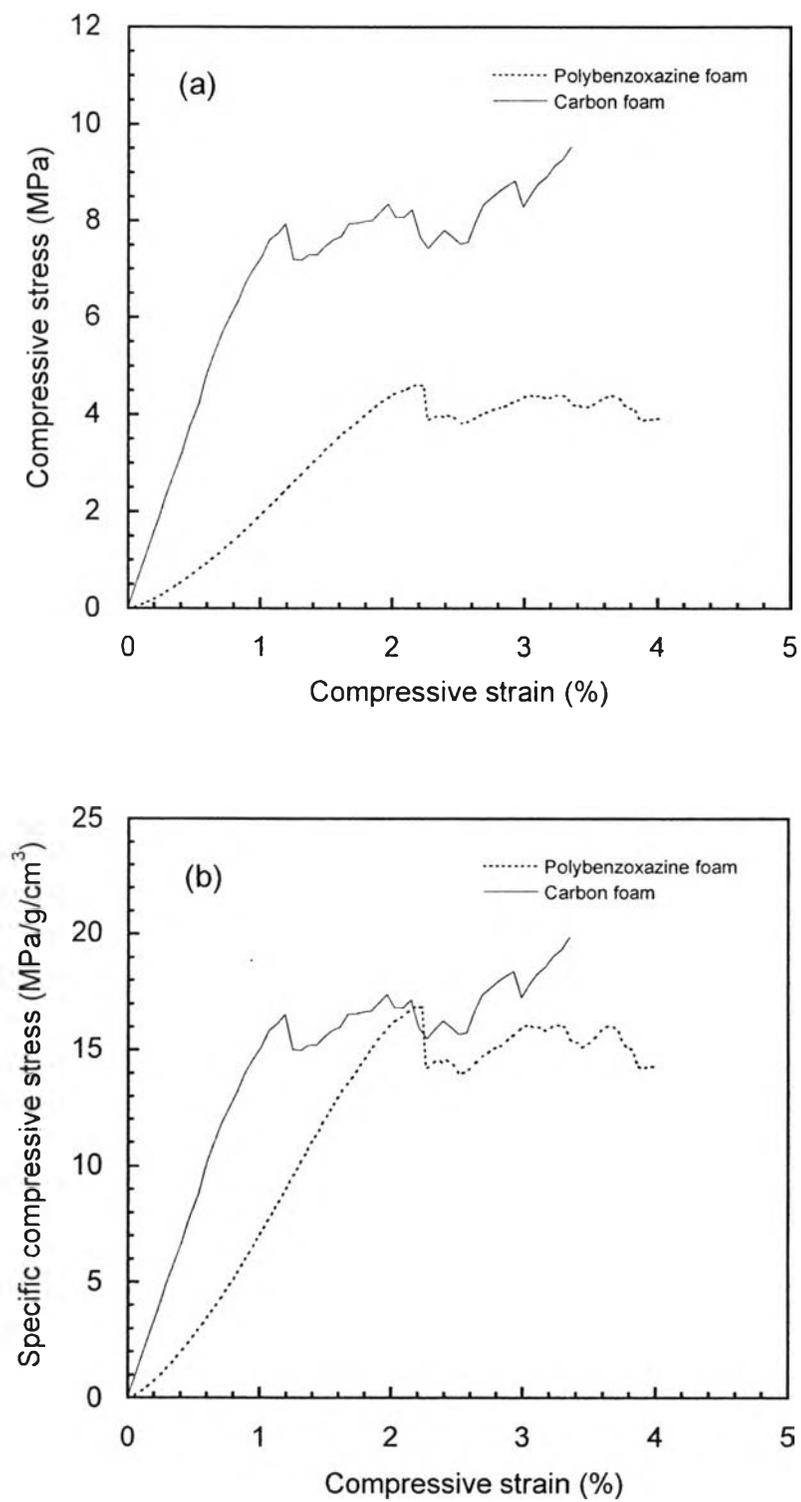


Figure 6.10 Comparison between (a) stress-strain curve and (b) specific stress-strain curve of polybenzoxazine foam and the corresponding carbon foam.

Table 6.1 Physical and compressive properties of polybenzoxazine foams with different AZD contents

Foaming agent content (wt%)	Density (kg/m ³)	Void content (vol%)	Specific compressive strength (MPa/g/cm ³)	Specific compressive modulus (MPa/g/cm ³)
1%	407±4	65.8±0.4	1670±88	30.4±2.4
3%	378±8	68.3±0.7	1313±69	26.0±1.9
5%	339±8	71.5±0.7	1093±74	20.5±1.7
7%	306±9	74.3±0.8	1046±28	18.8±0.5
10%	273±7	77.1±0.6	980±64	19.1±1.6

Table 6.2 Physical and compressive properties of the resulting carbon foam

Density	Compressive strength	Compressive modulus	Volume shrinkage	Electrical Conductivity (Foaming direction)
(kg/m ³)	(MPa)	(MPa)	(%)	(Ohm ⁻¹ cm ⁻¹)
480	9.5	829	67.7	0.005