ผ้าไม่ทอพอลิพรอพิลีนที่ถูกเพิ่มหมู่ฟังก์ชันคาร์บอกซิเลทสำหรับการกำจัดไอออนของแคดเมียม

Carboxylate-Functionalized Polypropylene Nonwoven Fabrics for Removal of Cadmium Ions

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บทคัดย่อ

งานวิจัยนี้อธิบายการปรับปรุงวัสดุผ้าไม่ทอสังเคราะห์สำหรับการกำจัดไอออนของแคดเมียมจากน้ำเสีย ประสิทธิภาพด้านความจุในการจับกับแคดเมียมของผ้าพอลิพรอพิลีนก่อนและหลังการปรับปรุงด้วยหมู่ฟังก์ชันคาร์บอกซิลเลท ผ้าไม่ทอพอลิพรอพิลีนได้ถูกเพิ่มหมู่ฟังก์ชันด้วยการกราฟท์พอลิเมอร์ที่ถูกเหนี่ยวนำด้วยรังสีแกมมาของมอนอเมอร์ชนิดกรดอะคริลิกและกรดไอทาคอนิก ในงานวิจัยนี้ได้มีการศึกษาผลกระทบของปริมาณรังสีแกมมาและระยะเวลาในการให้ความร้อนในระหว่างการกราฟท์พอลิเมอร์ และมีการวิเคราะห์ทางสเปกโตรสโคปีเพื่อตรวจสอบคุณลักษณะของหมู่ฟังก์ชันของพอลิอะคริลิกแอซิดและพอลิไอทาคอนิกแอซิดที่ถูกปรับปรุงผ้าพอลิพรอพิลีนด้วย Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) จากการตรวจสอบพบว่าสเปกตรัมจาก ATR-FTIR แสดงถึงหลักฐานของหมู่คาร์บอกซิลของผ้าพอลิพรอพิลีนหลังจากถูกกราฟท์ด้วยพอลิอะคริลิกแอซิดเพียงเท่านั้น คุณภาพของเส้นใยและลักษณะสัณฐานวิทยาของพื้นผิวของเส้นใยพอลิพรอพิลีนทั้งก่อนและหลังการกราฟท์พอลิเมอร์ถูกวัดด้วยกล้องจุลทรรศน์แบบใช้แสงกล้องและจุลทรรศน์อิเล็กตรอนแบบส่องกราด ประสิทธิภาพของผ้าไม่ทอพอลิพรอพิลีนทั้งก่อนและหลังการปรับปรุงด้วยพอลิอะคริลิกแอซิดได้ถูกตรวจสอบด้วยการทดสอบการซึมผ่านของน้ำ (water permeability) และการทดสอบหาค่าความจุในการดูดซับแคดเมียมแบบสถิต (static cadmium adsorption capacity) จากการทดสอบพบว่าการกำจัดแคดเมียมของผ้าพอลิพรอพิลีนทั้งก่อนและหลังการปรับปรุงด้วยพอลิอะคริลิกแอซิดมีค่าไม่ต่างกัน เนื่องจากการกราฟพอลิเมอร์มีผลกระทบต่อคุณสมบัติความชอบน้ำของวัสดุพอลิพรอพิลีนไม่เพียงพอ

คำสำคัญ: การกราฟท์พอลิเมอร์ ผ้าไม่ทอ การกำจัดแคดเมียม พอลิพรอพิลีน พอลิอะคริลิกแอซิด

Abstract

This research describes a modification of synthetic nonwoven materials for cadmium ion removal from wastewater. The performance of cadmium binding capacities of polypropylene (PP) fabrics with and without the modification of carboxylate functional groups was studied. PP nonwoven fabrics were functionalized by gamma radiation-induced polymer grafting of an acrylic acid and an itaconic acid monomers. Effects of gamma radiation dose and heating time on polymerization grafting were studied. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) analyses were performed to characterize the functional groups of poly (acrylic acid) (PAA) and poly (itaconic acid) (PIA) modified PP fabrics. ATR-FTIR spectra showed evidence of carboxyl groups of PP fabrics after grafting by only PAA. The fiber quality and surface morphology of PP fibers before and after polymer grafting were examined by optical microscope and scanning electron microscopy. Water permeability and static cadmium adsorption capacity measurements were conducted to show the performance of PP fabrics before and after PAA modification. It was found that the static cadmium adsorption capacities of PAA functionalized PP fabrics were not different from PP fabrics without the modification due to too low impact of hydrophilic property by PAA grafting.

Keywords: Polymer grafting, nonwoven, cadmium removal, polypropylene, poly (acrylic acid)

1. Introduction

Currently, plastic industry has been growing consistently. Consequently, plastic wastes such as polyethylene (PE) and polypropylene (PP) has been generated and causing environmental issues. It was reported that in 2015, only 9% of global plastic waste had been recycled, 12% was burned, and 79% was disposed to landfills [1] . PP, a thermoplastic polymer, has been used widely for various applications due to low cost, stability and good chemical and heat resistant properties [2]. The literatures also showed that PP materials were produced 7,190 thousand tons while only 40 thousand tons were recycled [3]. As a result, only 0.55% of PP materials were recycled due to difficulty and costliness of recycle process. Moreover, PP materials were not degradable easily by microorganisms [4]. Furthermore, the most of recycling process was used for nonfiber plastic waste while there was a low level of plastic fiber recycling [1]. Therefore, it was possible that textile wastes are incinerated or dumped to the landfill site [1]. To deal with this issue, reusing process of PP was proposed in this paper.

Generally, PP materials show hydrophobic property [5] that is not suitable for specific purposes such as water purification. Functionalization was selected to be a process to reuse PP for the specific purpose. Polymer grafting by irradiation-induced polymerization method with gamma ray was used to functionalize PP materials because of a simple procedure [6]-[8]. Due to hydrophobic property of PP, hydrophilic polymers such as poly (acrylic acid) (PAA) and poly (itaconic acid) (PIA) were chosen to convert property of PP to have a strong affinity for water. Several literatures showed that PAA was easily grafted onto PP. However, it is challenging to graft PIA onto PP surfaces due to too slow grafting rate [9]. Additionally, carboxylate-functional groups enable to ion exchange with toxic positive ions such as cadmium and nickel in wastewaters [9]-[12]. Cadmium was selected to be a representative of highly toxic heavy metals since it causes an acute and chronic disorder called Itai-Itai disease even in low levels [9]. Furthermore, cadmium adsorption onto carboxylate modified PP surfaces in aqueous solution has never been studied previously.

In this work, PP nonwoven was reused by surface chemistry modification. Acrylic acid (AA) and itaconic acid (IA) were used as monomers for polymer grafting onto PP surfaces by irradiation-induced polymerization method using gamma ray with different grafting conditions. The final modified products were characterized and tested for membrane performances including water permeability measurement and static cadmium adsorption capacity.

2. Experimental Section

2.1 Materials

Acrylic acid with inhibitor (AA, 99%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), ethanol (EtOH, reagent grade), itaconic acid (IA, ≥99%) and Sodium hyrodoxide (NaOH) were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received. Silica gel (SiO_2) was purchased from EMD Millipore Corporataion (Billerica, MA, USA). PP nonwoven fabrics were obtained from the Department of Textile Engineering at Rajamangala University of Technology Thanyaburi, Thailand.

2.2 Surface Modification

PP nonwoven fabric was cut into 3 × 3 cm^2 and placed into glass bottle 20 mL for 7 samples. AA solution was removed inhibitor by passing through SiO_2. Thereafter, monomers including AA and IA solutions (10 wt% and 5 wt% in EtOH respectively) for 15 mL were added into each bottle of prepared PP nonwoven samples. The whole preparation step was done inside nitrogen glove box to prevent a reaction with oxygen gas.

All samples were placed inside Gamma Cell 220 (Nordion, Canada) with velocity of 0.89 Gy/s for different duration times (1 and 5 h) to obtain different radiation intensities (3.2 and 16.0 kGy) and heated in water bath at 60 to 70 °C for different duration times (1,3 and 5 h) following Table 1. The nomenclatures of samples in Table 1 were representatives of grafted polymer types, gamma radiation inducing times, and heating times for example PPAA_1_1 sample was PAA-grafted PP nonwoven with 1 h of gamma radiation time and 1 h of heating time. Afterward, deionized (DI) water was used to rinse samples for 2 times to remove the unpolymerized monomers (AA and IA). Before characterizations and testing of performance properties, all obtained PP nonwoven samples were dried in oven at 70° C for 2 hrs.

2.3 Characterizations

Surface Chemistry. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) technique was operated by using PerkinElmer Frontier model (Waltham, MA, USA) and Omnic software. All samples were measured using number of scans at 16 and 4 cm resolution with an automatic signal. Before each sample measurement, scanning background was done. An ATR correction was made to the spectrum, and manual baseline correction was purposed consistently for all spectra.

Physical properties. Tensile strengths of unmodified PP and PPAA_1_1 samples were measured by a tensile tester (Instron Tensile Tester Model 5560, Norwood, MA, USA) using the procedures outlined in ASTM D5035-06 (strip test) for nonwoven fabrics [13] with a 10 kN load cell maintaining 25±2 mm gage length and 50 mm/min crosshead speed. Both samples were cut to rectangle shape (1 cm × 6 cm) for at least 15 pieces before testing.

Table 1 Radiation induced polymerization conditions.

	Sample name	Materials	Monomer	% Polymer by wt	Solvent	Gamma Ray (time, h)	Heating (time, h)
1	PPAA_1_1	PP	Acrylic acid	10%	Ethanol	1	1
2	PPAA_1_5	PP	Acrylic acid	10%	Ethanol	1	5
3	PPAA_5_1	PP	Acrylic acid	10%	Ethanol	5	1
4	PPAA_5_5	PP	Acrylic acid	10%	Ethanol	5	5
5	PPIA_5_1	PP	Itaconic acid	5%	Ethanol	5	1
6	PPIA_5_3	PP	Itaconic acid	5%	Ethanol	5	3
7	PPIA_5_5	PP	Itaconic acid	5%	Ethanol	5	5

2.4 Performance Properties

Flux measurement. Unmodified PP and PPAA_1 _1 fabric samples were cut into round shape and put into a 200 mL direct-flow stirred cell of Amicon (Model 8200, EMD Millipore, Billerica, MA) to conduct the flux measurements. DI water was delivered to the stirred cell linked to a nitrogen cylinder to apply constant inlet pressures at 34.47, 48.26, and 68.95 kPa, which were read by a pressure gauge. The filtrate masses, filtration times, inlet pressures and sample area contact sizes were used to calculate the permeabilities of each experiment. At each applied pressure, 3 measurements were done with rising applied pressures to check the membrane compaction following the procedure in the literature [9].

Static cadmium adsorption capacity. Cadmium solutions with concentrations of 1000 mg/L in DI water were formulated from $Cd(NO_3)_2 \cdot 4H_2O$ powder and diluted to 10, 60, and 100 mg/L. PAA and PIA-modified nonwoven fabrics were hydrolyzed by sodium hydroxide solution (0.25 M) for 1 h. Unmodified and hydrolyzed nonwoven fabrics were cut into small pieces and weighed before soaking in 2 solutions of cadmium ions (3 mL) for longer than 16 h to reach equilibrium following the procedure in the literature [9]. Cadmium ions concentrations before and after adsorption with unmodified and successfully modified PP samples were examined by inductively coupled plasma optical emission spectroscopy or ICP-OES (Perkin Elmer, 2000DV model, Waltham, MA, USA). The peak areas for cadmium ions both before and after adsorption were measured 3 times for each sample and also calibration solutions. The static cadmium adsorption capacity were calculated from the loss of cadmium (mg) after adsorption process divided by fabric sample weight. The standard deviation represent uncertainties of results between 2 samples.

3. Results and Discussion

3.1 Characterizations

ATR-FTIR. The characteristics of the functional groups on the surface of PP nonwoven samples with and without modification of PAA and PIA polymers by Gamma radiation induced-polymerization were conducted by using ATR-FTIR spectroscopy. Fig. 1 and Fig. 2 display the FTIR spectra of unmodified, PAA and PIA modified PP nonwoven and IR adsorptions of functional groups of PP, PAA and PIA were shown in Table 2. According to Fig. 1, PAA modified PP nonwoven obviously exhibited the absorbance by C=O stretching of COOH at 1710-1730 cm^{-1}

as reported in the literature of PAA functionalized membranes [6]-[8].

Unfortunately, the absorbance by C=O stretching of COOH did not appear for the spectra of PIA modified PP fabrics based on Fig. 2. This evidence shows the successful of surface modification of only PAA on PP surfaces by Gamma-induced irradiation polymerization with different conditions. However, PP was not be able to be grafted by PIA. This might be caused by slow kinetics of PIA polymerization as shown in the literature that up to 60 h was required to obtain PIA grafted onto membranes materials [14].

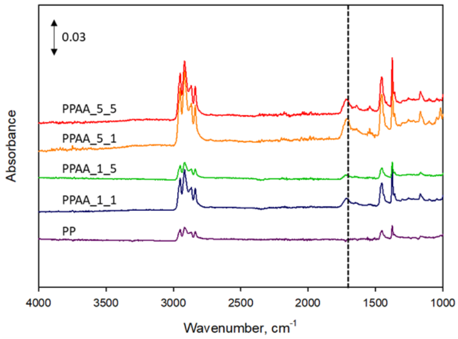

Figure 1 ATR-FTIR spectra of unmodified and PAA-modified PP nonwoven fabrics.

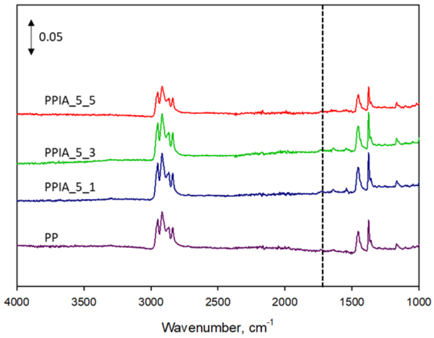

Figure 2 ATR-FTIR spectra of unmodified and PIA-modified PP nonwoven fabrics.

Table 2 ATR-FTIR absorbance.

Wavenumber (cm^{-1})	Functional groups
2950	CH_3 asymmetrical stretching of polypropylene
2920	CH_2 asymmetrical stretching of polypropylene
2870	CH_3 stretching of polypropylene
1710-1730	C=O stretching of COOH

OM images. Fig. 3 provides representative OM images of unmodified PP and PPAA_1_1 samples. In relation to Fig. 3, there is no difference in terms of fiber quality and sizes between PP with and without modification of PAA. However, from OM images, it is still unclear about surface morphology of fiber surfaces after functionalization.

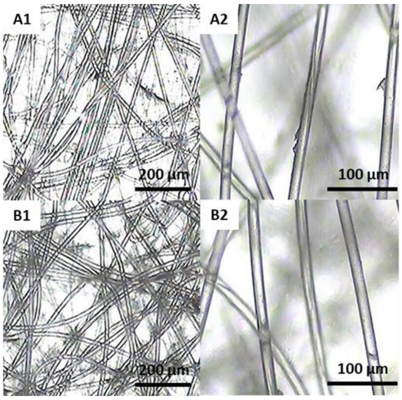

Figure 3 OM images of unmodified PP nonwoven (A1: 4× and A2: 10× magnifications) and PPAA_1_1 (B1: 4× and B2: 10× magnifications).

SEM images. Since SEM could be captured the fiber surfaces at higher magnification than OM, it was used to investigate the surface morphology of unmodified PP and PPAA_1_1 samples as shown in Fig. 4. It was found that the individual fibers were slightly merged together and there are agglomerates attached on the fiber surfaces for PPAA_1_1 sample (B1 and B2) while unmodified PP nonwoven exhibited smooth surfaces (A1 and A2). The result of agglomerates might be caused by polymer grafting as discussed by Barsbay and Güven that PAA grafted by conventional technique exhibited polymer gelation on PE/PP surfaces [8] and it was agree with the result of ATR-FTIR spectra as stated previously.

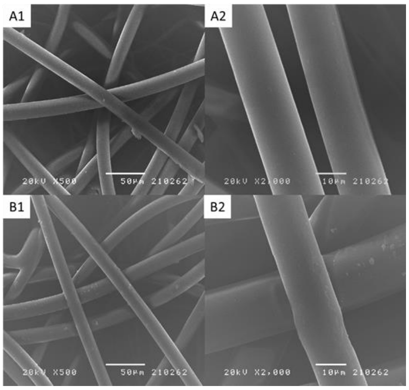

Figure 4 OM images of unmodified PP nonwoven (A1: 4× and A2: 10× magnifications) and PPAA_1_1 (B1: 4× and B2: 10× magnifications).

Physical properties. The high strength of fabrics is required for membrane system especially with direct-flow filtration. The maximum loads and extension at break values of unmodified PP nonwoven and PPAA_1_1 samples were measured. According to Fig. 5, the average maximum loads of PP samples barely increased after PAA grafting. Conversely, the average extension at break of fabric samples slightly decreased insignificantly after functionalization. Possibly, the higher strength is a result of polymer agglomerates attachment on fiber surfaces as shown in SEM images (Fig. 4). The actual tensile test values are shown in Table 3.

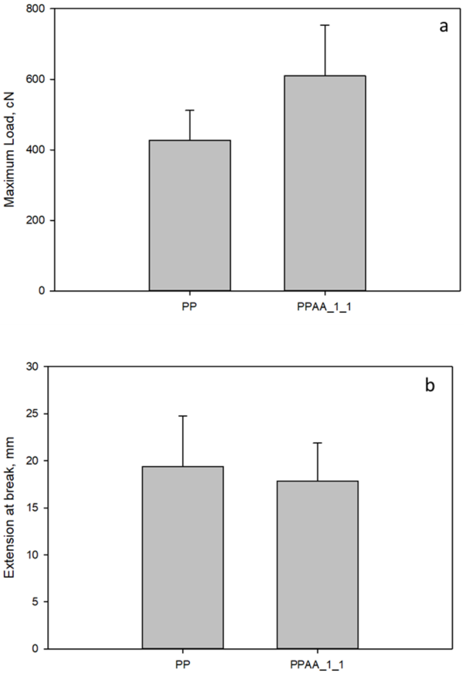

Figure 5 Tensile measurements: (a) Maximum load (cN) and (b) Extension at break (mm).

Table 3 Tensile test values.

Sample	Maximum Load (cN)	Extension at Break (mm)
PP	427.47 ± 84.5	19.39 ± 5.37
PPAA_1_1	609.54 ± 144.36	17.86 ± 4.04

3.2 Performance Properties

Flux measurement. Permeability experiments were conducted to compare the flowabilities of pure water throw PP fabrics. Fig. 6 demonstrates the water permeability of PPAA_1_1 insignificantly increased after the PAA functionalization. Error bars indicate standard deviation obtained from 3 times of each sample measurement. This negligible changes might be a result of polymer grafting on the PP fiber surfaces. Even though the decrease of permeabilities due to fabrics compaction with higher applied pressures was observed, PPAA_1_1 still exhibited 800 to 1000 times higher water permeability values than conventional membranes such as reverse osmosis (RO) and nanofiltration (NF) [9].

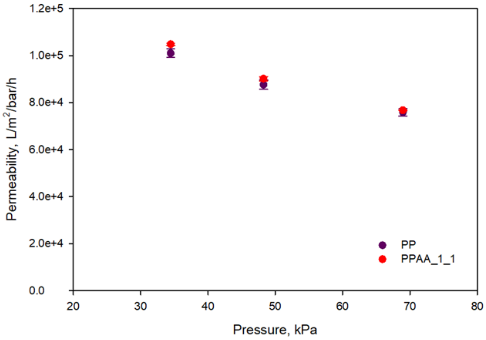

Figure 6 Water permeability measurements.

Static cadmium adsorption capacity. Only PP nonwoven fabrics with successful PAA grafting were investigated the static adsorption capacities under different cadmium ions initial concentrations (10-100 mg/L) at room temperature. Usually, carboxylate functional groups of polymers reveal ion exchange property with positive ions such as cadmium ion (Cd^{2+}) [9]-[12]. Langmuir model was generally applied to explain ion exchange process of this type of adsorption material [9]-[10]. Unfortunately, based on Fig. 7, the PAA modified PP nonwoven fabrics did not show any improvement of cadmium binding property. It was also observed that functionalized PP was not completely immersed in cadmium solutions. It might be explain that the interaction between targeted ions, solvents and adsorption materials is an important factor for adsorption ability [5]. Therefore, although PAA displays hydrophilicity which is an advantage for metals adsorption under water system, in this case the polymer chain might not be long enough to shift the hydrophobic property of PP fabrics to be hydrophilic to be able for capturing cadmium ion in aqueous solutions. It was also shown in the literatures that the radiation dose or time and amount of monomers affected to degree of grafting [15], [16]. For that reason, longer radiation time and more amount of monomers to obtain higher degree of grafting will be considered for further work. It was also reported that the water permeability increased with ion exchange value due to increased hydrophilicity of PP membranes [17]. That means the hydrophilic property of PP material is a main factor to show ability of PP ion exchange material in aqueous system. To apply PAA grafted PP fabric to more appropriate applications, it possibly can be used in other systems such as nonpolar systems [18], [19].

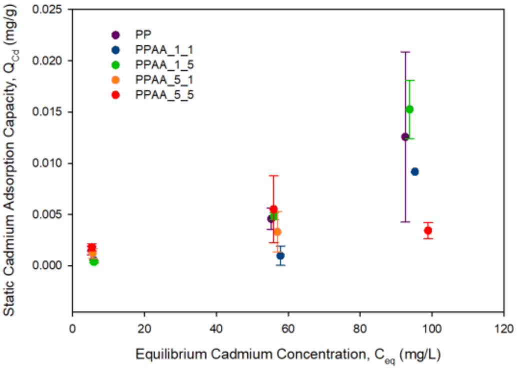

Figure 7 Static cadmium adsorption capacity.

4. Conclusions

Carboxylate functionalized materials were created by polymer grafting with Gamma ray inducing onto the surfaces of PP nonwoven fabrics for metals ions removal applications. PAA and PIA were selected to improve the hydrophilic property of PP fabrics. Although ATR-FTIR showed the success of PAA modification, modified samples exhibited opposite results of cadmium adsorption capacity in hydrophilic system due to too short polymer chain of PAA. However, different grafting conditions to obtain longer polymer grafting chain and cadmium adsorption experiment in hydrophobic system should be further studied to develop the materials performance. Also, hydrophilicity of materials should be measured by contact angle experiment to confirm the result of surface modification.

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