

Enhancement of carbon dioxide adsorption performances by hydrazinolysis of poly(n-vinylformamide) grafted fibrous adsorbent

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Abstract. Emission of carbon dioxide (CO₂) becomes a main concern in battling issues of global warming. The strategy to reduce the concentration of CO₂ could be achieved by implementing carbon capture and storage (CCS) technology such as adsorption by solid adsorbents. In this work, hydrazone containing adsorbent was prepared by radiation induced grafting of N-vinylformamide (NVF) onto polyethylene coated polypropylene (PE/PP) fibrous sheets and subsequent hydrazinolysis for CO₂ capture. Hydrazinolysis of the amide group to hydrazone moieties was accelerated by the addition of ammonium salts. These newly prepared adsorbent was characterized by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). The adsorption tests of pure CO₂ and N₂, and their mixture were carried using the gravimetric method. The result revealed that the obtained adsorbent was highly CO₂ selective and attained remarkably higher CO₂ sorption capacity of 3.1 mmol/g at 30 bar and room temperature compared to 0.3 mmol/g for amide-containing sample. The new adsorbent could be used for few repeated cycles with negligible loss in sorption capacity. Overall, the hydrazone-containing adsorbent has storing potential for CO₂ capture, and more studies need to be conducted for further development.

Keywords: CO₂ capture; solid adsorbent; radiation induced grafting; PE/PP non-woven sheet.

1. Introduction

Recently, there has been a rising concern about global warming and climate change. CO₂ is generally recognized as a greenhouse gas that contributed significantly to global warming, causing major concern for the global climate. The emission of greenhouse gases is generated from anthropogenic activities include burning of fossil fuels, production of electricity, agricultural practices, transportation and manufacturing. At present, carbon capture and sequestration (CCS) is considered as one of the most promising solutions to mitigate the CO₂ emissions [1, 2]. There are three methods for CCS: pre-combustion capture, oxy-fuel process, and post-combustion capture. Among them, post-combustion capture is more feasible capture methodology due to its flexible operation and minimal requirements for retrofitting existing power plants which is consistent with the current industrial infrastructures.

Based on economic and environmental considerations, it is necessary to apply efficient and suitable technology for CO₂ separation with low operating cost and energy consumption. Up to now, there are



several gas separation technologies being investigated for post-combustion capture namely, absorption, adsorption, cryogenic distillation, and membrane separation. Among them, the use of liquid amine is the most mature method, and which offers higher capture efficiency. This process typically operates at 50-60°C, and the saturated alkanolamine is regenerated at 110-130°C, which require high regeneration energy, cause corrosion to equipment, and change in viscosity thus ended with flow problems. As a result, solid adsorbent has been widely studied and recommended to be an alternative technology due to its simplicity, low operational requirements, low cost, ease of control, and high adsorption efficiency.

Generally, various types of solid adsorbent have been explored to have a suitable candidate for CO₂ capture, including mesoporous silicon [3-6], activated carbon [7], carbon nanotube [8], metal-organic framework [9], zeolite [10], aerogel [11, 12], polymers [13] and many others. Porous organic polymers are broadly exploited and have been classified into various forms such as hyper-cross-linked polymers, conjugated microporous polymers and grafted fibrous sheets. Of all, aminated fibrous polymeric materials have been investigated in the past several years and found to be attractive solid adsorbents for CO₂ adsorption. The availability of various fibrous polymer substrates with low cost provides an attractive opportunity to develop fibrous adsorbent containing ligands with various of amine end groups.

Amine-containing solid adsorbents have recently received a widespread attention in CO₂ capture applications due to their tunable structures and availability of wide range of modifiable inorganic and polymeric substrates and low regeneration energy. Yang and co-workers prepared an adsorbent for CO₂ capturing by grafting of allylamine onto polyacrylonitrile fibers [14]. Despite the good adsorption capacity, this adsorbent has serious disadvantages including the use of very hazardous allylamine monomer and the addition of chemical initiator. Another adsorbent for CO₂ was prepared by radiation induced grafting of glycidyl methacrylate (GMA) onto PE/PP nonwoven fabric followed by amination [15]. As an alternative route to GMA grafting and subsequent amination, the introduction of primary amine to porous ultrahigh molecular weight polyethylene (UHMWPE) substrates by grafting of NVF and subsequent hydrolysis was reported [16]. The content of amide grafts was found to be dependent on the grafting parameters. Then, simple hydrolysis of the amide group was achieved after chemical treatment with sodium hydroxide (NaOH), resulted in amine containing adsorbent. In another study, Zubair et al. has grafted the NVF monomer onto another lower cost substrates namely PE/PP fibrous sheet with the use of lower concentration of NVF monomer [17]. The adsorbent containing poly(vinylamine) obtained by the hydrolysis of the grafted poly(NVF) chains showed a remarkable CO₂ adsorption capacity of 1.36 mmol/g at room temperature.

The objective of the present study is to investigate a new method involving radiation induced grafting of NVF onto PE/PP fibrous sheet and subsequent hydrazinolysis to convert the grafted poly(NVF) chains to hydrazone containing adsorbent. Hydrazones consist of the amine structure and also nitrogen bonded atom imine, which improved the affinity of the adsorbent towards CO₂. The adsorbent was mainly characterized by Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The suitability of the obtained hydrazone containing adsorbent for CO₂ capturing was performed by evaluating its adsorption capacity, selectivity and stability.

2. Experimental

2.1. Materials

PE/PP fibrous sheets were obtained from Kurashiki Co., Japan. The NVF monomer with a purity of 98% was obtained from Sigma Aldrich (Saint Louis, MO, USA) and used without any further purification. Solvents such as ethanol and N-methylformamide (DMF) were research-grade and supplied by Merck (Darmstadt, Germany). Hydrazine hydrate and ammonium iodide was obtained by Sigma Aldrich. Deionized water (DI) was obtained from Barnstead Nanopure Diamond Lab Water Purification System (ThermoFisher, Waltham, USA) and used for washing of all samples and preparation of solution. CO₂ and N₂ gas were supplied by Linde Malaysia Sdn. Bhd.

2.2. Radiation Induced Grafting

The PE/PP samples were thoroughly washed with ethanol under sonication for 3 h to remove any impurities. The samples were dried under vacuum and placed in zipped plastic bags, which were deaerated

by purging with pure nitrogen gas and thermally sealed. The bags containing samples were placed in a tray on a dry ice loaded on a conveyer and irradiation by an electron beam [17] accelerator (NHVNissin High Voltage, EPS3000) operated at an acceleration energy and a beam current of 2 MeV and 10 mA, respectively. Dry ice was used to stabilize radicals formed in the PE/PP non-woven sheets and prevent any possible damage to the samples as a result of temperature increase during irradiation. The total doses were from 100 kGy at 25 kGy/pass.

The reaction was carried out in the grafting consists of a glass ampoule connected to vacuum pump (10–3 torr) and glass vessel having a bubbler (dip-in tube) from one side and an outlet tube that can be connected to the evacuated glass ampoule by a tri-way stopcock to allow monomer solution transfer from the vessel to the ampoule. The irradiated PE/PP substrates were weighed and placed in the glass ampoules, which were evacuated for 30 min. Meanwhile, the glass vessels containing 25% NVF monomer solutions diluted with toluene were de-aerated by bubbling with purified N₂ for 30 min. Subsequently, the NVF solutions were transferred to the irradiated PE/PP substrates in the evacuated glass ampoules through the tri-way stopcock. The glass ampoules were sealed and kept in a water bath at temperatures of 60 °C to initiate grafting. After the reaction was completed, the grafted PE/PP substrates were removed and thoroughly washed with methanol 5 times and later rinsed for 1 h in methanol under sonication. The clean samples were removed, vacuum dried and their weight increases were recorded. The amount of amide grafts incorporated in the samples or degree of grafting (G%) was calculated using equation 1:

$$(G\%) = \frac{W_f - W_i}{W_i} \times 100 \quad (1)$$

where, W_i and W_f are the initial and final weights of PE/PP substrates after grafting, respectively.

2.3. Hydrazinolysis of Amide grafted PE/PP

Hydrazinolysis of formamide groups in the grafted substrates into hydrazone was set up by dissolving hydrazine hydrate in DMF. 2% of ammonium iodide was added to the mixture solution to accelerate the hydrazinolysis of the amide bond. The solution was then put in a round bottom flask containing the grafted amide samples equipped with a reflux condenser and placed in an oil bath. The reaction was performed at 80°C for 6h. Subsequently, the treated samples were rinsed in deionized water, immersed in ethanol overnight, vacuum dried at 80°C and eventually weighed.

2.4. Characterization

SEM images of the samples before and after grafting and subsequent hydrazinolysis were obtained by a Phenom PRO scanning electron microscope (Thermo Fisher Sci., USA). The samples were carbon-coated and operated at an accelerating voltage of 2 kV. The chemical changes in vacuum dried samples were investigated with a Perkin Elmer Spectrum One FTIR spectrometer coupled with an attenuated total reflectance. Measurements were made in the frequency range of 500-4000 cm⁻¹ at a resolution of 4 cm⁻¹.

2.5. CO₂ adsorption measurement

The CO₂ adsorption and regeneration were performed using Isosorp[®] Gravimetric Analyzer from RUBOTHERM (Bochum, Germany), which is controlled by the RSCS software allowing automated operation and data collection. A blank measurement without any sample was carried out to determine the volume of the container using N₂ gas at room temperature after evacuation. Later, samples of pristine PE/PP, PE/PP-g-Amide and PE/PP-g-Hydrazone weighing 0.1-0.2 g were inserted in the sample containers before they were pre-treated at 90°C for 3h under vacuum and the true weights and volumes of the samples were determined using buoyancy mode prior to adsorption tests. In the adsorption test, a pure and mixture of CO₂ and N₂ gases is flowed to the system at a 500 ml/min flow rate at a temperature of 30°C. The pressure was varied in the range of 0-30 bar and the adsorption capacity was determined at each pressure for each sample.

3. Results & Discussion

Figure 1 shows FTIR spectra of original PE/PP, PE/PP-g-Amide and hydrazone-containing sample after

hydrazinolysis. The spectrum of the original substrate showed typical features of PE sheath layer that completely covered PP core of the fibres. This was evidence from the peaks at 2917 and 2847 cm^{-1} representing the antisymmetric and symmetric CH_2 stretching vibrations together the peaks at 1480 and 725 cm^{-1} assigned for CH_2 bending and rocking vibrations for PE. The absence of CH_3 representing peaks further confirm the absence of PP. Similar, observation was reported in literature for similar PE/PP fibrous sheet obtained from the same supplier [18]. The introduction of amide grafts into PE/PP substrate was evident from the appearance of few new peaks. For instance, the sharp peak at 1650 cm^{-1} resembles the stretching vibration of carbonyl group ($> \text{C}=\text{O}$) originated from amide (I) group. This was coupled with other formamide features such as N–H bending vibration at 1542 cm^{-1} and –CN stretching vibration at 1270 cm^{-1} from in addition to N–H stretching vibration at 3280 cm^{-1} belonging to amide (I). The conversion of the amide to hydrazone after hydrazinolysis of the grafted sample was confirmed from the presence of peaks in 1780 represent the $\text{C}=\text{N}$ imine, and the peak at 990 cm^{-1} represent the CN- heterocycle and 3360 cm^{-1} representing NH_2 group. It can be concluded that NVF was grafted on PE/PP fibrous substrates and the incorporated amide was almost fully converted to hydrazone after hydrazinolysis. Figure 2 shows a proposed schematic diagram for the preparation of hydrazone containing adsorbent by RIG of NVF onto PE/PP substrate and subsequent hydrazinolysis.

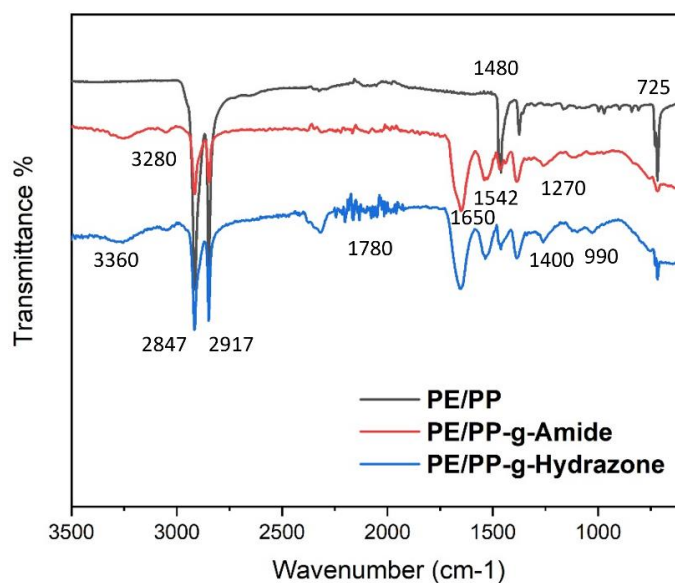


Figure 1. FTIR spectra of original PE/PP substrate, amide containing PE/PP, and hydrazone containing PE/PP.

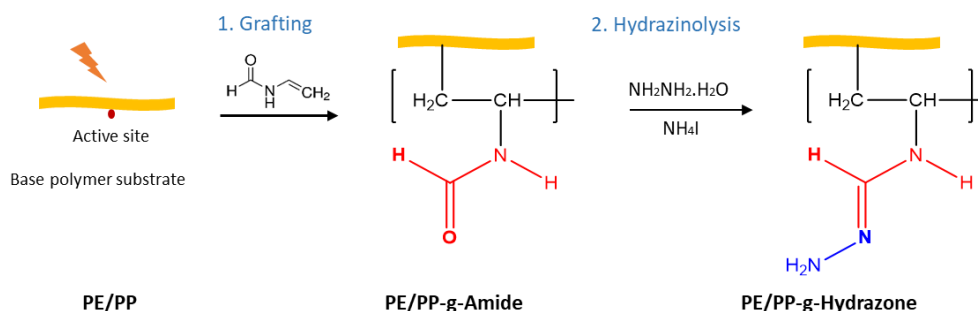


Figure 2. Reaction scheme for modification of polymeric fibrous adsorbent by RIG of NVF onto PE/PP nonwoven sheet and subsequent hydrazinolysis.

SEM images of the pristine PE/PP and the corresponding amide grafted PE/PP together with hydrazone containing sample are shown in Figure 3. As can be observed, the fibres display changes in their diameters after grafting. Particularly, the average fibre diameter was found to increase by the incorporation of amide grafts. For instance, the average diameter of the fibre of the pristine PE/PP increased from $15 (\pm 6.42)$ to $20 (\pm 10.70)$. The increments are coming from the coating of poly(NVF) around the fibre strands. Followed by hydrazinolysis, the average diameter is reduced around $\sim 10\%$ together with remarkable roughness attained after hydrazinolysis. The polymer eventually shrunk due to the bonding of the polymer chains in the initial stage of crosslinking, resulting from decreasing in average diameter after the treatment.

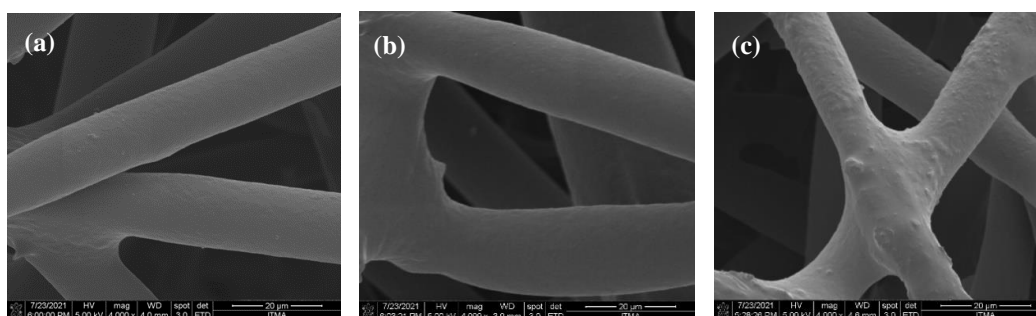


Figure 3. SEM images of (a) original PE/PP substrate, (b) amide containing PE/PP and (c) hydrazone containing PE/PP.

Figure 4(a) presents the CO_2 adsorption performance carried out using the gravimetric method as explained in section 2.5. The test was carried out in 100% CO_2 with a flow rate of 500ml/min at 30°C and pressure up to 30 bar. As can be seen, the amounts of CO_2 adsorbent increased with the increase in the pressure in all samples including pristine PE/PP. For instance, the pristine PE/PP recorded a CO_2 adsorption of 0.08 mmol/g. This likely due to the fibrous structure of the sheet that provided free volume in which, CO_2 interacted by a physical adsorption driven by van der Waals forces. The incorporation of poly(NVF) after grafting increased the CO_2 adsorption capacity to 0.25 mmol/g. This is caused by the formation of hydrogen bonds between N–H of amide and C=O of CO_2 . Despite being a type of dipole-dipole interaction, hydrogen bond is not a true chemical bond. When amide was converted to hydrazone in adsorbent, the CO_2 adsorption capacity became far greater and reached a value of 3.1 mmol/g. This was contributed by the amine and imine presence in the hydrazone containing adsorbent.

An effective adsorbent not only requires good adsorption capacity, but also the regeneration capacities over repeated adsorption and desorption cycles. Thus, eight adsorption cycles were conducted for the PE/PP-g-Hydrazone adsorbent, and the results are presented in Figure 4(b). The adsorption was carried out in pure CO_2 and desorption under vacuum condition at 80°C for 5h until a constant weight was measured. As shown, the adsorption capacity of the adsorbent decreased slightly after the first cycle of regeneration, which might be due to the removal of excess impurities that remain on the adsorbent surface after the washing process during the sample preparation, which hindered the excess of CO_2 molecules to the active site. However, after eight cycles, the adsorption capacity remains high, with value of 2.98 mmol/g (the adsorption capacity of the first cycle is 3.1 mmol/g). The negligible loss proved that the adsorbent can be used for a prolonged cyclic operation. The desorption method could completely remove the adsorbed CO_2 molecules at a low temperature, reducing energy consumption.

The effect of feed CO_2/N_2 gas mixture composition and operating pressure on adsorption capacity is shown in Figure 4(c). The result shows that the adsorption capacity increases with the increase of operating pressure and CO_2 composition. The adsorption capacity is in the following sequence at 30bar: 100% $\text{N}_2 < 25\% \text{CO}_2 < 50\% \text{CO}_2 < 75\% \text{CO}_2 < 100\% \text{CO}_2$ with their adsorption capacity such as 0.12 mmol/g, 1.60

mmol/g, 2.18 mmol/g, 2.70 mmol/g, and 3.10 mmol/g respectively. Furthermore, the degradation of adsorption capacity as the CO₂ composition lessening might occur due to competition for the active site of amine groups. Moreover, N₂ (28.01 g/mol) move faster compared to CO₂ (44.01g/mol) due to the smaller molecular weight as the rate of diffusion of a gas is inversely proportional to the square root of its molecular mass as per Graham's law of diffusion. Thus, it hindered the chance for CO₂ to access the amine group from the adsorbent.

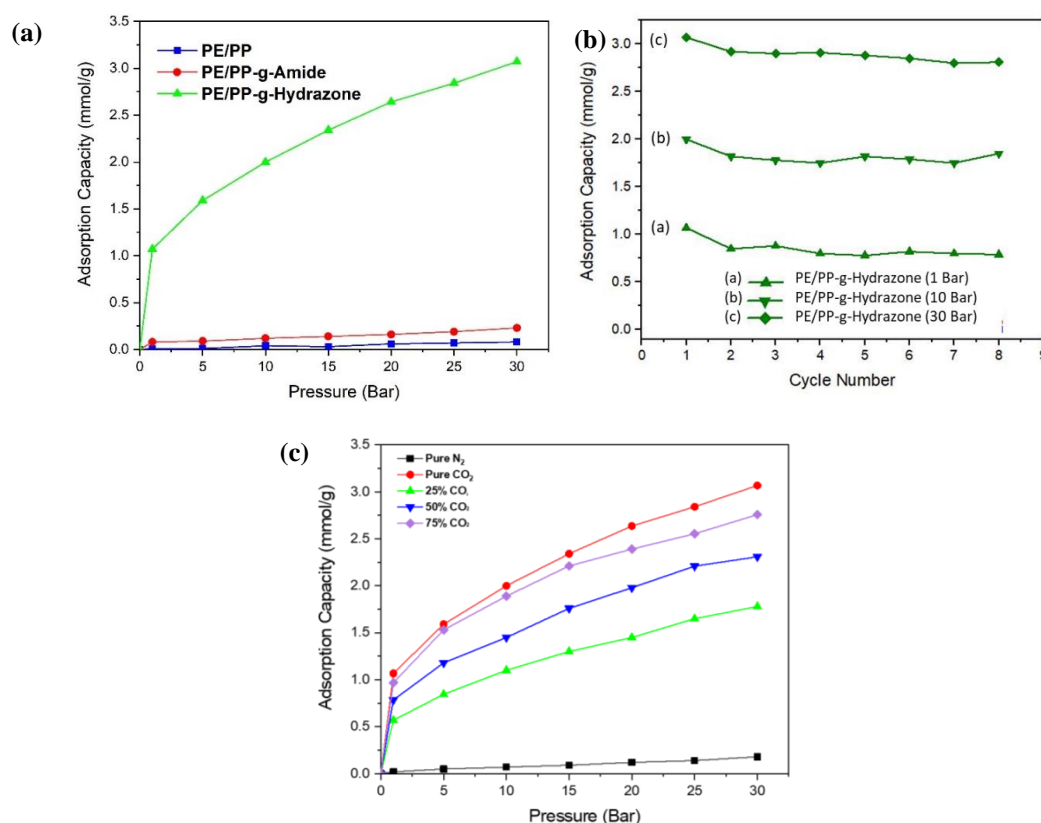


Figure 4. (a) CO₂ adsorption capacity of pristine PE/PP, amide containing PE/PP, and hydrazone containing PE/PP (b) The effect number of cycles on the adsorption performance at different pressure and (c) Adsorption capacity at different CO₂/N₂ gas composition for hydrazone containing PE/PP.

The result revealed that the obtained adsorbent was highly CO₂ selective and attained remarkably higher CO₂ sorption capacity of 3.1 mmol/g at 30 bar and room temperature compared to 0.3 mmol/g for amide-containing sample. The new adsorbent could be used for few repeated cycles with negligible loss in sorption capacity. Overall, the hydrazone-containing adsorbent has storing potential for CO₂ capture, and more studies need to be conducted for further development.

4. Conclusion

A fascinating fibrous adsorbent made of hydrazone containing PE/PP fibrous sheet was successfully prepared and tested for CO₂ adsorption. The results of this study suggest RIG of NVF onto PE/PP substrates and subsequent hydrolysis provides a highly effective and shorter route for the development of amine-containing adsorbent for potential application in CO₂ capture. The adsorbent was found to be highly selective for CO₂ over N₂ with a competitive adsorption capacity. Furthermore, the adsorbent was observed to have very good stability and can be easily regenerated at 80°C providing it suitable for column and scaled CO₂ capture applications.

Acknowledgement

The authors wish to acknowledge the financial support by Malaysia-Thailand Joint Authority (MTJA) research grant (Vote. No. R.J130000.7609.4C172). N.A. Zubair is grateful for Malaysia-Japan International Institute of Technology (MJIIT) for the Student Incentive Excellence Scheme.

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