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Radiation-induced and RAFT-mediated grafting of poly(hydroxyethyl methacrylate) (PHEMA) from cellulose surfaces

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HIGHLIGHTS

- Poly(hydroxyethylmethacrylate) was grafted from cellulose surface w/w a RAFT agent by gamma irradiation.
- Control of molecular weight and distribution of grafted chains were achieved in RAFT-mediated grafting reactions.
- Graft copolymers were characterized by FTIR-ATR, XPS, SEM, elemental analysis and contact angle measurements.

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ABSTRACT

This paper presents the results of RAFT mediated free-radical graft copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto cellulose fibers in a "grafting-from" approach under γ-irradiation. The effects of absorbed dose and monomer concentration on the graft ratios were investigated at different monomer (HEMA) to RAFT agent (cumyl dithiobenzoate, CDB) ratios. Cellulose-g-PHEMA copolymers with various graft ratios up to 92% (w/w) have been synthesized. The synthesized copolymers were characterized by ATR-FTIR spectroscopy, X-ray photoelectron spectroscopy, elemental analysis and scanning electron microscopy. The results of various techniques confirmed the existence of PHEMA in the copolymer composition.

1. Introduction

The modification of polymers through grafting has a bright future and the developments anticipated are practically boundless. In principle, graft co-polymerization is an attractive method to impart a variety of functional groups to a polymer and it can be initiated by chemical treatment, photo-irradiation, high-energy radiation, plasma-induced techniques, etc. (Nasef and Güven, 2012). In recent years, methods of controlled free-radical polymerizations (CRP) were developed to open up new potential for grafting reactions especially using ionizing radiation (Barsbay and Güven, 2009). Well-defined graft copolymers via CRP methods are most frequently prepared by either a "grafting through" or a "grafting from" polymerization process. In the "grafting from" technique, the initiators are initially anchored or active sites are generated on the surface and then they subsequently used to initiate the polymerization of monomer from the surface. Because the diffusion of monomer is not strongly hindered by the existing grafted polymer chains, this technique is more promising to achieve high graft densities. (Li et al., 2008).

Among the CRP techniques, RAFT (Reversible Addition/Fragmentation Chain Transfer) polymerization is one of the most versatile ones for providing living characteristics to radical polymerization (Barsbay et al., 2007; Moad et al., 2005). Advantages of RAFT polymerization include the ability to control polymerization of most monomers polymerizable by radical polymerization such as (meth)acrylates, (meth)acrylamides, acrylonitrile, styrenes, dienes, etc., tolerance of unprotected functionality in monomer and solvent, compatibility with reaction conditions (e.g., bulk, organic or aqueous solution, emulsion, mini-emulsion, and suspension) and ease of implementation and inexpensive relative to competitive technologies (Moad et al., 2005; Moad et al., 2009). RAFT polymerization at ambient temperature by means of γ-radiation has been successfully performed for a variety of monomers (Barsbay and Güven, 2009). In the course of γ-initiated RAFT mediated grafting; growing of both grafted polymer (on the surface) and free polymer (in the solution) are controlled by the same RAFT agent at the same time. Therefore, the molecular weights and molecular weight distributions of grafted and free polymers are almost the same when the grafting occurs on the surface of the substrate (Barsbay et al. 2007).

In this study, RAFT-mediated free-radical graft polymerization of 2-hydroxyethyl methacrylate (HEMA) onto cellulose fibers in a

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"grafting-from" approach under the γ-irradiation has been investigated. To the best of our knowledge this is the first report dealing with the γ-initiated RAFT polymerization of HEMA and investigating the grafting of this monomer from cellulose surface using the RAFT technique. Over the past decade, modification of cellulose as the base material for the development of new materials has received increasing attention (Malmström and Carlmark, 2012; Roy et al., 2009). Cellulose is the most abundant natural polymer and finds applications in areas as diverse as composite materials, textiles, drug delivery systems and personal care products (Roy et al., 2009). Poly(2-hydroxyethyl methacrylate) (PHEMA) has been used as an important material in drug delivery and tissue engineering (Ratner et al., 1996). It has been reported that grafting of PHEMA to cellulose increases the diffusive permeabilities of cellulose membranes (Nishioka et al., 1989). Worthley et al. (2011) have reported greater resistance to seawater microbial biofouling for PHEMA grafted cellulose acetate membranes with respect to pristine ones, especially in the case of the low graft densities. Cellulose has been chemically modified with PHEMA to mimic the behavior of bone proteins responsible for mineralization (Mircea et al., 2010). Considering the previous works and inherent characteristics of PHEMA and cellulose, we anticipate that the copolymers synthesized may have potential use in biomedical applications.

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA) was purified by passing through a column with aluminum oxide (activated, basic). HEMA, 2-phenyl-2-propyl benzodithioate (cumyl dithiobenzoate, CDB), and DMF were purchased from Sigma-Aldrich, high purity grade. Whatman No. 1 filter paper was used as cellulose substrate due to its high cellulose content (98% α-cellulose), lesser amount of impurities, and ease of chemical modification (Barsbay et al., 2007). Each cellulose sample was cut into approximately 1.5 cm × 1.0 cm dimensions with a weight of approximately 0.015 g.

2.2. Irradiation

Gammacell 220 ^{60}Co source with a dose rate of 0.26 kGy/h as determined by Fricke dosimetry was used for the irradiation of the samples at room temperature. Various absorbed doses, e.g. 2.1, 3.3, 5.0, 8.0, 10.0, and 12.5 kGy, were applied throughout the study.

2.3. Grafting

In a typical RAFT-mediated grafting, cellulose film was immersed at room temperature into a grafting solution containing the monomer (HEMA) and the RAFT agent (CDB) in solvent, e.g. DMF. The polymerization solution in purgeable glass was then connected to N_2 bubbling at room temperature for 10 min, then the glass tube was sealed and placed in the γ-irradiator for predetermined time intervals. The grafted film was washed with DMF and then Soxhlet extracted in boiling DMF for 10 h to remove free homopolymer. The film was dried to constant weight under vacuum at room temperature. The degree of grafting (%) was calculated using the formula given below:

$$\text{Degree of grafting } (\%) = \frac{w_2 - w_1}{w_1} \times 100 \quad (1)$$

where w_1 (g) is the weight of the pristine cellulose film and w_2 (g) is the dry weight of the PHEMA grafted film. In most cases, RAFT agent concentration is adjusted so that free PHEMA with expected molecular weight of 94,200 g/mol will be formed at complete conversion of the monomer. This has been determined to be [HEMA]/[CDB]=722:1. Along with this value, [HEMA]/[CDB] ratios of 361, 462, 1083 and 1444 were also studied to investigate the effect of target molecular weight on the degree of grafting. In parallel conventional grafting studies, cellulose films were treated identically with the samples subjected to grafting procedure in the absence of CDB, i.e. RAFT agent.

2.4. Gel permeation chromatography (GPC)

The molecular weight analysis of free (non-grafted) PHEMA formed during the grafting was performed in DMF as the eluent at room temperature (flow rate: 1 mL min^{-1}) using a Waters Gel Permeation Chromatograph equipped with a Waters 515 model HPLC pump. The system was equipped with Styragel HR4 and HR3 columns and Waters 2414 model refractive index detector. A universal calibration was prepared with 8 PS standards in molecular weight range of 1990 to 2×10^6 g mol^{-1}. The Mark–Houwink constants used in constructing the universal calibration were as follows: $K = 31.8 \times 10^{-3}$ mL/g; $a = 0.603$ for PS and $K = 10.6 \times 10^{-3}$ mL/g; $a = 0.70$ for PHEMA (Brandrup and Immergut, 1989).

2.5. ATR-FTIR spectroscopy

FTIR spectra of the films were obtained with a Nicolet Magna-IR 750 spectrometer equipped with a DGTS detector. Spectra were recorded in Attenuated Total Reflexion mode (ATR) using a diamond-crystal with single reflection.

2.6. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded on a Thermo spectrometer with a mono-chromatized Al Kα X-ray source (1486.6 eV photons). The details of the technique were given elsewhere (Barsbay et al., 2009).

2.7. Elemental analysis

The elemental composition of the samples was analyzed using AI/AS 3000 series autosampler and Flash 2000 (Thermo Scientific) automatic elemental analyzer equipped to analyze carbon, hydrogen, sulfur and nitrogen atoms. Samples were analyzed in tin capsules using 5-bis-5-tert-butyl-2-benzoxazolylthiophene (BBOT) as the calibration standard and vanadium pentoxide (V_2O_5) as the catalyst.

2.8. Scanning electron microscopy (SEM)

SEM pictures were taken using a FEI Quanta 200F microscope. All the samples were gold coated prior to scanning.

2.9. Contact angle

Wetting of pristine cellulose and cellulose-g-PHEMA copolymers were characterized by the sessile drop method, that is, by measuring the contact angle formed between the water droplet (10 μL) and solid surface, using Krüss DSA 100 model contact angle (CA) goniometer. The water droplet was placed on the surface of dry samples.

3. Results and discussion

Among the copolymerization techniques, graft copolymerization is an attractive one as it imparts a variety of functional groups especially to the surface of a polymer. Historically, one of the most common applications of γ radiation in polymer modification has been in grafting (Chapiro, 1962). This is due to the fact that γ

radiation is an excellent method for generating radicals on many substrates. During the γ-initiated RAFT mediated grafting of HEMA from cellulose, γ radiation generates radicals on the cellulose and in the monomer solution. Monomer radicals and radicals formed on the surface initiate propagating chains, which subsequently add to the thiocarbonyl group of the RAFT agent. It is reported in previous works that grafting occurs mainly at the surface of cellulose; no proceeding of grafting towards the bulk of the cellulose fibers is reported (Barsbay et al. 2007, 2009; Roy et al. 2005). Therefore, while some of HEMA is grafted from the cellulose surface some portion is homopolymerized in the solution. It has been noted that the growing of surface-grafted polymer chains are in a dynamic equilibrium with free polymer chains in the solution (Barsbay et al., 2007; Li et al., 2008). So, the free polymers formed in the solution can be analyzed to estimate the molecular weight, M_n, and polydispersity, PD, of surface-grafted polymer chains. We, therefore, analyzed the free PHEMA in solution not only to gain information on soluble part of the irradiated samples but also to estimate the characteristics of the surface grafted PHEMA chains. It should be mentioned here that when the grafting proceeds via the front mechanism where the grafting diffuses towards the bulk of the substrate, the characteristics of the chains grafted inside the matrix are expected to be different than those of the surface grafted chains and free homopolymers (Barsbay et al., 2013; Barsbay and Güven, in press).

Table 1 presents the comparison of M_n and PD values of free PHEMA formed during conventional and RAFT mediated grafting. RAFT mediated samples yield significantly lower M_n values even at higher doses compared to conventional ones. This shows that the increase of molecular weight with conversion is depressed considerably in the presence of the RAFT agent, CDB. However it is difficult to claim a full control over the molecular weight as the change of M_n with conversion is not yielding a straight line. Although the PD values were found to be significantly lower compared to polymerization in the absence of RAFT agent, they are still indicating broad molecular weight distributions near 2. The multimodal GPC chromatograms with very high PDs up to ~19 observed for conventional polymerization were replaced with monomodal distributions for the RAFT mediated ones as can be seen in Fig. 1. The RAFT agent used, CDB, is classified as a suitable agent for the controlled polymerization of HEMA (Moad et al., 2006). It is reported that the impurities in CDB cause a significant retardation effect during the RAFT polymerization (Plummer et al., 2005). However, these impurities actually depend on how CDB was synthesized and stored (Moad et al., 2013). It was shown that samples of CDB purified by column chromatography on silica gave a significant inhibition period even when used immediately following purification (Plummer et al., 2005). On the other hand,

Table 1
Comparison of M_n (g mol^{-1}) and PD obtained for RAFT mediated and conventional grafting.

Entry	Dose (kGy)	M_n (g mol^{-1})[a]	PD[a]
1	1.04	1830	2.27
2	2.08	11,000	1.62
3	3.12	29,800	2.11
4	4.94	51,650	2.12
5	5.98	97,500	2.51
6	7.02	148,300	3.12
Control[b]	0.52	481,400	19.58
Control[b]	1.04	985,900	19.74
control[b]	1.30	875,600	18.55

[a] Number-average molecular weight, M_n, and polydispersity, PD, determined via gel permeation chromatography, GPC, using DMF as eluent with polystyrene (PS) standards.
[b] Conventional grafting where no RAFT agent, CDB, added.

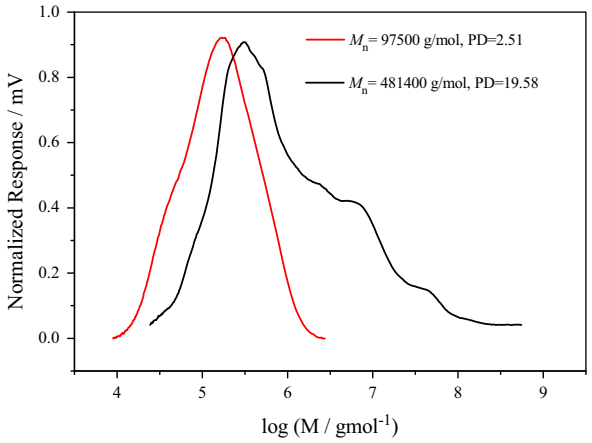

Fig. 1. GPC chromatograms for free PHEMA synthesized during (—) RAFT mediated and (−) conventional grafting. Dose rate: 0.26 kGy h^{-1}, room temperature and total dose absorbed is 5.98 kGy.

CDB purified by column chromatography on alumina with hexane as eluent and stored at 4 °C in the absence of light remains fully effective for more than 2 years (Moad et al., 2013; Moad et al., 2000). We have bought CDB with the highest commercial purity (99%) and stored it in freezer in dark. Therefore, the difficulties encountered in fully controlling the molecular weights and PDs are expected to be related mainly with the effects of γ radiation on PHEMA rather that the properties of the RAFT agent employed.

Diego et al. (2007) irradiated solid PHEMA samples in air for a broad absorbed dose range of 7–50 kGy with gamma rays and they reported that PHEMA degrades very rapidly through chain scission under γ-radiolysis. On the other hand, Hill et al. (1996) investigated the effect of high energy radiation on PHEMA by irradiating powdered PHEMA samples under vacuum for various doses up to 9 kGy using ^{60}Co source (dose rate = 1.65 kGy h^{-1}). They reported that the ESR spectrum of PHEMA irradiated at ambient temperature is a combination of two types of radicals; methacrylate main chain scission radical and methylene radical on the main chain. The high stability of the latter radical at room temperature and under vacuum increases the possibility of crosslinking due to labile hydrogen atoms in the side chain. In our case, simultaneous homo and graft polymerization of monomer, HEMA, take place in polymerization solution where solvent, DMF and substrate, cellulose are present in the medium under inert atmosphere. Monomer radicals and radicals formed on the cellulose surface initiate propagating PHEMA chains either as free homopolymers or grafts on cellulose backbone. The radicals formed on the PHEMA chains as a result of radiation may cause branching rather than crosslinking considering the accessibility of monomer molecules in close proximity. The difficulty of control over the molecular weight and broad PDs in this work with PHEMA can therefore be attributed to these probable branching or above discussed chain scission/crosslinking reactions that might occur in PHEMA structure under γ-radiolysis. The degree of grafting of the substrate, on the other hand, changes almost linearly with the [HEMA]/[CDB] ratio, Fig. 2. This shows that although the experimental M_ns are not in very good agreement with the theoretically calculated ones due to radiation effects on PHEMA, still the degree of grafting can be controlled by adjusting the [HEMA]/[CDB] ratio.

The effect of absorbed dose on grafting percentages for both RAFT mediated and conventional grafting methods is presented in Fig. 3. For both methods, degree of grafting increases with increasing absorbed dose. However, for the RAFT mediated method the grafting is significantly slower which in fact enables a better control for the achievement of a desired target degree of grafting. The amount of grafting depends on the monomer concentration, and it has been

often reported that the grafting efficiency increases with monomer concentration up to a certain limit (Bhattacharya and Misra, 2004). This is simply due to an increase of the monomer concentration in close proximity to the substrate grafted. As can be seen in Fig. 4, degree of grafting increases with increasing HEMA concentration for both RAFT and conventional processes as expected.

For spectroscopic characterization of the graft copolymers ATR-FTIR and XPS analyses were made. FTIR spectra of pristine cellulose, PHEMA and copolymers with various grafting percentages are presented in Fig. 5. The band at ~1750 cm^{-1} corresponds to C=O stretching vibrations of PHEMA. This band appears in the spectra of grafted samples and the intensity increases with increasing PHEMA content in copolymer composition. X-ray photoelectron spectra of pristine cellulose and cellulose-*g*-PHEMA samples are shown in Fig. 6. The surface chemical compositions calculated using the peak areas of the XPS spectra are inserted into the survey wide scans. As can be seen from these values, the amount of carbon atoms for the cellulose-*g*-PHEMA copolymers increase from 60.4% up to 68.1% whereas the amount of oxygen atoms decreases due to attachment of PHEMA to cellulose. The change is more evident in the C1s spectra: The C1s spectrum of native cellulose consists of a main peak with a bonding energy (BE) of 286.5 eV attributed to C–O bonds. However with grafting,

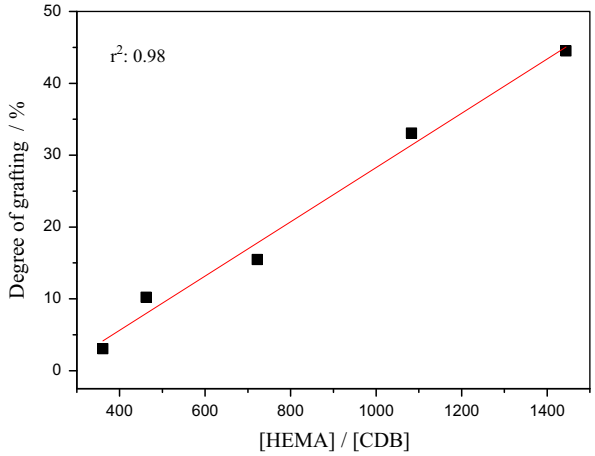

Fig. 2. Effect of [HEMA]/[CDB] ratio on degree of grafting. Dose rate: 0.26 kGy h^{-1}, solvent: DMF, room temperature and total absorbed dose is 5.98 kGy.

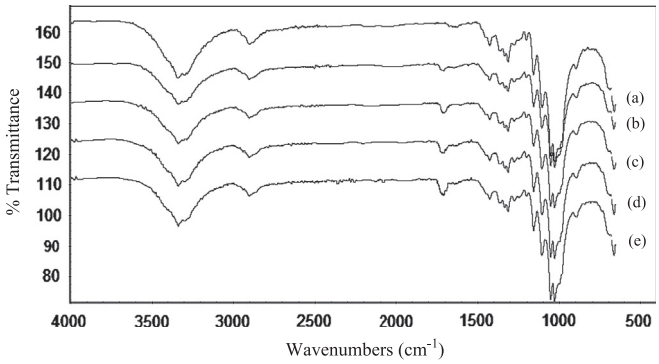

Fig. 5. FTIR spectra of pristine cellulose (a) and cellulose-*g*-PHEMA copolymers with % grafting of 10 (b), 19 (c), 31 (d), and 44.5 (e).

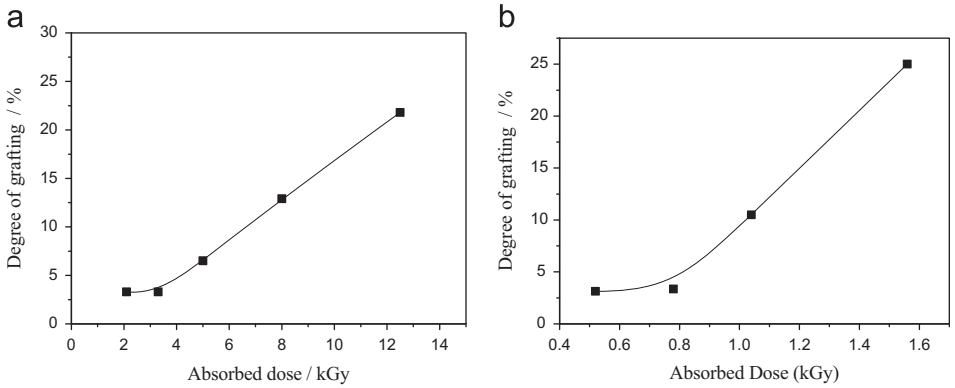

Fig. 3. Effect of absorbed dose on degree of grafting; (a) RAFT mediated, (b) conventional grafting. Dose rate: 0.26 kGy h^{-1}, solvent: DMF, room temperature.

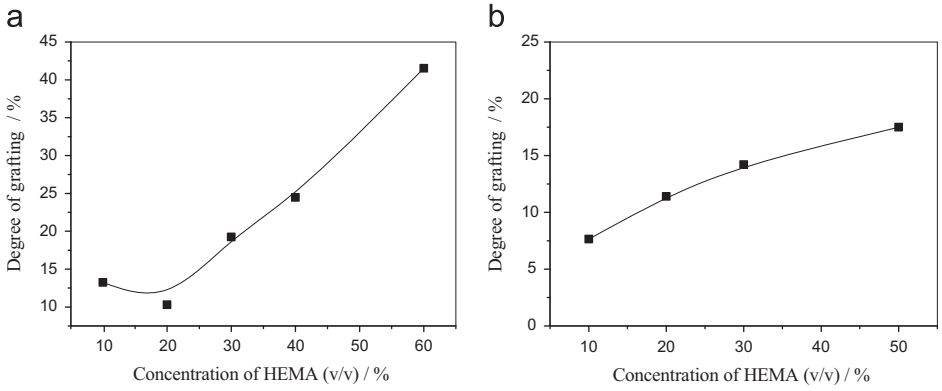

Fig. 4. Effect of HEMA concentration on degree of grafting; (a) RAFT mediated, (b) conventional grafting. Dose rate: 0.26 kGy h^{-1}, solvent: DMF, room temperature. Total dose absorbed are 10.4 kGy and 0.8 kGy for RAFT mediated and conventional polymerizations, respectively. [HEMA]/[CDB] is 722 for RAFT mediated grafting.

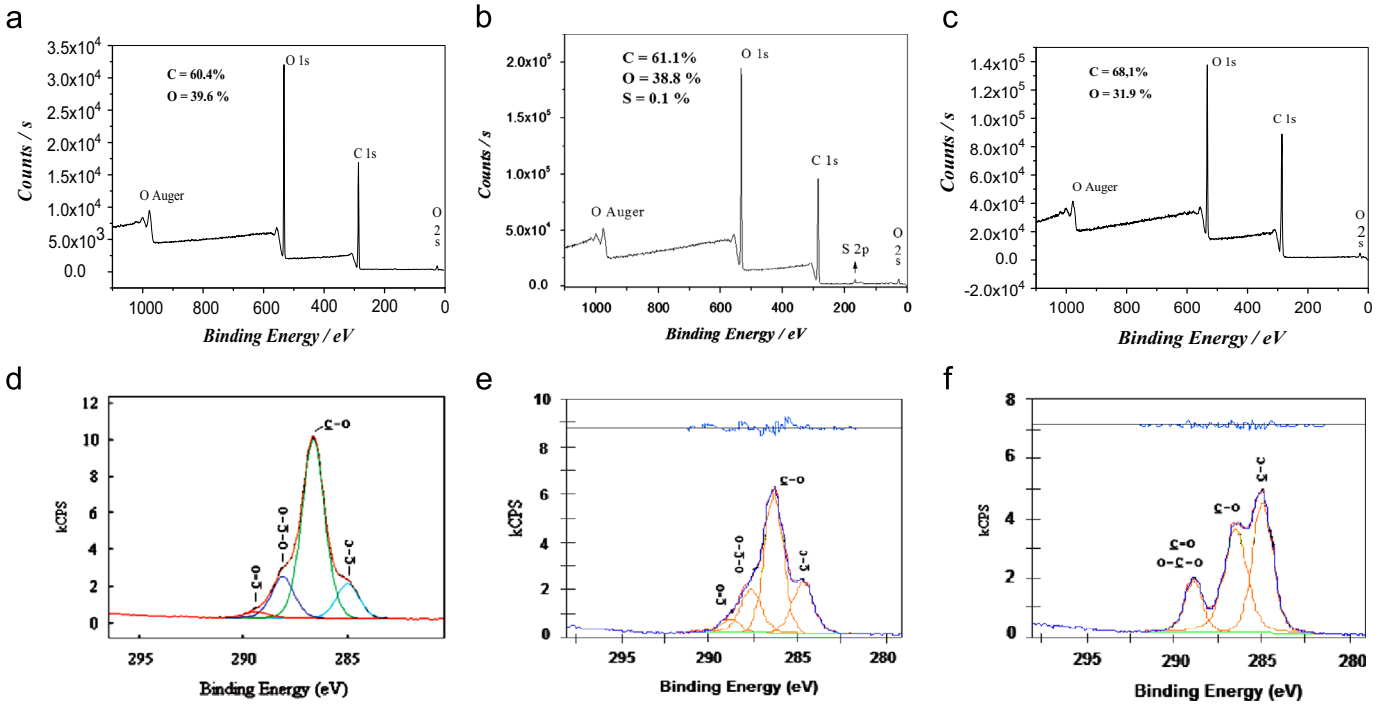

Fig. 6. XPS survey wide scans of (a) pristine cellulose, (b) cellulose-*g*-PHEMA, 44.5%, (c) cellulose-*g*-PHEMA, 92% and C1s XPS spectra of (d) pristine cellulose, (e) cellulose-*g*-PHEMA, 44.5%, and (f) cellulose-*g*-PHEMA, 92%.

Table 2
Elemental analysis results of pristine cellulose and copolymers with various degrees of grafting[a].

Sample	*C* (%)	*H* (%)
Pristine cellulose	42.12	6.01
PHEMA-*g*-cellulose, 13.4% grafting	44.16	6.30
PHEMA-*g*-cellulose, 44.5% grafting	46.22	6.50
PHEMA-*g*-cellulose, 92.4% grafting	48.42	6.69

[a] Sulfur atoms existing as chain end moieties of the grafted chains could not been detected due to the detection limits of the instrument.

the main peak appears at 284.9 eV, attributed to C–C bonds. Moreover, with the addition of PHEMA to the structure the amount of C=O peak at ~289.1 eV increases as expected. These changes are further confirmation of grafting of PHEMA from cellulose. As can be seen in Fig. 6b, S2p peak also appears in the survey wide scan of cellulose-*g*-PHEMA with 44.5% grafting at 168.8 eV, which indicates the presence of the RAFT end group of PHEMA. This shows that in spite of the radiation effects discussed above, the growing of PHEMA chains mainly obeys the RAFT mechanism.

It is reported in previous works that grafting occurs mainly at the surface of cellulose substrates (Barsbay et al. 2007, 2009; Roy et al. 2005) and XPS analysis is an excellent method for the surface characterization as it gives information on the top ~5 nm surface to the fullest extent of the polymer structure. In order to investigate the composition of the synthesized copolymers, i.e. including the bulk not only the surface, elemental analysis has been performed, Table 2. As can be seen from the results, sulfur atoms expected to exist at chain-ends as RAFT agent moieties cannot be detected in elemental analysis due to their low amounts. The amount of C atom increases with increasing grafting as expected considering the chemical structures of cellulose and PHEMA. The subtraction of percentages of carbon and hydrogen atoms from 100% indicates the amount of oxygen atoms which decreases with grafting as has already been revealed by XPS.

SEM was used to investigate the surface changes occurred during the grafting. In the SEM image of pristine cellulose, Fig. 7a, the cellulose fibers are clearly seen and the surface looks free from any spurious matter. As for the PHEMA grafted copolymers, surface features are quite different from that of native cellulose. As the grafting occurs mainly at the surface of cellulose fibers, the fibers are covered by the grafted polymers and the surface morphology changes significantly as clearly seen in Fig. 7b–d.

By controlling the type, structure and graft density of the surface-attached polymers, surface hydrophobicity/hydrophilicity of substrate materials can be significantly modified, which further affects other properties including adhesion, wettability, compatibility and solubility. It is cited that pure PHEMA surface has a contact angle, CA, of approximately 52° (Li et al., 2008). The CA of pristine cellulose could not be measured as it is very hydrophilic. However, for the PHEMA grafted samples, as the degree of grafting increased CA also increased, indicating a decrease in hydrophilicity due to the grafted PHEMA layer (Fig. 8a–c). For the copolymer samples, the water droplet was gradually absorbed by the substrate (Fig. 8c–e) and finally disappeared at the end of the first minute.

4. Conclusions

We managed to graft PHEMA from cellulose surface using cumyl dithiobenzoate (CDB) as the RAFT agent and γ irradiation as the source of initiation. The results indicated that the degree of grafting of PHEMA can be controlled smoothly by changing the [HEMA]/[CDB] ratio in RAFT mediated grafting which was not possible with conventional polymerization. However, a full control over the molecular weight and PDs could not be achieved due to

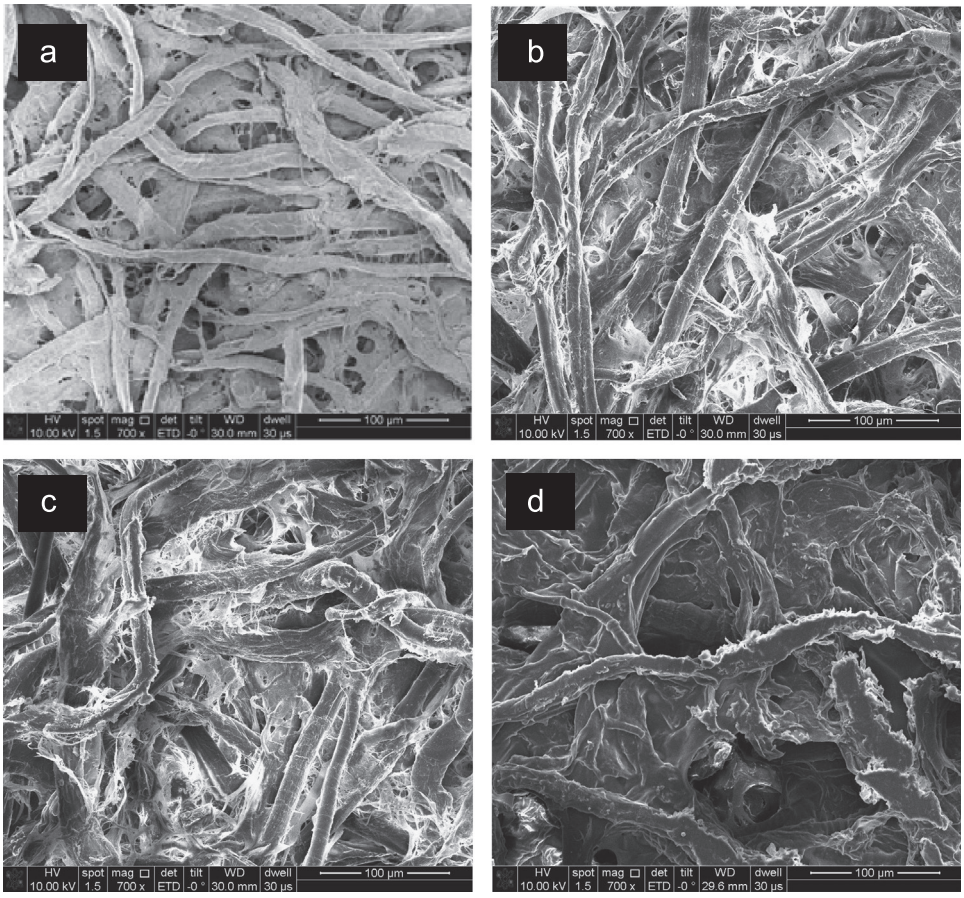

Fig. 7. SEM images of (a) pristine cellulose, (b) cellulose-*g*-PHEMA, 24%, (c) cellulose-*g*-PHEMA, 44.5%, and (d) cellulose-*g*-PHEMA, 92%.

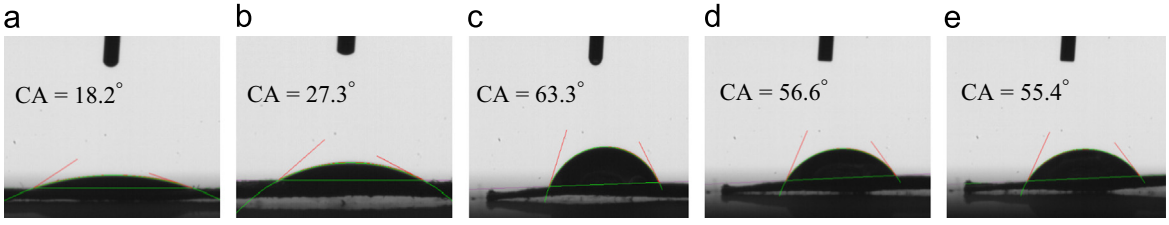

Fig. 8. Change of contact angle (CA) of PHEMA grafted cellulose surfaces at the end of indicated periods for: (a) 11% grafting, 2 s; (b) 21% grafting, 2 s; (c) 44.5% grafting, 2 s; (d) 44.5% grafting, 6 s; and (e) 44.5% grafting, 10 s.

probable radiation effects on PHEMA structure such as branching or chain scission/crosslinking reactions.

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