Poly(2-hydroxyethyl methacrylate) (PHEMA) grafted polyethylene/polypropylene (PE/PP) nonwoven fabric by γ-initiation: Synthesis, characterization and benefits of RAFT mediation

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HIGHLIGHTS

- PHEMA was grafted to PE/PP nonwoven fabric via the RAFT polymerization.
- Diffusion-controlled grafting was observed in compliance with 'front mechanism'.
- FTIR, XPS, SEM, TGA and contact angle measurements were used for characterization.

ARTICLE INFO

ABSTRACT

Polyethylene/polypropylene (PE/PP) nonwoven fabrics were functionalized by γ-initiated RAFT mediated grafting of 2-hydroxyethyl methacrylate (HEMA), and the characterization of the grafted samples was carried out using various techniques. FTIR and XPS analysis showed an increase in the oxygenated content till a certain degree of grafting. The results implied a grafting process following the concept of 'front mechanism'. The initial grafting occurred on the topmost surface layer, and then moved further into the bulk of the polymer matrix. Reversible addition-fragmentation chain transfer (RAFT) mediated grafting yielded a better controlled grafting when compared to those obtained in conventional grafting.

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1. Introduction

Modifying the surface properties of polymers is not only desirable but also vital to control the surface interactions and responses which are required especially in adsorption, separation, and biotechnology applications. Physical, chemical, mechanical and biological methods can be employed for the modification of polymeric surfaces (Hoffman, 1996). Among techniques used, grafting is one of the growing and promising methods for the surface modification as it enables the preparation of new materials from known and commercially available polymers having desirable bulk properties in conjunction with advantageous newly tailored surface properties (Nasef and Güven, 2012; Uyama et al., 1998). The grafting technique can be improved and yield superior results when it is performed in company with the controlled radical polymerization (CRP) techniques instead of conventional free-radical polymerization methods (Barsbay et al., 2013; Barsbay and Güven, 2013).

The advent of CRP methods combining the inherent advantages of free-radical polymerization with that of living polymerization methods in their own way enabled the synthesis of well-defined, narrowly dispersed polymers with designed architectures and molecular weights. Among the CRP methods, the reversible addition–fragmentation chain transfer (RAFT) polymerization is considered as advantageous in terms of applicability to most monomers that reacts through radical polymerization, compatibility with various reaction conditions and simplicity of execution compared to competitive techniques (Chiefari et al., 1998; Perrier and Takolpuckdee, 2005; Moad et al., 2005, 2006; Barner et al., 2007; Barsbay et al., 2007). In addition, RAFT mechanism can successfully be utilized in radiation-induced polymerizations which enables the synthesis of tuneable surfaces in a controlled manner by a one-step method that leads to stable and robust bonding between the surface and the grafted polymer under mild conditions (e.g. at room temperature) without any pre-functionalization step (Barsbay and Güven, 2009).

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Poly(2-hydroxyethyl methacrylate) (PHEMA), was the first synthetic hydrogel used in the medical and pharmaceutical applications due to its high biocompatibility (Wichterle and Lim, 1960). PHEMA-based materials are still widely used in many biomedical applications (Hoffman, 2012; Montheard et al., 1992; Tomić et al., 2010). Nonwoven fabrics are porous materials with great surface area and they have the potential for use in separation and purification of a large range of materials from metal ions to biomolecules after proper surface activation and modification (Kavaklı et al., 2007; Barsbay et al., 2010; Barsbay and Güven, 2013). Considering their inherent characteristics, PHEMA grafted PE/PP nonwoven copolymers may have potential use, especially in biomedical applications. The synthesized nonwoven fabrics may also lead to more complex structures via further chain growth or block extension by subsequent addition of monomer due to post-polymerization activity of their chain that ends as grafting was performed in the presence of so-called RAFT agents.

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA) was passed through a column with aluminum oxide (activated, basic) to remove the inhibitor. HEMA, Cumyl dithiobenzoate (CDB) and solvents with high purity grade were purchased from Sigma-Aldrich. PE/PP nonwoven fabric was supplied by Kurashiki Sen-I Kako Co. Okayama, Japan.

2.2. Irradiation

The irradiation was performed at room temperature in N_2 atmosphere by using a Gammacell 220 ^{60}Co source at a dose rate of 0.26 kGy h^{-1} as determined by Fricke dosimetry. The samples were taken from the chamber at different predetermined time intervals to achieve absorbed doses of 0.20, 0.26, 0.39, and 0.52 kGy for conventional grafting and 4.94, 5.98, 7.10, 8.06, 9.50, 10.4 and 16.6 kGy for RAFT mediated grafting.

2.3. Grafting

PE/PP nonwoven pieces with approximately 1.5 cm × 1.5 cm dimensions and a weight of ∼0.02 g was immersed into grafting solutions prepared by dissolving desired amounts of the monomer (HEMA) and the RAFT agent (CDB) in solvent, e.g. DMF, prior to a typical RAFT-mediated grafting. The polymerization solution in purgeable glass was then connected to N_2 bubbling at room temperature for 10 min. The samples were placed in the sample chamber of a ^{60}Co γ-irradiator at ambient temperature and taken from the chamber at different time intervals. PE/PP-g-PHEMA copolymer samples were repeatedly washed with DMF and THF to remove surface contaminations. The copolymers were then Soxhlet extracted in boiling DMF for 10 h to remove free homo-polymer. Finally, the PE/PP-g-PHEMA samples were dried to constant weight under vacuum at 45 °C. The degree of grafting (DG, wt%) was calculated using the following equation:

$$DG, \% = \frac{w_2 - w_1}{w_1} \times 100 \qquad (1)$$

where w_1 (g) is the weight of the pristine PE/PP fabric before grafting and w_2 (g) is the dry weight of the PHEMA grafted copolymer. In most cases, RAFT agent concentration is adjusted so that free PHEMA with expected theoretical molecular weight ($M_{n,Th.}$) of ∼94.000 g/mol will be formed at complete conversion of

the monomer. This has been chosen in accordance with our previous work (Kodama et al. 2014) and determined to be [HEMA]/[CDB]=722:1 using the following equation:

$$M_{n,Th.} = M_{CDB} + \frac{[HEMA]}{[CDB]} \times M_{HEMA} \times overall\ conversion$$

where $M_{n,Th.}$ is the theoretical number-average molecular weight of polymer; [HEMA] is the initial molarity of the monomer, i.e., HEMA; M_{HEMA} is the molecular weight of HEMA; [CDB] is the initial molarity of the RAFT agent; M_{CDB} is the molecular weight of the RAFT agent, CDB.

Along with the [HEMA]/[CDB] ratio of 722, other values of 361, 462, 1083 and 1444 were also studied to investigate the effect of target molecular weight on grafting. The advantages associated with RAFT mediated grafting was investigated by carrying out parallel conventional grafting studies where PE/PP nonwoven fabrics were treated identically with the exception that no RAFT agent was added to the medium.

2.4. FTIR-ATR Spectroscopy

FTIR spectra of the films were obtained using a Nicolet Magna-IR 750 spectrometer equipped with a DGTS detector. Spectra were collected by cumulating 64 scans at 4 cm^{-1} resolution in Attenuated Total Reflexion mode (ATR) using a diamond-crystal with single reflection.

2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded using 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). Surface elemental compositions were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ± 5%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

2.6. Scanning electron microscopy (SEM)

FEI Quanta 200FEG Scanning Electron Microscope was employed to analyze the surface morphology of PE/PP nonwoven fabrics.

2.7. Contact angle (CA)

Static contact angles (CA) of dry sample surfaces were measured using a Krüss DSA100 model contact angle goniometer at an ambient temperature. Drop volumes of ultra-pure water were 10 μL and the average CA value was obtained by measuring the same sample at three different positions.

2.8. Thermogravimetric analysis (TGA)

Perkin-Elmer thermogravimetric analyzer (Pyris 1 TGA) was employed to record the thermal decomposition properties of polymers over the temperature range from 25 to 700 °C with a programmed temperature increment of 10 °C min^{-1} under N_2 atmosphere.

3. Results and discussion

3.1. Synthesis of PE/PP-g-PHEMA copolymers via RAFT-mediated and conventional γ-initiated grafting methods

A group led by Rizzardo from the Commonwealth Scientific and Industrial Research Organization (CSIRO) first described the concept of using a thiocarbonylthio compound as a chain transfer agent (CTA) to create a living free-radical polymerization system in 1998 (Chiefari et al., 1998; Le et al., 1998). Three years after this discovery, Pan and coworkers were the first to employ γ-radiation for the generation of radicals in a RAFT polymerization (Bai et al. 2001a, 2001b; You et al., 2001; Hong et al., 2001). Since these initial reports, there has been a considerable effort extended to radiation-induced RAFT-mediated homo- and co-polymerizations of a large number of monomers (Barner et al., 2003; Barsbay and Güven, 2009). This facile combination has also been employed to impart a variety of functional groups to the polymeric surfaces in a controlled manner via graft copolymerization technique (Barner et al., 2006; Kiani et al., 2007; Barsbay et al., 2007, 2009). We have recently reported the γ-induced and RAFT-mediated grafting of PHEMA from cellulosic filter paper surface (Kodama et al., 2014). CDB mediated RAFT polymerization of HEMA did not yield a full molecular weight control and very low dispersity under γ-irradiation most probably due to branching, chain scission (Diego et al., 2007) or crosslinking (Hill et al., 1996) reactions that might have occurred on PHEMA structure as a result of radiolysis. The strong radical storage effect associated with CDB at an ambient temperature may also have been effective in the difficulties encountered (Barner-Kowollik et al., 2002; Barner et al., 2003; Feldermann et al., 2004). Multimodal GPC chromatograms with very high polydispersities up to ~19 observed for conventional polymerization, however, were replaced with significantly narrower monomodal chromatograms in case of CDB-mediation. Moreover, the degree of grafting of PHEMA could be controlled smoothly by changing the [HEMA]/[CDB] ratio (Kodama et al., 2014). In the following part of this paper, the predominant variables influencing the degree of grafting (DG) of PHEMA to PE/PP nonwoven fabric and advantages associated with RAFT-mediation are discussed.

Fig. 1 compares the DG values obtained at 30% HEMA (v/v) solution in DMF as a function of absorbed radiation dose for RAFT-mediated and conventional grafting. For both grafting techniques DG increases rapidly with absorbed dose at an initial stage, and then it levels off at higher doses. This is simply attributed to the decrease of monomer concentration available for grafting with increasing conversion with dose. It is further seen in Fig. 1 that grafting is significantly faster in conventional grafting compared to RAFT mediated grafting; e.g. conventional grafting yields a DG of 6.15% at an absorbed dose of 0.52 kGy while a similar DG value, i.e. 6.4%, is attained at a higher dose of 5.98 kGy in the latter method. Polymerization of HEMA in the absence of CDB is very rapid; full monomer conversion is reached in about 3 h, and the final product in solution is usually a cross-linked PHEMA gel. The PHEMA gel entangled in between the micro-scale fibers of PE/PP fabric is difficult to remove from the copolymers synthesized, which causes an erroneous contribution to DG. Therefore, the content of the sealed ampoule in conventional grafting was opened to air at the end of second hour, i.e. in pre-gelation stage, in order to stop the polymerization before reaching the full monomer conversion and to prevent gel formation. In contrast, RAFT-mediated polymerization of HEMA is remarkably slower due to the chain transfer reactions and radical storage effect associated with CDB (Barner-Kowollik et al., 2002; Barner et al., 2003; Feldermann et al., 2004); full monomer conversion is observed after around 64 h without yielding an insoluble gel. At such a high irradiation time, the number of free radicals produced in PE/PP would be significantly higher. These radicals would initiate more grafting chains. Moreover, longer polymerization time is also beneficial in enabling the diffusion of more HEMA monomer into the bulk of the PE/PP fibers. This increases the degree of grafting inside the bulk of the substrate. We have previously showed that grafting of acrylic acid to PE/PP nonwoven fabric proceeds via front mechanism, where it starts at the surface which is in intimate contact with the monomer solution, and then proceeds inward towards the bulk of the fibers by progressive diffusion through the swollen grafted layers (Barsbay and Güven, 2013). Grafting process proceeding via front mechanism is reported for similar systems by other groups as well (Ikram et al., 2011; Hegazy et al., 1986; Hidzir et al., 2012). The grafting of PHEMA to PE/PP nonwoven fabric proceeding via front mechanism will be discussed in more detail in the later parts of this report. It is well known that the diffusion of monomer towards the bulk is very much a function of monomer transport rate, and hence on polymerization time (Barsbay and Güven, 2013). Consequently, the RAFT mediated grafting method achieves a higher degree of grafting compared to conventional technique in pre-gelation stage due to enhanced amount of monomer diffusion towards the bulk of the fibers within the longer polymerization time applied. Obtaining a slower grafting rate by RAFT mediation is beneficial also for controlling the degree grafting (DG).

Fig. 2 shows that achievement of a target DG can also be provided by varying the [HEMA]/[CDB] ratio. Decreasing the
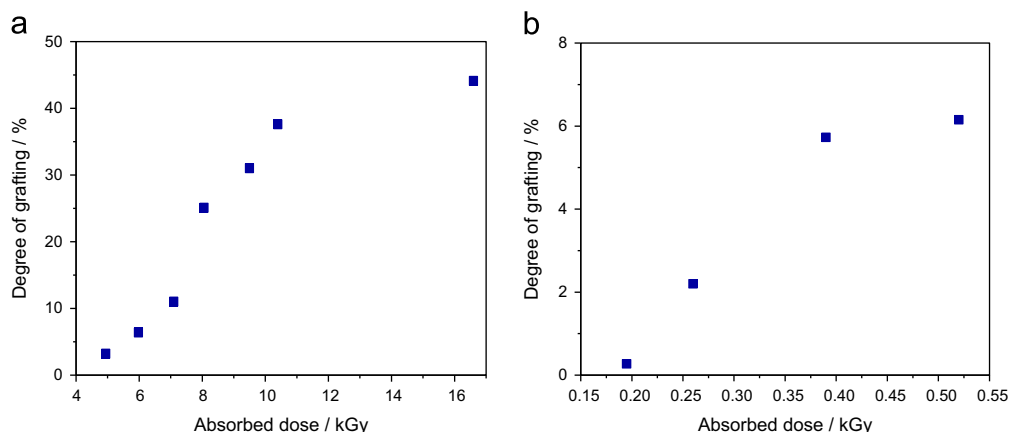

Fig. 1. Effect of absorbed dose on degree of grafting for (a) RAFT mediated, and (b) conventional grafting. Dose rate: 0.26 kGy h^{-1}, solvent: DMF, monomer concentration: 30% (v/v), room temperature. [HEMA]/[CDB] is 722 for RAFT mediated grafting.

concentration of RAFT agent results in an increase in the polymerization rate. Consequently, the monomer conversion, i.e. fraction of the monomer polymerized, increases at a given reaction time, yielding a gradual increase in DG with [HEMA]/[CDB] ratio. The dependency of DG on monomer concentration is shown in Fig. 3. The amount of monomer diffused into fibers at a given reaction time increases when there are more monomer molecules in close proximity to the substrate grafted. Therefore, DG increases with monomer concentration for a given absorbed dose as seen both in Fig. 3a andb. Comparison of these figures reveals that RAFT mediated grafting yields remarkably higher graft degrees compared to the conventional grafting. However, this is attributed to the longer polymerization time, i.e. higher absorbed doses, applied during the RAFT mediated grafting.

The advantages of RAFT mediation to achieve higher and relatively controllable graft degrees compared to conventional grafting method are clearly revealed by above discussions. However, it should further be mentioned here that the benefit of RAFT mediated grafting was not that clear when a substrate like cellulose was used instead of PE/PP. Grafting occurs only on the surface of cellulose, and does not proceed towards the bulk via front mechanism (Kodama et al., 2014). The lowered rate of polymerization provided by RAFT mechanism seems to be advantageous in obtaining higher DG values when a substrate like PE/PP nonwoven fabric is used, where a diffusion-controlled grafting process occurs via front mechanism.
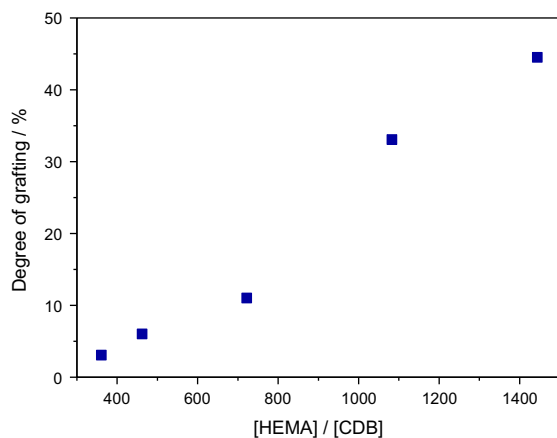
3.2. Characterization of PE/PP-g-PHEMA copolymers

FTIR spectroscopic analysis was used to determine the composition of PHEMA grafted nonwoven fabric copolymers, Fig. 4. In the spectrum of pristine PE/PP fabric, characteristic absorption bands of $-CH_3$ antisymmetric, $-CH_2$ antisymmetric, and $-CH_2$ symmetric stretching vibrations were observed at 2966 cm^{-1}, 2917 cm^{-1} and 2847 cm^{-1}, respectively (Kavaklı et al., 2007). The incorporation of PHEMA in copolymers was confirmed by two characteristic peaks at around 3400 cm^{-1} and 1718 cm^{-1} corresponding to hydroxyl (OH) and carbonyl (C=O) stretching vibration bands, respectively (Perova et al., 1997). The depth of penetration of the incident beam in FTIR-ATR spectroscopy increases as the wavenumber decreases and it is about a few microns depending on the material (Betz et al., 1994; Barsbay et al., 2013). It is clearly seen in Fig. 4 that the intensities of the hydroxyl and carbonyl peaks increase with increasing amount of PHEMA in copolymer composition at initial stages of grafting, but the spectra of copolymers with DG of 97% and 150% are quite similar to each other. This indicates that the depth analyzable in FTIR-ATR is saturated by the grafted PHEMA chains beyond a certain degree of grafting. This finding is supported by the XPS analysis to be discussed below and it is in very good agreement with the previous data (Saxena et al., 2010).

XPS is a very powerful surface-sensitive quantitative spectroscopic technique that can be used to investigate the top~5–10 nm surface layers of a material. XPS survey wide scans of pristine

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 7.10 kGy.
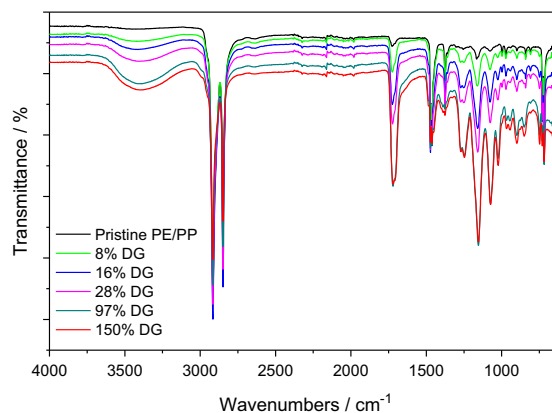

Fig. 4. FTIR spectra of pristine PE/PP nonwoven fabric and PE/PP-g-PHEMA copolymers with various degree of grafting (DG).
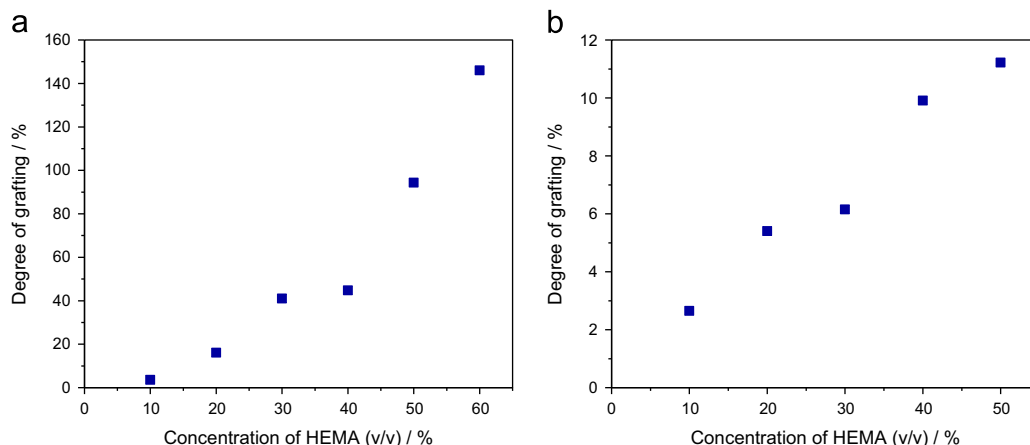

Fig. 3. Effect of monomer feed concentration on degree of grafting for (a) RAFT mediated, and (b) conventional grafting. Dose rate: 0.26 kGy h^{-1}, solvent: DMF, room temperature. Total doses absorbed during RAFT mediated and conventional grafting are 10.4 kGy and 0.52 kGy, respectively. [HEMA]/[CDB] is 722 for RAFT mediated grafting.

PE/PP nonwoven fabric and PHEMA grafted copolymers with various DGs are shown in Fig. 5. Survey wide scan spectrum of pristine PE/PP shown in Fig. 5a consists of two characteristic peaks corresponding to C 1 s and O1s at 285.0 eV and 532.1 eV, respectively. Around 4.5% O content of pristine fabric is attributed to the surface oxidations and catalyst residues that may exist in commercial PE/PP and other polyolefin fabrics (Zheng et al., 2010; Barsbay and Güven, 2013). A remarkable increase in O content is observed in the composition of copolymer with DG of 37%, demonstrating the grafting of PHEMA. However, the O content seems to remain almost constant for the rest of the copolymer samples. This is clearly shown in Fig. 6 where the change of oxygen content (O1s/C1s) is presented as a function of DG. Fig. 6 shows that surface has already been saturated by O atoms at a DG of 37%, yielding almost no change thereafter all along the graft level of 112.6%. Moreover, the O/C ratio obtained after grafting, which is about 0.1 depending on the DG, is far lower than the theoretically calculated value from the chemical structure of PHEMA where O/C should be equal to 0.50. This suggests that
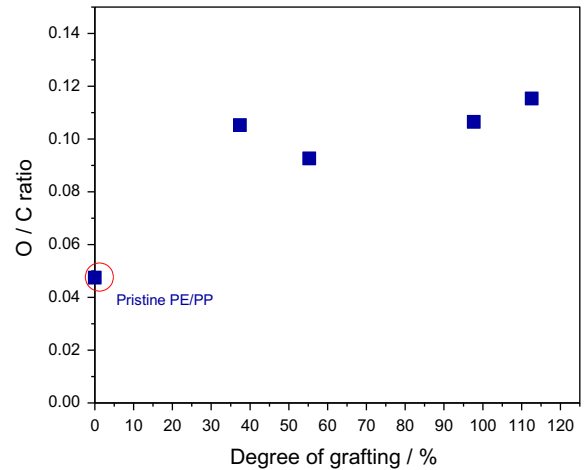

Fig. 6. Change of the O/C ratio calculated from XPS spectra for pristine PE/PP nonwoven fabric and PE/PP-g-PHEMA copolymers with DG of 37.4%, 55.3%, 97.7%, and 112.6%.
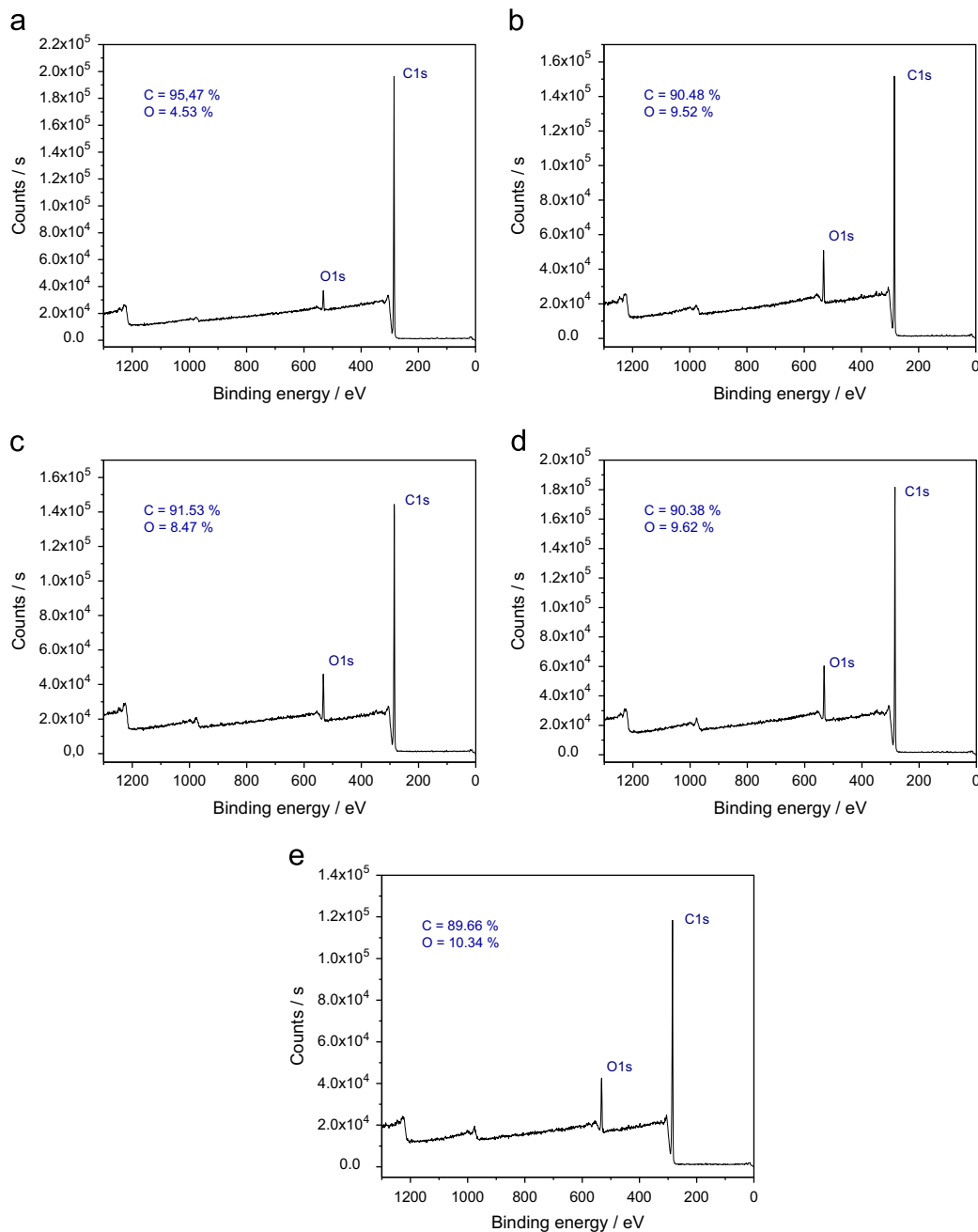

Fig. 5. XPS survey wide scan of (a) pristine PE/PP nonwoven fabric and PE/PP-g-PHEMA copolymers with degree of grafting (DG) of (b) 37.4%, (c) 55.3%, (d) 97.7%, and (e) 112.6%.

PE/PP substrate substantially contributes to the composition on the top ~5–10 nm surface depth, that is the top surface layers are not constituted solely of pure PHEMA chains. Therefore, it is expected that the grafting proceeds deep inside the surface layers by creating new fronts and enriching them without significant contribution to the already grafted zones after a certain saturation degree. This degree is probably a function of the distribution of
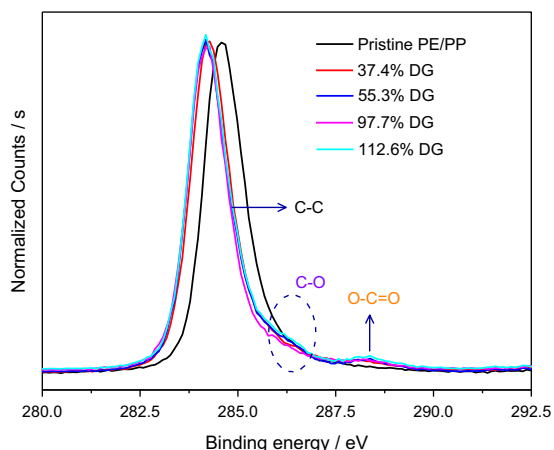

Fig. 7. C1s XPS spectra for pristine PE/PP nonwoven fabric and PE/PP-*g*-PHEMA copolymers with various degree of grafting (DG).
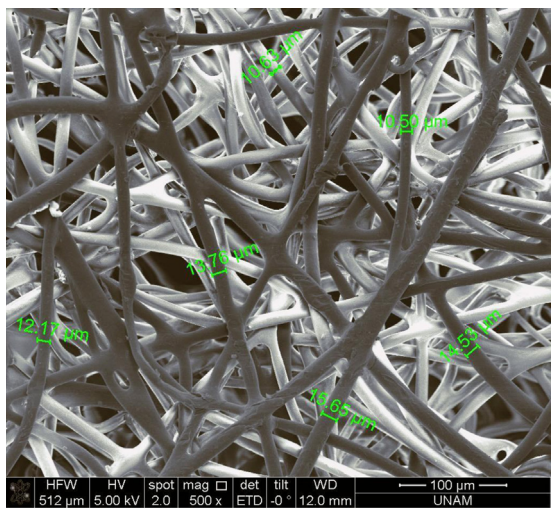

Fig. 8. SEM image of porous PE/PP nonwoven fabric.

amorphous domains where grafting is mainly occurred through the bulk of the matrix (Choi et al., 2001).

C1s core level spectra shown in Fig. 7 compares the C atoms existing in pristine PE/PP and copolymers with regard to their composition and different forms. Detailed chemical analysis on the spectra of the copolymers reveals that two new peaks due to PHEMA appear at around 288.4 eV and 286.2 eV due to the carboxylate carbon (O–C=O) and carbon in C–O groups, respectively (Kodama et al., 2014). The intensities of these peaks seem almost the same for all copolymers, indicating a grafting saturation at the top layers as mentioned above. The main peak appeared below 285 eV can be assigned to the non-oxygenated C atoms existing in PE/PP and grafted PHEMA structures. It is clearly seen that this peak shifts to lower binding energies after grafting, indicating a certain change in electron cloud density around C atoms due to the incorporation of PHEMA into the copolymer composition.

We have previously showed that the surface hydrophobicity of PE/PP nonwoven fabric is completely altered even at very low DG values of acrylic acid, e.g. DG < 3% (Barsbay and Güven, 2013). A water droplet applied to the surface of hydrophobic pristine PE/PP fabric disappears within less than a second, rendering measurement of the contact angle impossible. The water droplet simply rolls off around the PE covered fibers through the pores and fills the gaps. The porous structure of the nonwoven fabric is clearly seen from the SEM image in Fig. 8. On the other hand, when a polymer like PHEMA is grafted the fibers become more hydrophilic. This imposes a certain restriction against flowing of water droplets through the fabrics, enabling the measurements of contact angle (CA) as seen in Fig. 9. The measured CAs are quite stable and change just a few degrees within the first 10 min, in very good agreement with our previous observations (Barsbay and Güven, 2013). This shows that the grafting of PHEMA to PE/PP nonwoven fabric completely alters the composition and properties of the outermost surface layer even at low DG values such as 3.5% (w/w), Fig. 9a. However, the effect of DG on the hydrophilicity of surface is not clear, as the surface characterization of nonwoven fabric via CA measurements is not straightforward due to the inherent porous structure of the nonwoven surface.

TGA was performed to examine the effect of composition on the thermal properties of PHEMA grafted copolymers. The dynamic and derivative thermograms of the pristine PE/PP, PHEMA and graft copolymers are shown in Fig. 10. The thermal degradation of PE/PP proceeds by a one-step process with the maximum decomposition temperature at ~458 °C, in agreement with previous reports (Kavaklı et al., 2007; Barsbay et al., 2010). Degradation of nonwoven starts at around 330 °C and continues till ~500 °C, giving almost no residue at 700 °C. As seen in Fig. 10b, the area of the curve at ~458 °C decreases with increasing DG, indicating the gradual decrease of PE/PP component in copolymer
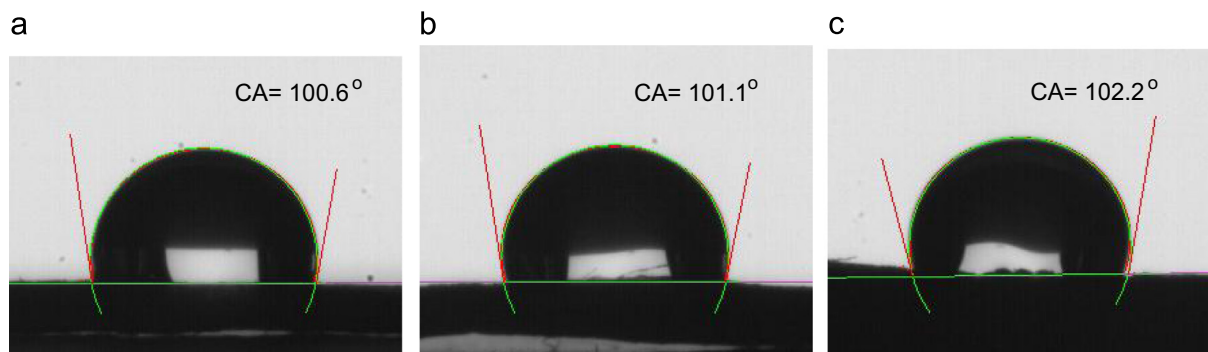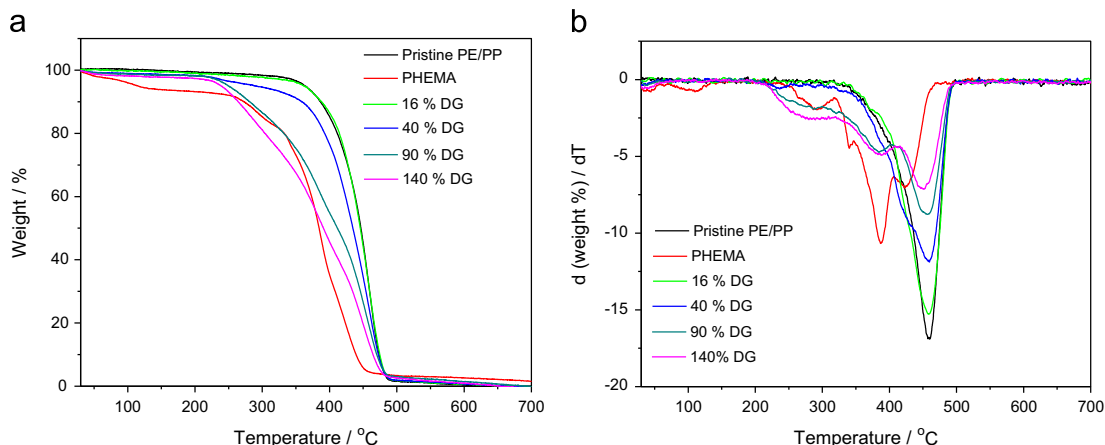

Fig. 9. Contact angle (CA) values at the end of 1st minute for PE/PP-*g*-PHEMA copolymers with degree of grafting (DG) of (a) 3.5%, (b) 55.3%, (c) 97.7%.

Fig. 10. (a) Thermogravimetry (TG), and (b) derivative thermogravimetry (DTG) curves of pristine PE/PP nonwoven fabric, PHEMA, and PE/PP-*g*-PHEMA copolymers with various degree of grafting (DG).

composition. The thermogram of PHEMA presents a multi-step degradation profile with a residue of 1.5% (w/w) remained at 700 °C. The copolymers also present multiple degradation profiles that seem more or less superposition of those obtained for PHEMA and PE/PP.

4. Conclusions

We have synthesized PHEMA grafted PE/PP nonwoven fabric via γ-initiated RAFT mediated graft copolymerization technique. The grafting process follows the concept of front mechanism. The main emphasis is that the employment of RAFT polymerization in grafting proceeding via front mechanism may be beneficial for obtaining higher DG values in a controlled fashion when a substrate suitable for the front mechanism and a rapidly polymerizing monomer are used.

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