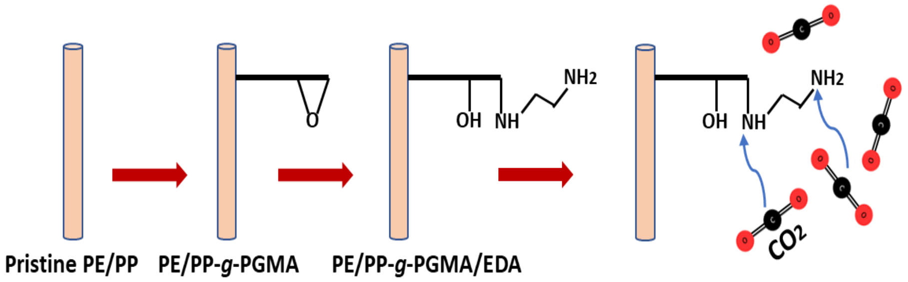
Effect of amine head group imparted to poly (glycidyl methacrylate) grafted fibrous adsorbent for CO_2 adsorption

Noor Ashikin Mohamad[a,b] and Mohamed Mahmoud Nasef[a,b*]

[a]Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia
[b]Advanced Materials Research Group, Center of Hydrogen Energy, Universiti Teknologi Malaysia, Jalan Semarak 54100, Kuala Lumpur, Malaysia.

Email: mahmoudeithar@cheme.utm.my

Graphical abstract



Abstract. The demand to develop adsorbents for CO_2 capture with high performance continued to grow extensively. Adsorbents with covalently bonded amine groups based on fibrous substrate modified by radiation-induced grafting copolymerization (RIGC) of glycidyl methacrylate (GMA) and amination treatment have emerged recently. In this study, GMA was grafted onto a polyethylene/polypropylene (PE/PP) fibrous sheet and the grafted intermediate was used to incorporate two different amine-containing agents, namely polyethyleneimine (PEI) and ethylenediamine (EDA) for CO_2 adsorption. The chemical structural and morphological changes in the two aminated adsorbents were evaluated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. A low and equal amination level of 20% was achieved in PEI-containing and EDA-containing adsorbents. The CO_2 adsorption from a binary mixture of CO_2/N_2 (40:60 v/v) was not satisfactory despite a 30% higher adsorption capacity (50.44 mg/g) demonstrated by EDA-containing adsorbent compared to 34.51 mg/g for PEI-containing counterpart at 30 bar and at room temperature. More work is needed to elevate the CO_2 adsorption capacity levels in such adsorbents by increasing the amination level via optimization of reaction parameters.

Keywords: Amine head group, Fibrous adsorbent; Radiation-induced grafting, Polyethyleneimine; Ethylenediamine; CO_2 adsorption

1. Introduction

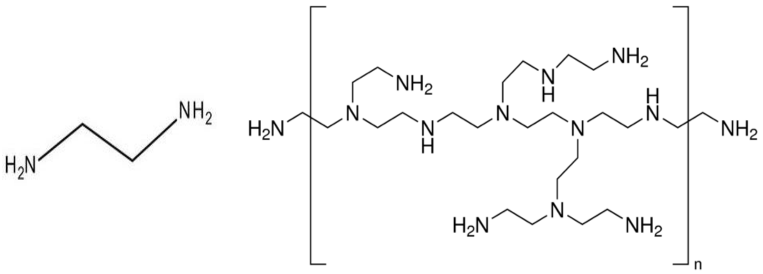
Carbon capture and storage (CCS) has received a lot of interest because of its potential to mitigate climate change. Thus, academia and industry actively promote CCS technologies development. CCS involves removing CO_2 directly from industrial or energy generation plants and subsequently storing it in a secured reservoir [1]. Currently, 85% of world energy demand is supplied by fossil fuels, including coal, oil, and gas. Unfortunately, such fuel utilization processes produced 40% of total CO_2 emissions into the atmosphere, and the contribution comes mainly from the coal-fired power plant [2]. Hence, it is crucial to have a system that can capture the CO_2 before its release into the atmosphere to control concentration and cut emissions.

The absorption method using monoethanolamine (MEA) is often regarded as the most mature and documented technology for CO_2 capture from power plants. This is required to eliminate pollutants that can produce acids in the presence of water causing corrosion in pipelines and other equipment. However, this CO_2 separation method is considered a high operational cost process requiring high regeneration energy and a short equipment lifespan due to corrosion [3]. The studies on different types of solid-based adsorbents have been widely explored for CO_2 capture via physisorption or chemisorption interaction, including carbon-based materials, zeolite, mesoporous silica, porous coordination polymer (PCPs) and microporous organic polymer (MOPs) [4].

Among solid adsorbents, fibrous polymeric adsorbents have shown advantages such as high flexibility, low-pressure drop, short transit distance, easy regeneration, and high selectivity [5]. These adsorbents were introduced with various amine-containing moieties with weakly bonded (impregnated) or covalently bonded (grafted). The impregnated adsorbents were prepared by physical adsorption through facile impregnation of amines into supports (e.g., activated carbon). However, impregnated amine sorbent often exhibits high CO_2 adsorption capacity but lacks stability due to the amine leaching over regeneration cycles [6]. On the other hand, grafted or covalently bonded amines were designed through the chemical tethering of amines to the adsorbent surface upon functionalization.

Covalent bonding (grafting) is a practical approach to produce a strong bonded between amine and polymer adsorbent surfaces. Chemical-induced graft copolymerization (CIGC) is a well-established method to impart desired functionality to the polymeric surface through covalent interaction. However, this method causes environmental concerns due to the use of hazardous chemical initiators and solvents and the difficulty in controlling the grafting level. Alternatively, radiation-induced graft copolymerization (RIGC) provided a versatile means to produce the desired grafting level and modify various types of polymer surfaces without environmental burden. Interestingly, grafting polar monomers enables the incorporation of side chains ending with functional groups capable of hosting CO_2 to the polymer surface [7].

As amine polymers for preparing CO_2 adsorbents, branched polyethyleneimines (PEI) have been frequently impregnated into porous inorganic supports because of their high amine content and low material cost [8]. Hence, the objective of this study is to identify the most prominent amine structure either linear or branched to enhance the CO_2 adsorption capacity. This study aims to briefly report the preparation of CO_2 adsorbent obtained by RIGC the GMA onto polyethylene-coated polypropylene (PE/PP) and followed by amination reaction with two different amines such as ethylenediamine (EDA) and polyethyleneimine (PEI) that attained an equal amine content to observe the effect of different amine chemical structure as presented in Figure 1 on the CO_2 adsorption capacity performance.



Ethylenediamine (EDA) **Polyethyleneimine (PEI)**

Figure 1. Chemical structure of ethylenediamine and polyethyleneimine.

2. Materials and methods

2.1. Chemicals and reagents

The PE/PP nonwoven sheet grafted with poly (glycidyl methacrylate) (PE/PP-*g*-GMA) with a degree of grafting of 160% was prepared as reported elsewhere [9]. EDA (purity ≥99) was purchased from Merck Millipore and used without further dilution. PEI (purity 50wt% aqueous solution, branched) was purchased from Acros Organics and further dilute with dimethylformamide (DMF) and isopropanol. DMF and isopropanol were analytical grade and purchased from Merck Millipore. Ethanol was obtained from Merck Millipore. Deionized water (DI) was produced by Barnstead Nanopure Diamond Lab Water Purification System (ThermoFisher) and used for solution dilution and sample washing. Lastly, pure carbon dioxide (CO_2) gas (99.8%), pure nitrogen (99.999%) and Pure methane (CH_4) gas (99.995%) were supplied by Alpha Gas Solution (Sdn Bhd).

2.2. Apparatus and measurements

The EDA or PEI functionalized PE/PP-*g*-GMA adsorbent was characterized using Fourier transform infrared (FTIR, Nicolet iS50, Thermo Fisher Scientific Inc.) spectroscopy in the range of 500 to 4500 cm^{-1} and 32 scans with 4 cm^{-1} resolution. The crystallinity of the adsorbents was observed using the X-ray diffraction (XRD) (PANalytical Empyrean) pattern in the range of 5° to 80°. Scanning electron microscopy images were recorded using GEMINISEM 500 (Germany) with a magnification of 500x to study the surface morphological properties of the samples.

2.3. Amine Functionalization

A sample of PE/PP-*g*-GMA substrate was added in a pure EDA amine in a 100 ml round bottom flask containing 30 ml solution. The reaction was carried out under reflux conditions at a temperature of 83 ºC for 24 h duration. Another sample of PE/PP-*g*-GMA was immersed into a mixture of DMF, isopropanol and PEI solution (64%, 16%, and 20%) in a total volume of 30 ml. The reaction was allowed for 24 hours at a temperature of 90 ºC. Finally, the amine-functionalized substrates were removed and washed repeatedly with distilled water and ethanol before placing them in an oven at 60 ºC for overnight. The following equation was used for calculating the amine percentage:

$$\text{Percent of amination (\%)} = \frac{(\mathrm{Wa}-\mathrm{Wg})\,/W_{amine}}{(\mathrm{Wa}-\mathrm{Wo})/W_{\mathrm{GMA}}}\; x100\% \quad (1)$$

where W_{GMA} and W_{amine} are the molecular weight of GMA and EDA (g/mol), respectively, W_a and W_g are the weight (g) of the PE/PP-*g*-GMA substrate before and after amination. The W_o is the weight of pristine PE/PP polymer before grafting. The amine-functionalized substrate was denoted as PE/PP-*g*-GMA-EDA or PE/PP-*g*-GMA-PEI.

2.4. CO_2 adsorption tests

The CO_2 adsorption capacity measurement studies were carried out using magnetic suspension balance (MSB) from isoSORP® gravimetric analyzer, and it was manufactured by RUBOTHERM (Bochum, Germany). A complete set of adsorption measurements consists of three steps comprising pre-treatment, buoyancy, and adsorption capacity measurement. All data were recorded by RUBOTHERM system control software (RSCS-2016), and each measurement was configured step by step. First, a pre-treatment was performed by heating the samples at 80ºC for 3 h under vacuum until a constant weight was measured to eliminate any retained moisture. Secondly, the buoyancy measurement was conducted to determine the weight and volume of adsorbents using purified Helium gas at the required adsorption temperature in varying pressure from vacuum condition to 30 bar. Finally, the adsorption measurements were carried out using gaseous mixtures composed of 40 % CO_2 and 60 % N_2 at a total flow rate of 500 ml/min at a temperature of 30 ºC and a pressure up to 30 bar.

3. Results and discussions

3.1. Structural Characterization

Fourier transform infrared spectroscopy (FTIR) analysis was used to track the chemical changes in the pristine PE/PP substrate after grafted with GMA and subsequently functionalized with amine from either EDA or PEI. The FTIR spectra of pristine PE/PP, PE/PP-*g*-PGMA, PE/PP-*g*-PGMA-EDA, and (d) PE/PP-*g*-PGMA-PEI are shown in Figure 2. Three peaks appeared at 840 cm^{-1}, 905 cm$^{-1,}$ and 1740 cm^{-1}, indicating the epoxy group and –C=O stretching band of PGMA chains grafted to the PE/PP backbone polymer [10]. The disappearance of peaks at 840 cm^{-1} and 905 cm^{-1} provides evidence for the successful epoxide ring-opening and introduction of EDA or PEI amines [11]. Furthermore, the emergence of the –NH bond at 1658 cm^{-1} and 1572 cm^{-1} confirms the presence of EDA or PEI amines after the amination reaction [12].

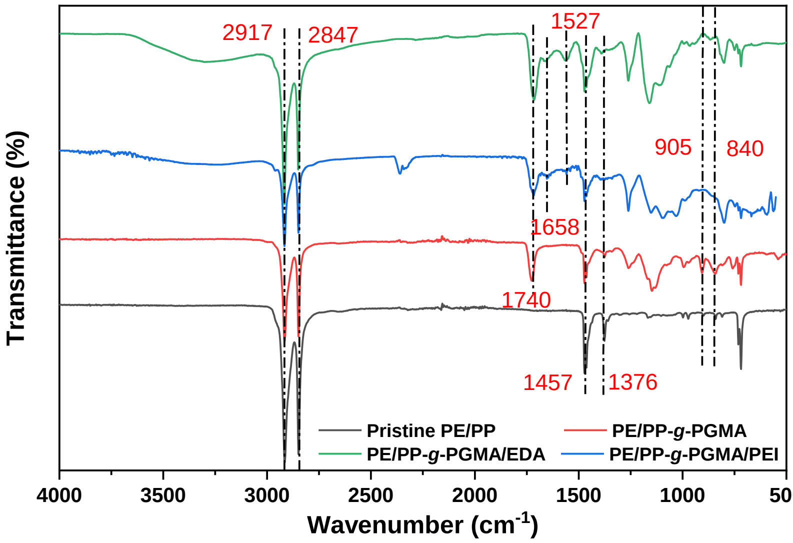


Figure 2. FTIR spectra of Pristine PE/PP, PE/PP-*g*-PGMA, PE/PP-*g*-PGMA-EDA, and PE/PP-*g*-PGMA-PEI.

Figure 3 shows the XRD diffractograms of PE/PP, PE/PP-*g*-PGMA, PE/PP-*g*-PGMA-EDA and PE/PP-*g*-PGMA-PEI samples. The XRD measurements were carried out to investigate the changes in crystallinity of pristine PE/PP after PGMA and EDA or PEI incorporation. As can be seen, all crystallinity representing peaks showed a minor shift in Bragg's angle in pristine PE/PP after grafting and amination, suggesting minor crystal disruption. The intensity of the prominent characteristic peaks was slightly reduced for all three samples, especially the PEI sample. This can be attributed to the dilution of the inherent crystallinity by incorporating amorphous PGMA and EDA or PEI amines. It can be concluded the crystallinity changes are in the forms of dilution and partial disruption in the crystal structure of PE/PP took place during grafting the amination reaction [13,14].

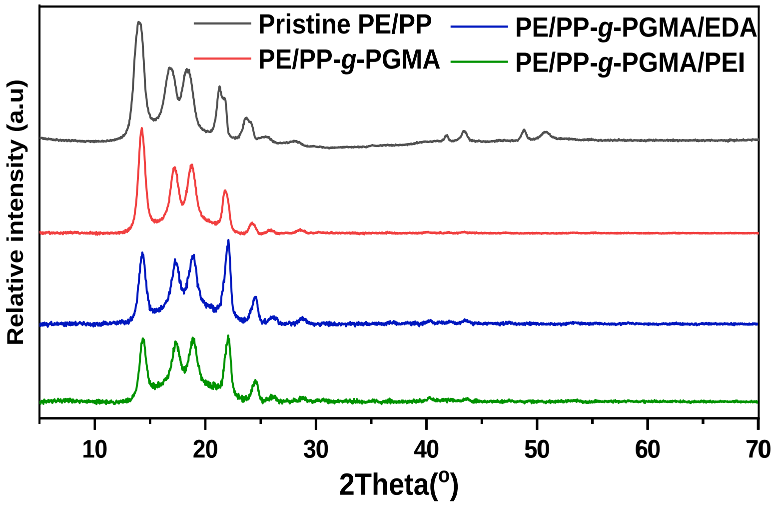


Figure 3. X-ray diffraction pattern of Pristine PE/PP, PE/PP-*g*-PGMA, PE/PP-*g*-PGMA-EDA and PE/PP-*g*-PGMA-PEI.

The scanning electron micrograph (SEM) shown in Figure 4 portrays the changes in the fiber diameters after grafting and amination. The average fiber diameter of pristine PE/PP was around 15.3 ± 3.2 µm. However, it is observed that the average diameter is increased after grafting with PGMA and recorded 20.0 ± 5.7 µm. Such an increase is due to the incorporation of PGMA grafting in PE/PP fibers [15]. After amination with EDA, the average fiber diameter was reduced by ~8% reaching a value of 18.5 ± 5.5 µm. This suggests a degradation that happened at a part of fiber surfaces, which is likely caused by the collision between magnetic stirrer and sample during the amination.

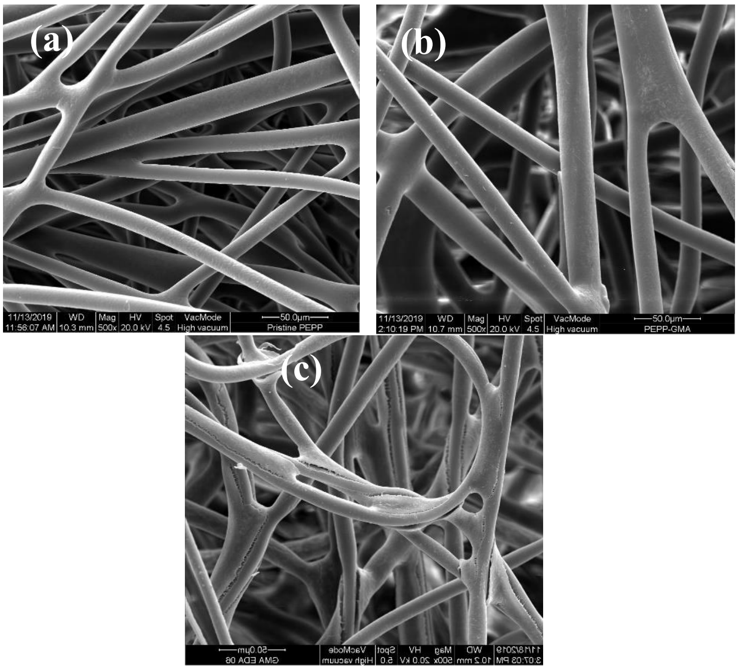


Figure 4. SEM image of (a) Pristine PE/PP, (b) PE/PP-*g*-PGMA and (c) PE/PP-*g*-PGMA-EDA.

3.2. CO_2 adsorption

The two adsorbents showed low yet equal amine content of 20% after treatments with EDA and PEI. The performance concerning CO_2 adsorption capacity of PE/PP-*g*-PGMA-EDA and PE/PP-*g*-PGMA-PEI adsorbents were presented in Figure 5. The CO_2 adsorption test was carried out at 30 °C adsorption temperatures with 40 v/v% of CO_2/N_2 gas mixture of 500 ml/min total flow rate. Both adsorbents showed an increased adsorption capacity trend with the rise in pressure. Remarkably, the adsorption capacity initially increased in a steep manner followed by a gradual increase, which was more profound with the adsorbent having PEI than that containing EDA as the pressure increases.

Interestingly, the CO_2 adsorption capacity of EDA was 50.44 mg/g, which is 32% higher than that of PEI adsorbent (34.51 mg/g) at 30 bar. The increasing capacity trend with pressure is generally due to the increase in the diffusion of CO_2 gas, allowing more access to amine groups [16]. The results suggest EDA-bearing adsorbent outperformed EDA-containing counterpart despite having smaller numbers of basic sites with linear structure than the branched PEI, which has 4 amine sites. A similar trend was observed for the CO_2 adsorption performance of adsorbent having a linear structure of tetraethylenepentamine (TEPA) which exhibited a 43% higher adsorption than the branched structure of PEI containing adsorbent [8]. The reason is that TEPA has a very small tertiary amine content compared to PEI, where tertiary amine provides a weak interaction with CO_2 molecules. Tertiary amine does not bind with CO_2 molecules without water molecules (dry condition)[17]. The experiment was conducted in a dry environment, which explains why the performance of PEI-adsorbent, which carries a substantial quantity of tertiary amine, is significantly lower than that of EDA-adsorbent, which only contains primary amine. Furthermore, as compared to the linear shape of EDA-adsorbent, the bulky structure of PEI-adsorbent produced a small free volume, indicating lower working capacity [18].

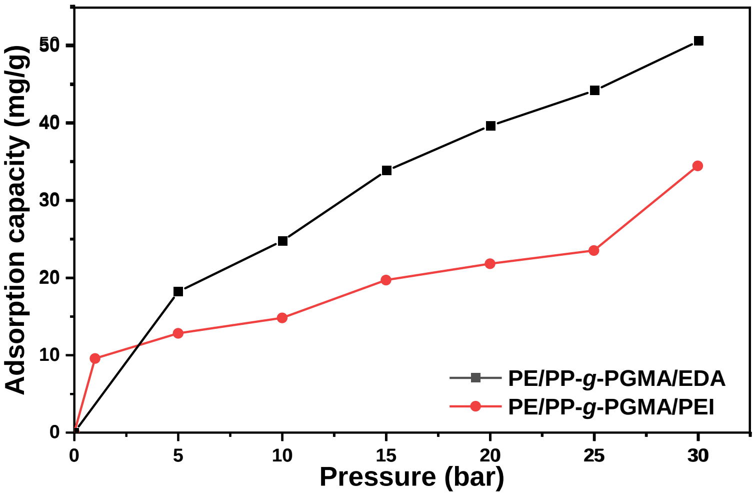


Figure 5. CO_2 adsorption capacity isotherm of PE/PP-*g*-PGMA-EDA and PE/PP-*g*-PGMA-PEI

4. Conclusion

Two adsorbents: PE/PP-*g*-PGMA-EDA and PE/PP-*g*-PGMA-PEI, were successfully prepared by RIGC of GMA followed by amination treatments as confirmed by FTIR, XRD and SEM analysis. Both adsorbents achieved 20% amination level with EDA and PEI despite the difference in the applied treatment conditions. The effect of the amine group structure attached to PGMA grafts covalently bonded PE/PP sheet on CO_2 adsorption capacity was investigated. Interestingly, the performance test showed that PE/PP-*g*-PGMA-EDA adsorbent attained higher CO_2 adsorption capacity than PE/PP-*g*-PGMA-PEI as indicated by the capacity value of 50.44 mg/g for the former and 34.51 mg/g for the latter. More work is needed to reduce the degree of grafting in the grafted precursor and optimize the amination conditions to increase the amination level.

Acknowledgment

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