CHAPTER V

RESULTS AND DISCUSSION

(CARBON MATERIALS FROM POLYBENZOXAZINE

FOR CARBON DIOXIDE ADSORPTION APPLICATION)

5.1 Characterization of Adsorbents

In current work, due to the presence of the nitrogen functionalities in the structure of polybenxzoxazine-derived carbon materials, it was aimed to improve the textural parameters of these materials via a sol-gel technique, using xylene as a solvent. After obtaining the carbon aerogel, polybenzoxazine-based aerogel from two different amines of diethylenetriamine (DETA) and pentaetylenehexamine (PEHA) were carbonized under N_2 atmosphere and then activated with CO_2 at two activation temperatures of 800 °C and 900 °C. Moreover, the concentrations of benzoxazine monomer were varied at 30, 35 and 40 wt% in order to tune the surface properties of these aerogel materials. Furthermore, the influence of carbon aerogels loading with PEG-PPG-PEG block copolymer as non-ionic surfactant on CO_2 adsorption performance was investigated in both types of amine precursors

5.1.1 Adsorbents Characterization

The BET surface area was analyzed using the BET (Brunauer-Emmett-Teller) theory. Micropore volume was calculated using the HV (Horvath Kawazoe) theory. Mesopore volume was calculated using the BJH (Barrett-Johner-Halendar) theory. Table 5.1 shows the textural parameters of activated carbon derived from PBZ, PBZ-based organic aerogels, and PBZ-based carbon aerogels from two different amine types (e.g., DETA and PEHA).

As for the activated carbon prepared from the bulk polymerization technique, activated carbon from PEHA-derived PBZ exhibited higher surface area than DETA-derived PBZ activated carbon to 238 m^2/g with pore volume of 0.477 cm^3/g as a result of the generating on small pores on the surface of carbon materials as observed in Figure 5.1.

In case of all adsorbents from a sol-gel technique, all of carbon materials showed a dramatic increase in the specific surface area and pore volume, especially for the micropore volume, compared to those organic aerogels. It was because the volatile matters evolved and created pores during the carbonization and activation steps, leading to the rise of the number of micropores and mesopores, resulting in the increasing of the surface area. These results were similar to the other studies on the preparation of carbon materials (Li *et al.*, 2002; Al-Muhtaseb and Ritter, 2003; Lee *et al.*, 2014).
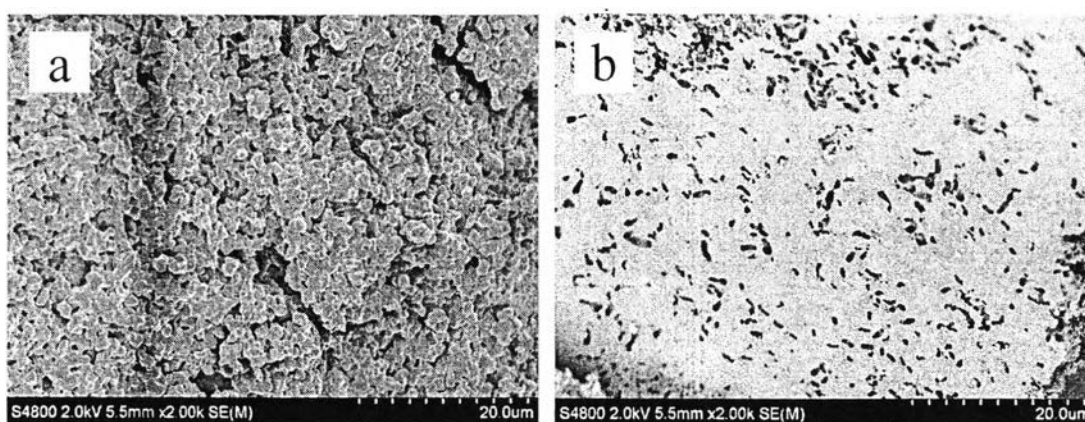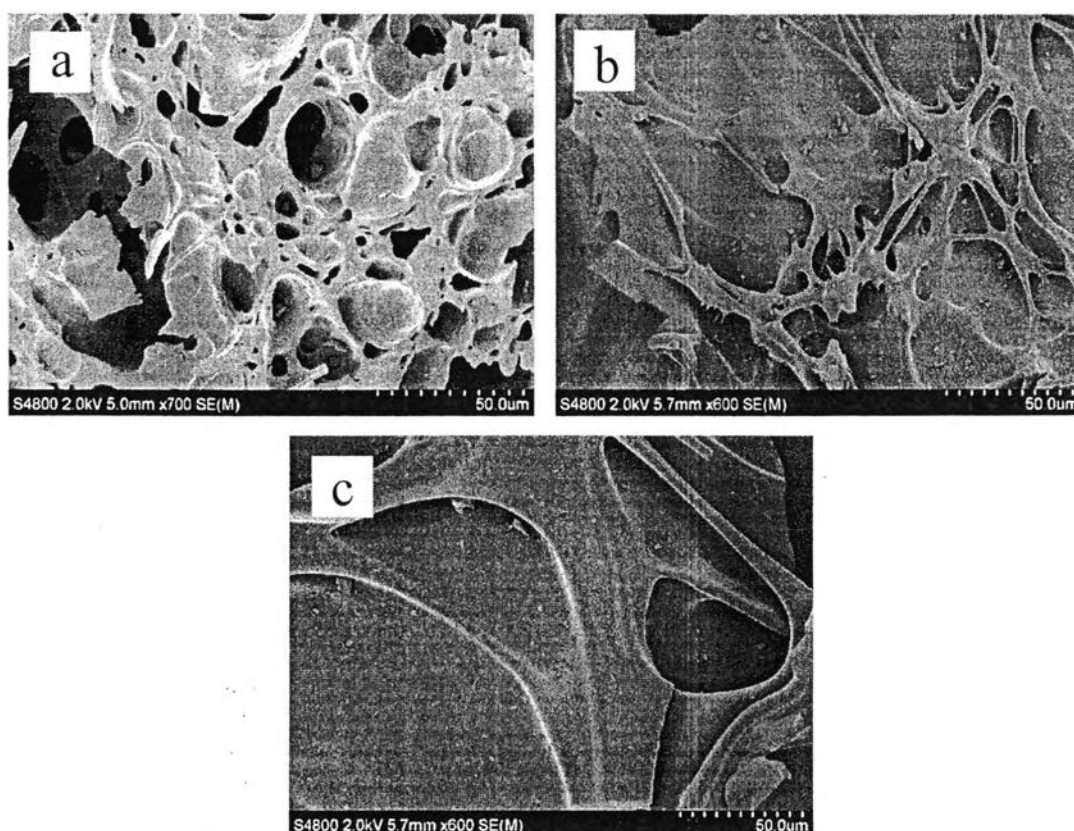

Figure 5.1 SEM images of (a) activated carbon from DETA-derived PBZ, (b) activated carbon from PEHA-derived PBZ with a magnification of 2,000 times.

Turning to consider about the effect of benzoxazine concentrations on aerogel materials, both series of organic aerogels show that the surface area and other pore properties did not change significantly with increasing the amount of benzoxazine monomer as obsreved in a series of DETA-based carbon aerogels as shown in Table 5.1. However, as benzoxazine comncentration higher the PEHA-derived PBZ carbon aerogels exhibited the decrease in surface area, leading to the decrease in the BET surface area and total pore volume due to damaging of pores within the aerogel structure during carbonization and activation steps as a result of pore collapse which obviously observed in Figure 5.2.

Table 5.2 displays the surface properties of PBZ-based activated carbons, carbon aerogels derived from PBZ, and carbon aerogels containing non-ionic

surfactant (by 6 wt% of benzoxazine monomer) from two amine precursors at the activation temperature of 900 °C. For activated carbons derived from PBZ, they provided gently increase in surface area and pore volume owing to the activation at higher temperature. Interestingly, at higher activation of carbon aerogels, they reveal the significant improvement of the surface properties, especially in 30 wt% of DE-TA-based carbon aerogel with a specific surface area of 695 m^2/g and pore volume of 0.396 cm^3/g. It was because a higher activation temperature led to the increase in the generation of micropores in the structure of materials as agreed with several other works (Robertson and Mokaya, 2013; Burhenne and Aicher, 2014). Not only these carbon aerogels operated at high activation temperature would help create a high surface area, but their structures prepared via a sol-gel technique also have a dominant influence to generate the high surface area during carbonization and activation steps.

Figure 5.2 SEM images of (a) PEHA-derived PBZ carbon aerogel at 30 wt%, (b) 35 wt%, and (c) 40 wt% of monomer solutions with magnification of 600 times.

Table 5.1 The surface property of activated carbon from polybenzoxazine, a series of organic aerogels and carbon aerogels at activation temperature of 800 °C

Adsorbents	BET Surface Area (m^2/g)	Micropore Volume (cm^3/g)	Mesopore Volume (cm^3/g)	Total Pore Volume (cm^3/g)	Pore Size (nm)
AC (DETA)	167	0.088	0.071	0.181	1.84
AC (PEHA)	238	0.121	0.155	0.477	0.78
BA from DETA-30w%t	47	0.017	0.029	0.093	2.33
BA from DETA-35wt%	14	0.007	0.070	0.050	1.60
BA from DETA-40wt%	21	0.011	0.063	0.174	2.66
BA from PEHA-30wt%	14	0.007	0.019	0.120	2.17
BA from PEHA-35wt%	52	0.018	-	0.127	2.14
BA from PEHA-40wt%	28	0.013	-	0.052	2.76
CA from DETA-30wt%	312	0.165	0.016	0.258	1.15
CA from DETA-35wt%	368	0.193	0.053	0.288	1.09
CA from DETA-40wt%	376	0.202	0.084	0.344	1.20
CA from PEHA-30wt%	114	0.059	0.015	0.124	1.29
CA from PEHA-35wt%	85	0.045	0.004	0.099	2.48
CA from PEHA-40wt%	44	0.024	0.007	0.155	2.40

*AC = Activated carbon, BA = Organic aerogel, and CA = Carbon aerogel

Table 5.2 The surface property of activated carbon from polybenzoxazine, carbon aerogels, and carbon aerogels containing with non-organic surfactant (P_{123}) at activation temperature of 900 °C

Adsorbents	BET Surface Area (m^2/g)	Micropore Volume (cm^3/g)	Mesopore Volume (cm^3/g)	Total Pore Volume (cm^3/g)	Pore Size (nm)
AC (DETA) at 900 °C	178	0.094	0.047	0.297	1.82
AC (PEHA) at 900 °C	295	0.151	0.238	0.433	0.77
CA from DETA-30wt% (900 °C)	695	0.359	-	0.396	0.65
CA from PEHA-30wt% (900 °C)	304	0.161	0.013	0.179	0.78
CA from DETA-30wt%+P_{123} (900 °C)	665	0.343	0.043	0.386	0.76
CA from PEHA-30wt%+P_{123} (900 °C)	502	0.273	0.007	0.285	0.77

*AC = Activated carbon, BA = Organic aerogel, CA = Carbon aerogel, and P_{123} = Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

As per carbon aerogels loading with non-ionic surfactant (PEG-PPG-PEG block copolymer), PEHA-derived PBZ carbon aerogel with surfactant demonstrates that non-ionic surfactant could help increase the surface area from 304 m^2/g to 502 m^2/g and micropore volume from 0.161 cm^3/g to 0.273 cm^3/g in the structure of carbon aerogel because these non-ionic surfactant would help disperse the aggregated molecules of polybenzoxazine which caused from the strong bonding (hydrogen bond) between the polymer chains. A similar result of loading non-ionic surfactant in polybenzoxazine was found in the study of Thubsuang (2015). Nevertheless, the PEG-PPG-PEG block copolymer was not affected on the textural properties of DETA-derived PBZ carbon aerogel as evidenced in Table 5.2.

5.1.2 Ultimate Analysis

CHN analyzer was employed to investigate the three elemental compositions including carbon (C), hydrogen (H) and nitrogen (N) of the materials. Table 5.3 demonstrates the ultimate analysis of benzoxazine monomers, polybenzoxazines, activated carbons derived from PBZ, a series of organic aerogels, a series of carbon aerogels, and carbon aerogel loading with non-ionic surfactant (PEG-PPG-PEG block copolymer, with 6 wt% of benzoxazine monomer) by two different amine reactants (e.g., DETA and PEHA). In case of organic and carbon aerogels, the monomer solution concentrations were varied and kept at 30, 35 and 40 wt% of monomer in xylene.

According to the results, it can be inferred that the concentration of mono-mer solution does not have a significant effect on the amount of nitrogen content for both polybenzoxazine-based organic aerogels synthesized from the DETA and PEHA precursors which perform the nitrogen composition at approximately 11.00 and 14.59 wt%, respectively. However, the amount of nitrogen content of organic aerogel by PEHA was higher than the organic aerogel by DETA for all the aerogel conditions due to the higher content of nitrogen in PEHA-derived benzoxazine as compared to the DETA-derived benzoxazine (14.61 and 10.71%, respectively). In the same case, carbon aerogels with different benzoxazine concentrations by DETA and PEHA as amine precursors provided the nitrogen content at about 6.35 and 7.82 wt%, respectively.

Table 5.3 Ultimate analysis of all materials

Materials	%C	%H	%N	%O
BZ (DETA)	63.54	7.14	10.71	18.61
BZ (PEHA)	60.91	8.11	14.61	16.37
PBZ (DETA)	67.17	7.09	10.73	15.01
PBZ (PEHA)	65.86	8.26	14.39	11.49
BA from DETA-30wt%	72.15	7.25	11.22	9.38
BA from DETA-35wt%	72.15	7.25	11.00	8.83
BA from DETA-40wt%	71.49	7.46	11.00	9.99
BA from PEHA-30wt%	67.25	8.05	14.32	10.38
BA from PEHA-35wt%	67.92	8.73	14.59	8.76
BA from PEHA-40wt%	69.57	8.49	14.67	7.27
AC (DETA) at 800 °C	82.50	0.82	6.33	10.35
AC (PEHA) at 800 °C	75.30	0.67	5.21	18.82
CA from DETA-30wt% (800 °C)	82.40	1.15	6.35	10.10
CA from DETA-35wt% (800 °C)	82.80	0.78	5.75	10.67
CA from DETA-40wt% (800 °C)	82.50	0.69	6.48	10.33
CA from PEHA-30wt% (800 °C)	76.90	0.82	7.74	14.54
CA from PEHA-35wt% (800 °C)	76.20	0.59	7.82	15.39
CA from PEHA-40wt% (800 °C)	76.80	1.52	8.61	13.07
AC (DETA) at 900 °C	82.90	0.62	5.14	11.34
AC (PEHA) at 900 °C	81.80	0.58	4.12	13.50
CA from DETA-30wt% (900 °C)	86.30	0.82	5.29	7.59
CA from PEHA-30w% (900 °C)	85.40	0.70	6.74	7.16
CA from DETA-30wt%+P_{123} (900 °C)	84.10	0.86	4.31	10.73
CA from PEHA-30wt%+P_{123} (900 °C)	82.40	0.71	4.75	12.14

*BZ = Benzoxazine monomer, PBZ = Polybenzoxazine, AC = Activated carbon, BA = Organic aerogel, CA = Carbon aerogel, and P_{123} = Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

After carbonization under nitrogen atmosphere and activation with CO_2 at 900 °C for 2 hours, all carbon materials (e.g., activated carbons from PBZ and carbon aerogels) by DETA and PEHA as precursors shows that their nitrogen content decreased with increasing activation temperature. The same trend was observed by several works (Robertson and Mokaya, 2013; Wickramaratne *et al.*, 2014).

5.1.3 Surface Analysis by XPS

The type of functional groups and surface composition information in mainly three components including carbon, oxygen, and nitrogen were determined by XPS analyzer with the scanning modes of wide and narrow. Tables 5.4 – 5.9 show the binding energy and percentage of functional groups in each component obtained from the deconvoluted XPS spectrum of the samples. Moreover, the assignments of each component are displayed in Table 4.10.

The data in Tables 5.4 – 5.9 exhibits that the type of functional groups on the surface in all materials were similar. The deconvoluted spectra for C 1s composed of four binding energies at 284.3 ± 0.1, 285.0 ± 0.1, 285.4 ± 0.2, 285.8 ± 0.1, 286.6 ± 0.2, and 288.2 ± 0.3 eV corresponding to Graphite, Aliphatics, C with N, Hydroxyl/Ether, Carbonyl, and Carboxyl/Ester, respectively, as proposed from other studies of Burg *et al.* (2002); Plaza *et al.* (2013). For the XPS spectra of O 1s, they consisted of only two elements at the binding energies of 531.3 ± 0.1 and 532.9 ± 0.1 eV corresponding to Carbonyl/Carboxyl group and Ether/Carboxylic/Hydroxyl group, respectively, as the same reference above. In addition, the N 1s spectra exhibited six functional groups at the binding energy of 398.2 ± 0.4, 399.4 ± 0.4, 400.3 ± 0.1, 401.4 ± 0.3, and 403.6 ± 0.1 eV associated with Pyridinic-N, Amine, Pyrrolic-N, Quaternary-N, and N-Oxide, respectively, as suggested by Adelodun (2014); Coutinho *et al.* (2012); Wickramaratne *et al.* (2014).

For the green materials like benzoxazine monomers, polybenzoxazines, and PBZ-based organic aerogels, only amine functional group was present on the surface as listed in Table 5.4 and 5.5 for DETA-derived PEHA-derived, respectively. Besides, these materials indicated only ether type and/or carboxylic and/or hydroxyl oxygen functionalities because the chemical structure of polybenzoxazine contained mainly amine and phenolic groups (see Figure 5.3).
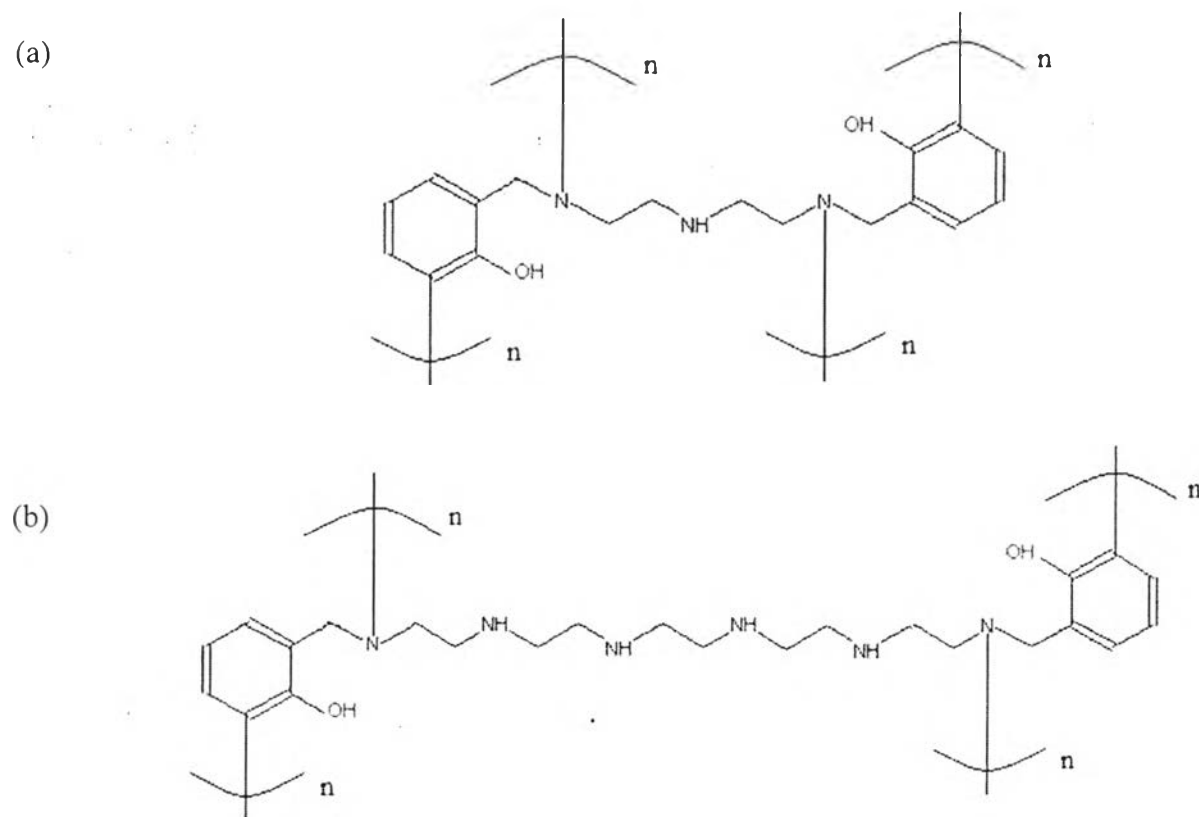
Figure 5.3 The chemical structures of (a) DETA-derived polybenzoxazine and (b) PEHA-derived polybenzoxazine.

Table 5.4 Deconvolution results of polybenzoxazine and PBZ-based organic aerogels by DETA as precursor

Region	Position (eV)	Intensity (%)				Assignment
		PBZ (DETA)	BA from DETA-30 wt%	BA from DETA-35 wt%	BA from DETA-40 wt%	
C 1s	284.3 ± 0.1	43.10 %	32.97 %.	29.20 %	43.09 %	Graphite
	285.0 ± 0.1	19.07 %	18.44 %	25.84 %	17.76 %	Aliphatics
	285.4 ± 0.2	13.27 %	13.50 %	13.89 %	13.65 %	C with N
	285.8 ± 0.1	10.81 %	15.59 %	9.96 %	12.59 %	Hydroxyl or Ether
	286.6 ± 0.2	11.40 %	16.91 %	12.90 %	9.99 %	Carbonyl
	288.2 ± 0.3	2.35 %	2.60 %	8.20 %	2.91 %	Carboxyl or Ester
O 1s	532.9 ± 0.1	100 %	100 %	100 %	100 %	Ether or Carboxyl or Hydroxyl
N 1s	399.4 ± 0.4	100 %	100 %	100 %	100 %	Amine

*PBZ = Polybenzoxazine and BA = Organic aerogel

Table 5.5 Deconvolution results of polybenzoxazine and PBZ-based organic aerogels by PEHA as precursor

Region	Position (eV)	Intensity (%)				Assignment
		PBZ (PEHA)	BA from PEHA-30 wt%	BA from PEHA-35 wt%	BA from PEHA-40 wt%	
C 1s	284.3 ± 0.1	36.74 %	32.96 %	29.68 %	35.84 %	Graphite
	285.0 ± 0.1	19.62 %	17.71 %	22.57 %	21.07 %	Aliphatics
	285.4 ± 0.2	16.59 %	18.32 %	18.20 %	16.20 %	C with N
	285.8 ± 0.1	13.44 %	14.96 %	10.81 %	8.70 %	Hydroxyl or Ether
	286.6 ± 0.2	4.53 %	11.41 %	10.52 %	12.17 %	Carbonyl
	288.2 ± 0.3	9.09 %	4.63 %	8.22 %	6.03 %	Carboxyl or Ester
O 1s	532.9 ± 0.1	100 %	100 %	100 %	100 %	Ether or Carboxyl or Hydroxyl
N 1s	399.4 ± 0.4	100 %	100 %	100 %	100 %	Amine

*PBZ = Polybenzoxazine and BA = Organic aerogel

Table 5.6 Deconvolution results of activated carbon from PBZ and carbon aerogels from derived PBZ by DETA as precursor at activating temperature of 800 °C

Region	Position (eV)	Intensity (%)				Assignment
		AC(DETA)	CA from DETA-30 wt%	CA from DETA-35 wt%	CA from DETA-40 wt%	
C 1s	284.3 ± 0.1	52.97 %	52.87 %	39.49 %	46.60 %	Graphite
	285.0 ± 0.1	17.04 %	15.82 %	20.57 %	21.12 %	Aliphatics
	285.4 ± 0.2	9.92 %	9.42 %	10.98 %	9.84 %	C with N
	285.8 ± 0.1	7.05 %	6.66 %	9.00 %	7.90 %	Hydroxyl or Ether
	286.6 ± 0.2	8.16 %	8.27 %	8.24 %	8.25 %	Carbonyl
	288.2 ± 0.3	4.87 %	6.96 %	11.72 %	6.29 %	Carboxyl or Ester
O 1s	531.3 ± 0.1	78.35 %	73.50 %	64.41 %	81.68 %	Carbonyl or Carboxyl
	532.9 ± 0.1	21.63 %	26.50 %	35.59 %	18.32 %	Ether or Carboxyl or Hydroxyl
N 1s	398.2 ± 0.4	35.65 %	35.79 %	44.77%	44.85 %	Pyridinic-N
	400.3 ± 0.1	37.29 %	35.11 %	28.90 %	28.61 %	Pyrrolic-N
	401.4 ± 0.3	15.43 %	16.03 %	14.36 %	15.68 %	Quaternary-N
	403.6 ± 0.1	11.63 %	13.06 %	11.97 %	10.87 %	N-Oxide

*AC = Activated carbon and CA = Carbon aerogel

Table 5.7 Deconvolution results of activated carbon from PBZ and carbon aerogels from derived PBZ by PEHA as precursor at activating temperature of 800 °C

Region	Position (eV)	Intensity (%)				Assignment
		AC(PEHA)	CA from PEHA-30 wt%	CA from PEHA-35 wt%	CA from PEHA-40 wt%	
C 1s	284.3 ± 0.1	33.93 %	41.56 %	46.52 %	49.53 %	Graphite
	285.0 ± 0.1	23.14 %	18.86 %	18.70 %	17.97 %	Aliphatics
	285.4 ± 0.2	12.42 %	12.80 %	12.52 %	12.31 %	C with N
	285.8 ± 0.1	9.87 %	8.44 %	8.24 %	5.60 %	Hydroxyl or Ether
	286.6 ± 0.2	12.01 %	7.62 %	7.56 %	8.72 %	Carbonyl
	288.2 ± 0.3	8.64 %	10.73 %	6.46 %	5.87 %	Carboxyl or Ester
O 1s	531.3 ± 0.1	73.50 %	70.13 %	73.83 %	66.18 %	Carbonyl or Carboxyl
	532.9 ± 0.1	26.50 %	29.87 %	26.17 %	33.82 %	Ether or Carboxy l or Hydroxyl
N 1s	398.2 ± 0.4	33.56 %	43.35 %	40.76 %	43.90 %	Pyridinic-N
	400.3 ± 0.1	30.44 %	27.38 %	33.96 %	36.80 %	Pyrrolic-N
	401.4 ± 0.3	22.56 %	13.35 %	12.64 %	14.01 %	Quaternary-N
	403.6 ± 0.1	13.45 %	15.91 %	12.65 %	5.29 %	N-Oxide

*AC = Activated carbon and CA = Carbon aerogel

Table 5.8 Deconvolution results of carbon materials by DETA as precursor at activation temperature of 900 °C

Region	Position (eV)	Intensity (%)			Assignment
		AC(DETA)	CA from DETA-30 wt%	CA from DETA-30 wt% + P_{123}	
C 1s	284.3 ± 0.1	48.05 %	47.60 %	53.31 %	Graphite
	285.0 ± 0.1	22.34 %	22.42 %	16.76 %	Aliphatics
	285.4 ± 0.2	8.9 %	7.49 %	7.13 %	C with N
	285.8 ± 0.1	5.97 %	7.00 %	8.75 %	Hydroxyl or Ether
	286.6 ± 0.2	8.65 %	9.93 %	7.87 %	Carbonyl
	288.2 ± 0.3	6.50 %	5.56 %	6.19 %	Carboxyl or Ester
O 1s	531.3 ± 0.1	67.52 %	51.18 %	70.75 %	Carbonyl or Carboxyl
	532.9 ± 0.1	32.48 %	48.82 %	29.25 %	Ether or Carboxyl or Hydroxyl
N 1s	398.2 ± 0.4	35.96 %	34.28 %	37.23 %	Pyridinic-N
	400.3 ± 0.1	34.99 %	35.25 %	28.85 %	Pyrrolic-N
	401.4 ± 0.3	21.08 %	20.24 %	23.48 %	Quaternary-N
	403.6 ± 0.1	7.96 %	10.22 %	10.44 %	N-Oxide

*AC = Activated carbon, CA = Carbon aerogel, and P_{123} = Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

Table 5.9 Deconvolution results of carbon materials by PEHA as precursor at activation temperature of 900 °C

Region	Position (eV)	Intensity (%)			Assignment
		AC(PEHA)	CA from PEHA-30 wt%	CA from PEHA-30 wt% + P_{123}	
C 1s	284.3 ± 0.1	58.33 %	51.82 %	47.55 %	Graphite
	285.0 ± 0.1	16.61 %	18.31 %	21.60 %	Aliphatics
	285.4 ± 0.2	6.58 %	9.46 %	9.61 %	C with N
	285.8 ± 0.1	6.07 %	6.32 %	8.08 %	Hydroxyl or Ether
	286.6 ± 0.2	7.69 %	7.23 %	8.03 %	Carbonyl
	288.2 ± 0.3	4.72 %	6.85 %	5.14 %	Carboxyl or Ester
O 1s	531.3 ± 0.1	51.16 %	60.15 %	64.38 %	Carbonyl or Carboxyl
	532.9 ± 0.1	48.84 %	39.85 %	35.62 %	Ether or Carboxyl or Hydroxyl
N 1s	398.2 ± 0.4	40.91 %	38.34 %	39.49 %	Pyridinic-N
	400.3 ± 0.1	.28.71 %	32.53 %	24.47 %	Pyrrolic-N
	401.4 ± 0.3	20.21 %	20.59 %	23.91 %	Quaternary-N
	403.6 ± 0.1	10.17 %	8.57 %	12.12 %	N-Oxide

*AC = Activated carbon, CA = Carbon aerogel, and P_{123} = Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

Table 5.10 Assignments of deconvoluted peaks as characterized by XPS

Region	Binding Energy (eV)	Assignment	References
C 1s	284.3 ± 0.1	Graphite	
	285.0 ± 0.1	Aliphatics	
	285.4 ± 0.2	C with N	Burg *et al.* (2002);
	285.8 ± 0.1	Hydroxyl or Ether	Plaza *et al.* (2013)
	286.6 ± 0.2	Carbonyl	
	288.2 ± 0.3	Carboxyl or Ester	
O 1s	531.3 ± 0.1	Carbonyl or Carboxyl	Plaza *et al.* (2013)
	532.9 ± 0.1	Ether or Carboxyl or Hydroxyl	
N 1s	398.2 ± 0.4	Pyridinic-N	
	399.4 ± 0.4	Amine	Adelodun (2014);
	400.3 ± 0.1	Pyrrolic-N	Coutinho *et al.* (2012);
	401.4 ± 0.3	Quaternary-N	Wickramaratne *et al.* (2014)
	403.6 ± 0.1	N-Oxide	

After carbonization under N_2 atmosphere and activation with CO_2, the new species of nitrogen functionalities were formed on the surface of carbon materials which exhibited the XPS spectra between 398.2 and 403.6 eV which composed of pyridinic-N, pyrrolic-N, quaternary-N, and N-oxide as agreed with the works of Pevida *et al.* (2008); Sevilla *et al.* (2011), while the formation of new oxygen functionalities was occurred at the binding energy of 531.3 eV, namely, carbonyl and/or carboxyl groups.

5.2 Effect of Preparation Method on CO_2 Adsorption Performance

In this study, the porous carbons were prepared from two different methods, namely, a bulk polymerization technique and a sol-gel technique. These carbon materials were synthesized from two amine types of DETA and PEHA. Moreover, the

CO_2 adsorption capacity of these adsorbents was measured by using a simultaneous thermal analyzer (STA). Figures 5.4 and 5.5 show the adsorption/desorption isotherms of activated carbons derived from PBZ and carbon aerogels from 30 wt% of benzoxazine solution by DETA and PEHA as reactants at the adsorption temperature of 40 °C and 1 bar. The results indicated that both carbon aerogels from DETA and PEHA provided higher CO_2 uptake than those activated carbons derived from PBZ, with CO_2 uptake of 1.46 and 1.27 $mmol_{CO_2}/g_{adsorbent}$, respectively. It was because DETA-derived PBZ carbon aerogel contained a larger surface area of 312 m^2/g and higher pore volume of 0.258 cm^3/g compared to DETA-based activated carbon from bulk polymerization, AC (DETA), as shown in Table 5.1. In addition, amines in the form of diethylenetriamine (DETA) are embedded in the structure of adsorbent during the synthesis of polybenzoxazine which had more potential to increase the amount of CO_2 adsorbed as supported from the work of Plaza *et al.* (2007).
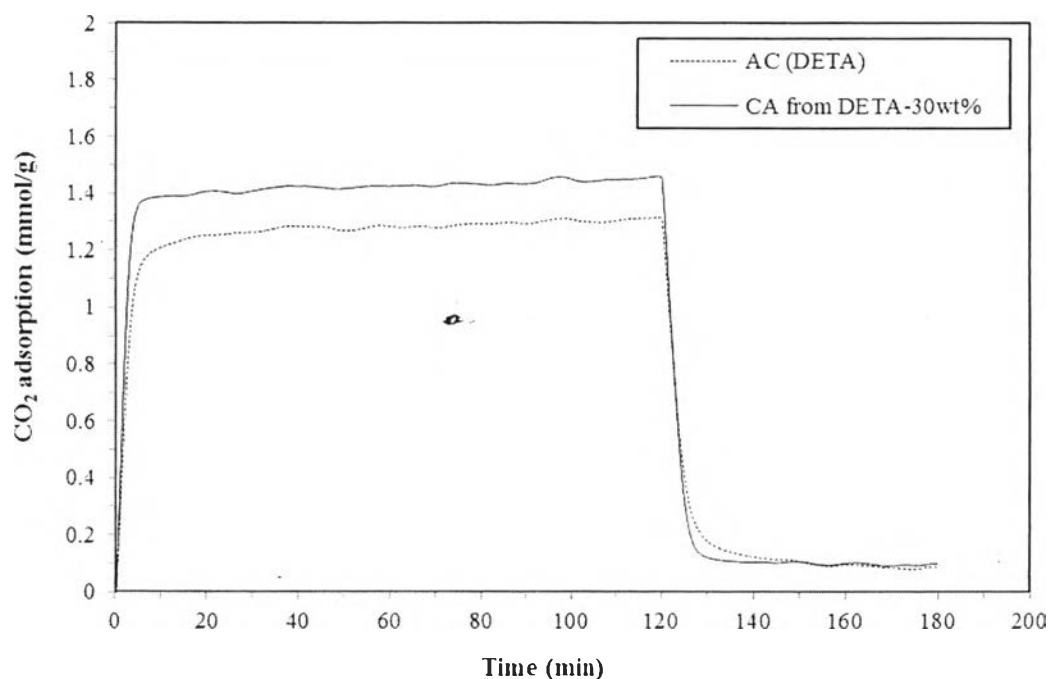
Figure 5.4 Adsorption/desorption isotherms of carbon materials from PBZ prepared by two preparation methods: a conventional technique and a sol-gel technique by DETA as precursor (at 40 °C and 1 bar).
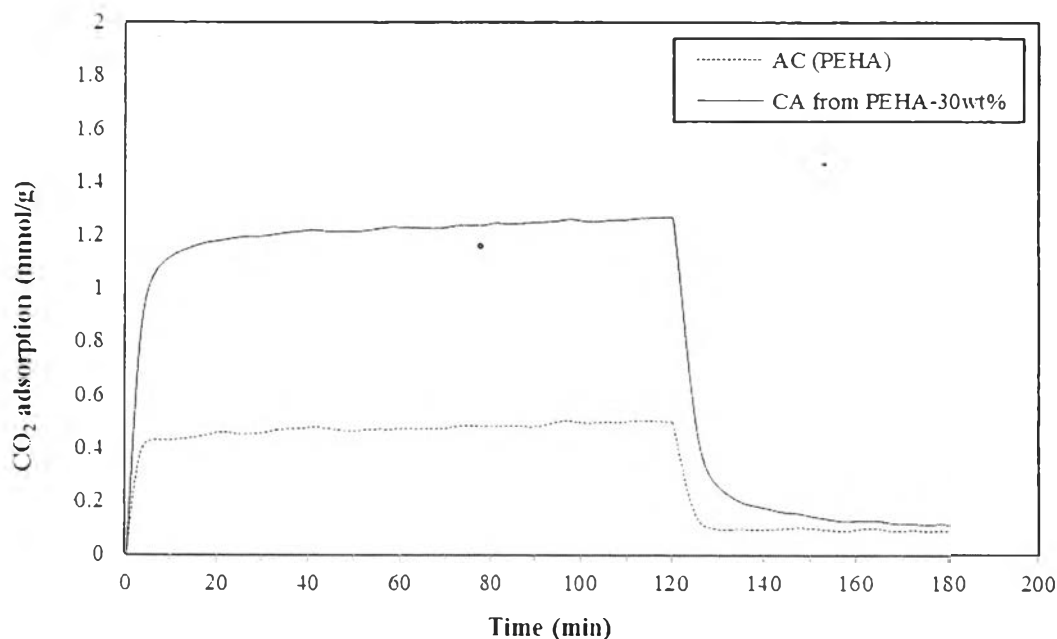
Figure 5.5 Adsorption/desorption isotherms of carbon materials from PBZ prepared by two preparation methods: a conventional technique and a sol-gel technique by DETA as precursor (at 40 °C and 1 bar).

Even though the surface area of PEHA-derived PBZ carbon aerogel was lower than the AC (PEHA), i.e. 114 m2/g v.s. 238 m2/g (see Table 5.1), its nitrogen content was higher than activated carbon from PEHA-derived PBZ as evidenced from the ultimate analysis in Table 5.3.

5.3 Effect of Benzoxazine Concentrations on CO_2 Adsorption Performance

Figure 5.6 and 5.7 display the adsorption/desorption isotherms at 40 °C and 1 bar of carbon aerogels derived from PBZ at three different benzoxazine concentrations of 30, 35, and 40 wt% with DETA and PEHA as precursors. In case of carbon aerogels from DETA as reactant, the CO_2 adsorption capacities did not change significantly when increasing the amount of benzoxazine content during the aerogel preparation due to their similar surface properties as observed in Table 5.1. Their CO_2 adsorption performances were in the ranges from 1.46 to 1.59 mmol$_{CO_2}$/g $_{adsorbent}$ at adsorption condition of 40 °C and 1 bar.

For PEHA-derived PBZ carbon aerogels, raising the concentration of benzoxazine had negative effect to their surface properties which provided the surface areas of 114, 85, and 44 m^2/g for carbon aerolgels at 30, 35, and 40 wt% of benzoxazine solutions because of the unsuccessful in aerogel preparation at high concentration of monomer as observed in Figure 5.2. Their CO_2 adsorption capacities exhibited similar values in the ranges from 1.27 to 1.34 $mmol_{CO_2}/g_{adsorbent}$ at adsorption condition of 40 °C and 1 bar. Although the surface area of PEHA-derived aerogels were low, the amount of CO_2 adsorbed was only slightly lower than those DETA-derived aerogels. A the amount of nitrogen functionalities on the carbon surface had more predominant influence over the textural properties as supported from the data of ultimate analysis in Table 5.3.

Furthermore, Varying in benzoxazine concentrations did not have a significant influence on the adsorbed amount of CO_2 on all carbon aerogels derived from PBZ by DETA and PEHA as reactants at all adsorption conditions (see Table 5.11 and 5.12).
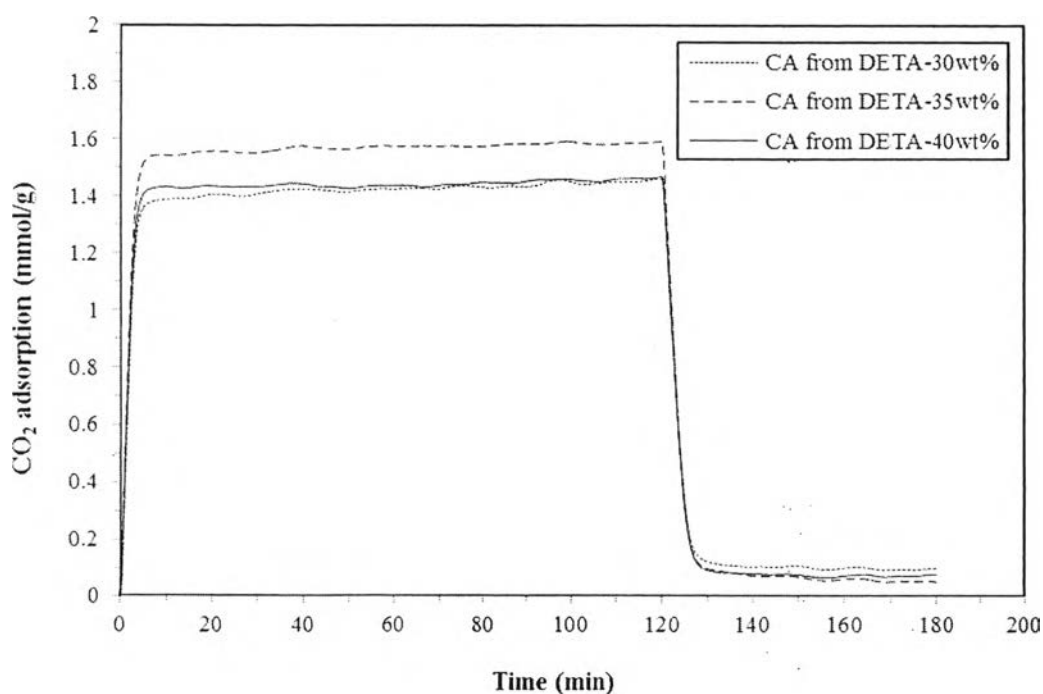
Figure 5.6 Adsorption/desorption isotherms of carbon aerogels at different benzoxazine concentrations by DETA as precursor (at 40 °C and 1 bar).
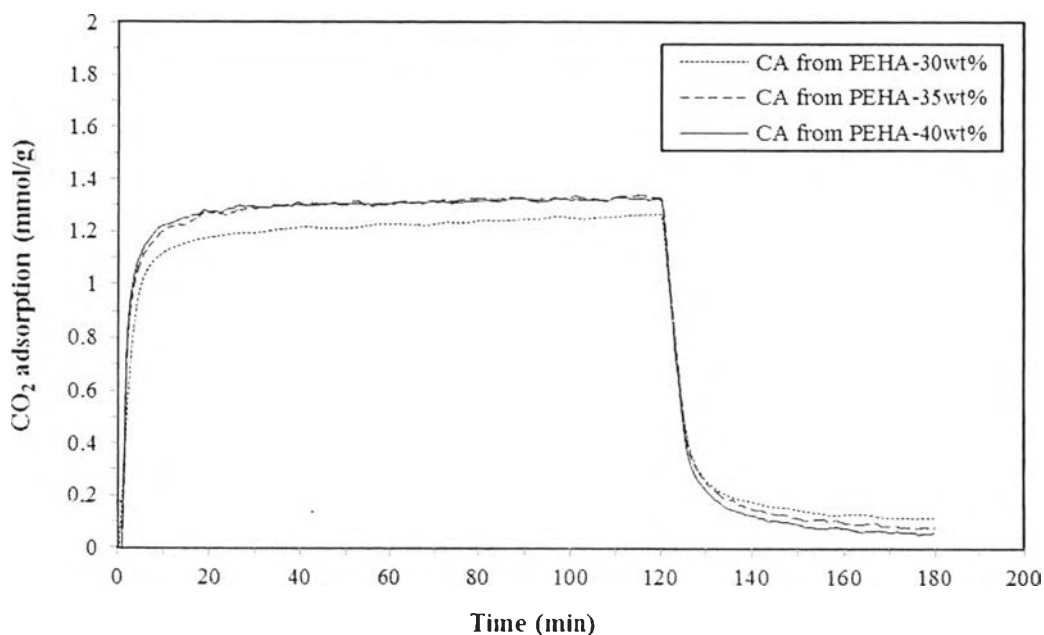
Figure 5.7 Adsorption/desorption isotherms of carbon aerogels at different benzoxazine concentrations by PEHA as precursor (at 40 °C and 1 bar).

5.4 Effect of Chain Lengths of Amine Precursors on CO_2 Adsorption Performance

Figures 5.8 - 5.9 exhibit the adsorption/desorption isotherms of activated carbon from PBZ and PBZ-based carbon aerogels from 30 wt% of benzoxazine solution by DETA and PEHA as reactants at the adsorption condition of 40 °C under atmospheric pressure. In case of PBZ-based activated carbon, the results reveal that the CO_2 adsorption performance on PEHA-based activated carbon was 0.50 $mmol_{CO_2}/g_{adsorbent}$ at 40 °C and 1 bar, whereas the CO_2 uptake was 1.31 $mmol_{CO_2}/g_{adsorbent}$ for DETA-based activated carbon. The higher amount of CO_2 adsorption from DETA-based activated carbon was attributed to a higher nitrogen content of activated carbon from DETA-derived PBZ compared to PEHA-based activated carbon, with 6.33 and 5.22 wt%, respectively (see Table 5.3). In addition, other adsorption conditions of DETA-based activated carbon also gave higher CO_2 uptake than PEHA-based activated carbon as the same reason above (see Table 5.11 and 5.12).
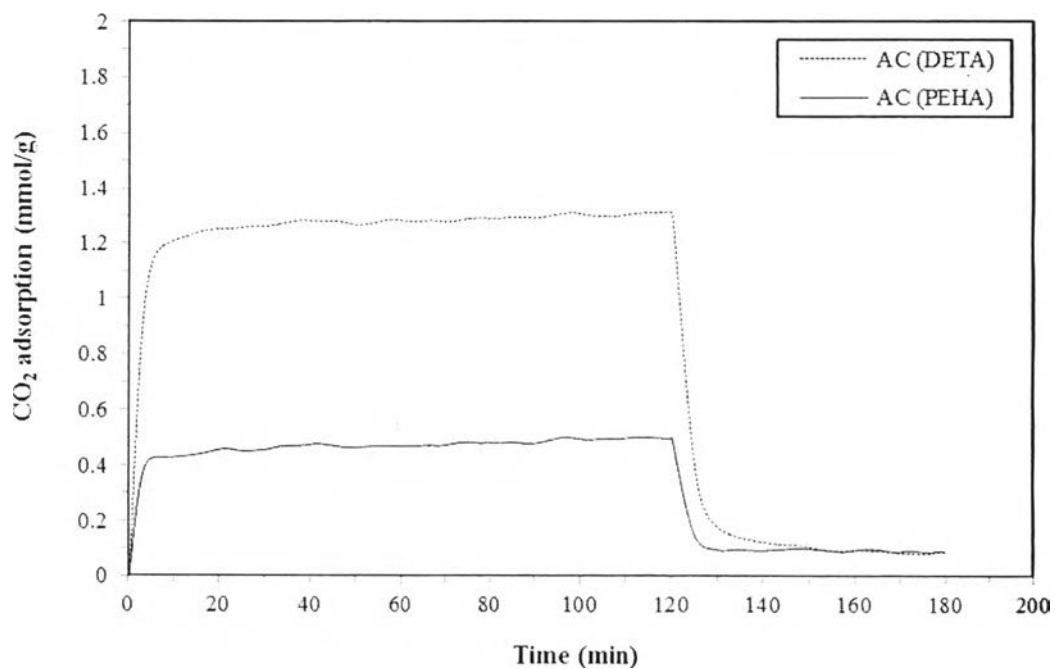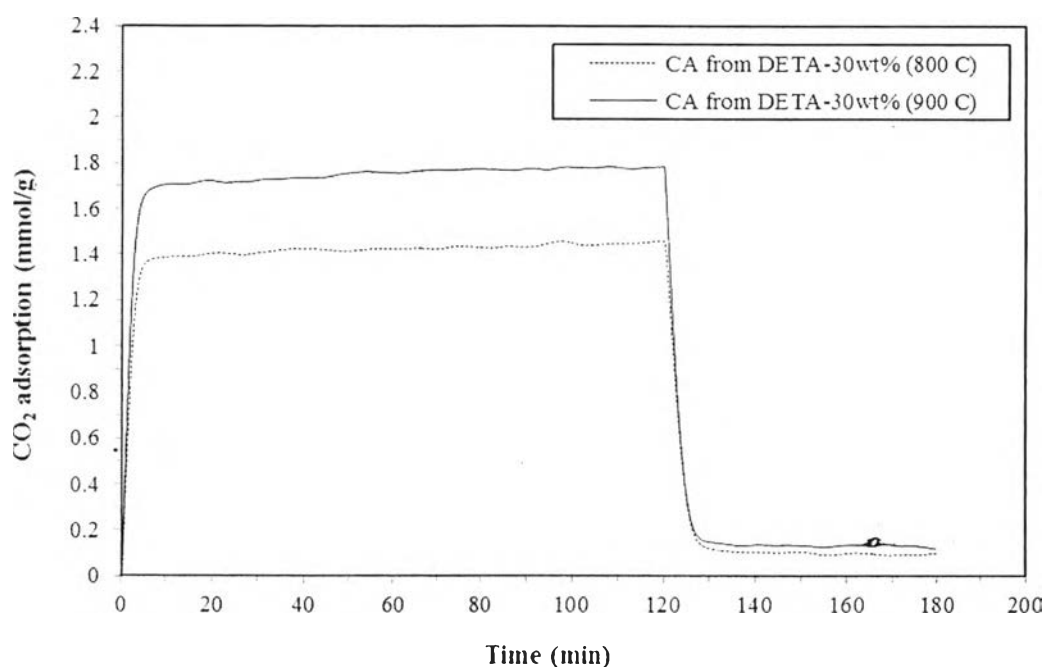
Figure 5.8 Adsorption/desorption isotherms of activated carbons derived from PBZ by DETA and PEHA as amine precursors (at 40 °C and 1 bar).
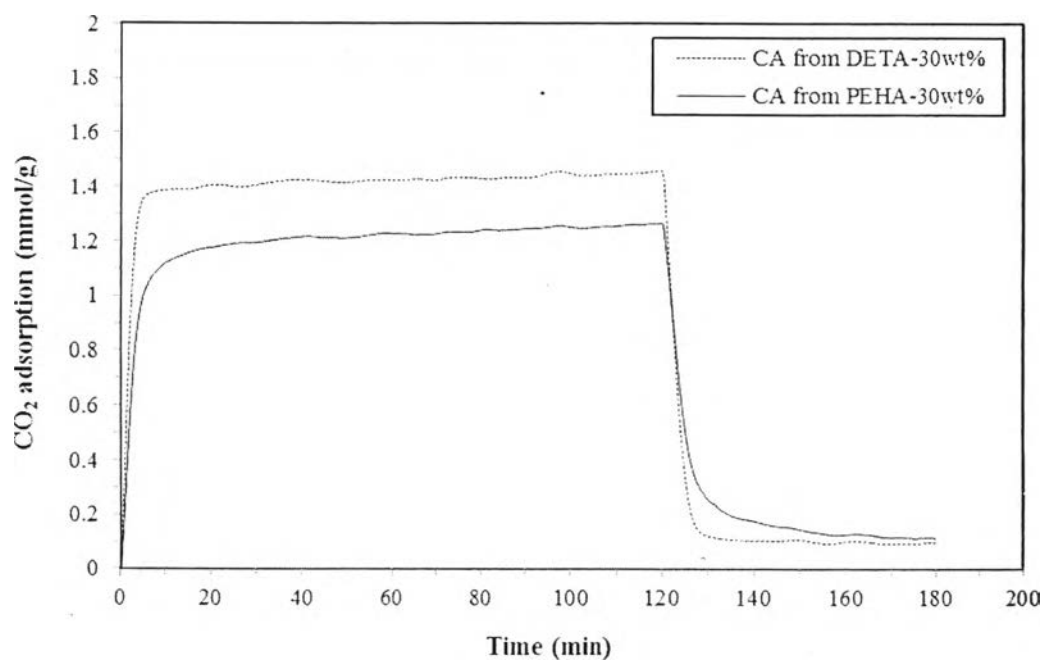
Figure 5.9 Adsorption/desorption isotherms of carbon aerogels from 30 wt% of benzoxazine solution by DETA and PEHA as amine precursors (at 40 °C and 1 bar).

For carbon aerogels, DETA-derived PBZ carbon aerogel provided a higher adsorbed amount of CO_2 than PEHA-based carbon aerogel for all conditions of adsorbed temperatures (see Table 5.11 and 5.12). It was directly because the textural property from Table 5.1 indicates that DETA-based carbon aerogel had a larger surface area and pore volume than PEHA-based carbon aerogel, with 312 and 114 m^2/g, respectively.

5.5 Effect of Activation Temperatures of Carbon Aerogels on CO_2 Adsorption Performance
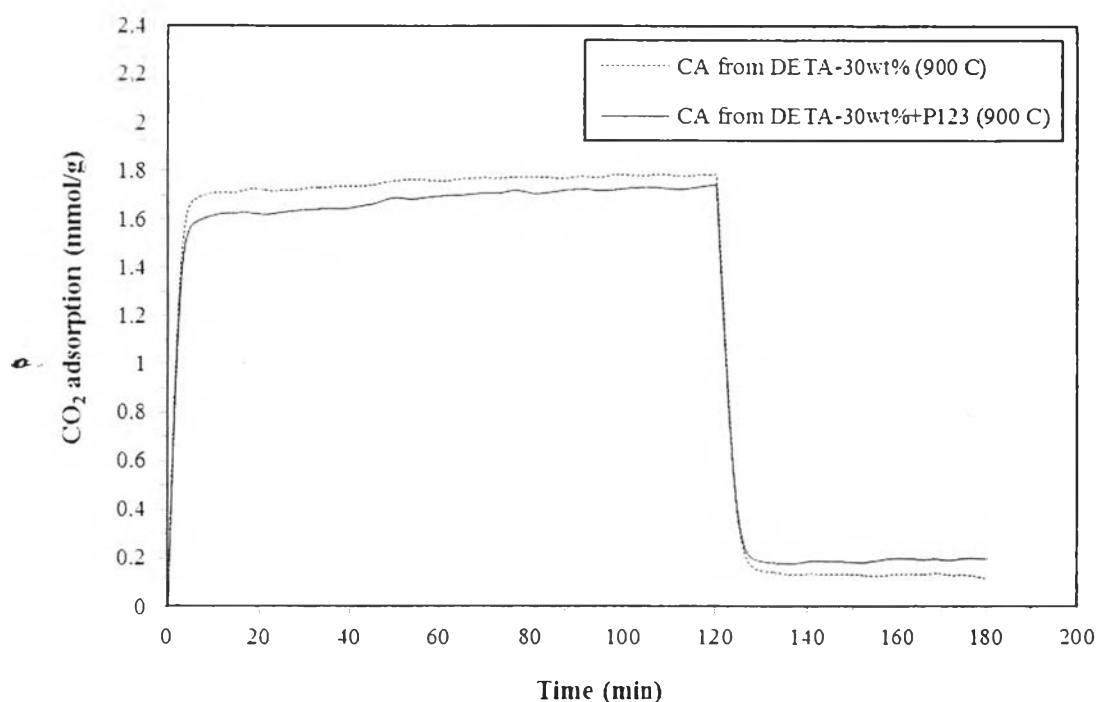

Figure 5.10 Adsorption/desorption isotherms of carbon aerogels from 30 wt% of benzoxazine solution with different activation temperatures of 800 ° and 900 °C by DETA as precursor (at 40 °C and 1 bar).

Tables 5.10 and 5.11 show the adsorption/desorption isotherms of PBZ-based carbon aerogels from 30 wt% of benzoxazine solution by DETA and PEHA as reactants at the adsorption temperature of 40 °C and 1 bar. After activation with CO_2 at 900 °C for 2 hours, both carbon aerogels from different amine types of DETA and

PEHA were higher CO_2 adsorption performances of 1.79 and 1.40 $mmol_{CO2}/g_{adsorbent}$, respectively, compared to DETA and PEHA-based carbon aerogels which were activated at 800 °C under the same condition with 1.46 and 1.24 $mmol_{CO2}/g_{adsorbent}$, respectively. These comparatively high adsorption capacities were mainly due to the high surface area and pore volume of both types of carbon aerogels after activation temperature of 900 °C as evidenced from the textural properties in Table 5.1 and 5.2.
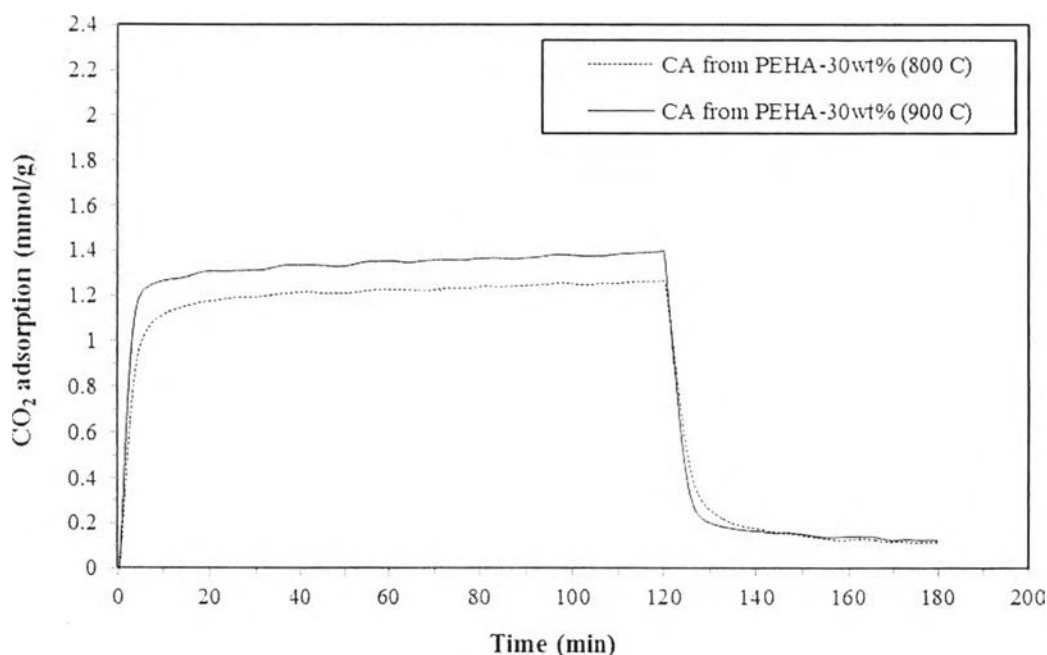
Figure 5.11 Adsorption/desorption isotherms of carbon aerogels from 30 wt% of benzoxazine solution with different activation temperatures of 800 ° and 900 °C by PEHA as precursor (at 40 °C and 1 bar).

5.6 Effect of Non-ionic Surfactant (PEG-PPG-PEG Block Copolymer) in Polybenzoxazine-Based Carbon Aerogel on CO_2 Adsorption Performance

Figures 5.12 and 5.13 respectively display the adsorption/desorption isotherms at 40 °C and 1 bar of DETA-derived and PEHA-derived PBZ-based carbon aerogels from 30 wt% of benzoxazine solution with and without PEG-PPG-PEG block copolymer as non-ionic surfactant at the activation temperature of 900 °C. For carbon aerogels from DETA as amine precursor, the adsorbed amount of CO_2 on
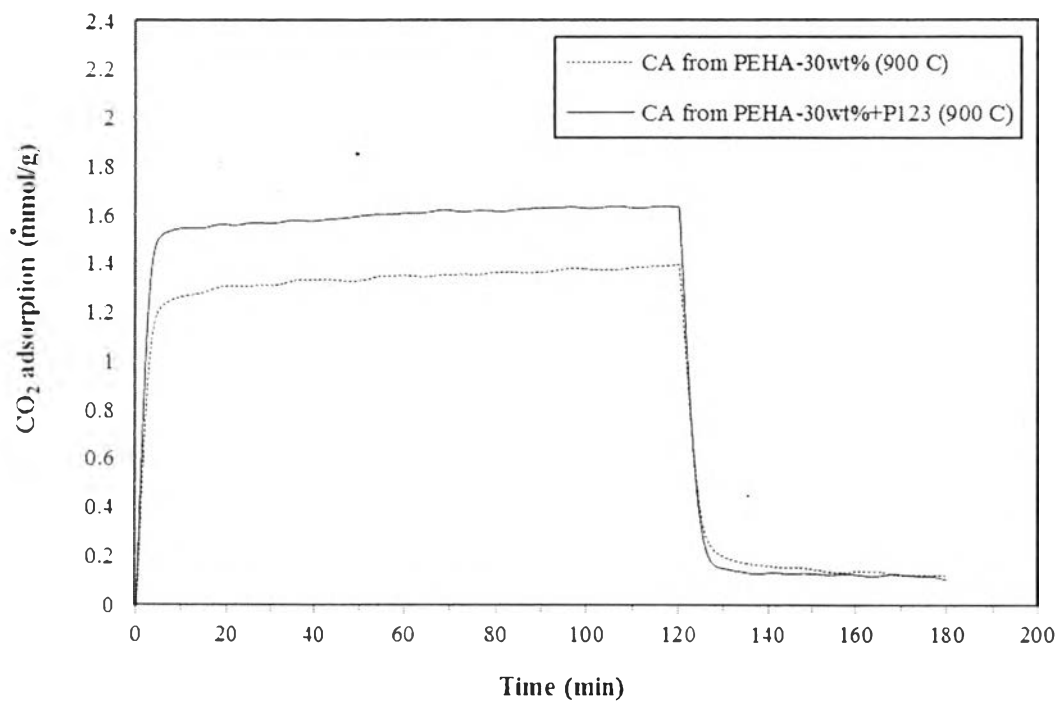
carbon aerogel with and without non-ionic surfactant performed the similar values at 1.79 and 1.74 $mmol_{CO_2}/g_{adsorbent}$, respectively, due to the indifference of surface properties in both carbon aerogels as observe in Table 5.2.

In case of carbon aerogels from PEHA as amine type, carbon aerogel loading with non-ionic surfactant presented CO_2 adsorption capacity of 1.64 $mmol_{CO_2}/g_{adsorbent}$ at 40 °C and 1 bar, while carbon aerogel without non-ionic surfactant provided CO_2 uptake of 1.40 $mmol_{CO_2}/g_{adsorbent}$ at the same adsorption condition. The higher capacity of the adsorbent could be mainly ascribed to an improved textural property as evidenced from the BET surface area and other pore characteristics in Table 5.2. Furthermore, this evidence revealed that PEG-PPG-PEG block copolymer had a predominant influence to generate more porosity in the structure of PEHA-derived polybenzoxazine.

Figure 5.12 Adsorption/desorption isotherms of carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by DETA as precursor (at 40 °C and 1 bar).

Figure 5.13 Adsorption/desorption isotherms of carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by PEHA as precursor (at 40 °C and 1 bar).

5.7 Effect of Adsorption Temperatures on CO_2 Adsorption Performance

Tables 5.11 and 5.12 display the CO_2 adsorption capacity of all adsorbents derived from polybenzoxazine at the adsorption conditions of 40, 75, and 110 °C and 1 bar. The results indicate that all carbon materials from PBZ performed a low CO_2 uptake when increasing the adsorption temperature owing to the limitation of chemisorption at higher temperature. Moreover, carbon aerogels at higher activation temperature (900 °C) showed a higher CO_2 adsorption capacity than those carbon aerogels which activated at 800 °C. This was mainly due to the physisorption as evidenced from the textural properties in Tables 5.1 and 5.2.

Table 5.11 The CO_2 adsorption performances of activated carbons and organic aerogels from PBZ at different adsorption temperatures of 40, 75, and 110 °C and 1 bar

Adsorbents	CO_2 Uptake (mmol/g) at 40 °C	CO_2 Uptake (mmol/g) at 75 °C	CO_2 Uptake (mmol/g) at 110 °C
AC (DETA) at 800 °C	1.31	0.71	0.38
AC (PEHA) at 800 °C	0.50	0.23	0.16
BA from DETA-30wt %	0.13	N/A	N/A
BA from DETA-35wt%	0.08	N/A	N/A
BA from DETA-40wt%	0.09	N/A	N/A
BA from PEHA-30wt%	0.08	N/A	N/A
BA from PEHA-35wt%	0.13	N/A	N/A
BA from PEHA-40wt%	0.11	N/A	N/A

*AC = Activated carbon, BA = Organic aerogel, and N/A = Not available

Table 5.12 The CO_2 adsorption performances of carbon materials from PBZ at different adsorption temperatures of 40, 75, and 110 °C and 1 bar

Adsorbents	CO_2 Uptake (mmol/g) at 40 °C	CO_2 Uptake (mmol/g) at 75 °C	CO_2 Uptake (mmol/g) at 110 °C
CA from DETA-30wt% (800 °C)	1.46	0.95	0.49
CA from DETA-35wt% (800 °C)	1.59	0.93	0.48
CA from DETA-40wt% (800 °C)	1.47	0.80	0.47
CA from PEHA-30wt% (800 °C)	1.27	0.73	0.43
CA from PEHA-35wt% (800 °C)	1.34	0.71	0.41
CA from PEHA-40wt% (800 °C)	1.33	0.72	0.36

Table 5.12 The CO_2 adsorption performances of carbon materials from PBZ at different adsorption temperatures of 40, 75, and 110 °C and 1 bar (Con't.)

Adsorbents	CO_2 Uptake (mmol/g) at 40 °C	CO_2 Uptake (mmol/g) at 75 °C	CO_2 Uptake (mmol/g) at 110 °C
AC (DETA) at 900 °C	1.12	0.63	0.29
AC (PEHA) at 900 °C	0.40	0.17	0.08
CA from DETA-30wt% (900 °C)	1.79	0.91	0.55
CA from PEHA-30wt% (900 °C)	1.40	0.74	0.41
CA from DETA-30wt%+P_{123} (900 °C)	1.74	0.84	0.48
CA from PEHA-30wt%+P_{123} (900 °C)	1.64	0.86	0.44

*AC = Activated carbon, CA = Carbon aerogel, and P_{123} = Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

5.8 Effect of Regenerations on Carbon Materials

Tables 5.13- 5.15 and Figures 5.14 - 5.19 demonstrate the regeneration efficiency and desorption isotherms of carbon materials from polybenzoxazine at the desorption temperatures of 40, 75, and 110 °C. After desorption at 40 °C for 1 hour under N_2 atmosphere, the results show that all adsorbents were not complete to regenerate at 100 percent due to the chemisorption from bonding between CO_2 and nitrogen functional groups on the surface of adsorbents. Moreover, the regeneration efficiency of all carbon materials was performed in the range from 87.50 to 96.86 percent at desorption condition of 40 °C and 1 bar. Conversely, the regeneration of all adsorbents was perfect when rising the desorbed temperature to 75 °C (or 110 °C) because the CO_2 molecules on the surface could easily be regenerated at higher temperature.

Table 5.13 The regeneration percentages of activated carbons from PBZ, carbon aerrogels at different monomer concentrations of 30, 35, and 40 wt% by DETA and PEHA as amine precursors at desorption temperatures of 40 and 75 °C (all these carbon materials were activated at 800 °C)

Regeneration Temperatures	Carbon Materials	%Regeneration
40 °C	AC (DETA)	93.13
	CA from DETA-30 wt%	93.84
	CA from DETA-35 wt%	96.86
	CA from DETA-40 wt%	94.56
	AC (PEHA)	92.00
	CA from PEHA-30 wt%	91.34
	CA from PEHA-35 wt%	94.03
	CA from PEHA-40 wt%	95.49
75 °C	AC (DETA)	100.00
	CA from DETA-30 wt%	100.00
	CA from DETA-35 wt%	100.00
	CA from DETA-40 wt%	100.00
	AC (PEHA)	100.00
	CA from PEHA-30 wt%	100.00
	CA from PEHA-35 wt%	100.00
	CA from PEHA-40 wt%	100.00

*AC = Activated carbon and CA = Carbon aerogel

Table 5.14 The regeneration percentages of activated carbons from PBZ, carbon aerrogels at different monomer concentrations of 30, 35, and 40 wt% by DETA and PEHA as amine precursors at desorption temperature of 110 °C (all these carbon materials were activated at 800 °C)

Regeneration Temperatures	Carbon Materials	%Regeneration
110 °C	AC (DETA)	100.00
	CA from DETA-30 wt%	100.00
	CA from DETA-35 wt%	100.00
	CA from DETA-40 wt%	100.00
	AC (PEHA)	100.00
	CA from PEHA-30 wt%	100.00
	CA from PEHA-35 wt%	100.00
	CA from PEHA-40 wt%	100.00

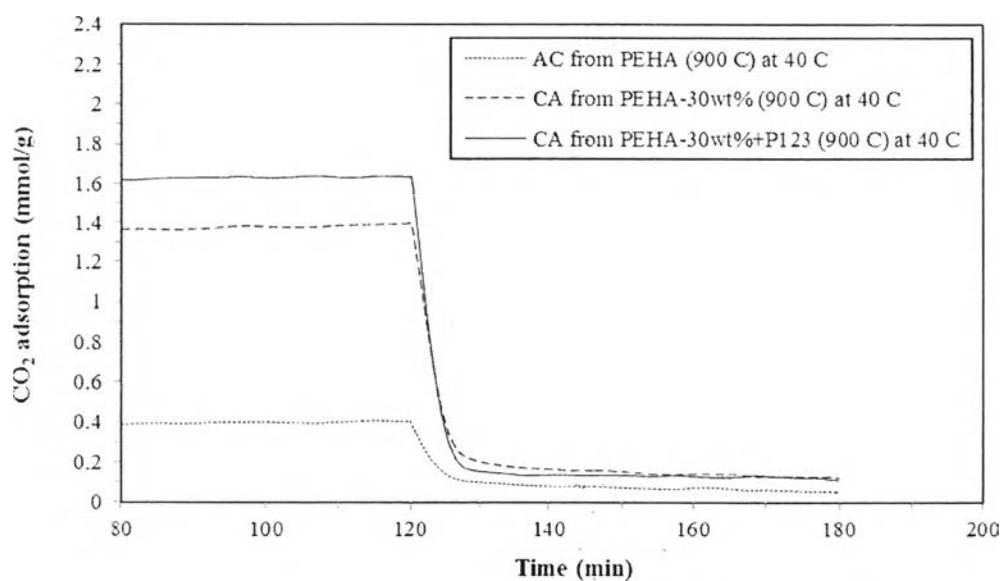*AC = Activated carbon and CA = Carbon aerogel

Table 5.15 The regeneration percentages of activated carbons from PBZ, carbon aerrogels from 30 wt% of benzoxazine solution, and carbon aerogels from 30 wt% of benzoxazine solution with non-ionic surfactant by DETA and PEHA as reactants at desorption temperatures of 40, 75, and 110 °C (all these carbon materials were activated at 900 °C)

| Regeneration Temperatures	Carbon Materials	%Regeneration
40 °C	AC (DETA)	91.07
	CA from DETA-30 wt%	93.29
	CA from DETA-30 wt%+P_{123}	89.08
	AC (PEHA)	87.50
	CA from PEHA-30 wt%	91.42
	CA from PEHA-30 wt%+P_{123}	93.29
75 °C	AC (DETA)	100.00
	CA from DETA-30 wt%	100.00
	CA from DETA-30 wt%+P_{123}	100.00
	AC (PEHA)	100.00
	CA from PEHA-30 wt%	100.00
	CA from PEHA-30 wt%+P_{123}	100.00
140 °C	AC (DETA)	100.00
	CA from DETA-30 wt%	100.00
	CA from DETA-30 wt%+P_{123}	100.00
	AC (PEHA)	100.00
	CA from PEHA-30 wt%	100.00
	CA from PEHA-30 wt%+P_{123}	100.00

*AC = Activated carbon, CA = Carbon aerogel, and P_{123} = Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)
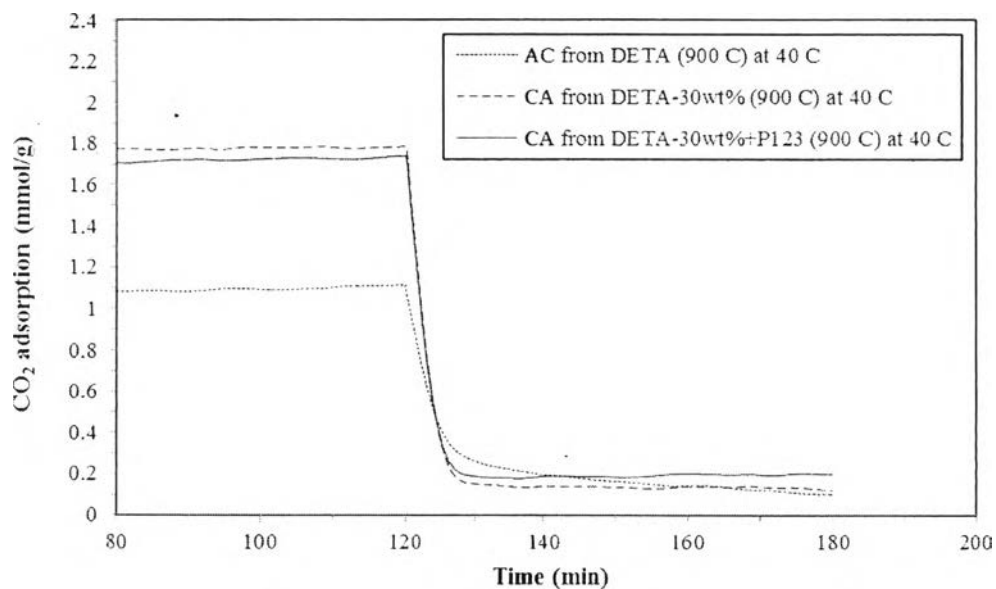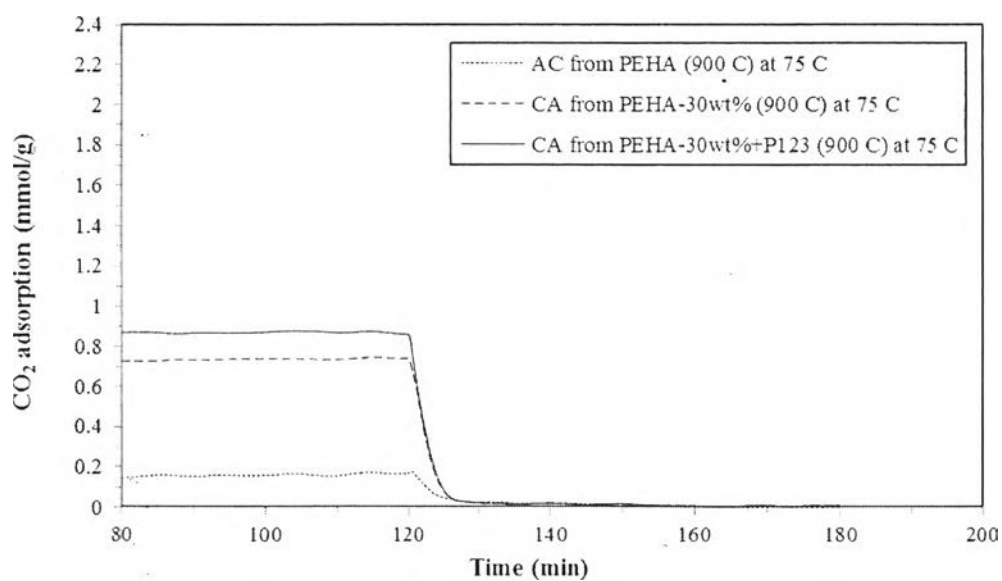
Figure 5.14 Desorption isotherms of activated carbon from PBZ, carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by DETA as precursor (at 40 °C and 1 bar).
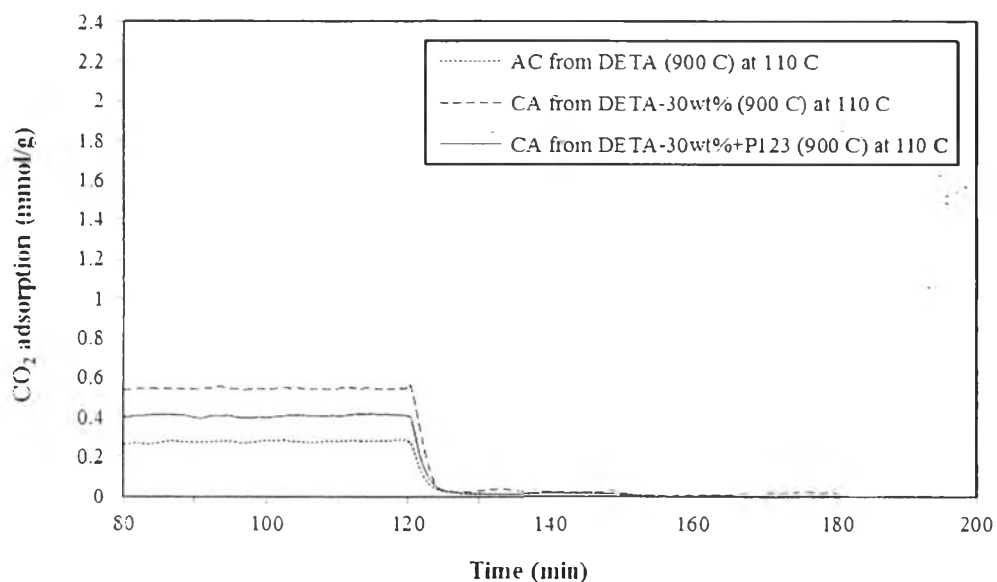

Figure 5.15 Desorption isotherms of activated carbon from PBZ, carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by PEHA as precursor (at 40 °C and 1 bar).
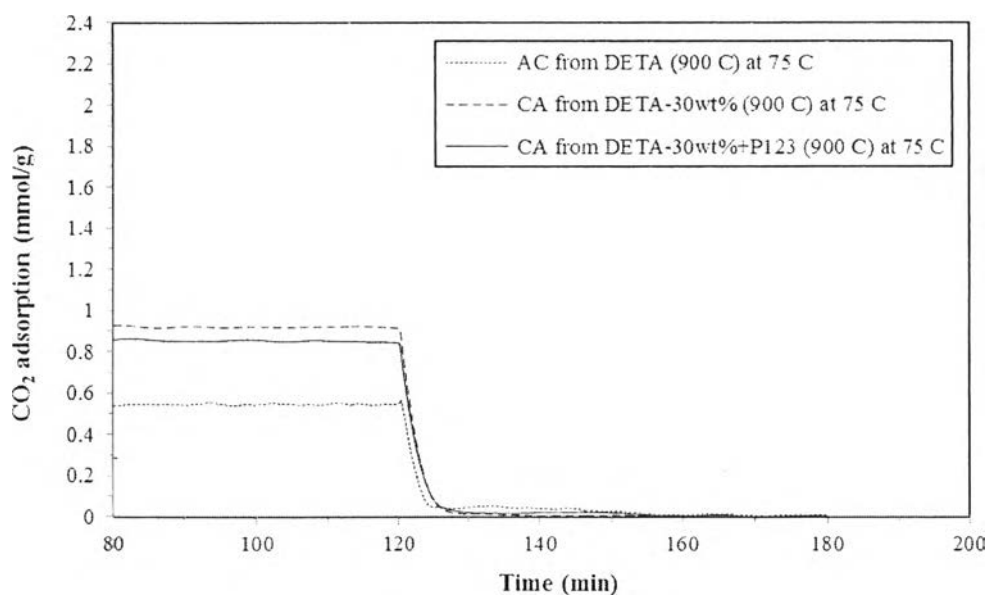
Figure 5.16 Desorption isotherms of activated carbon from PBZ, carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by DETA as precursor (at 75 °C and 1 bar).
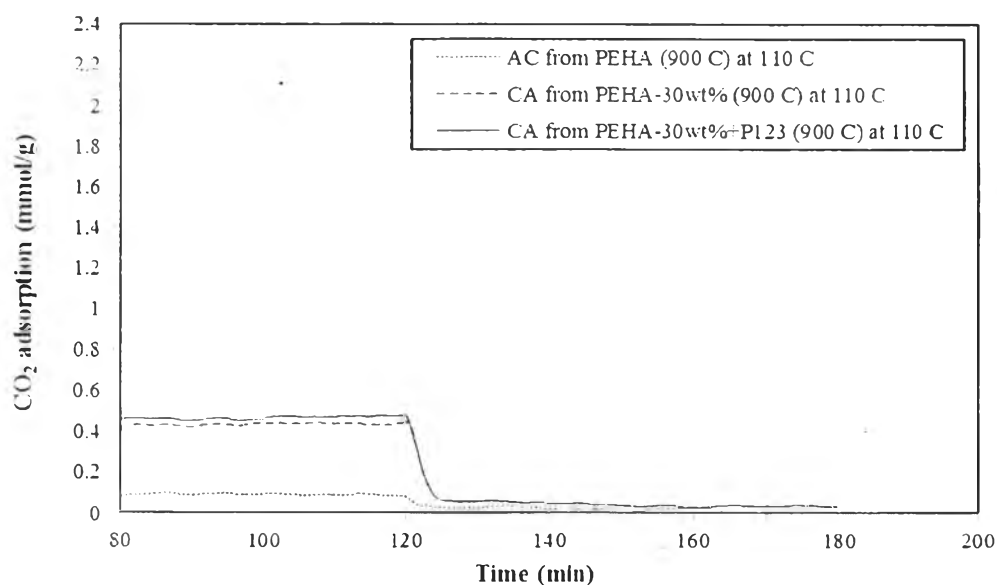

Figure 5.17 Desorption isotherms of activated carbon from PBZ, carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by PEHA as precursor (at 75 °C and 1 bar).

Figure 5.18 Desorption isotherms of activated carbon from PBZ, carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by DETA as precursor (at 110 °C and 1 bar).

Figure 5.19 Desorption isotherms of activated carbon from PBZ, carbon aerogels from 30 wt% of benzoxazine solution with and without non-ionic surfactant at activation temperature of 900 °C by PEHA as precursor (at 110 °C and 1 bar).