

Radiation induced graft copolymerization of amine-containing monomer onto polyethylene coated propylene for CO₂ adsorption

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Abstract. Modification of polyethylene coated polypropylene by radiation-induced graft copolymerization (RIGP) of N-vinylformamide film followed by hydrolysis was studied to produce polyvinylamine (PVAm) containing adsorbent for CO₂ adsorption. A number of grafting parameters such as irradiation dose, monomer concentration, and reaction temperature were investigated to obtain desired degree of grafting (DOG) prior to hydrolysis. The DOG was found to be a function of reaction parameters and achieved a desired value of 131% at 40 wt% NVF concentration in toluene, 300 kGy dose, 70°C temperature and 1h reaction time. Subsequently the hydrolysis of formamide groups in the grafted films into amine functionalities was carried out in basic medium. Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) confirmed the NVF monomer was successfully grafted on PE/PP and consequently the hydrolysis of amide into amine functionalities has occurred in the grafted substrates. The CO₂ adsorption capacity of PVAm modified adsorbent was brought to be a function of DOG, which is corresponding to the amine content after hydrolysis. The adsorbent showed the highest CO₂ adsorption capacity of 1.32 mmol/g when tested with gas composition of 40% CO₂ and 60% nitrogen at room temperature.

1. Introduction

CO₂ is the most serious greenhouse gas released into the atmosphere and become a critical issue over the past 50 years. This vast amount of CO₂ causes global warming that contribute to climate change include the sun's intensity, volcanic eruptions, and changes in naturally occurring greenhouse gas concentrations. Currently, liquid amine absorption, also known as amine scrubbing is the main commercial method used for CO₂ capturing. This method involves the use of monoethanolamine (EA), diethanolamine, or methyldiethanolamine solutions for CO₂ removal [1]. However, the process involves a number of serious challenges including high regeneration energy, large equipment size, amine degradation, and equipment corrosion [2].



Recently, solid adsorption has become the most preferable technique for CO₂ capturing. Among solid adsorbents, polymeric fibres containing amine functional groups have shown some advantages compared to other adsorbents [3, 4]. Modification of polymers by radiation induced grafting polymerization (RIGP) of functional monomers is a flexible method for imparting desired chemical and physical properties to various substrates and allowing tuned compositions. The grafted materials were found suitable for adsorption and separation processes and energy applications [5]. This method offers some advantages in preparation of functionalised polymeric materials such as the ability to control the graft copolymer composition by selecting the suitable grafting conditions [6], in addition to its procedural simplicity and environmental friendliness [7].

In RIGP, various substrates (sheets and fibres) have been frequently used as starting materials for development of variety of membranes and adsorbents. For example grafting of amide or amine-containing groups onto different substrates have been reported in literature and recently proposed for important materials such as adsorbents [8] and catalyst [9]. Particularly, an adsorbent for CO₂ capturing was obtained by RIG of allylamine onto polyacrylonitrile fibres and demonstrated good adsorption capacity [10]. Another CO₂ adsorbent was prepared by RIG of GMA onto PE/PP non-woven sheet followed by amination [11]. The selection of PE/PP as a substrate was motivated by its high chemical stability, mechanical strength, thermal resistance and reasonable cost and ability to form relatively stable radicals upon radiation at room temperature [12].

Recently Rojek *et al.* (2017) studied RIG of N-vinylformamide (NVF) monomer into porous ultrahigh molecular weight polyethylene (UMWPE) films and the obtained membrane was used as a CO₂ adsorbent. A noticeably high concentrations of monomer in the range of 80-100% were used [8]. Thus, it would be highly interesting to graft NVF at lower concentrations and modified with amine functionalities for CO₂ adsorbent to reduce the cost of the graft copolymer. Therefore, the objective of the present study is to investigate the behaviour of grafting reaction parameter of NVF onto fibrous PE/PP sheets and testing its hydrolysed copolymer for CO₂ adsorption. The evidence of formation of poly(NVF) in the grafted fibrous sheets is provided using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Moreover, the potential of using the obtained functionalised adsorbent for CO₂ adsorption was evaluated.

2. Materials and methodology

2.1. Materials

PE/PP fibrous sheets were obtained from Kurashiki Co., Japan. NVF with a purity of 98% was obtained from Sigma Aldrich and used without any further purification. Ethanol and toluene (reagent grade) were purchased from Merck. All chemicals were used as received without further treatment.

2.2 Irradiation of PE/PP substrates

PE/PP substrates were rinsed in ethanol for few hours under sonication, then removed and vacuum dried and placed in zipped plastic bags. The substrates were irradiated by an electron beam [4] accelerator (NHV-Nissin High Voltage, EPS3000) operated at an acceleration energy of 2 MeV, a beam current of 10 mA and a dose of 25kGy/pass.

2.3. Graft polymerization

The irradiated PE/PP substrates were transferred to an ampoule containing de-oxygenated NVF solutions diluted with toluene to various concentrations in the range of 10 wt% to 40 wt% and bubbled with N₂ for 30 minutes. Subsequently, the NVF solution was transferred to evacuated glass ampoules hosting the irradiated PE/PP substrates. The glass ampoule was sealed and kept in water bath at different temperatures (ranged from 40 to 70°C) to initiate the graft polymerization. After completion of the reaction, the grafted PE/PP substrates were removed, washed with methanol and rinsed in a methanol-containing vessel under sonication for 1h to remove the residual monomer and occluded

homopolymer. The grafted substrates were dried under vacuum oven and the amount of NVF monomer grafted onto PE/PP substrates was evaluated by the DOG using equation (1).

$$\text{Degree of grafting, DOG (\%)} = \frac{W_f - W_i}{W_i} \times 100\% \quad (1)$$

where, W_i and W_f are the initial weights of substrates and their weight after grafting, respectively.

2.4. Hydrolysis of poly(NVF) grafted PEPP

Hydrolysis of formamide group in the grafted substrates into amine group was carried out in basic medium using 2M NaOH solution at 80°C for 4h under reflux as reported in literature [8]. After treatment, the substrates were removed, washed with deionized water repeatedly and immersed in ethanol overnight. The substrates were removed and vacuum dried at 80°C and eventually weighed.

2.5. Characterization of the grafted fibres

A phenom PRO scanning electron microscope (SEM) was used to obtain images of the substrates before and after grafting. A Perkin Elmer Spectrum One FTIR Spectrometer equipped with an attenuated total reflectance was used to analyse the substrates in the frequency range 500 – 4000 cm^{-1} at a resolution of 4 cm^{-1} . Prior to FTIR measurements, the substrates were dried in a vacuum at 40°C overnight.

2.6. CO₂ adsorption test

The adsorption measurement was performed using a Rubotherm gravimetric sorption analyser. Substrates weigh of 0.1-0.2 g of hydrolysed PE/PP-g-poly(VAM) were placed inside the substrate container. The substrates were pre-treated at 80°C for 2h under vacuum prior to adsorption test. The buoyancy mode was selected to obtain the weight and volume of the substrate. The buoyancy measurements were performed in N₂ gas with 500 ml/min flow rate and operating temperature of 30°C with pressure range of 0 to 30 bar. In the adsorption test, the mixture of CO₂ and N₂ gases with a total flow rate of 500 ml/min was used in 30°C temperature and pressure range of 0-30 bar.

3. Results and discussion

3.1. Effect of grafting parameters on degree of grafting

3.1.1. *Effect of irradiation dose.* Figure 1 shows the effect of absorbed dose on DOG of NVF onto PE/PP substrates. The grafting parameters including time, temperature and monomer concentration were set at 1h, 70°C and 20 wt% NVF. As can be seen, the DOG increases with the increase in the dose from 50 to 300kGy. This is due to the increase in the number of radicals generated in the system, and as a result, more radicals contribute to initiation reaction. This high number of radical will participate in the graft polymerisation reaction leading to higher DOG. Similar dose trends were observed for RIGP of acrylic acid onto nylon-6 membrane [13] and grafting of acrylamide and acrylic acid onto nylon-6 fabric [14].

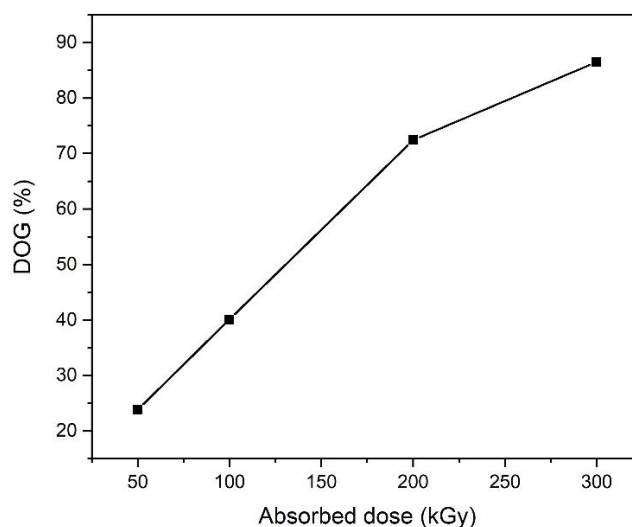


Figure 1. Variation of the degree of grafting with the absorbed dose for grafting of NVF onto PE/PP. Grafting parameters: 20 wt% GMA, 70°C and 1h

3.1.2. Effect of monomer concentration. Figure 2 shows the effect of variation of monomer concentration on DOG. It can be seen that DOG increases with the increase in monomer concentration from 10 wt% to 40 wt%. This can be attributed to the increase of the number of monomer molecules diffused to the grafting zone, leading to abundant monomers for grafting percentage. A further increase in the monomer concentration leads to arise in the viscosity that hinders the monomer diffusion to the radicals' sites and eventually reduces the rate of grafting reaction. The increasing viscosity of reaction medium enhanced the homopolymer formation as indicated by the increase in the viscosity of the grafting residues. Similar behaviour was reported for grafting of VBC onto poly(ether ketone) film [15] and butyl-spacer styrenic monomer onto ETFE [16].

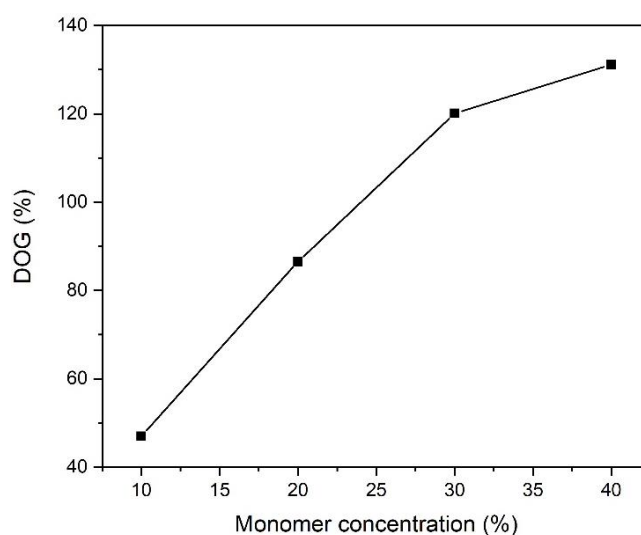


Figure 2. Variation of the degree of grafting with the monomer concentration for grafting of NVF onto PE/PP. Grafting parameters: 300kGy, 70°C and 1h.

3.1.3. Effect of reaction temperature. Figure 3 shows the effect of variation of reaction temperature on DOG of NVF onto PE/PP. The DOG increased with the increase in temperature from 40°C to 70°C. The results have shown that the rate of grafting increased

sharply during the initial period of the reaction. This trend is very popular in various grafting systems and can be attributed to the acceleration in chain mobility leading to the enhancement in the monomer diffusion to the grafting zone, which is accompanied by an increase in the rate of initiation and propagation. This behaviour is going along with grafting of VBC onto poly(hexafluoropropylene- co-tetrafluoroethylene) films [17] and grafting of dimethylamino ethylmethacrylate onto PE/PP nonwoven fabric [18]. Further temperature increases up to 70°C resulting in a higher amount of homopolymer contamination on the PE/PP substrates.

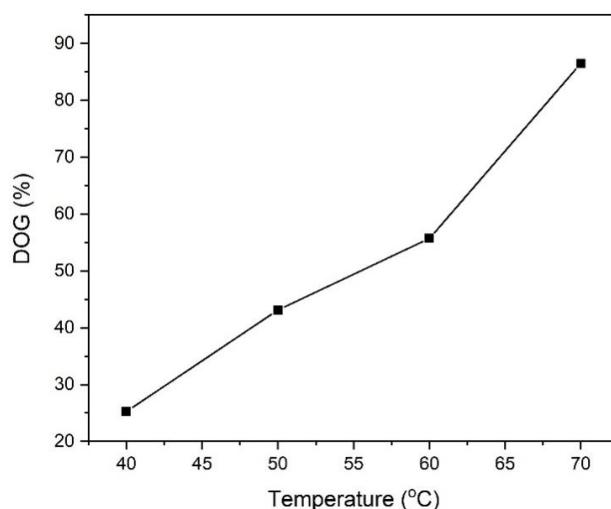


Figure 3. Variation of the degree of grafting with temperature for grafting of NVF onto PE/PP. Grafting parameters: 20 wt%, 300kGy and 1h.

3.2 Evidence of grafting

SEM images of pristine PE/PP and the corresponding poly(NVF) grafted PE/PP with two different DOG are shown in Figure 4. The average fibre diameter was found to increase by the incorporation of poly(NVF) grafts. For instance, the average diameter of fibre of the pristine PE/PP increased from 15 to 20 mm by incorporation of poly(NVF) and rise to 22 mm when DOG increased from 40 to 60. The hydrolysis resulted in no significant changes in fiber size. It can be resolved that the grafted monomer unit is assumed to remain the same before and after hydrolysis.

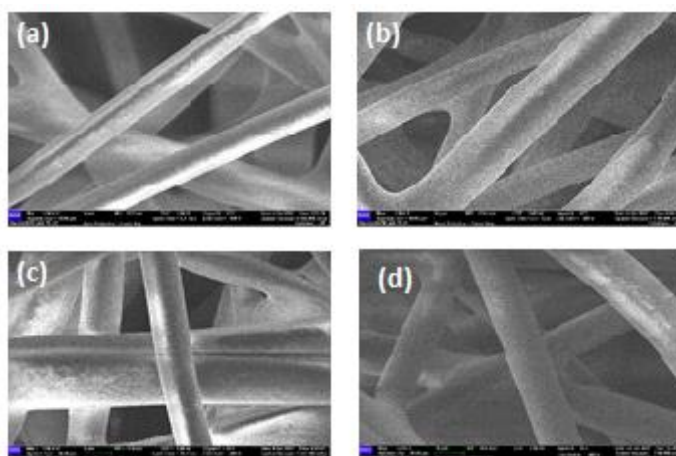


Figure 4. The SEM images of a) pristine PE/PP b) poly(NVF) grafted PE/PP with DOG of 40% and c) poly(NVF) grafted PE/PP with DOG of 60% (d) hydrolysed poly(VAm).

Figure 5 shows FTIR spectra of pristine PE/PP and grafted PE/PP substrates at different degrees of grafting. The incorporation of poly(NVF) grafts to PE/PP substrate was confirmed by the appearance of new characteristic peaks such as the absorption band at 1270 and 1354 cm^{-1} which is due to N–H stretching vibration of pendant chain of NVF molecule resulted from the interaction between N–H bending vibration and –CN stretching vibration, respectively. The peak at 1750 cm^{-1} which appeared in both grafted PE/PP with different DOG was assigned for to C=O stretching vibration of secondary amide present in the pendant chain attached to PE/PP. It is evident that NVF was successfully grafted on PE/PP fibrous substrates. The hydrolysis of amide to amine is confirmed by the disappearance of a sharp peak at 1750 cm^{-1} and the appearance of a broad peak at 3360 cm^{-1} .

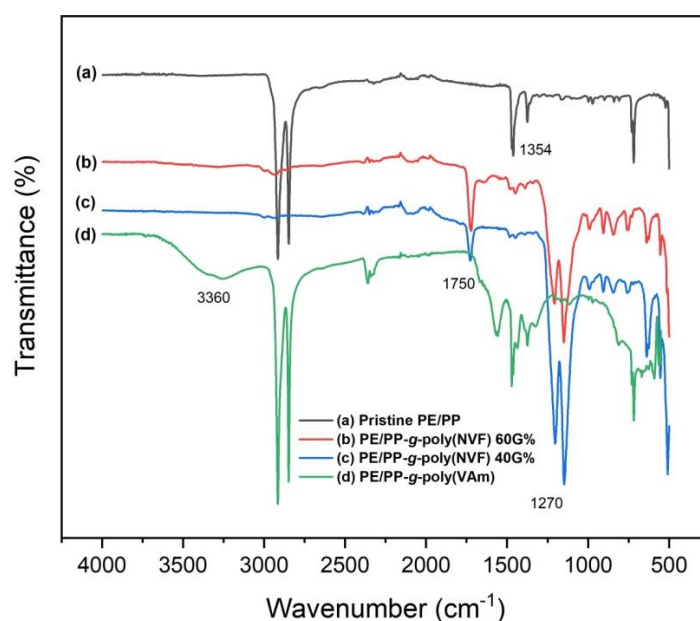


Figure 5. FTIR spectra of original PE/PP substrate, grafted PE/PP with different degree of grafting and PE/PP-g-poly(VAm).

3.3. CO₂ adsorption

Figure 6 shows CO₂ adsorption isotherms for pristine PE/PP substrate, PE/PP-g-poly(NVF) and PE/PP-g-poly(VAm) fibrous adsorbents (DOG = 131%) under different pressures at 30°C. As can be seen the amounts of CO₂ adsorbent increased with the increase in the pressure in all substrates. However, it can be obviously seen that CO₂ adsorption capacity of PE/PP-g-poly(VAm) fibrous adsorbent is far greater than that of PE/PP-g-poly(NVF) substrate which in turn has 3 times (0.25 mmol g^{-1}) higher CO₂ capacity than pristine PE/PP substrate (0.08 mmol g^{-1}) at all pressure values. The hydrolysis of amide to amine provides basic active sites on adsorbent surfaces that improves the affinity for CO₂ adsorbates.

Particularly, the isotherm of PE/PP-g-poly(NVF) showed a sharp increase until a pressure of 5 bar beyond which it continued to increase but at a slower rate and tended to level off with the pressure increase up to 30 bar. This isotherm seems to follow type I, which resembles Langmuir adsorption model in which monolayer chemisorption in microporous structure is taking place [19]. A maximum CO₂ adsorption capacity of 1.32 mmol g^{-1} was achieved at 30 bar and at room temperature. It can be concluded that RIG of NVF onto PE/PP substrates and subsequent hydrolysis reaction is highly effective and shorter route for imparting CO₂ capturing group. Moreover, the CO₂ adsorption capacity of this fibrous adsorbent is a pressure dependent.

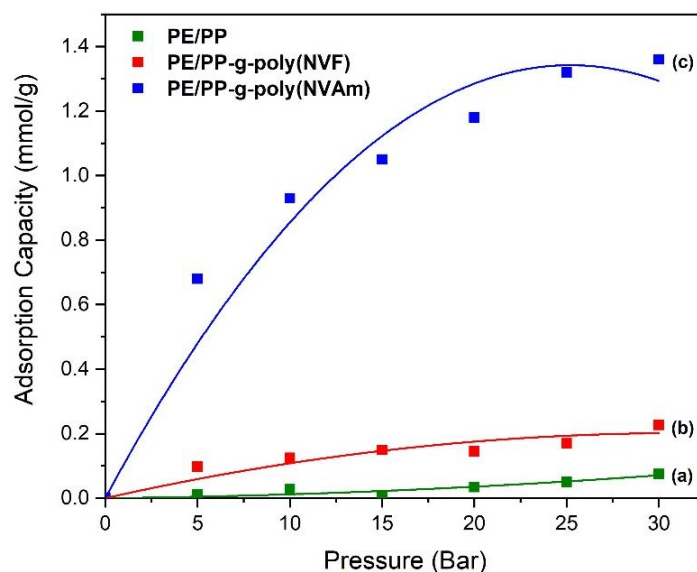


Figure 6. The adsorption capacity of original PE/PP substrate, grafted PE/PP and hydrolysed PE/PP

4. Conclusion

In this study, NVF was grafted onto pre-irradiated PE/PP by RIGP followed by hydrolysis to introduce amine functional group for CO₂ adsorption. The reaction parameter during the grafting was optimised to obtain desired DOG. The DOG was found to be the function of the reaction parameters such as irradiation dose, monomer concentration and reaction temperature. The results of SEM and FT-IR revealed that NVF was successfully grafted onto the PE/PP nonwoven sheet, and the hydrolysed copolymer has high potential to be applied as CO₂ adsorbent.

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