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Grafting of Cellulose: Synthesis and Characterization

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Abstract

In this study, cellulose methacrylate was firstly prepared by the reaction of methacryloyl chloride with primary OH groups on raw cellulose. The graft copolymerization of cellulose was made with our own synthesized 2-(4-Methoxyphenylamino)-2-oxoethyl methacrylate (MPAEMA) monomer by method of free radical polymerization. Cellulose, cellulose methacrylate and its graft copolymer (Cell.met-g-MPAEMA) were characterized by FT-IR spectra, elemental and thermal analysis.

Key Words: Cellulose, cellulose methacrylate, graft copolymer, 2-(4-Methoxyphenylamino)-2-oxoethyl methacrylate

1. Introduction

The importance of polymers is increasing as well as their utilization. Particularly, there is great progress towards the development and different properties of polymers with many industrial uses. Polymer and its derivatives have a wide range of uses due to their low density, low heat and electrical conductivity, high mechanical strength and flexibility, and they can be used at a low cost compared to other materials [1]. One of the most commonly used species to improve the functionality of polymers is acrylate and methacrylate derivatives. One of the most important properties of acrylate group monomers is their optical permeability. Due to their high light transmittance, good mechanical and thermal resistance, they have a wide range of applications. The application of monomers and polymers containing acrylate and methacrylate is very wide and this area is increasing day by day. Therefore, scientific studies have rapidly shifted towards this area. Apart from resistance to physical properties; its use as a biologically active substance has found work in many fields such as medicine, orthopedics, dentistry and dental fillings, drug delivery systems, biochemical sensors, and soft tissue studies [2-5].

The most important advantages of biopolymers are they being renewable, decomposable, and abundant in nature and low cost [6]. In recent years, due to pollution and global warming, unlike petrochemical polymers, environmentally friendly biopolymers with minimal harm to the environment are being studied and this issue is being developed [7]. Cellulose is a polysaccharide present in plants in which a large number of glucose molecules bind to the β-(1,4) glycoside bond. It is an odorless, tasteless and white color natural polymer which is obtained from cotton and wood. It has a linear structure and consists of repetitive units containing a long macro molecular chain [8-9]. The chemical structure of cellulose is shown in Figure 1. The cellulose molecule is a linear and natural polymer with three hydroxyl groups (-OH) on each monomer unit. The -OH groups have the property of binding another cellulose chain to the -OH group. These hydrogen bonds provide the hydrophilic properties of cellulose molecules. The modified cellulose obtained by various methods has a wide range of uses: Food, paint, cleaning and pharmaceutical industry, clothing, furniture fittings, varnishes-lacquers, films, explosives etc. [10]. Examples of chemically modified cellulose derivatives include cellulose acetate, methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and hydroxypropyl methylcellulose [10-13]. In order to obtain a semi-synthetic natural polymer which is a cellulose derivative, various chemicals containing functional groups are used. Many studies have been carried out on the synthesis and characterization of cellulose derivatives [7-17].

This study describes the esterification of a part of OH cellulosic groups with methacryloyl chloride as well as graft copolymerization of cellulose with certain monomer 2-(4-methoxyphenylamino)-2-oxoethyl methacrylate. Besides we have studied characterization and thermal stabilities behaviors of the graft copolymer.

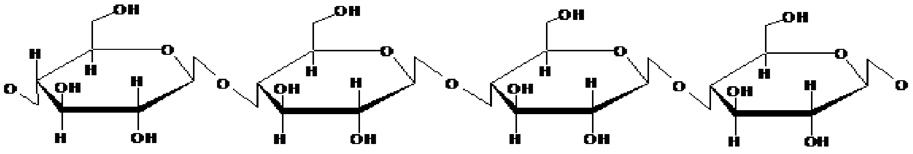


Fig.1. The chemical structure of cellulose

2. Materials and Methods

2.1. Materials and Instrumental Measurements

For monomer synthesis, p-methoxyaniline, chloroacetyl chloride, triethylamine, and sodium methacrylate, (Aldrich) were used as received. For to grafting cellulose, potassium tert-butoxide, methacryloyl chloride, acetonitrile (Aldrich) were used as received.

For FT-IR (Fourier Transform Infrared) spectrum; Perkin Elmer Spectrum One FT-IR spectrometer and Perkin Elmer Spectrum Two (UATR) IR spectrometer, for thermal analysis; Shimadzu TGA-50, and for elemental analysis; LECO-932 CHNS-O spectrometer were used.

2.2. Synthesis of Cellulose Methacrylate and its Graft Copolymer

In order to obtain the cellulose graft copolymer with MPAEMA (2-(4-methoxyphenylamino)-2-oxoethyl methacrylate) monomer, cellulose methacrylate was first synthesized. Cellulose methacrylate (Cell.met) [11,16] and MPAEMA monomer [1,5] were synthesized in a similar method to our previous work. The synthesis reaction of the Cell.met and MPAEMA are shown in Figure 2 and 3, respectively. 0.5 g of Cell.met, 2.5 g of MPAEMA monomer and benzoyl peroxide as a free radical initiator were refluxed for 48 hours by continuous stirring in the acetonitrile solvent. Grafted copolymer was filtered and thoroughly washed with acetonitrile and certain solvent to eliminate oligomers and homopolymers formed in the reaction as products. The synthesis reaction of the grafting of Cell.met with MPAEMA monomer is shown in Figure 4.

3. Results and Discussion

3.1. Grafting of Cellulose and its Characterization

The primary OH group in cellulose was transformed to ester groups with methacryloyl chloride and Cell.met was synthesized (Figure 2). Grafting reaction was done of Cell.met with MPAEMA monomer (Figure 3), by free radical polymerization initiator, benzoyl peroxide (Figure 4), and thus Cell-g-MPAEMA was synthesized.

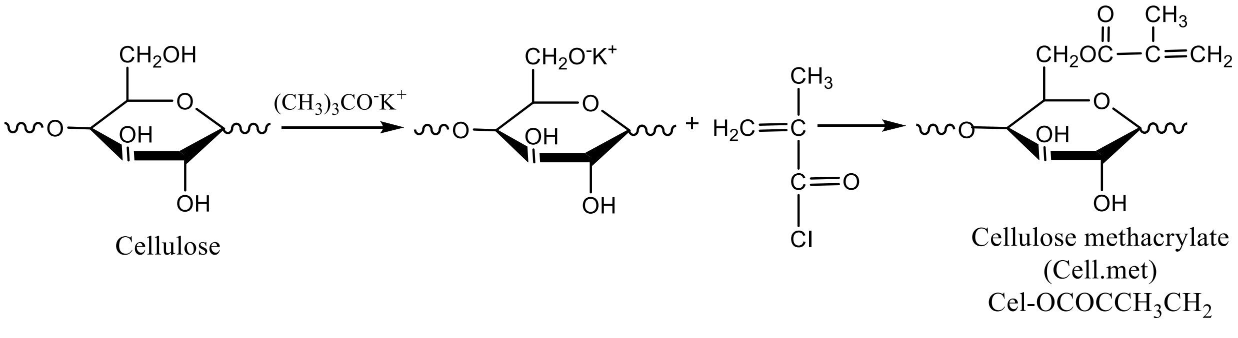
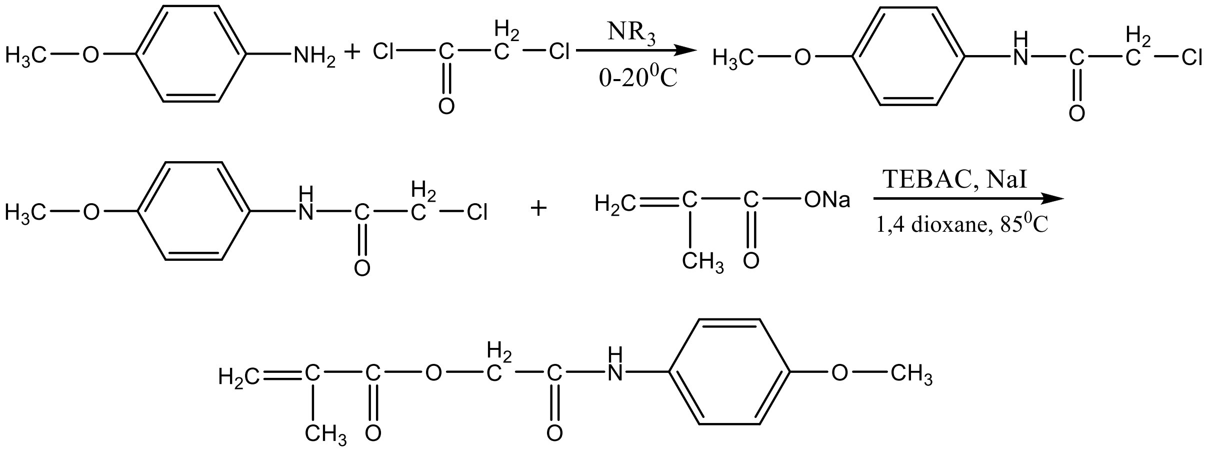
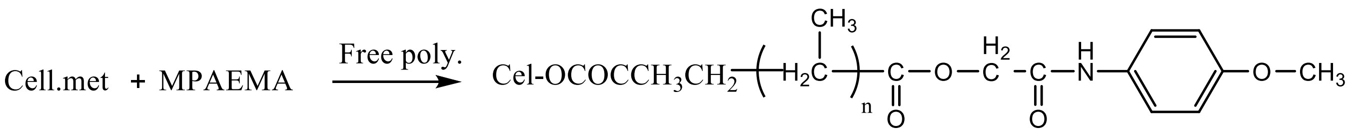


Figure 2. Synthesis of cellulose methacrylate (Cell.met)



2-(4-methoxyphenylamino)-2-oxoethyl methacrylate
(MPAEMA)

Figure 3. Synthesis of MPAEMA monomer



Cell-g-MPAEMA

Figure 4. The grafting of cellulose with MPAEMA monomer

FT-IR spectra of Cell.met and the graft copolymer with poly(MPAEMA) are shown in Figure 5. The presence of a new band 1730 cm^{-1} (-C=O stretching), in which there is no band for cellulose, indicates that the methacrylate group has become attached to the cellulose. Both amide stretching (1650 cm^{-1}) and ester band increase is seen for Cell-g-MPAEMA, which is a characteristic peak.

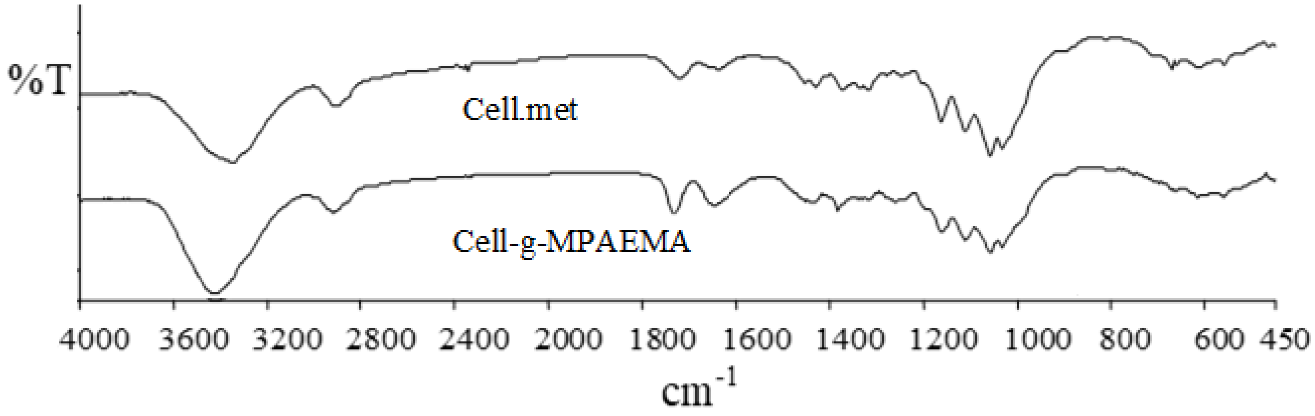


Figure 5. FT-IR spectra of the cellulose methacrylate and its graft copolymer

The degree of substitution in the glucose units of cellulose was 21.3% by mole (y) from and 27.8% by weight (Y) the percentage of carbon [14-17]. This calculation made on the amount of carbon in the elemental analysis, the graft copolymer was formed with MPAEMA monomer. According to the results of elemental analysis; from the amount of 48.3% Carbon, the weight ratio of the monomer (x) in the graft copolymer was 0.22. In the literature such calculations have been made and these results are compatible.

3.2. Thermogravimetric Analysis

The thermal properties of cellulose, Cell.met and Cell-g-MPAEMA graft copolymer were determined by thermal gravimetric analysis (TGA). The Thermogravimetric curves for polymers, which are obtained from room temperature to 500 °C at a heating rate of 10 °C/min nitrogen flow, are given in Figure 6. The initial decomposition temperature (IDT) and the temperature at 50% weight loss are taken as a measure of thermal stability. It has been observed that degradation from the thermogram occurs at one level. It has been seen that all the grafting processes and also the substitution have decreased the thermal stability of the raw cellulose. While the initial decomposition temperature (IDT) of cellulose is about 290 °C, Cell.met for which it is about 270 °C. The residue left by the cellulose was 7%, the Cell.met was 9% and the residue of the graft copolymer was 12%. The temperature of a weight loss of 50% by the cellulose was 370 °C, the Cell.met was 340 °C and the graft copolymer was 323 °C.

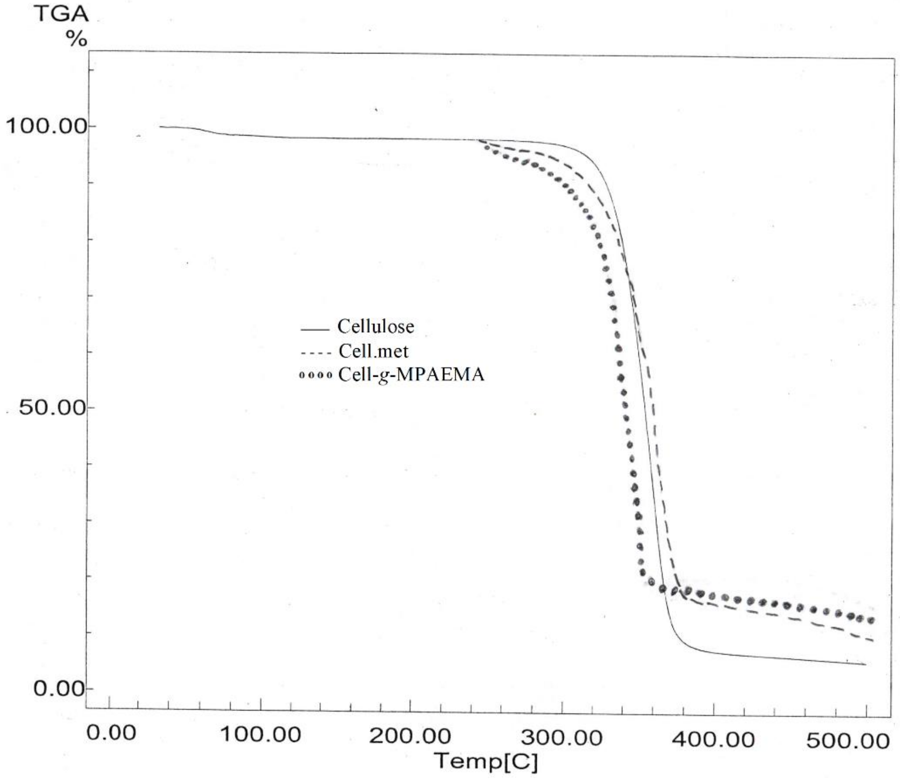


Figure 6. TGA curves of the cellulose, cell.met and its graft copolymer

4. Conclusions

In this study, cellulose methacrylate was first prepared by esterification of primary -OH group with methacryloyl chloride. 2-(4-Methoxyphenylamino)-2-oxoethyl methacrylate (MPAEMA) monomer was grafted onto the cellulose methacrylate via free radical polymerization using benzoyl peroxide as initiator. Cellulose, cellulose methacrylate and its graft copolymer (Cell.met-g-MPAEMA) were characterized by FT-IR spectra, elemental analysis and thermal analysis. Thermal stabilities of the polymers were determined by TGA method and thermal stability of the cellulose methacrylate and graft copolymer are decreased with grafting. The newly synthesized biopolymer-containing graft polymers will increase the application area.

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