Photo-grafting polymerization, microstructure and hydrophilicity of spun-blown polypropylene nonwoven fabrics

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Abstract. The non-polarity and poor hygroscopicity of polypropylene (PP) impede its wide application. The polar monomers, glycidyl methacrylate (GMA), hydroxyethyl methacrylate (HEMA) and methacrylamido propyl trimethyl ammonium chloride (MAPTAC) were grafted onto the spun-blown polypropylene nonwoven fabric (SMS) under ultraviolet irradiation, and the subsequent functionalization of the grafted fabrics was implemented as well. The results show that both the monomer and the polymer of HEMA are hydrophilic and are grafted uniformly onto the fabric surface as well as into the melt-blown layer with the hydrophilicity being enhanced slightly, whereas the hydrophilic monomer yet the hydrophobic polymer of MAPTAC prefer to be grafted onto the melt-blown fibre with the wicking effect. Both the monomer and the polymer of GMA are hydrophobic and are favourably grafted into the melt-blown layer with no hydrophilicity being improved. The grafting diminishes the fibre crystallinity and melting temperature, especially significant for the graftings of hydrophobic polymers, PGMA and PMAPTAC. All the grafting reduces the water flux of the grafted fabrics no matter what the grafting polymers are hydrophilicity or hydrophobicity not.

1. Introduction

The chemical grafting polymerization modification is one of most important techniques to provide polarity and functionality for the hesitant polymers. The usual and ready modification methods include ultraviolet, gamma-ray, electron beam and plasma irradiations. It seems that ultraviolet irradiation is cost-effective, little damage and readily implemented. Some non-polarity monomers are easily adsorbed onto the PP surface and readily converted into polarized substance. The PP substrate can be fibers, films, membranes and fabrics. The large specific area usually can uptake a plenty of monomers. Among them, the melt-blown nonwoven fabrics often adsorb much more non-polar monomers than the others since the fiber diameter in the fabric is much small. In this work, GMA, HEMA and MAPTAC were grafted onto the SMS fabrics respectively, and the subsequent functionalization of the grafted fabrics was implemented as well. The grafting, microstructure and hydrophilicity of the grafted nonwoven fabrics were investigated.

2. Experimental

2.1. Photo-grafting polymerization

The SMS fabric (100g/m2) was washed with acetone, water, and dried at vacuum oven. The grafting solution consisted of monomer, crosslinkers [N,N'-Methylene bisacrylamide (MBAA) for MAPTAC, and pentaerythritol triacrylate (PATA) for GMA and HEMA], benzophenone BP, surfactant Tween 60 and the dispersion medium methanol/water. The imbibed PP fabric was sent into glass vessel of UV-light reactor, being vacuum and nitrogen purged, at the irradiation power 300W and time 30min. The grafted fabric was rinsed with acetone/methanol and water sequentially, and finally dried in vacuum. The grafting yield was calculated based on the mass gain. In addition, the sulfonation of epoxy group of the PP fabric grafted with GMA was realized by treating sodium sulfite, and quaternization with glycidyl trimethyl ammonium chloride (GTMAC) to hydroxyl group of the HEMA-grafted fabrics.

2.2. Characterization of structure and properties of the grafted fabrics
The morphologies of fabric and fibre cross-section were observed with scanning electron microscope, Hitachi TM3030. The compositional structure of the grafted fabrics was characterized with Fourier transform infrared spectroscopy, Nicolet 5700. The crystallinity and melting temperature of the samples were determined with differential scanning calorimetry (DSC Diamond 5700, Perkin-Elmer, USA).Water contact angle measurement was implemented with Contact Angle System OCA21, Dataphysics Co., Germany with the water drop size of 0.2μL. X-ray photoelectron spectroscopy (XPS) was used to characterize the functionalization of the GMA- and HEMA-grafted SMS with SHIMADZU/KRATOS Axis Ultra HAS. The crystallinity of the SMS nonwoven was analyzed by XRD using an advanced diffractometer (X 'Pert-Pro MRD) with CuKα radiation (40kV, 40mA).

3. Results and Discussion

3.1. Grafting of the SMS fabric
Figure 1 gives the infrared spectra of the raw and the grafted SMS fabrics. The adsorption peaks of the pristine PP fabric at 1458, and 1378cm^{-1} are attributed to the asymmetric bending of C-H in methyl and methylene groups and symmetric bending of C-H in methyl group. The three peaks at 1166, 999 and 975cm^{-1} may relate to the helix configuration of isotactic PP. The peaks appeared at 1724, 1196 and 1062cm-1 come from the ester group of GMA-grafted fabric. Similarly, the peaks appeared at 1730, 1255 and 1078cm^{-1} are assigned to the hydroxyethyl ester of HEMA-grafted fabric. The peaks at 1640, 1530 and 1205cm^{-1} are allocated to the amide group whereas the adsorptions at 1477cm^{-1} may relate to the symmetric bending of the methyl group[1]. Therefore, all the three monomers are grafted onto the SMS nonwoven fabrics.
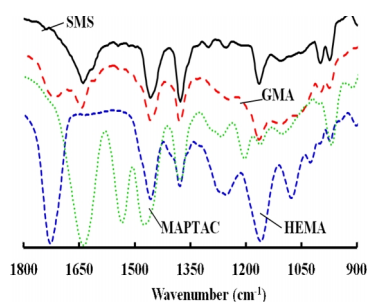

Figure 1. Infrared spectra of the raw and the grafted SMS nonwoven fabrics (GMA81.4%, HEMA70.3%, MAPTAC 67.6%)

Figure 2 give the SEM images of the raw and the GMA-grafted fabrics. In the figure 2a, there is trace amount of PGMA grafted onto the fabric surface, while in the left side of figure 2b there gather a plenty of the grafted polymer. This implies the grafting takes place in the inner part and preferably in the one side of the fabric. Figure 2c displays the sectional morphology of the raw SMS fabric, and the fiber diameter in the inner melt-blown layer is much smaller than that of the two outside spun-bonded layers. Therefore, the finer diameter inner layer is supposed to uptake more monomer than the larger diameter spun-bonded layers during the imbibing process. The asymmetric distribution of the grafting polymer can be attributed to the sample setup during grafting process, since the side faced the UV light will polymerize intensively in comparison with the side opposite to UV light. Figure 3

demonstrate the relative reflection intensities of the SMS fabric, and it can be found that the crystallinity of the melt-blown layer is much smaller than those of the two spun-bonded layers. Thus, it is the small diameter and the low crystallinity that make grafting to prefer in the melt-blown layer.
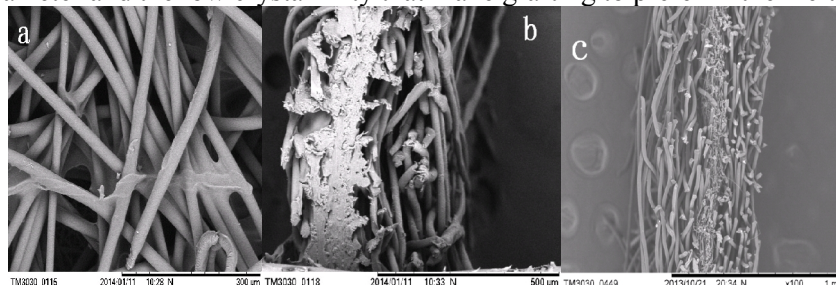

Figure 2. SEM images of the SMS fabric grafted with GMA at the yield of 60.9% (a: nonwoven surface morphology, b: the nonwoven section, c the blank SMS section)
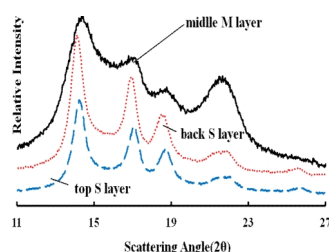

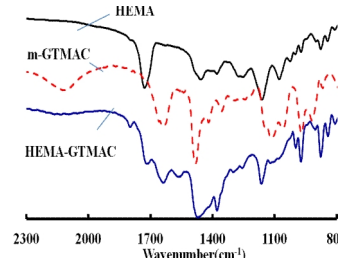**Figure 3.** Diffractiograms of the component layers of the SMS fabric

Figure 4. Infrared spectra of the modified SMS fabrics (HEMA means SMS-g-HEMA, m-GTMAC means molecule GTMAC, HEMA-GTMAC means SMS-g-(HEMA-GTMAC))

3.2. Functionalization of epoxy- and hydroxy-groups containing SMS fabrics

Figure 4 indicates the infrared spectra of the functionalized HEMA-grafted SMS fabrics. The peak at $2123cm^{-1}$ comes from the alpha mode of translation of water molecule associated with GTMAC [2]. The peak ca. $1720cm^{-1}$ from the ester's carbonyl stretching vibration in HEMA-GTMAC is slightly red-shifted due to the functionalization. The peak at $1646 cm^{-1}$ is assigned to the delta (O-H) deformation of associated water molecule. The two peaks at 1382 and $1477cm^{-1}$ are originated from the bending of methyl group respectively. The peak at $921cm^{-1}$ of the molecule GTMAC disappears at the spectrum of the functionalized HEMA-grafted SMS fabric. All of which indicates that the epoxy group of GTMAC has reacted with the hydroxyl group of HEMA-grafted fabric.

Figure 5 show the X-ray photoelectron spectra of the SMS-g-(HEMA-GTMAC) fabric. C1s chemical shift of PP is generally thought to appear in the vicinity of 284.5eV. There also appear overlapped peaks at ca. 286 and 289eV due to the sizing agent on the fiber surface and/or thermo-oxidation while the SMS fabric was being processed. When HEMA was grafted onto the SMS surface, and there appears a wide plateau at the high chemical shift wing up to 292eV, which are attributed the carbon atoms from ester and hydroxyl groups. However, it is puzzled why the peak red-shifts down to ca. 286eV and the plateau seems cut-off at the high chemical shift since the reaction of epoxy with hydroxyl groups never means to "swallow" ester group up. It may be postulated that the introduction of the bulky quaternary ammonium with three methyl groups blocks the carbon atoms connected to the original ester and hydroxyl groups, and the binding energy of the carbon atoms from the methyl group increases slightly due to the increase of C-N bond and the electron abstract of nitrogen cation in comparison with the common and aliphatic carbon atoms [3]. Usually there should be no oxygen present in the raw SMS fabric, and the peak is indeed very small as indicated in O1s spectra in figure 5. While PHEMA was grafted onto polypropylene surface, and there are a large number of ester groups in the grafting polymer with two kind of oxygen atoms in the sense of chemical environment. As mentioned before, the bulky quaternary ammonium loaded with three methyl groups again blocks

the oxygen atoms of ester group but with the oxygen atoms from original epoxy group being shown up. The chemical shift at ca. 398eV is derived from the nitrogen atom in the N1s spectra. Thus, it can be proved that the HEMA and the GTMAC are connected to the polypropylene surfaces, especially the quaternary ammonium uniformly covers on the PP fabric.
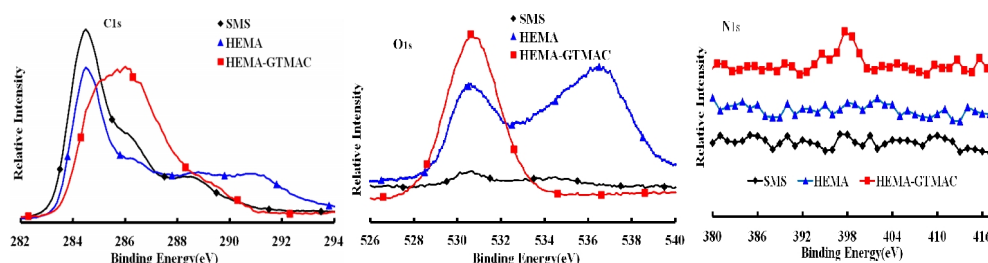

Figure 5. X-ray photoelectron spectra of SMS-g-(HEMA-GTMAC)

Figure 6 show the X-ray photoelectron spectra of the GMA-grafted and the subsequently sulfonated fabrics. In the C1s spectra, after the grafting of GMA, namely the introduction of the carbons from ester carbonyl and epoxy groups, there appear two overlapped peaks at high chemical shift side. However, after the reaction between epoxy group and sodium sulfite has occurred, the original epoxy group is transformed into a secondary hydroxyl and a sulfonic acid groups, and the two slightly new carbons are formed due to the secondary hydroxyl and the methylene connected to sodium sulfonate. In the O1s spectra, since the three kind of oxygen atoms in the ester group are present after GMA being grafted onto the SMS fabric, so there should be three chemical shift peaks to be appeared. However, the close to the chemical environment of the oxygen atoms from epoxy group and ester single bond causes to merge into one big peak. Similarly, after the reaction between the epoxy and sodium sulfite, it seems to appear two mergers of the oxygen atoms from the single ester bond and secondary hydroxyl group and from sulfonic acid and ester carbonyl groups. The size of peak at high chemical shift, namely ca. 534eV, is larger than that at ca. 530eV simply due to more oxygen from the sulfonate and carbonyl groups. In the Na1s spectra, a twin-peak at 1070-1073eV separated by ca. 3eV should be derived from the newly formed sodium sulfonate and residual sodium sulfite as well. Actually sodium sulfite was also found in IR spectra. In the S2p spectra, because 2p-orbit electron will split into two small peaks, $S_{2p3/2}$ and $S_{2p1/2}$ with the separation ca.1.18eV were found in the spectrum.
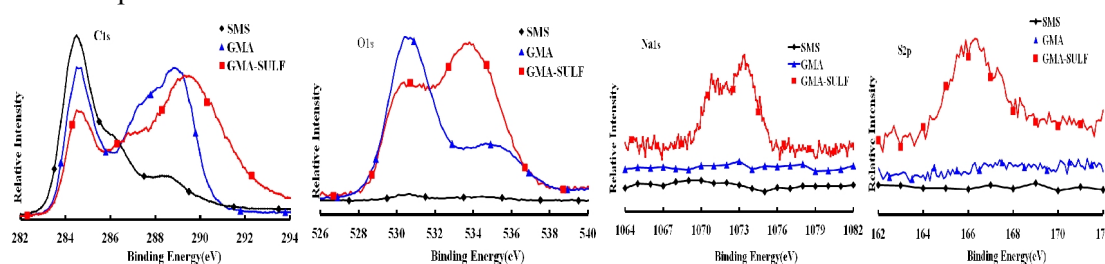

Figure 6. X-ray photoelectron spectra of SMS-g-(GMA-SULF)
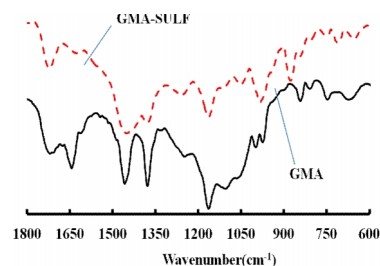

Figure 7. Infrared spectra of the modified SMS fabrics (GMA means SMS-g-GMA, GMA-SULF means SMS-g-(GMA-SULF))
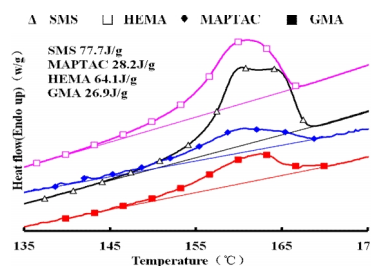

Figure 8. Differential scanning thermograms of the SMS and the grafted fabrics (MAPTAC 128.9%, HEMA 20.5%, GMA 135.8%)

Figure 7 shows the infrared spectra of the GMA-grafted and the subsequently sulfonated fabrics. The peaks at f 1267 and 1060cm^{-1} are assigned to the stretching vibrations -SO$_3$- from sulfonic acid group. The peak at 880cm^{-1} may relate to the residual sodium sulfite. The shoulder peak at ca.1430cm^{-1} is associated with the new generation of secondary hydroxyl group, and the peak at 848 cm^{-1} from the epoxy group is weakened simultaneously. The results evidence the happening of the reaction between sodium sulfite and epoxy group. This is consistent with the Takeda et al's finding [4].

3.3. Microstructure of the grafted SMS fabrics
Figure 8 demonstrates the differential scanning thermograms and the enthalpy of fusions of the pristine and grafted SMS fabrics. The double melting point phenomenon of the pristine SMS can be attributed to the re-organisation and re-crystallisation during the hot air drawing. The higher melting endotherm in the twin-peak corresponds to the fusion of lamellar crystals formed during the primary crystallisation process, whereas the lower corresponds to the melting of crystals grown mainly in the inter-fibriliar regions during the secondary crystallization process [5]. The enthalpy of fusion of complete alpha-spherulite is 209J/g [6], and thus the crystalline degree of the raw SMS fabric is 37.2%. The shape and position of the melting peak didn't change very much for the HEMA-grafted fabric, with the degree of 30.7%, in comparison with the un-grafted one. However, the twin-peak of the GMA- and MAPTAC-grafted fabrics seems to merge into an extended one, and the crystallinities of the two versions were decreased remarkably down to 12.9% and 13.5% respectively. Generally the grafting modification is believed to take place in the amorphous regions, and the grafting tends to erode the microcrystalline domain and finally destroy small crystallites.

The good wettability of GMA insoluble in water onto the PP surface is expected and this is benefit to grafting, while the water soluble of both the monomer and polymer of HEMA are difficult in wetting and grafting. However, although MAPTAC is hydrophilic, its hydrophobic polymer can wet PP surface and dominate its high grafting yield.

3.4. Hydrophilicity of the grafted SMS fabrics
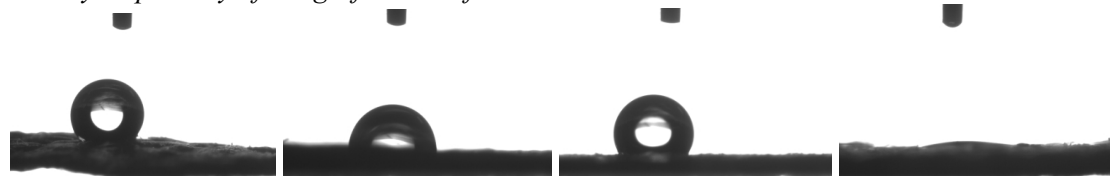
SMS blank, 132.1°///HEMA-61.9%, 89.2° ///GMA-96.6%, 121.4°///MAPTAC-129.0%,0°
Figure 9. Water contact angles of the pristine and the grafted SMS fabrics

Figure 9 display the water contact angle of the pristine and the grafted fabrics. The apparent water contact angles (θ_a) of the blank SMS, HEMA-grafted, GMA-grafted, and MAPTAC-grafted fabrics are 132.1°, 89.2°, 121.4° and 0° respectively. Theoretically the large water drop may be also suspended by the air entrapped in the SMS fabric. Therefore, and the real water contact angle should be calculated according to the Cassie-Baxter equation. If the volume fraction of air entrapped of pristine SMS fabric is 0.55, namely, f2=0.55, and f1=0.45, then the real contact angle of the raw PP will be ca. 105.5°. This value is almost consistent with the result of the literature [7]. The grafting and filling of hydrophobic PGMA diminishes the porosity of fabric. If the volume fraction of the entrapped air is 0.45, and f1=0.55, then the real angle of the GMA-grafted PP fiber will be ca. 97.4°. Similarly, the real contact angle of the HEMA-grafted PP fiber will be ca. 32.5°. It sounds reasonable. However, the grafting of partially hydrophilic polymer, PMAPTAC improves the water wettability of PP surface, and the porous structure produces a capillary effect or a wicking effect, and thus the Cassie-Baxter equation cannot work well.

Table 1 gives the water permeability of the raw and the GMA- and HEMA-grafted SMS fabrics. The water flux of the raw fabric was increased but the increase rate of flux was decreased with the increase of pressure. This may imply that the pressure gets the fabrics dense. In fact, the water flow

volume under pressure was decreased with pressure. For the grafted fabrics, all the grafting reduces the water flux no matter what the grafting polymers are hydrophilic or hydrophobic. The increase of grafting degree all weakens the flowability across the fabrics. Whether the grafted fabrics are hydrophilic or hydrophobic doesn't present significant difference.

Table 1. Water flux of the blank and the grafted fabrics

Fabrics	Vaccum(mmHg)	Water flux(L/m^{2}h)	Water flow volume under pressure (L/(m$^2\cdot$h$\cdot$atm))	
SMS	70	610	6623	6623
	228	1825	6083	6083
	350	2625	5700	5700
GMA (54.9%)	66	180	2073	3211
	352	550	1188	1839
GMA (71.8%)	72	100	1056	1813
	364	310	647	1112
HEMA (37.8%)	78	200	1949	2685
	356	850	1815	2501
HEMA (66.5%)	75	100	1013	1687
	358	480	1019	1697

Note: the water flow in second column is obtained by discounting grafting polymers

4. Conclusions

The three monomers were grafted onto the SMS fabrics under ultraviolet irradiation, and the sequential sulfonation and the quaternization of the grafted fabrics were implemented as well. The hydrophilic HEMA is grafted uniformly onto the fabric surface and into the interior fabric with the hydrophilicity improved slightly, whereas the hydrophilic monomer yet hydrophobic polymer of MAPTAC prefer to be grafted onto the melt-blown layer with the wicking effect. The hydrophobic GMA is favourably grafted into the interior melt-blown layer with no hydrophilicity improved. The grafting diminishes the fibre crystallinity and melting temperature, especially for the graftings of hydrophobic GMA and MAPTAC. All the grafting reduces the water flux of the fabrics no matter what the grafting polymers are hydrophilicity or hydrophobicity not.

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