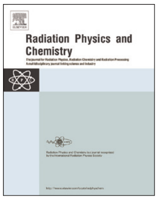
Radiation Physics and Chemistry 115 (2015) 143–147

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Modification of microcrystalline cellulose by gamma radiation-induced grafting

Jordan F. Madrid*, Lucille V. Abad

Chemistry Research Section, Atomic Research Division, Philippine Nuclear Research Institute, Department of Science and Technology, Diliman, Quezon City 1101, Philippines

HIGHLIGHTS

- RIGP of GMA onto microcrystalline cellulose was successfully performed.
- TGA, ATR–FTIR and wettability analysis confirmed successful grafting.
- XRD data showed that RIGP did not significantly affect the crystallinity of MCC.

ARTICLE INFO

Article history:
Received 20 April 2015
Received in revised form
6 June 2015
Accepted 27 June 2015
Available online 4 July 2015

Keywords:
Microcrystalline cellulose
Radiation-induced graft polymerization
Glycidyl methacrylate
Degree of grafting
Gamma radiation

ABSTRACT

Modified microcrystalline cellulose (MCC) was prepared through gamma radiation-induced graft polymerization of glycidyl methacrylate (GMA). Simultaneous grafting was employed wherein MCC with GMA in methanol was irradiated with gamma radiation in nitrogen atmosphere. The effects of different experimental factors such as monomer concentration, type of solvent and absorbed dose on the degree of grafting, Dg, were studied. The amount of grafted GMA, expressed as Dg, was determined gravimetrically. Information from grafted samples subjected to Fourier transformed infrared spectroscopy (FTIR) in attenuated total reflectance (ATR) mode showed peaks corresponding to GMA which indicates successful grafting. The X-ray diffraction (XRD) analysis revealed that the crystalline region of MCC was not adversely affected after grafting with GMA. The thermogravimetric analysis (TGA) data showed that the decomposition of grafted MCC occurred at higher temperature compared to the base MCC polymer.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Cellulose is a renewable polymer that is generally synthesized through photosynthesis in plants. It is an abundant biopolymer, renewable, biodegradable, and it can be processed to yield functionalized products. Microcrystalline cellulose (MCC), a plant-derived form of cellulose, possesses the merits of cellulose. Moreover, it has good mechanical properties which make it a good reinforcement in polymeric matrices (Wittaya, 2009). However, the inherent hydrophilicity of microcrystalline cellulose limits its dispersion and compatibility with hydrophobic matrices. This results to low interface bonding strength which affects the properties of composites containing MCC. Consequently, modification of MCC to enhance its hydrophobicity is of interest in order to improve its compatibility with various hydrophobic matrices.

Many methods have been proposed for the modification of cellulose, including chemical processing using acetic anhydride (Kim et al., 2002) and fatty acids (Freire et al., 2006) as reactive agents, surface derivatization (Hafren et al., 2006), application of surfactants (Bonini et al., 2002) and graft copolymerization (Takacs et al., 2005; Sokker et al., 2009).

Graft copolymerization is a well-established method for chemical modification of surfaces of both natural and synthetic polymers (Desmet et al., 2011; Sekine et al., 2010; Seko et al., 2010; Takacs et al., 2010; Wojnarovits et al., 2010). Different grafting techniques have been employed for surface modification of polymers, such as chemical grafting, photochemical grafting, plasma grafting, enzymatic grafting, living radical polymerization and radiation grafting using ionizing radiation (Wojnarovits et al., 2010). Surface functionalization via radiation-induced graft polymerization (RIGP) presents unique advantages over other methods. These advantages include the absence of catalyst or additives in the initiation step, homogeneous and temperature-independent initiation, relative ease of variation of the grafting parameters and that materials can be modified in different prefabricated form (O'Connell et al., 2008, Wojnarovits et al., 2010).

---

* Corresponding author.
E-mail addresses: jfmadrid@pnri.dost.gov.ph, jordan.madrid@yahoo.com.ph (J.F. Madrid).

http://dx.doi.org/10.1016/j.radphyschem.2015.06.025
0969-806X/© 2015 Elsevier Ltd. All rights reserved.

The advancement of grafting in cellulose based trunk polymers can be followed gravimetrically or through Fourier transformed infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Using FTIR in diffuse reflectance mode, Takacs et al. (2012) found that the peak intensity of C=O from glycidyl methacrylate is proportional to the degree of grafting. Gravimetry is commonly used to evaluate the degree of grafting after drying the samples subjected to ionizing radiation-induced grafting processes.

The objective of this work is to introduce glycidyl methacrylate (GMA) on MCC through RIGP using simultaneous irradiation method. Post-grafting reactions of GMA leads to addition of functional groups that imparts advantageous tailored properties to the surface of the base polymer. The effects of absorbed dose, solvent, and monomer concentration on the grafting of GMA onto MCC were studied. Pristine and grafted MCC were examined using FTIR in attenuated total reflectance (ATR) mode, XRD and TGA.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (Merck) with a density of 1.5 g/cm^3 was used for grafting. Analytical grade glycidyl methacrylate (GMA, $>97\%$, Aldrich), methanol ($>99.8\%$, Tedia), acetone ($>99.5\%$, Univar) and dimethylformamide ($>99.8\%$, RCI Labscan) were used as received. Deionized water was obtained from an ultra-pure water system Milli-Q plus (Millipore).

2.2. Grafting procedure

GMA was dissolved in methanol to prepare monomer solutions with different concentrations (2%, 5%, 7% and 10% w/w). A weighed amount of MCC was mixed with the GMA solution and then the MCC/GMA mixture was deoxygenated by bubbling with high purity N_2 gas for 10 min. The deoxygenated mixtures were irradiated with gamma rays from a ^{60}Co source (absorbed dose=2, 5, 10, 20 kGy; dose rate=approximately 8 kGy h^{-1}) at room temperature. The absorbed dose was determined by an ethanol–chlorobenzene dosimetry system which is traceable to the National Physical Laboratory, United Kingdom and prepared using ASTM 51538. After irradiation, the grafted MCC was filtered from the mixture. The homopolymers and unreacted monomers were removed by acetone in a Soxhlet extraction setup for 24 h. The samples were then dried at room temperature for 24 h.

2.3. Characterization

The degree of grafting (Dg, $\% = 100 \times (w_g - w_u)/w_u$) was determined from the weights of the dried samples before (w_u) and after (w_g) grafting. Two parallel samples were grafted and Dg value was reported as an average.

The X-ray diffraction (XRD) patterns were taken using an X-ray diffractometer setup, with Siemens Kristalloflex 760 X-ray Generator with Cu as anode material and Philips PW 1050/80 vertical goniometer equipped with a detector assembly, graphite crystal secondary monochromator and collimators. The X-ray diffractometer was set at 34 kV and 20 mA. Samples were scanned from $2\theta = 10–30°$ using the CuKα radiation ($\lambda = 1.54$ Å). The crystallinity index, I_C, of the grafted and ungrafted MCC was calculated according to Segal empirical equation: $I_C = (I_{002} - I_{am})/I_{002}$, where I_{002} is the maximum intensity of diffraction of the (0 0 2) lattice peak at a 2θ angle between 22° and 23° and I_{am} is the intensity of diffraction of the amorphous material, which is taken at a 2θ angle between 18° and 19° where the intensity is at a minimum (Rosa et al., 2012).

Fourier transformed infrared spectroscopy (FTIR) analysis was carried out using a Spectrum Frontier FT-IR Spectrometer System (Perkin Elmer) with Single Reflection Diamond Universal Attenuated Total Reflection (ATR) accessory (Golden Gate Single Reflection Diamond ATR, Specac-Teknokroma). Samples were scanned in the range 600–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

Thermogravimetric measurement of the fiber samples was carried out using a Shimadzu TGA-50 instrument with platinum cell. The samples were heated from 25 to 800 °C at a rate of 10 °C per minute and maintained under nitrogen atmosphere at flow rate of 50 mL min^{-1}.

3. Results and discussion

The extent of grafting, i.e. Dg, of different monomers on various polymeric matrices is dependent on different experimental variables such as type of solvent, monomer concentration and absorbed dose. In this work, the effects of each parameter on Dg and properties of grafted MCC were systematically studied.

3.1. Effect of solvent

In graft polymerization, the solvent plays important roles in several key aspects of grafting. Solvent radiolysis affects both monomer and the formation of active sites on microcrystalline cellulose (i.e. indirect effect of solvent). Free radicals are created upon irradiation of the solvent. These radicals are capable of abstracting hydrogen atom from cellulose which gives additional grafting sites (Sokker et al., 2009). The nature and presence of solvent also influences grafting kinetics and enhance uniformity of the grafted chains.

Fig. 1 demonstrates the variation of Dg with type of solvent for grafting of MCC with GMA in methanol, 1:1 water/methanol solution, 1:1 water/acetone solution, and dimethylformamide. It shows that Dg was dependent on the type of solvent used during grafting. Graft levels of GMA increased in the order of DMF $<$1:1 acetone/H_2O ~methanol $<<$1:1 CH_3OH/H_2O. The results indicated that the maximum weight increment was achieved when 1:1 CH_3OH/H_2O was used as the solvent for GMA. However, the obtained Dg might not be accurate because there were visible homopolymers attached to some of the grafted MCC even after extraction with acetone for more than 24 h. Although 1:1 CH_3OH/H_2O solvent system resulted to the highest Dg after grafting, it was not chosen for the subsequent grafting experiments because of too much homopolymer formation.

The cellulose used in this study was in microcrystalline form. Cellulose is a carbohydrate comprising of β-D-glucopyranose units bonded together by β-1,4-glycosidic linkages. The glucose units are

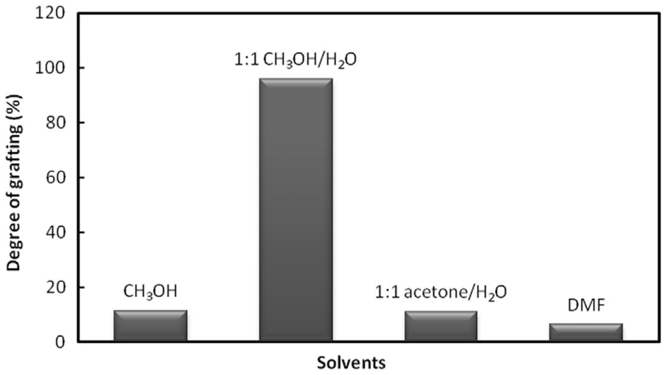


Fig. 1. Effect of solvent on the degree of grafting at 7% (w/w) GMA concentration, 10 kGy absorbed dose and 8 kGy/h dose rate.

Download English Version:

https://daneshyari.com/en/article/8252798

Download Persian Version:

https://daneshyari.com/article/8252798

Daneshyari.com