PC06: กราฟต์โคพอลิเมอไรเซชันของเมทิลอะคริเลตบนเส้นใยเซลลูโลสโดยการใช้รังสีแกมมา

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บทคัดย่อ

งานวิจัยนี้ทำการเตรียมกราฟต์โคพอลิเมอร์ของเมทิลอะคริเลต (Methyl Acrylate, MA) บนเส้นใยเซลลูโลส โดยใช้เทคนิค Simultaneous Irradiation ซึ่งใช้รังสีแกมมาเป็นตัวริเริ่มปฏิกิริยาการกราฟต์ ตัวแปรหลักที่ทำการศึกษาได้แก่ ปริมาณรังสี ความเข้มข้นของมอนอเมอร์ และอัตรส่วนของเมทานอลต่อน้ำ ในการทดลอง Trunk polymer ที่ใช้คือเส้นใยเซลลูโลสของผ้าฝ้าย 100 % ซึ่งมีน้ำหนักต่อหน่วยพื้นที่ 150 กรัมต่อตารางเซนติเมตรสภาวะที่เหมาะสมที่สุดต่อการเกิดปฏิกิริยากราฟต์โคพอลิเมอไรเซชันเมทิลอะคริเลตบนเส้นใยเซลลูโลส คือในสารละลายผสมของเมทิลอะคริเลต 45% (โดยปริมาตร) กับ สารละลายผสมเมทานอลต่อน้ำ (ในอัตราส่วน 1:1) ที่ปริมาณรังสี 50 กิโลเกรย์ สภาวะดังกล่าวให้ค่า Degree of Grafting เท่ากับ 135 (6.67 มิลลิโมลต่อกรัม ของหมู่ เมทิลอะคริเลต) วิเคราะห์ลักษณะสมบัติของโคพอลิเมอร์ด้วย Fourier transform Infrared (FTIR) Spectroscopy

คำสำคัญ: กราฟต์โคพอลิเมอร์ เมทิลอะคริเลต เซลลูโลส รังสีแกมมา

Graft Copolymerization of Methyl Acrylate onto Cellulose Fiber by Gamma Radiation

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Abstract

This research investigated the graft copolymerization of methyl acrylate (MA) onto cellulose fiber by simultaneous irradiation technique induced by gamma radiation. Major parameter included total dose (kGy), monomer concentration, and methanol-to-water ratio. The 100% cotton fabric of 150 g/cm^2 was used as a trunk polymer. The optimum condition for grafting methyl acrylate onto cotton fabric was found at the following condition: mixture

solution of 45% MA (v/v) and methanolic solution (Methanol:H_2O = 1:1) at the radiation dose of 50 kGy. The degree of grafting at this condition was 135 (6.67 mmol/g of MA group). Characterization of grafted copolymers was done by FTIR spectroscopy.

Keywords: Graft Copolymer, Methyl Acrylate, Cellulose, Gamma Radiation

1. Introduction

Radiation-induced graft polymerization (RIGP) is a powerful method for preparation of polymeric materials with new properties for practicable application.[1-3] The advantages of this method include: (1) it can give uniform and rapid creation of active radical sites,allowings a high degree of penetration of graft chains in the polymer matrix, (2) it can be effectively and conveniently carried out at room temperature, (3) polymer containing functional groups con be added without significant changes in the properties of the trunk polymers, (4) various side reactions are minimal, (5) a wide range of shapes and qualities of polymers can be selected as a trunk polymer according to mechanical, thermal, and chemical stability required by the practicable applications,and (6) the distribution of the introduced functional groups is easily achieved by controlling the irradiation energy.

Natural polymers such as starches, cellulose, chitin and chitosan are natural materials with high potential for various applications from medical to environmental, due to their unique properties, especially biodegradability and biocompatibility. The development of novel materials by radiation processing is therefore a promising method to increase the values of these natural polymers which are abundant and inexpensive.

Cotton is a natural polymer fiber that consists of cellulose with 1, 4 D-glucopyranose as its repeating unit.[4] Although cellulose has good properties, it also has some undesirable properties such as low tensile strength high, and moisture transmission. Grafting of polymer by ionizing radiation can modify their physical and chemical properties such as hydrophilic or hydrophobic character, thermal stability and resistance to chemical and biological reagents.[5-7] In this work, methyl acrylate (MA) was grafted onto cellulose fiber by simultaneous irradiation induced by gamma-ray. Graft polymerizations were studied with regard to various parameters of importance: absorbed dose, concentration of MA, and methanolic solution.

2. Experimental

2.1 Materials

Cotton fabric was obtained from Thai Num Chok Company. Before use, it was extracted by boiling in ethanol for 5 h followed by boiling in 1% sodium hydroxide solution for 3 h. Treated cotton was then repeatedly washed with distilled water until neutral washing were obtained. The sample was dried at 50 ^{o}C and stored in desiccators for future use. Reagent grade methyl acrylate was purchased from Aldrich, and was used as received. All the other chemicals and solvents were also used without further purification.

2.2 Graft copolymerization of methyl acrylate onto cellulose fiber

The trunk polymer fabrics were cut into a 3 cm × 3 cm rectangle and immersed in methyl acrylate solution. The samples in glass tube were purged with N_2 gas for 5 minutes before tightly closed, and the irradiated under gamma ray (Co-60 source,Gammacell 220 Excel). After irradiation, the sample was removed from the tube, and washed several times with dimethylformamide (DMF). Homopolymer was extracted off the grafted copolymer by soxhlet extraction in DMF for 40 hours. After the grafted copolymer was dried. Degree of grafting (Dg) was determined by the following equation :

$$Dg\ (\%) = (W_1 - W_0) / W_0 \times 100$$

Where W_0 and W_1 are the weights (g) of trunk polymer and graft copolymer , respectively.
The density of MA graft chains was determined as follows:

$$MA\ (mmol/g) = [(W_1 - W_0) / W_1] \times (1{,}000/M_{MA})$$

Where the molecular weight of MA (M_{MA}) is 86.09.

2.3 FTIR Analysis

Fourier transform infrared (FTIR) spectroscopy was done using Bruker, Tensor 27.

The wave number range was used in this study was 600-3600 cm^{-1} in order to detect the function groups of trunk, grafted copolymer. Acquired in absorbance mode, the spectra were collected with 16 scans co-added at a resolution of 2 cm^{-1}.

3. Results and discussion

3.1 Effect of absorbed dose on degree of grafting

Figure 1 shows the effect of absorbed dose on degree of grafting. The degree of grafting increased with increasing adsorbed dose up to 50 kGy. The increase in dose enhance the formation of the free radicals, resulting in high degree of grafting. The degree of grafting reached about 60% at the absorbed dose of 50 kGy. At the absorbed dose of 60 kGy, the degree of grafting decrease because of the degradation of the trunk polymer.

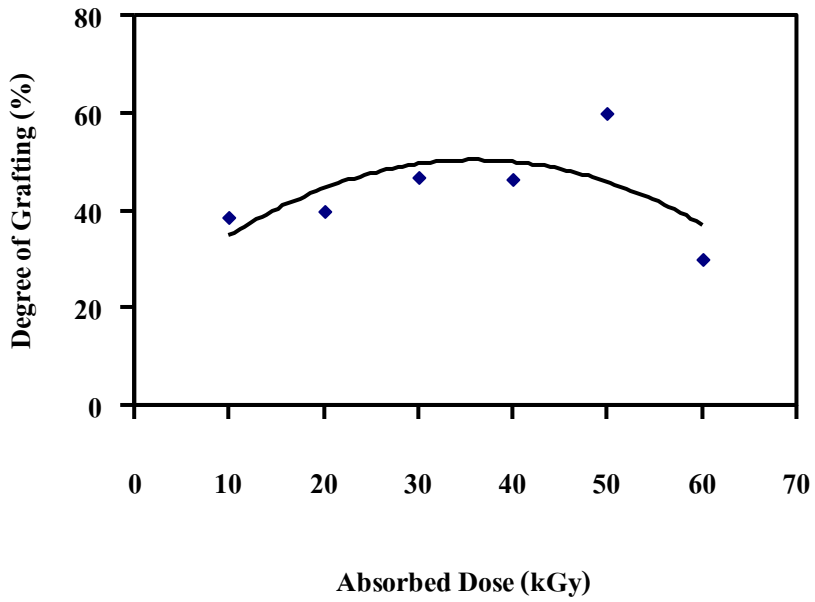

Figure 1. Effect of absorbed dose on degree of PMA grafting onto cellulose fiber : 20% MA(v/v), ((MeOH:H_2O), (v/v)) (1:1) and dose rate 0.1367 kGy/min.

3.2 Effect of MA concentration on degree of grafting

Figure 2 represents the effect of MA concentration on the degree of MA grafting onto trunk polymer. As the monomer concentration increased, the degree of grafting was found to be increased. At higher monomer concentration, radicals generated on the trunk polymer are able to interact with more

monomer molecules. However, at the monomer concentration higher than 50% v/v the mixture separated into two phases. The degree of grafting 135% at MA concentration 45% v/v.

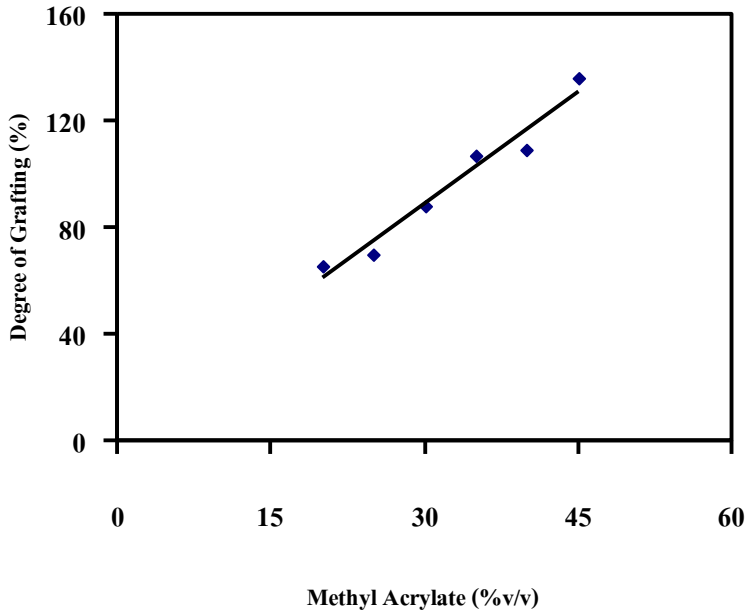

Figure 2. Effect of MA concentration on degree of grafting : ((MeOH:H_2O), (v/v)) (1:1) absorbed dose 50 kGy and dose rate 0.1367 kGy/min.

3.3 Effect of Methanolic solution (MeOH:H_2O) (v/v) on degree of grafting

Figure 3 show the effect of methanolic solution ([(MeOH:H_2O), (v/v)]) on degree of grafting. Suitable condition for high degree of grafting about 135% is ((MeOH:H_2O), (v/v)) (1:1)

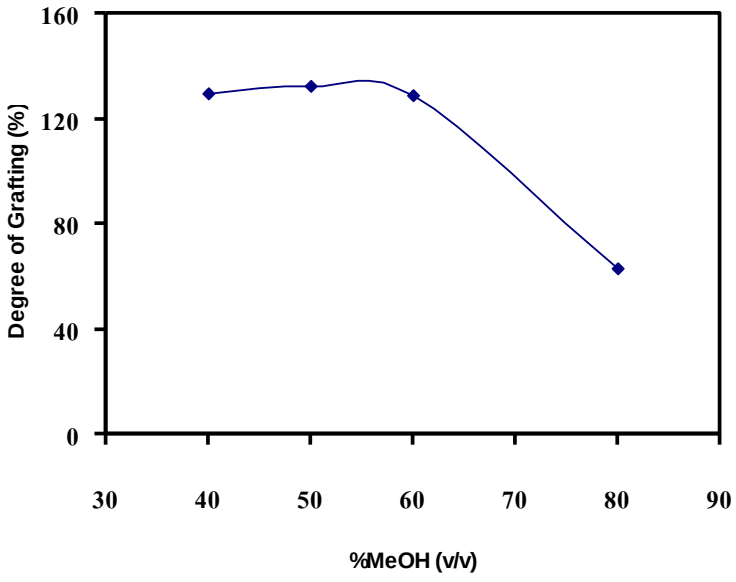

Figure 3. Effect of methanolic solution (MeOH:H_2O) (v/v) on degree of grafting 45% MA absorbed dose 50 kGy and dose rate 0.1367 kGy/min.

3.4 FTIR analysis

FTIR spectra of trunk polymer and graft copolymer are show in Figure 4. The FTIR spectrum of trunk polymer in Figure 4 (A) showed the characteristic absorption band at 3,311 cm^{-1} and 2,869 cm^{-1} due to O-H and C-H stretching mode of aliphatic carbon, respectively, and other absorption band at 1,051 cm^{-1} for C-H bending. While the FTIR spectrum of graft copolymer showed a new characteristic absorption band of an ester at 1,726 cm^{-1} due to C=O stretching mode in addition to the same absorption band of trunk polymer.

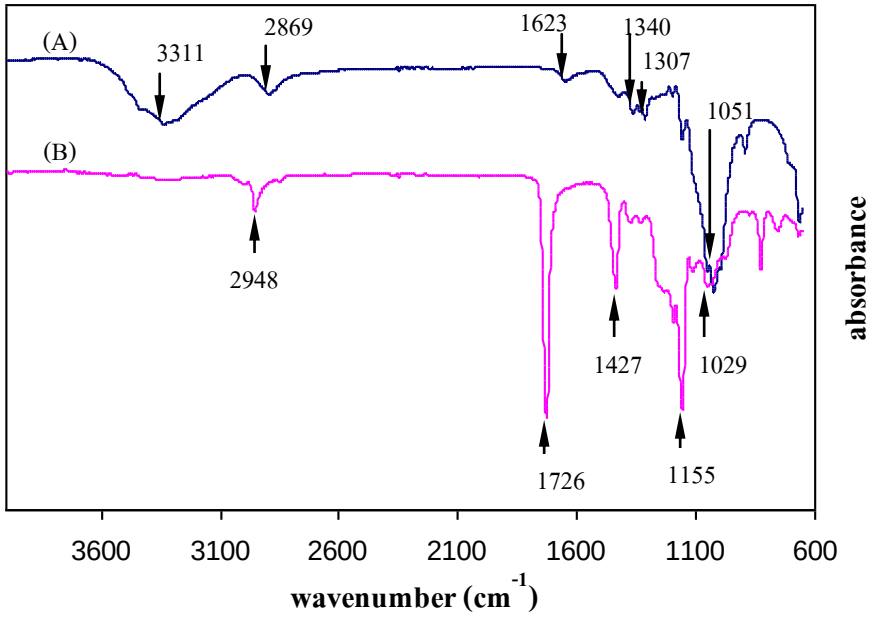

Figure 4 : FTIR spectra of (A) trunk polymer and (B) graft copolymer

4. Summary

PMA was successfully grafted onto the cotton cellulose fabric by simultaneous irradiation technique induced by gamma-ray. The grafted copolymer produced with 45%MA in methanolic solution (Methanol:H_2O) =1:1) using absorbed dose of 50 kGy (1:1) and dose rate of 0.14 kGy/min yielded 135% degree of grafting (6.67 mmol/g MA).

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