

A comparison of CO₂ adsorption behaviour of mono- and diamine-functionalised adsorbents

Noor Ashikin Mohamad¹, Ebrahim Abouzari Lotfi^{2*}, Mohamed M. Nasef^{3**}, Arshad Ahmad², and TAT Abdullah²

¹Advanced Material Research Group, Center of Hydrogen Energy, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra 54100, Kuala Lumpur, Malaysia.

²Department of Chemical Engineering, School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia.

³Chemical Engineering Department, Universiti Teknologi Petronas, 32610 Seri Iskandar, Perak, Malaysia.

*Corresponding Author: *: ebrahim@utm.my, **: mohamed.nasef@utp.edu.my

Abstract. The paper presents a study for investigating i) the effect of amination of poly(GMA)-grafted polyethylene/polypropylene (PE/PP) substrates with trimethylamine (TMA) and ethylenediamine (EDA) and ii) their impact on carbon dioxide (CO₂) adsorption capacity of the obtained adsorbents. The chemical, structural, and morphological changes of the aminated adsorbents were evaluated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM), respectively. The amination yield with TMA was 40% higher than EDA. However, the obtained adsorbent showed two times lower CO₂ adsorption capacity (at 30 bars) than the adsorbent with EDA and stood at 0.6 mmol g⁻¹ compared to 1.2 mmol g⁻¹.

1 Introduction

Excessive utilisation of natural resources such as fossil fuels (coal, petroleum, and natural gas) to produce energy releases unwanted pollutants such as carbon dioxide (CO₂), contributing to global warming [1], [2]. Thus, it is crucial to have a system that can capture CO₂ before it is released to the atmosphere. A current large-scale CO₂ capture technology is absorption with liquid amine. However, the operation of this technology is expensive, including high energy demand to regenerate amine solution, and accelerated corrosion causes short life-span to vessels and pipelines [3]–[5]. Solid adsorbents have been proposed to replace absorption technology including zeolites, metal organic frameworks, microporous organic polymers, carbonaceous materials (graphene, activated carbon, and carbon nanotubes), and ordered mesoporous silica that are driven by physical adsorption. Chemical adsorption is another mechanism that drives materials such as lithium-based materials, calcium-based materials, and amine-containing materials (amine impregnated or amine grafted) [6]–[8].

Solid amines obtained by grafting with amine groups are promising materials for effective CO₂ capture. Particularly, functionalised fibrous adsorbents are advantageous in terms of simple preparation procedure, high surface area, low regeneration temperature, and easy handling [9]. Fibrous adsorbents can be prepared using radiation-induced grafting

(RIG) technique [10]–[13] that allows functionalisation of an inert polymer substrate with vinyl or acrylic monomers such as glycidyl methacrylate (GMA) [14], leading to a precursor that can host Lewis base (e.g., amine) for CO₂ capture [15]. However, the level of CO₂ capture depends on the type of the incorporated amine group.

The aims of this study are to investigate the effect of amine type on the adsorption of CO₂ on adsorbents obtained by RIG of GMA onto polyethylene/polypropylene (PE/PP) and followed by amination reaction with two different amines: trimethylamine (TMA) and ethylenediamine (EDA).

2 Materials and methods

2.1 Chemicals and reagents

The adsorbent precursor PE/PP-*g*-GMA was prepared following the procedure reported in [16] and has a degree of grafting of 166%. TMA (50 wt. % aqueous solution) and EDA (≥99%) were purchased from Acros Organics and Sigma-Aldrich, respectively, and used without further dilution.

2.2 Apparatus and measurements

The chemical changes after amination were observed with Nicolet iS50 FTIR spectrometer in the wave number range of 500 to 4500 cm⁻¹ using 32 scans with 4 cm⁻¹ resolution. The structural changes were investigated using X-ray diffraction (XRD) with PANalytical Empyrean at 2θ in the range of 5° to 80°. The morphological changes were studied using GeminiSEM 500 microscope with 100× magnification. CO₂ adsorption capacity of the samples were analysed using gravimetric sorption analyser isoSORP® from Rubotherm-TA instrument at 30 °C and a pressure range of 0–30 bars. All the analysis were carried out using samples of pristine PE/PP, poly(GMA) grafted PE/PP (PE/PP-*g*-PGMA), and aminated PE/PP (PE/PP-*g*-PGMA-X), where X stands for TMA and EDA.

2.3 Amine functionalisation

0.1052 g of PE/PP-*g*-PGMA substrate was added to a 100 ml round-bottom flask containing 30 ml of amine solution. The reaction was carried out under reflux condition at 32 and 90 °C for TMA and EDA, respectively. After 24 h of reaction with TMA and 6 h of reaction with EDA, the amine functionalised substrates were removed and washed repeatedly with water and ethanol and dried at 60 °C for 5 h. The percentage of amination was calculated by taking the weight changes in PE/PP-*g*-PGMA samples after the reaction and compared with the initial weight. Then, amine percentage was calculated using the following equation:

$$\text{Percent of amination (\%)} = \boxed{100 - \left[\frac{[(m_g - m_o)/W_{\text{GMA}}] - [(m_a - m_g)/W_{\text{amine}}]}{m_g - m_o} \times 100\% \right]} \quad (1)$$

Where W_{GMA} and W_{amine} are the molecular weights of GMA and TMA or EDA (g mol⁻¹), respectively. m_o , m_g , and m_a are the mass (g) of pristine, grafted, and aminated PE/PP substrate, respectively. Figure 1 shows the reaction scheme for the preparation of CO₂ adsorbent starting from pristine PE/PP non-woven substrate using RIG and followed by amination with TMA or EDA.

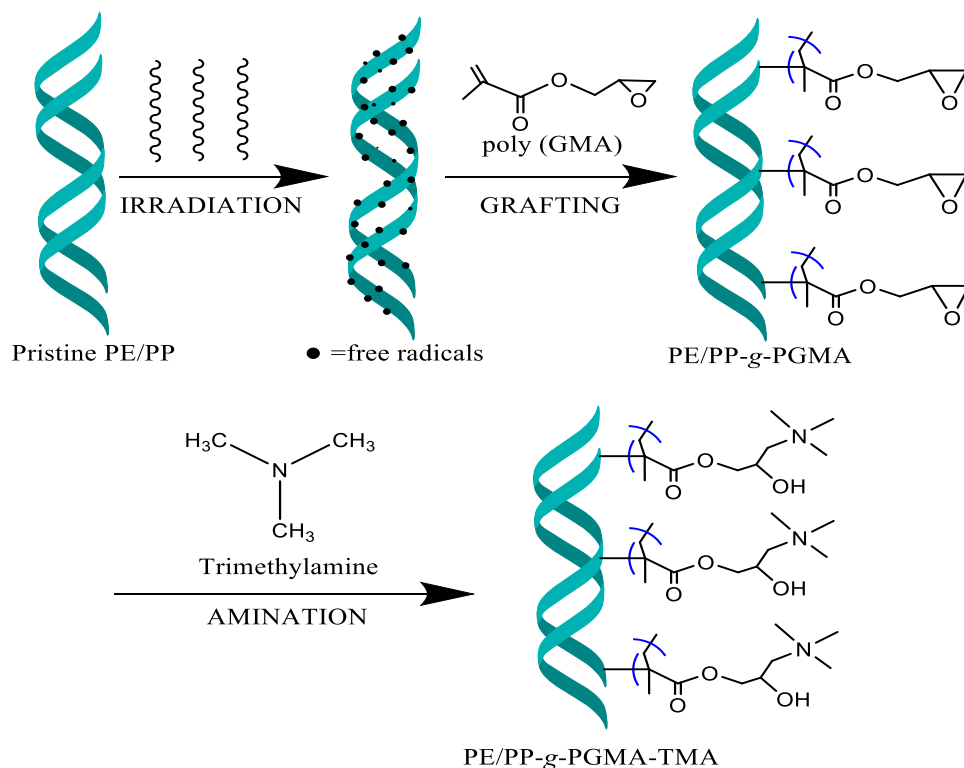


Fig. 1. Reaction scheme for the preparation of CO₂ fibrous adsorbent by radiation induced grafting of GMA onto PE/PP and subsequent amination.

2.4 CO₂ adsorption test

0.1052 g of PE/PP-g-PGMA-TMA and PE/PP-g-GMA-EDA substrates were placed inside the sample container of gravimetric sorption analyser. Prior to adsorption, the pre-treatment mode was applied to remove moisture content at 80 °C for 2 h under vacuum and subsequently, the buoyancy mode was selected to obtain accurate weight and volume of the substrate for correct weight of adsorption. Buoyancy was measured under nitrogen (N₂) gas flow rate of 500 ml min⁻¹ at 30 °C with pressure ranging from 0 to 30 bars. The mixture of CO₂/N₂ gases with 40 v/v % of CO₂ gas concentration with total flow rate of 500 ml min⁻¹ was used for adsorption test at 30 °C and pressure from 0 to 30 bars.

3 Results and discussion

3.1 Structural characterisation

Fourier transform infrared spectroscopy (FTIR) analysis was performed to observe the changes in composition of PE/PP after grafting with GMA and subsequent amination with TMA or EDA. Figure 2 shows FTIR spectra of pristine PE/PP, PE/PP-g-PGMA, PE/PP-g-PGMA-TMA, and PE/PP-g-PGMA-EDA. As can be seen, Figure 2(b) shows two peaks at 840 cm⁻¹ and 1740 cm⁻¹, providing evidence for the presence of epoxy group and -C=O stretching peak of grafted PGMA chains on the PE/PP backbone polymer structure after

grafted with poly(GMA) [10]. The disappearance of the peak at 840 cm^{-1} in Figures 2(c) and 2(d) proves successful epoxy ring-opening and introduction of TMA and EDA amines. The emergence of a broad band at 3500 cm^{-1} is due to -OH incorporated after ring opening and -NH peaks at 1658 cm^{-1} and 3300 cm^{-1} confirm the presence of TMA and EDA amines after the amination reaction [11], [17].

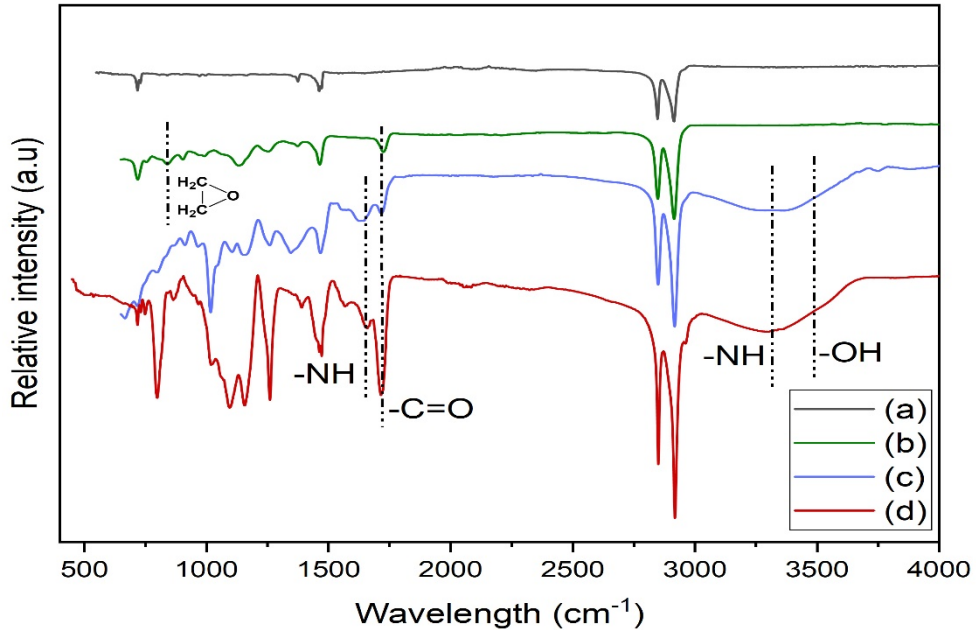


Fig. 2. FTIR spectra of (a) pristine PE/PP, (b) PE/PP-g-GMA, (c) PE/PP-g-GMA-TMA, and (d) PE/PP-g-GMA-EDA.

Figure 3 shows the XRD diffractograms of PE/PP, PE/PP-g-PGMA, PE/PP-g-PGMA-TMA, and PE/PP-g-PGMA-EDA samples. XRD analysis was conducted to investigate the changes in crystalline structure of PE/PP after grafting and subsequent amination. The positions of the crystallinity representing peaks occurred at the same angle (2θ in the range of $10\text{--}30^\circ$), indicating that there is a major disruption in the crystallites of PE/PP after grafting and amination, suggesting the presence of dilution effect. However, the intensity of the peaks was reduced and the significance of reduction was in the order of PE/PP-g-PGMA > PE/PP-g-PGMA-EDA > PE/PP-g-PGMA-TMA. This suggests that the dilution of inherent crystallinity occurred by incorporation of amorphous poly(GMA) increase by amination and it becomes more profound upon amination with TMA, suggesting severe disruption in the crystal structure of PE/PP [18], [19].

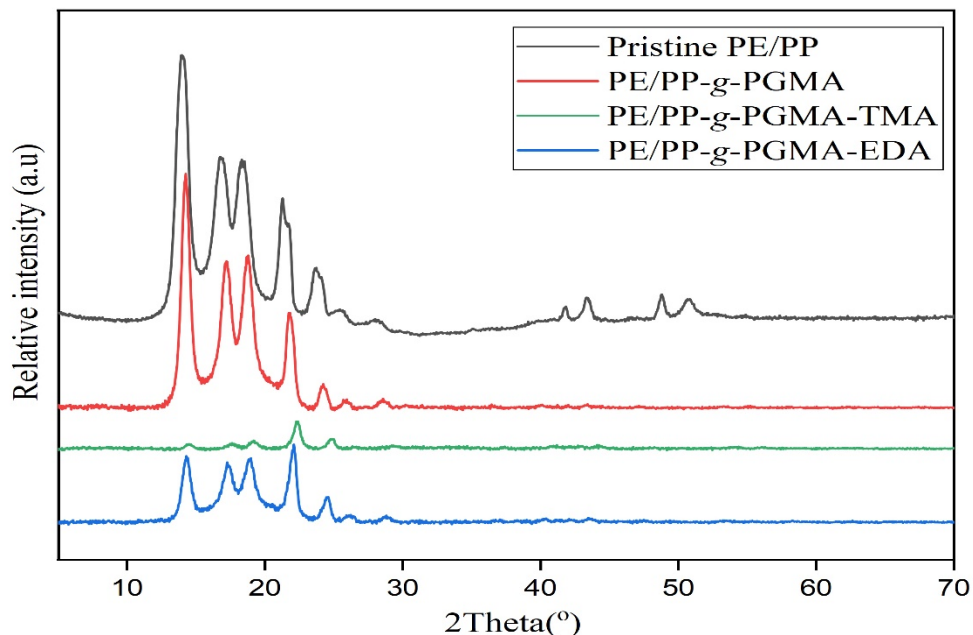


Fig. 3. XRD results for pristine PE/PP, PE/PP-g-GMA, PE/PP-g-GMA-TMA, and PE/PP-g-GMA-EDA.

Figure 4 shows the surface morphology of pristine PE/PP and PE/PP grafted with poly (GMA) with the degree of grafting of 166% obtained from the SEM images with a magnification of 100 \times . The fibre diameter of PE/PP-g-GMA substrate increased to almost two-folds compared to the pristine PE/PP sample. This provides additional evidence of GMA grafting.

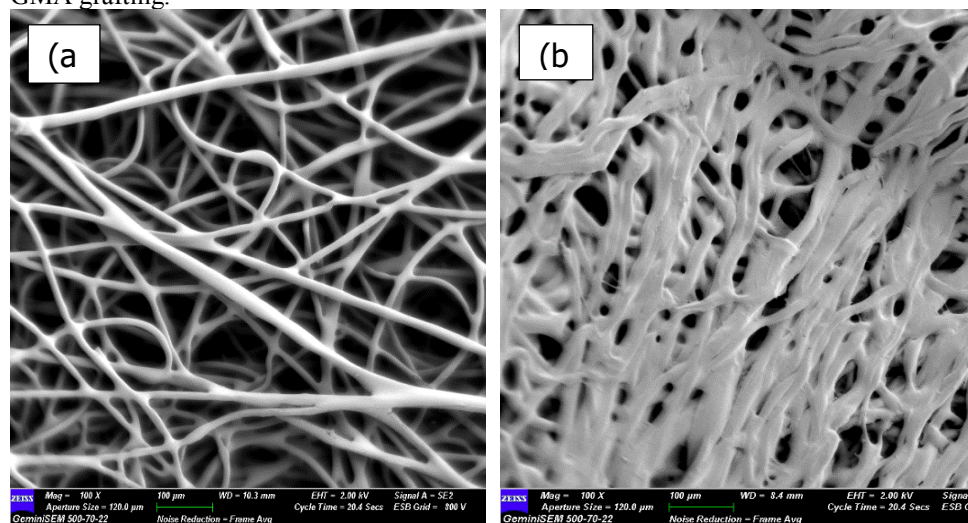


Fig. 4. SEM results for (a) pristine PE/PP and (b) grafted PE/PP-g-PGMA.

3.2 CO₂ adsorption test in gravimetric sorption analyser

The amination yield obtained for PE/PP-g-PGMA samples treated with TMA and EDA was 100% and 60%, respectively. The variation of CO₂ adsorption capacity of PE/PP-g-PGMA-TMA and PE/PP-g-PGMA-EDA adsorbents with pressure is presented in Figure 5. Pristine PE/PP and PE/PP-g-PGMA samples were included as references. As can be observed, very low CO₂ adsorption capacity was obtained with pristine PE/PP, which amounted to 0.2 mmol g⁻¹ at 30 bars for the corresponding PGMA grafted sample. This is due to entrapment of CO₂ in the structure of PGMA. Unlikely, the aminated samples showed a remarkable increase in CO₂ adsorption with increased pressure. At 30 bars, the CO₂ adsorption capacity of the adsorbent aminated with EDA was 1.2 mmol g⁻¹, which was two times higher than TMA with the capacity of 0.6 mmol g⁻¹. It shows that EDA substrate performed better despite low amination yield compared to TMA substrate. This might be due to the partially destructive structure of PE/PP during the amination procedure as presented in Figure 3, where the intensity peak of TMA sample reduced significantly.

TMA sample is known as monoamine, but it is also known as a tertiary amine and the diamine of EDA is also known as a primary amine. This statement explains that the size of amine affects CO₂ adsorption performance. The bulkier groups imply less working capacity compared to the primary amine due to a significant decrease in porous volume, which also causes a lower adsorption amount at high pressure [20]. The reaction of primary and tertiary amines with CO₂ is different, where the reaction from a primary amine forms carbamate and a tertiary amine forms bicarbonate from their mechanism and this is well explained in the study by [21]. From the mechanism, it can be explained that the tertiary amine does not bind with CO₂ molecules without the presence of water molecules (i.e., dry condition). However, this study was conducted in a dry condition to test the CO₂ adsorption performance; thus, the amine efficiency for TMA sample is much lower compared to EDA amine, practically and theoretically [22].

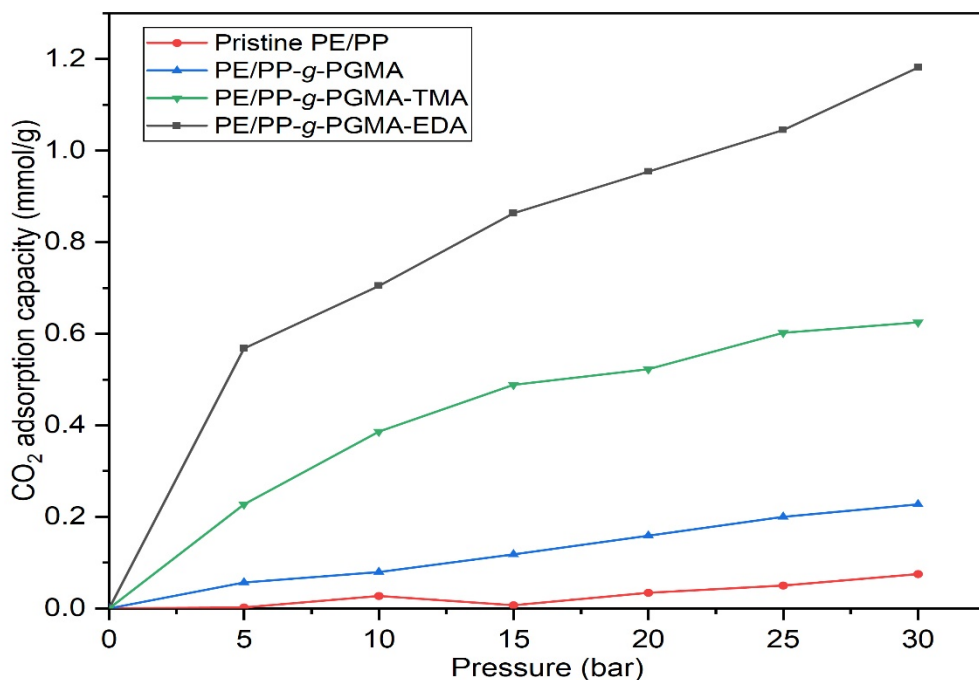


Fig. 5. CO₂ adsorption capacity at different pressures for pristine, grafted, and aminated PE/PP.

4 Conclusion

This study was conducted to determine the effect of types of amine towards CO₂ adsorption capacity. The percentage of amination obtained from the experimental work shows that PE/PP-g-GMA-TMA has higher value with 100% as compared to PE/PP-g-GMA-EDA with 60% amination. However, the CO₂ adsorption capacity performance test shows the opposite result, where at 30 bars, PE/PP-g-GMA-EDA obtained 1.2 mmol g⁻¹ and PE/PP-g-GMA-TMA obtained 0.6 mmol g⁻¹. From the results, the EDA sample demonstrates strong potential as a CO₂ adsorbent for future industrial application, with more studies are required to study other properties of the sample.

This work was supported by Universiti Teknologi Malaysia (UTM) and Malaysia-Thailand Joint Association (MTJA) under the grant (Vot. No. 4C116).

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