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journal homepage: www.elsevier.com/locate/radphyschemAmine functionalization of cellulose surface grafted with glycidyl methacrylate by γ -initiated RAFT polymerizationMurat Barsbay^{a,*}, Olgun Güven^a, Yasko Kodama^b^a Department of Chemistry, Hacettepe University, 06800 Beytepe, Ankara, Turkey^b Instituto de Pesquisas Energeticas e Nucleares – IPEN – CNEN/SP, Cidade Universitaria, Av. Prof. Lineu Prestes, 2242, 05508-000 Sao Paulo, Brazil

H I G H L I G H T S

- Ethylenediamine (EDA) was immobilized to cellulose-g-PGMA copolymers.
- FTIR, XPS, SEM, EA and CA measurements were used for characterization.
- The useful qualities of the RAFT were combined with the versatility of PGMA.

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This study presents the functionalization of poly(glycidyl methacrylate) (PGMA) grafted cellulose filter paper by a model compound, ethylenediamine (EDA), through the epoxy groups of PGMA. Cellulose based copolymers were prepared via the radiation-induced and RAFT-mediated graft polymerization. The samples were characterized by ATR–FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS), elemental analysis, contact angle measurements and scanning electron microscopy (SEM). An efficient modification density of around 1 mmol EDA/mg copolymer was attained within ca. 8 h, indicating that chemical composition of well-defined copolymers may further be tuned by appropriately selecting the reactive agents for use in many emerging fields.

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1. Introduction

Considering biopolymer-based materials, natural fibers have being foreseen for the last decades as potential environmentally friendly constituents that will become essential for various applications due to unique properties such as low-cost, biodegradability, recyclability, etc. Most natural fibers are primarily composed of cellulose, hemicellulose, and lignin. Cellulose is the most common natural polymer and a very important sustainable raw material. Over the last decade, research to utilize cellulose as a base for the development of new materials has intensified (Thakur et al., 2014; Belgacem and Gandini, 2008).

The molecular structure of cellulose is composed of linear chains with a large number of hydroxyl groups (three OH groups per repeating unit). These hydroxyls are capable of forming

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extensive hydrogen bonds between and within the chains, yielding a straight and crystalline chain nature (Klemm et al., 2005; Nishiyama et al., 2003). They also provide possibility to functionalize cellulose through the well-established methods such as esterification (Roy et al., 2009). Usually, such treatments maintain bulk properties practically intact, apart from a very thin external layer whose thickness can vary from a few nanometers to micrometers (Belgacem and Gandini, 2008). Graft copolymerization is an effective technique to obtain specific surface properties required for some special applications (Barsbay and Güven, 2009). The use of monomers carrying extra functional groups, that are inactive to polymerization process, allow for further chemical transformation once the grafted polymers are obtained. Consequently, by means of a single reactive polymer it would be possible to obtain a variety of different materials with characteristics achieved by the modifying reagent. Glycidyl methacrylate (GMA), having both vinyl and epoxy functions, is a reactive monomer which meets the requirements for post-polymerization modification. Moreover, following the modification of PGMA, the derivatized polymer can be further used for other reactions via the hydroxyl groups formed in the epoxide ring-opening reaction

(Benaglia et al., 2013).

Ionizing radiation induced grafting method is a very favorable grafting technique as it is simple, economically favorable, easily controllable and applicable for the grafting of a great number of monomers (Barsbay et al., 2013; Barsbay and Güven, 2013; Kodama et al., 2014a, 2014b). The grafting technique can be improved and yield superior results when it is performed in company with the controlled radical polymerization (CRP) techniques, such as Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization, instead of conventional free-radical polymerization methods. In a previous study of ours, we have synthesized PGMA grafted cellulosic surfaces via radiation induced RAFT mediated graft polymerization (Barsbay et al., 2014). Due to the versatility of the grafted polymer, i.e. PGMA, the synthesized cellulosic copolymers possess the attitude to formulate tailor-made and natural-based end products capable to meet a wide variety of demanding specifications. In this study, this attitude has been investigated by immobilizing a model compound, i.e. ethylenediamine (EDA), onto cellulose by opening the epoxy rings. Amine groups have been known as one of the most efficient functional species for removal of toxic heavy metal ions (Renbi and Chen, 2003; Li and Bai, 2005; Barsbay et al., 2010). Besides, applications such as enzyme immobilization (Petro et al., 1996) and gene delivery (Xua et al., 2011) have also been reported for EDA modified materials. The model modification process carried out in this study shows that it is possible to tune the chemical composition of the well-defined cellulosic copolymers by appropriately selecting the reactive agents for use in many emerging fields.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA) (Aldrich, 97%) was passed through a basic alumina column to remove the inhibitor. Ethylenediamine ($\geq 99\%$) and solvents with high purity grade were purchased from Sigma-Aldrich and used as received. Whatman no. 1 filter paper was used as cellulose substrate due to reported advantages (Barsbay et al., 2007).

2.2. EDA modification

In a typical immobilization reaction, a piece of cellulose-g-PGMA copolymer with a known degree of grafting (DG) was immersed into reaction solution prepared by dissolving EDA (10%, v/v) in DMSO at 60 °C for various periods. The synthesis of cellulose-g-PGMA copolymers was given elsewhere (Barsbay et al., 2014). EDA modified samples were repeatedly washed with THF and ethanol and dried to constant weight under vacuum at 45 °C. The

amount of immobilized EDA, namely EDA group density, was calculated by using the following equation:

$$\text{EDA group density (mmol/g)} = 1000 \times \frac{W_2 - W_1}{60.1 \times W_1} \quad (1)$$

where W_2 and W_1 are the weights of the EDA immobilized cellulose and PGMA grafted cellulose, respectively. The molecular weight of the EDA is 60.1.

2.3. ATR-FTIR spectroscopy

Spectra were recorded using Nicolet Magna-IR 750 spectrometer equipped with a DGTS detector by cumulating 32 scans at 4 cm^{-1} resolution in Attenuated Total Reflexion mode (ATR).

2.4. X-ray photoelectron spectroscopy (XPS)

Thermo spectrometer with a mono-chromatized Al $K\alpha$ X-ray source (1486.6 eV photons) was used in XPS analysis. The details of the technique were given elsewhere (Barsbay and Güven, 2013).

2.5. Elemental analysis (EA)

Flash 2000 (Thermo Scientific) automatic elemental analyzer equipped to analyze C, H, S and N atoms was used to analyze the elemental composition. BBOT and V_2O_5 were used as the calibration standard and catalyst, respectively.

2.6. Scanning electron microscopy (SEM)

FEI Quanta 200FEG Scanning Electron Microscope was used for the morphological analyses. Samples were sputter-coated with gold prior to scanning.

2.7. Contact angle (CA)

Krüss DSA 100 model CA goniometer was used to characterize the wettability of raw and EDA modified cellulose-g-PGMA copolymers at ambient temperature by placing a drop of water (10 μL) on the dry sample surface.

3. Results and discussion

The immobilization of the model compound, EDA, onto cellulose substrate was carried out via the opening of epoxy rings of PGMA grafts as represented in Fig. 1. DMSO was chosen as the solvent as complete conversion of the epoxide rings by many amines is reportedly reached in shorter reaction times in this solvent (Benaglia et al., 2013) compared to other organic solvents

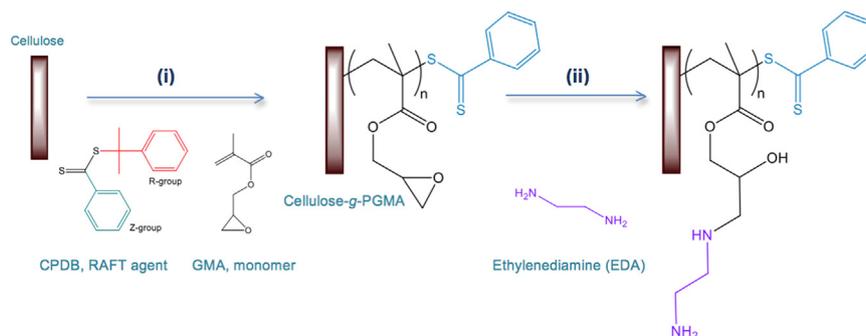


Fig. 1. Scheme showing the modification steps: (i) radiation-induced and RAFT-mediated grafting of PGMA from cellulose (Barsbay et al., 2014), (ii) post-polymerization treatment of PGMA, i.e. immobilization of EDA onto GMA units.

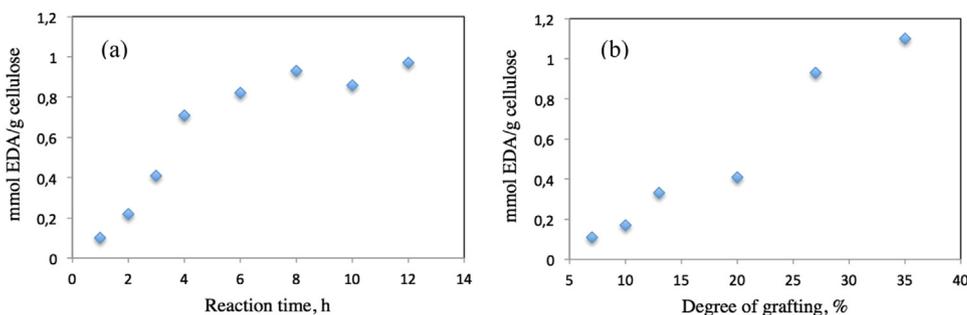


Fig. 2. Change of EDA group density with (a) reaction time and (b) degree of grafting (DG) of PGMA. The DG is 25% for (a) and the reaction time is 8 h for (b). Solvent is DMSO, 60 °C.

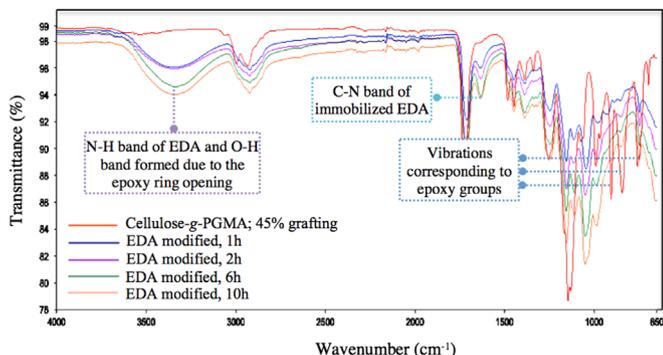


Fig. 3. FTIR spectra of raw cellulose-g-PGMA copolymer with DG of 45% and EDA modified samples at different reaction times.

such as acetonitrile (Gao et al., 2011) and THF/DMF (Xu et al., 2010).

Fig. 2 shows the immobilized EDA content of PGMA grafted cellulose as a function of reaction time and degree of grafting (DG). As can be seen in Fig. 2a, EDA content increase linearly with increasing reaction time up to ca. 4 h. Thereafter, the conversion of epoxy groups starts to level off, indicating completion of the chemical transformation. The plateau value is reached within 8 h. Fig. 2b shows that the amount of immobilized EDA groups increases almost linearly with DG as the number of reactive epoxy groups existing on PGMA grafts increases. The linearity indicates that the GMA units are easily available and no steric effect is encountered most probably due to the homogeneity and controlled chains lengths achieved by means of RAFT polymerization (Barsbay et al., 2013).

Fig. 3 compares the ATR-FTIR spectrum of cellulose-g-PGMA copolymer with those measured after amine functionalization at various reaction times. As seen in this figure, the measured depth

in FTIR is saturated mostly by the absorption bands of PGMA, indicating an efficient surface coverage at DG of 45%. The characteristic epoxy stretching vibrations observed at $750\text{--}950\text{ cm}^{-1}$ (Gudipati et al., 2008) disappear after amine functionalization due to the opening of the epoxy ring. An obvious new absorption peak assigned to the stretching band of C-N is observed at ca. 1640 cm^{-1} for the amine functionalized copolymers (Silverstein et al., 1991). The intensity of this peak increases with reaction time till the first 6 h. Thereafter, the intensities become quite similar, indicating completion of reaction in very good agreement with Fig. 2a. The broad peaks at $3600\text{--}3000\text{ cm}^{-1}$ are attributed both to the immobilized amine functionalities and -OH groups appearing due to the epoxy ring opening.

XPS is an effective technique for the surface-sensitive quantitative spectroscopic analysis. Fig. 4 presents the XPS spectra and calculated elemental surface compositions of cellulose-g-PGMA copolymer with DG of 30% and its EDA modified counterpart (modification time is 8 h). In the XPS wide scan spectrum of the unmodified copolymer, Fig. 4a, two characteristic peaks corresponding to C 1s at ca. 285 eV and O 1s at ca. 533 eV were observed along with a small S 2p peak centered at 169.4 eV arising from the presence of the RAFT chain-end moieties of PGMA (Barsbay et al., 2014). With the addition of EDA group to GMA repeating units, surface composition changes significantly as can be seen from the elemental percentages inserted into Fig. 4. The increase in C atom amount and the opposite situation observed for O atoms are in agreement with the chemical composition expected after the modification. For the EDA immobilized copolymer, Fig. 4b, the detection of N 1s peak reveals the success of the modification.

For better understanding of chemical changes occurred upon EDA modification, C 1s core level spectra depicted in Fig. 5 were investigated. For the raw copolymer, Fig. 5a, the C 1s spectrum can be curved-fitted with three peak components; hydrocarbon species (C-C) with binding energy (BE) at 284.7 eV, and ether (C-O)

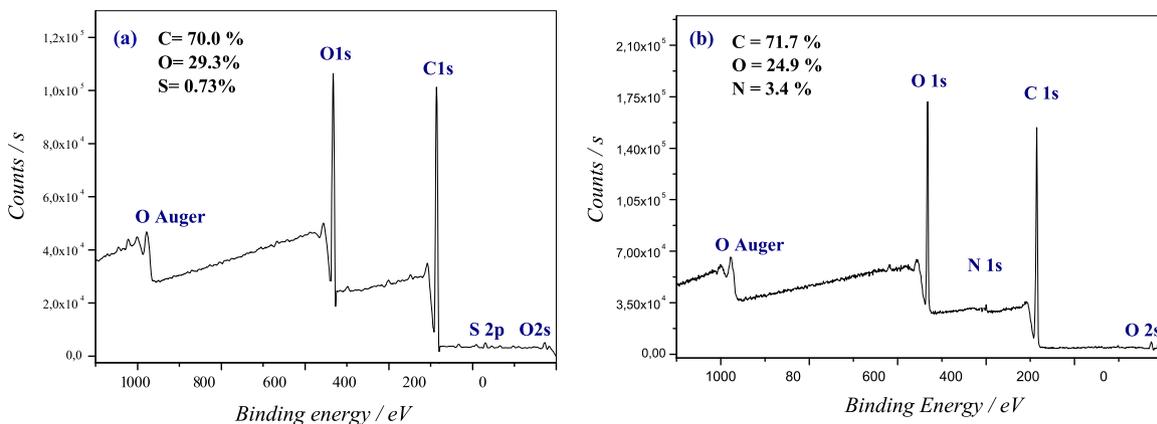


Fig. 4. XPS survey wide scan of cellulose-g-PGMA copolymer with DG of 30% before (a) and after (b) EDA modification.

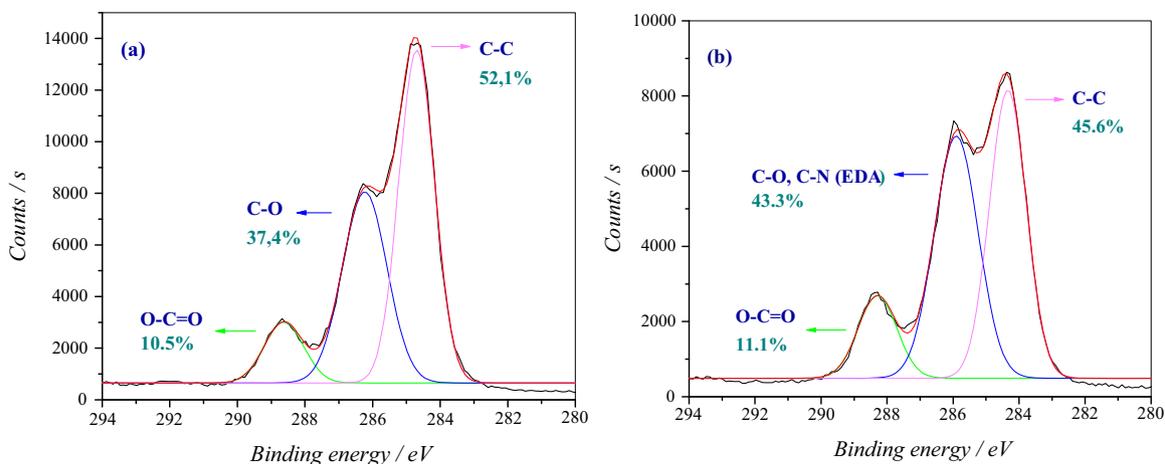


Fig. 5. C1 s XPS spectra of cellulose-g-PGMA copolymer with DG of 30% before (a) and after (b) EDA modification.

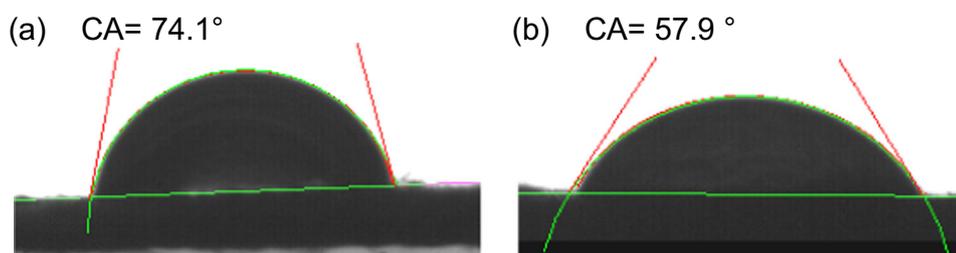


Fig. 6. Contact angle (CA) values at the end of 5th second for cellulose-g-PGMA copolymer with DG of 30% before (a) and after (b) EDA modification.

Table 1

Elemental analysis results of cellulose-g-PGMA copolymer with DG of 30% before and after EDA modification.

Sample	C %	H%	N%	O% ^a
Cellulose-g-PGMA	45.3	6.1	–	48.6
Cellulose-g-PGMA-EDA	45.8	6.1	0.7	47.4

^a Approximate amount of oxygen atoms by subtracting the percentages of C, H and N atoms from 100%.

and carboxylate (O–C=O) type oxygenated C atoms at around 286.2 eV and 288.7 eV, respectively (Barsbay and Güven, 2013). The C–N peak appearing due to the incorporation of EDA groups to GMA units is reported to appear at 285.9 eV (Lopez et al. 2005). This peak overlaps the C–O peak of the raw copolymer, yielding a significant increase at ca. 286 eV in the spectrum of EDA modified sample, Fig. 5b.

In order to further study the surface properties, contact angle

(CA) measurements were carried out. CA measurement of pristine filter paper was impossible as it uptakes water very quickly. We have previously verified that the surface wettability may completely be altered even at very low DG values (Barsbay and Güven, 2013). Consistent with this, cellulose-g-PGMA copolymer with 30% DG became hydrophobic with a CA value of 74.1° (Fig. 6a). Immobilization of EDA enriches the surface with hydrophilic amine functionalities. Due to the favorable interactions, water droplet spreads to the surface, yielding a lowered CA value after modification (Fig. 6b). The repeated measurements yielded almost the same CA value, suggesting sufficient and homogeneous surface coverage attained by means of RAFT polymerization.

Elemental analysis (EA) gives information on the fullest extent of the composition of copolymer. As seen in Table 1, immobilization of EDA results in a slight increase in C atom amount and a decrease in O amount, which is in agreement with XPS results. The amount of N atom detected by EA is significantly lower than that observed by XPS. This is a rather expected result, as the grafting of

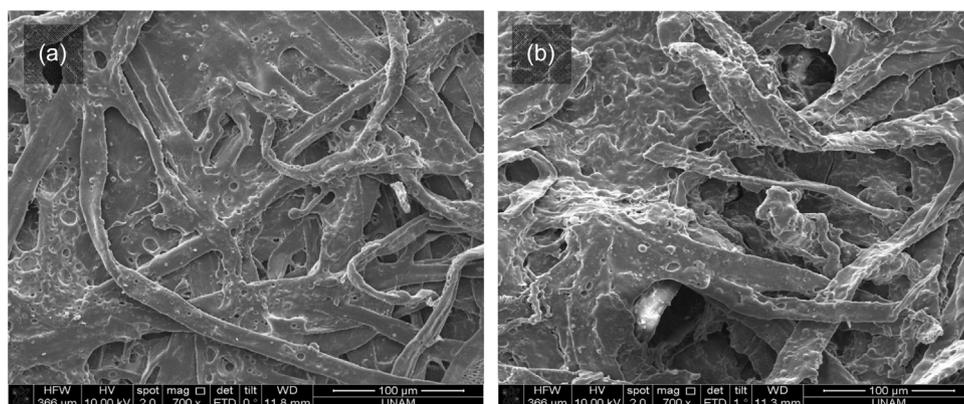


Fig. 7. SEM image of cellulose-g-PGMA copolymer with DG of 25% before (a) and after (b) EDA modification.

PGMA occurs mainly on the surface of cellulose, not inside its matrix (Barsbay et al., 2014).

Modification of EDA yields no change on the appearance of the cellulose-based copolymer. We have performed SEM analysis for better understanding of the morphological changes that might have occurred during the modification. It is seen from the SEM image of cellulose-g-PGMA copolymer (Fig. 7a) that the fibers of cellulose are apparent even though a layer of PGMA has entirely covered them. EDA modification yields almost no morphological change as seen in Fig. 7b, which may constitute an advantage in possible applications in terms of durability.

4. Conclusions

In summary, immobilization of EDA on PGMA grafted cellulose was successfully achieved as a model system. This study clearly shows that γ -initiated and RAFT mediated graft polymerization of GMA to cellulose yields copolymers possessing the attitude to formulate tailor-made and natural-based end products capable to meet a wide variety of demanding specifications by combining the useful qualities attained by RAFT polymerization, e.g. controlled polymer chain lengths and homogeneous grafting fashion, with the versatility of PGMA post-polymerization treatments.

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