Photoinduced Cografting of Vinyl Benzyl Trimethylammonium Chloride and 2-Hydroxyethyl Methacrylate onto Nylon Nonwoven Fabric for Preparing an Anion-Exchange Sorbent: Optimum Cografting Conditions and Characterization

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ABSTRACT: Vinyl benzyl trimethylammonium chloride (VBTAC) and 2-hydroxyethyl methacrylate (HEMA) were cografted onto nylon fiber by photoirradiation-induced graft polymerization with benzophenone (BP) as the photoinitiator and methanol (MeOH) as the solvent. The cografted VBTAC afforded an anion-exchange functionality to the nylon-*g*-HEMA–VBTAC fabric without any further modification. The concentration of each and the ratio of the HEMA and VBTAC monomers in solution were the most important factors determining the degree of grafting and anion-exchange capacity (AEC) of nylon-*g*-HEMA–VBTAC. With regard to the AEC of the grafted fabric, the optimal HEMA/VBTAC ratio was 10 : 7 (v/w), which gave a molar fraction of VBTAC of 0.286. The photoirradiation time, temperature of the reaction, and concentrations of BP and MeOH were opti-mized for the cografting of VBTAC and HEMA onto the nylon fabric. The molar ratio of VBTAC units in the grafted polymer was dependent on the photoirradiation time but not on the other parameters. The results showed that the AEC of nylon-*g*-HEMA–VBTAC was governed directly by its VBTAC density rather than by its degree of grafting. The grafted fabric was characterized in terms of its surface area, porosity, and surface charge density by Fourier transform infrared, ^{13}C-NMR, and scanning electron microscopy studies, and the regeneration efficiency was estimated. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2723–2733, 2010

Key words: copolymerization; degree of polymerization (DP); functionalization of polymers; photopolymerization; radical polymerization

INTRODUCTION

Various anionic species, inorganics and organics, are commonly encountered, environmentally important major or trace pollutants in both wastewater and drinking water. Because of their associated environmental impact and health risks, many of these anionic pollutants are subject to increasingly stringent environmental regulations, with concentration limits set at levels as low as tens of parts per million to parts per billion. A number of technologies have been developed for the removal of anionic pollutants from water and wastewater, including oxidation, coagulation, precipitation, electrolysis, ion exchange, adsorption, membrane separation, and reverse osmosis.[1–7] Among them, adsorption and ion exchange are expected to be the most convenient methods for the removal of ionic pollutants from water, particularly in terms of initial cost, simplicity of design, ease of operation, insensitivity to climate, and the prevention of the formation of potentially toxic byproducts.[8–10] Although various sorbents, such as activated carbon and clay minerals,[7,11] ferric and aluminum (hydr)oxides,[12–15] biomass,[16,17] and ion-exchange resins,[18–20] have been investigated for the removal of anionic pollutants from water and wastewater with varying degrees of success, the exploration of more effective and less expensive sorbents continues to be a hot topic. In recent years, graft polymerization has been widely used to develop sorbents with various functional groups, high efficiencies, and ion-selective properties because grafting can be restricted to the surface of the substrate polymer without affecting any bulk properties, and various shapes and qualities can be adopted for the substrate polymer. Many methods, such as photoirradiation, γ-ray irradiation, electron-beam irradiation, and plasma discharge grafting, have been investigated.[21–26] All of these techniques are both costly and time-consuming, especially the preparation of anion-exchange materials, because further chemical modification processes, such as amination[27–30] and amidoximation,[25] are required for the

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introduction of anion-exchange functional groups into the polymer chains. This generates a large amount of raw material waste and often requires pretreatment, such as chlorination, the addition of a catalyst, and/or high temperature, which further increases the production costs.

Tsuneda et al.[31] reported the cografting of vinyl benzyl trimethylammonium chloride (VBTAC) with 2-hydroxyethyl methacrylate (HEMA) onto a polyethylene (PE) film by electron-beam radiation and demonstrated its anion-exchange functionality. More recently, Kolhe and Kumar[32,33] grafted VBTAC with HEMA onto PE and nylon fabric by γ irradiation. The reports of these works are the basis of this study, in which the photoinduced graft polymerization of VBTAC with HEMA was performed on a nylon nonwoven fabric for the preparation of a novel anion exchanger. The effects of several parameters, including the ratio of monomers, photoirradiation time, reaction temperature, and concentrations of the solvent and photoinitiator, on the degree of grafting and anion-exchange capacity (AEC) of the product were investigated to determine the optimal grafting conditions. The physicochemical properties and the regeneration efficiency of the grafted fabric were examined.

EXPERIMENTAL

Materials

Nonwoven nylon fabric (120 g/m^2, 60% nylon fiber, 40% PE fiber) to be used as the substrate polymer for grafting was from the Samsung Nonwoven Fabric Co. (Seoul, Korea). The monomers used were HEMA (Aldrich Chemical, Inc., Milwaukee, WI) and VBTAC (Acros Organics, Geel, Belgium), the photoinitiator was benzophenone (BP; Yakuri Pure Chemical Co., Japan, Osaka, Japan), and the solvents used were methanol (MeOH) and deionized water. All reagents were of the highest grade available and were used as received.

Photografting procedures

The nylon fabric was cut into strips (1 cm wide and 10 cm long), washed with a neutral detergent solution, and then air-dried at 60°C. The monomer solution was prepared with 5–30% (v/v) MeOH as the solvent and contained 0–16% (v/v) HEMA, 0–8% (w/v) VBTAC, and 0.1–0.4% (w/v) BP. One piece of nylon fabric was placed in a Pyrex glass tube containing 20 mL of the monomer solution; this tube was purged with nitrogen gas to eliminate oxygen and then sealed. The tube was exposed to ultraviolet light under controlled conditions. The light source was a 400-W high-pressure mercury lamp (Miya Electric Co., Gwangju, Korea), and the glass tubes were rotated and revolved simultaneously around

the light source at a distance of 10 cm. After the grafting reaction, the nylon fabric was removed from the glass tubes, washed three times with hot water, then extracted with MeOH for 3 h in a Soxhlet apparatus to remove unreacted monomer and homopolymer, and air-dried at 60°C to a constant weight. The degree of grafting was calculated from the weight gain:

$$\text{Degree of grafting } (\%) = \frac{100(W_1 - W_0)}{W_0} \quad (1)$$

where W_0 and W_1 are the weight of the substrate and the weight of the grafted fabric, respectively. At least three parallel experiments were done under each set of conditions.

Characterization

The AEC (mequiv/g) of the nylon fabric with grafted HEMA and VBTAC (nylon-g-HEMA–VBTAC) was determined as described with 0.2M NH$_4$Cl and 0.2M KNO$_3$.[34] Nylon-g-HEMA–VBTAC was placed in a preweighed 50-mL centrifuge tube. We added 20 mL of 0.2M NH$_4$Cl. The tube was then shaken for 1 h and centrifuged; then, we discarded the supernatant. This process was repeated two more times. The same process was repeated three times with 0.04M NH$_4$Cl, and then, we weighed tube to determine the volume of the entrained solution. We added 20 mL of 0.2M KNO$_3$. The tube was then shaken for 1 h and centrifuged; we collected the supernatant in a 250-mL volumetric flask. We repeated this process two more times, combining the supernatants. This solution was analyzed for Cl$^-$ by a titration method as described in the literature.[35] AEC was calculated with the following equation:

$$\text{AEC(mequiv/g)} = \frac{V_s C_s - V_{en} C_{en}}{W_1} \quad (2)$$

where W_1 is the weight of nylon-g-HEMA–VBTAC (g); V_s and V_{en} are the volumes of the collected KNO$_3$ and entrained NH$_4$Cl (L), respectively; and C_s and C_{en} are the concentrations of Cl$^-$ in the collected KNO$_3$ and entrained NH$_4$Cl (mequiv/L), respectively.

The chemical structure of the substrate fabric, nylon-g-HEMA, and nylon-g-HEMA–VBTAC fabric was analyzed with a Shimadzu IR-435 infrared spectrophotometer (Kyoto, Japan) and a Varian Unity Infinity Plus 200 solid ^{13}C-NMR spectrometer (Palo Alto, CA). The ^{13}C-NMR spectra were recorded at ambient temperature with an acquisition time of 20.48 ms, a contact time of 2.0 ms, and a spin rate of 10 kHz. The nitrogen content of nylon-g-HEMA–VBTAC was determined for each degree of grafting with an elemental analyzer (Fision EA1108) to

evaluate the quantity of VBTAC units grafted onto the nylon along with HEMA. The density and the molar fraction of VBTAC in the grafted polymer were calculated with the mass balance of nitrogen:

$$W_V(g) = \frac{x_N W_1 - f_N W_0}{V_N} \quad (3)$$

$$W_H(g) = (W_1 - W_0) - W_V \quad (4)$$

Molar fraction of VBTAC units

$$= \frac{(W_V/211.74)}{(W_V/211.74 + W_H/130.14)} \quad (5)$$

$$\text{VBTAC density (mmol/g)} = \frac{1000 W_V}{211.74 W_1} \quad (6)$$

where W_V is the VBTAC weight in the graft chain, W_H is the HEMA weight in the graft chain, and x_N, f_N, and V_N are the nitrogen contents (%) of nylon-g-HEMA–VBTAC, the substrate nylon fabric, and VBTAC, respectively. The values 211.74 and 130.14 are the molecular masses of VBTAC and HEMA, respectively.

The surface area, total pore volume, and pore size distribution of the substrate nylon fabric, nylon-g-HEMA, and nylon-g-HEMA–VBTAC were analyzed by N_2 adsorption at a relative pressure of 0.3 at 77.3 K with a Micromeritics TriStar II 3020 surface area and porosity measuring system (Micromeritics Instrument Co., Norcross, GA). The surface morphology was observed with a Hitachi S-4800 field emission scanning electron microscope (Tokyo, Japan). The potentiometric titration method was used to evaluate the surface charge of the substrate nylon fabric, nylon-g-HEMA, and nylon-g-HEMA–VBTAC, as described in the literature.[36] The fabric was cut into pieces approximately 5×5 mm^2 and mixed with $0.01M$ NaNO$_3$ to obtain a 2 g/L suspension, which was stirred with a magnetic follower and kept at 20°C. Before the titration, the suspension was equilibrated until the pH was 7.0 ± 0.1. Titration was done by the addition of $0.1M$ HNO$_3$ and $0.1M$ NaOH with a micropipette. The pH range 2.0–12.0 was covered with an Orion 3-Star benchtop pH meter (Thermo Fisher Scientific Inc., Waltham, MA). The surface charge density was calculated as a function of pH from the difference between the total added acid or base and the equilibrium concentrations of H$^+$ and OH$^-$ for a given quantity of fabric with the following equation:

$$\sigma = \frac{F(C_A - C_B + [\text{OH}^-] - [\text{H}^+])}{WA} \quad (7)$$

where σ is the surface charge density (C/cm^2); W is the quantity (g/L) of fabric; F is Faraday's constant (96,490 C/mol); C_A and C_B are the concentrations

(mol/L) of the acid and base, respectively, after each addition during titration; [H$^+$] and [OH$^-$] are the equilibrium concentrations of H$^+$ and OH$^-$, respectively; and A is the surface area (cm^2/g) of the fabric used.

For regeneration experiments, nylon-g-HEMA–VBTAC used for the measurement of AEC was regenerated with $0.1M$ NaCl and then reused for sorption. The sorption and regeneration cycles were done five times, and after each regeneration cycle, nylon-g-HEMA–VBTAC was washed with deionized water and air-dried at 60°C to a constant weight.

RESULTS AND DISCUSSION

Effect of the mixing ratio of HEMA and VBTAC

In any cograft polymerization system, the ratio of monomers in the monomer solution is an important factor influencing the degree of grafting and the AEC of the grafted product. Thus, the effects of the ratio of monomers on the degree of grafting and the AEC of the resulting products were investigated with various HEMA/VBTAC ratios. The total concentration of monomers was 6% (w/v) in a 30 : 70% (v/v) MeOH/water mixture containing 0.2% (w/v) BP as a photoinitiator. The degree of grafting increased with increasing HEMA/VBTAC ratio, whereas the opposite was observed when the concentration of VBTAC was increased in the monomer solution (Table I). There was no grafting when VBTAC was used alone; this showed that the presence of HEMA was essential for the grafting of VBTAC onto nylon. The same observations has been reported for the grafting of VBTAC onto PE or onto nylon with an electron beam or γ rays as the source of radiation,[31–33] and those authors suggested that, because VBTAC has a highly ionizable group with a large hydration sphere, it is incompatible with a hydrophobic polymer. As shown in Table I, the AEC for the fabrics grafted under different HEMA/VBTAC ratios showed no linear relationship with

TABLE I
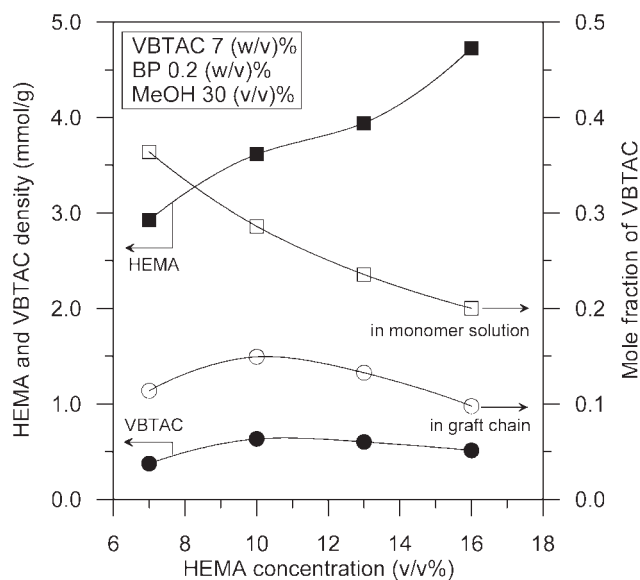**Effect of the Concentration of HEMA and VBTAC on the Degree of Grafting and AEC**

HEMA [% (v/v)]	VBTAC [% (w/v)]	Grafting (%)	AEC (mequiv/g)
6.0	0.0	85.10 ± 0.53	0.000
4.5	1.5	71.60 ± 0.36	0.514
4.0	2.0	65.81 ± 1.97	0.598
3.0	3.0	32.98 ± 0.44	0.584
2.0	4.0	18.25 ± 0.19	0.542
0.0	6.0	Not grafted	—

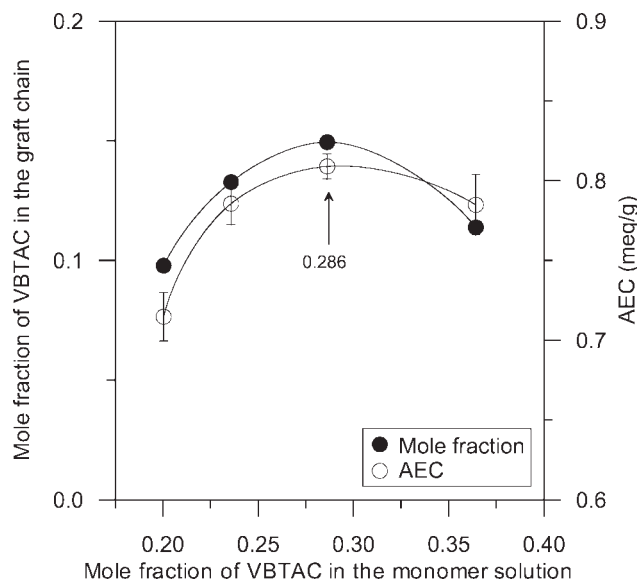The solvent was 70 : 30% (v/v) water/MeOH, the initiator was 0.2% (w/v) BP, and the irradiation lasted for 1 h at 60°C.
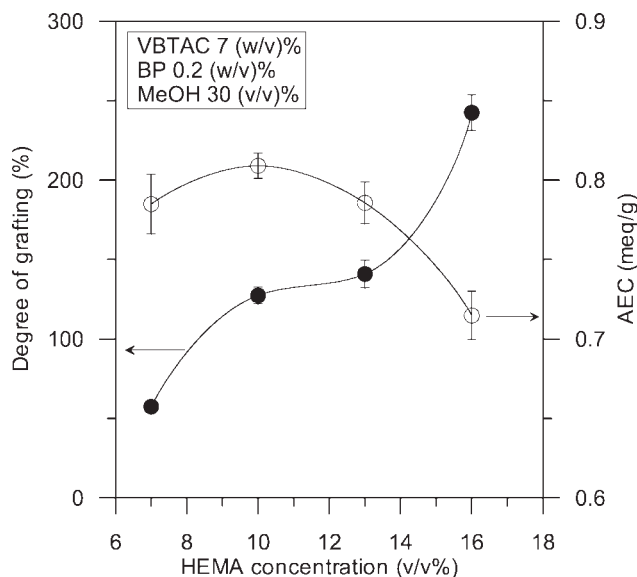
Figure 1 Effect of the concentration of HEMA on the degree of grafting and AEC of the grafted fabric (photoirradiation for 2 h at 60°C).


Figure 3 Molar fractions of VBTAC between the monomer solution and the grafted polymer chain and their effects on the AEC of the grafted fabric (data from Figs. 1 and 2).

the degree of grafting or even with the HEMA/VBTAC ratio. This was probably because of the inverse relationship between the degree of grafting and the concentration of VBTAC, where only VBTAC units in the grafted chain had an anion-exchangeable function. Thus, with increasing concentration of VBTAC in the monomer mixture, the VBTAC units in the grafted chain increased, whereas the degree of grafting (reflecting the amount of grafted chain) decreased. Nylon-*g*-HEMA–VBTAC prepared at an HEMA/VBTAC ratio of 2 : 1 exhibited the highest AEC, as shown in Table I. Consider-

ing the degree of grafting and the AEC of the grafted fabric, we found that HEMA/VBTAC ratios between 2 : 1 and 1 : 1 were optimal, and they were used for further experiments.

Figure 1 shows the degree of grafting and AEC of the resulting grafted polymer, nylon-*g*-HEMA–VBTAC, for various concentrations of HEMA. In all of the experiments, we used a monomer solution containing 7–16% (v/v) HEMA and a constant 7% (w/v) VBTAC with a photoirradiation time of 2 h at 60°C. The degree of grafting increased with increasing concentration of HEMA, although the change of grafting rate was not linear. On the other hand, the AEC of the grafted fabrics increased with the concentration of HEMA up to 10% (v/v) and decreased thereafter. Figure 2 shows the density of VBTAC and HEMA in nylon-*g*-HEMA–VBTAC and the molar fraction of VBTAC units in the grafted polymer chain for various concentrations of HEMA. The initial molar fraction of VBTAC in the monomer solution is also plotted in Figure 2. The density of HEMA in the grafted fabric increased consistently with increasing concentration of HEMA and corresponded well with the degree of grafting, whereas the density of VBTAC in the grafted fabric was maximal with 10% (v/v) HEMA and then decreased. The trend of the molar fraction of VBTAC units in the grafted polymer chain was similar to that of the VBTAC density and corresponded well with the AEC of the grafted fabric, as shown in Figure 3. These results show that the AEC of the grafted fabric was determined directly by the molar fraction of VBTAC units in the grafted polymer chain rather than that in the monomer solution and that there was an optimum HEMA/VBTAC ratio for the introduction of the highest
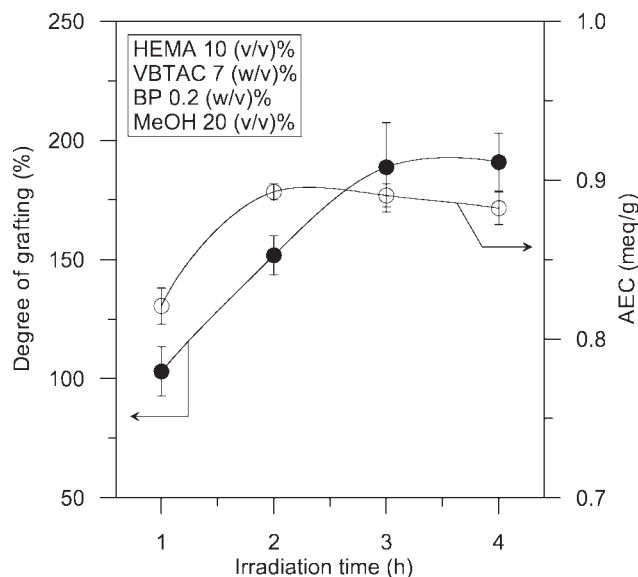

Figure 2 HEMA and VBTAC density and molar fraction of VBTAC in the grafted fabric (Fig. 1) as a function of the concentration of HEMA.
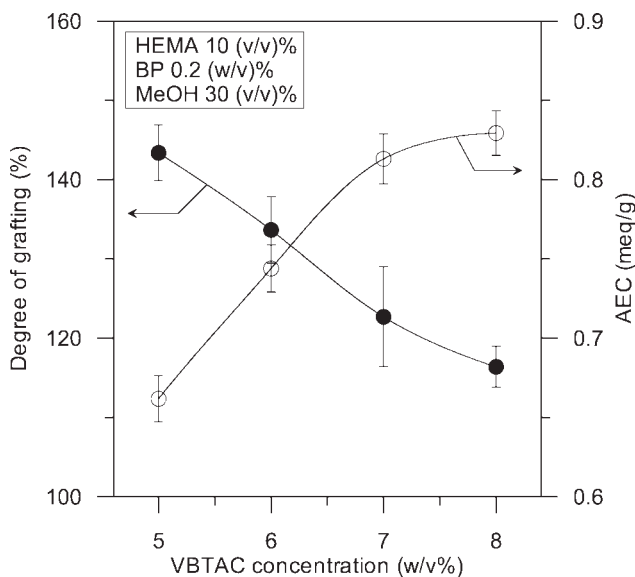
Figure 4 Effect of the concentration of VBTAC on the degree of grafting and AEC of the grafted fabric (photoirradiation for 2 h at 60°C).

Figure 5 Effect of the photoirradiation time on the degree of grafting and AEC of the grafted fabric (reaction temperature = 60°C).

molar fraction of VBTAC units to the polymer chain grafted onto nylon fabric along with HEMA. Under these experimental conditions, the optimum values were an HEMA/VBTAC ratio of 10 : 7 (v/w) and a molar fraction of VBTAC in the monomer mixture of 0.286. Figure 4 shows the degree of grafting and the AEC values of nylon-*g*-HEMA–VBTAC for various concentrations of VBTAC. The experiments were done at 60°C with a monomer solution containing 5–8% (w/v) VBTAC and 10% (v/v) HEMA and a photoirradiation time of 2 h. The degree of grafting decreased with increasing concentration of VBTAC. In contrast to the degree of grafting, the AEC of the grafted fabrics increased linearly with increasing concentration of VBTAC up to 7% (w/v) and then leveled off. This confirmed that an HEMA/VBTAC ratio of 10 : 7 (v/w) was optimal for the cografting of VBTAC and HEMA onto the nylon fabric.

Other important factors

The effects of photoirradiation time, reaction temperature, and concentrations of the solvent MeOH and photoinitiator BP on the graft polymerization were investigated to determine the best conditions for photografting.

Figure 5 shows the degree of grafting obtained at 60°C with 10% (v/v) HEMA, 7% (w/v) VBTAC, 0.2% (w/v) BP, and 20% (v/v) MeOH in deionized water and with photoirradiation times ranging from 1 to 4 h. The degree of grafting increased linearly with photoirradiation time up to 3 h; this confirmed the reinitiation ability of the polymer chain ends, as reported by Yang and Ranby.[37] However, the degree of grafting leveled off after 3 h, probably because of a large amount of homopolymer formation in the residual monomer solution, which would have

decreased the monomer available for graft polymerization. In contrast to the degree of grafting, the AEC of the resulting nylon-*g*-HEMA–VBTAC was maximal at a photoirradiation time of 2 h and then tended to decrease with further increases in time because the density of VBTAC units in nylon-*g*-HEMA–VBTAC, which acted as a functional group for capturing anions onto the graft polymer chain, increased with photoirradiation time up to 2 h and then decreased with further increases (Fig. 6). Furthermore, the molar fraction of VBTAC units in the grafted polymer chain was also maximized at a
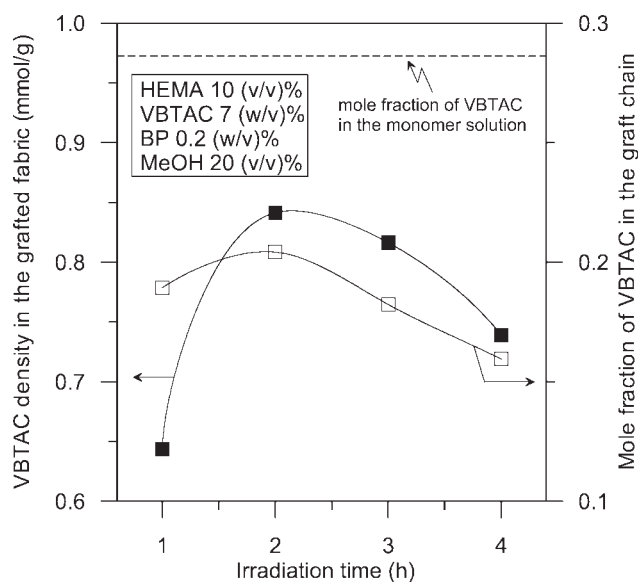
Figure 6 VBTAC density and molar fraction of VBTAC in the grafted fabric (Fig. 5) as a function of the photoirradiation time.
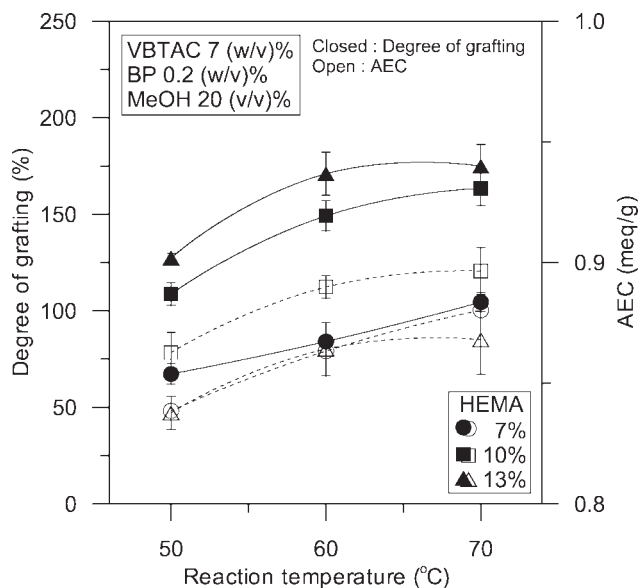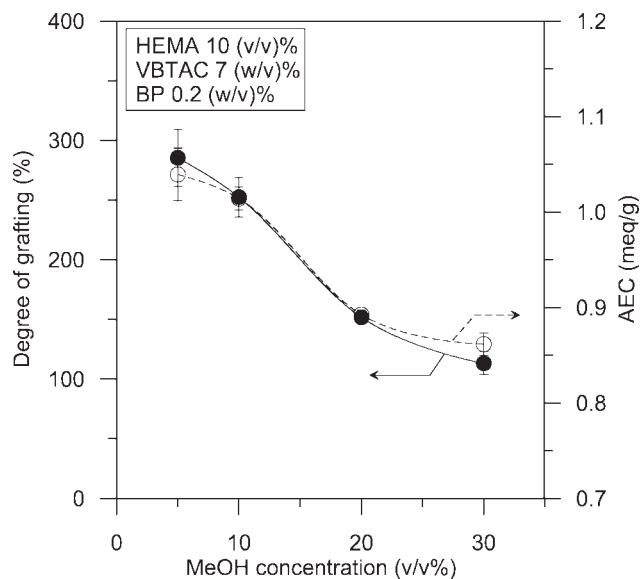
Figure 7 Effect of the reaction temperature on the degree of grafting and AEC of the grafted fabric (photoirradiation for 2 h).

Figure 8 Effect of the concentration of MeOH on the degree of grafting and AEC of the grafted fabric (photoirradiation for 2 h at 60°C).

photoirradiation time of 2 h and then decreased, similar to the density of VBTAC. This result indicates that HEMA and VBTAC had different grafting rates during the photoirradiation.

Figure 7 shows the degree of HEMA/VBTAC grafting onto nylon at different reaction temperatures. In general, the degree of grafting increased with increasing temperature, but the pattern of increase was not the same for all concentrations of HEMA. As the concentration of HEMA increased, the rate of increase of grafting was slower at temperatures higher than 60°C. The AEC of the resulting nylon-g-HEMA–VBTAC corresponded well with the degree of grafting and indicated no temperature-dependent difference in the grafting rate of HEMA and VBTAC.

These results show that a photoirradiation time of 2 h and a reaction temperature of 60°C were optimal, and these values were, therefore, used for subsequent experiments.

The degree of HEMA/VBTAC grafting onto nylon for different concentrations of MeOH and the AEC of the resulting nylon-g-HEMA–VBTAC are shown in Figure 8. All of these experiments were done at 60°C with 10% (v/v) HEMA, 7% (w/v) VBTAC, 2% (w/v) BP, and 5–30% (v/v) MeOH in deionized water and with a photoirradiation time of 2 h. As shown in Figure 8, the degree of grafting increased with decreasing concentration of MeOH in the monomer solution. The decreasing degree of grafting with high concentrations of MeOH may have been due to the fact that the hydrogen in MeOH was highly reactive to abstraction. The effect of the solvent on photografting was attributed directly to the

photoreduction reactivity of hydrogen in the solvent.[38,39] The AEC of the resulting nylon-g-HEMA–VBTAC tended to increase consistently with the degree of grafting and corresponded well with the density of VBTAC units in nylon-g-HEMA–VBTAC, as shown in Figure 9. Regardless of the degree of grafting or the density of VBTAC units, the molar fraction of VBTAC in the grafted polymer chain was nearly constant for different concentrations of MeOH; this indicated clearly that the concentration of MeOH in the monomer solution had a considerable effect on the degree of grafting and the VBTAC
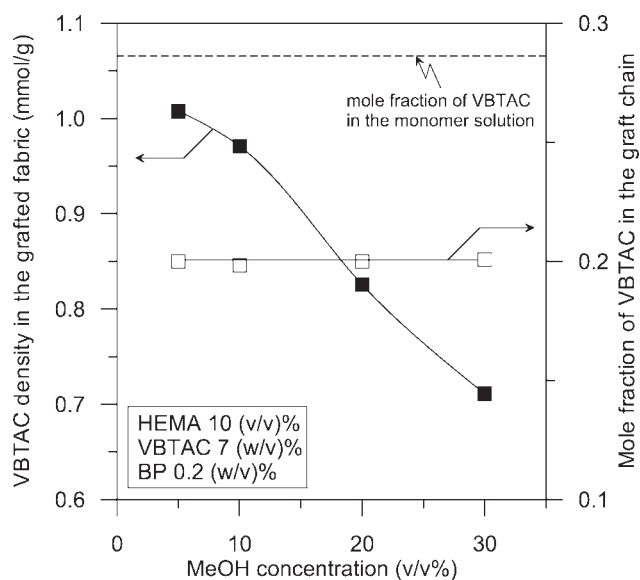
Figure 9 VBTAC density and molar fraction of VBTAC in the grafted fabric (Fig. 8) as a function of the concentration of MeOH.
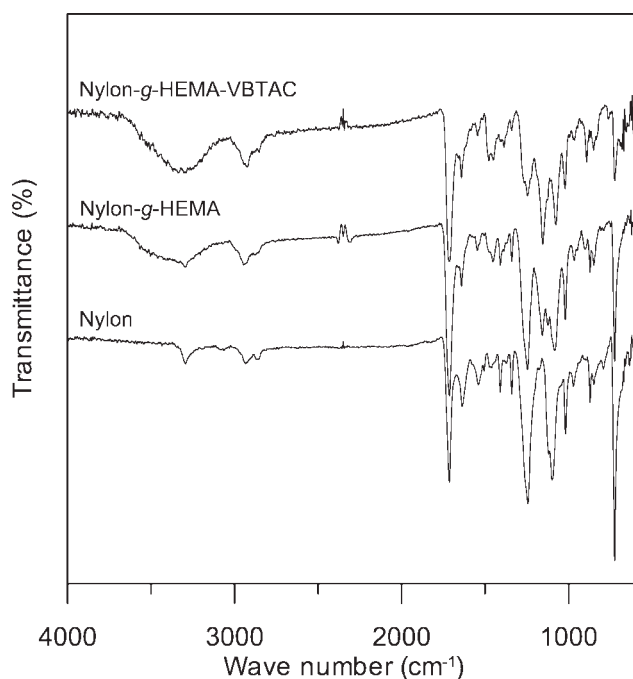
Figure 10 FTIR spectra of the nylon substrate, nylon-*g*-HEMA, and nylon-*g*-HEMA–VBTAC.

density in the grafted product but had no effect on the molar ratio of HEMA/VBTAC in the polymer chain grafted onto nylon. These results suggest that the use of MeOH should be minimized to obtain the maximum degree of grafting and, eventually, to maximize the AEC of the resulting products under the same experimental conditions. The use of some MeOH was essential because the photoinitiator BP was insoluble in water alone. In fact, when the concentration of MeOH in the monomer solution was 10% (v/v) or lower, BP tended to recrystallize and precipitate, especially when it was stored at low temperature and/or for a long time. Thus, it was important to ensure that the BP in the monomer solution was dissolved completely before use. We dissolved any recrystallized BP by the heating the monomer solution at 30°C or higher.

The degree of HEMA/VBTAC grafting onto nylon was maximal at a BP concentration of 0.2% (w/v) and then tended to decrease with further increases in BP. It is known that BP is excited to the triplet state by photoirradiation, which can abstract a hydrogen atom from the substrate polymer to yield polymer radicals capable of initiating the graft polymerization of the monomers.[40] BP excited to the triplet state also takes part in the homopolymerization of the monomer and a termination reaction by abstracting hydrogen from the solvent, the monomer, or any other molecule present in the monomer solution and by the recombination of semibenzopinacol radicals.[41] A decrease in the degree of grafting at high concentrations of BP may have been due to a more dominant homopolymerization and termination reaction, which were undesirable for the graft polymerization.

Structural characterization

The Fourier transform infrared (FTIR) spectra obtained from the substrate nylon fabric, grafted nylon-*g*-HEMA, and nylon-*g*-HEMA–VBTAC are presented in Figure 10. Compared with the spectrum of the substrate nylon fabric, several different absorption bands were observed in the spectrum of nylon-*g*-HEMA at about 900 and 1157 cm^{-1}, corresponding to the stretching vibrations of C=CH$_2$ and C—O, respectively. The absorption peak at 3300 cm^{-1}, corresponding to an N—H stretching vibration from the amide group in nylon, became a broad absorption band in the region 3060–3690 cm^{-1}; this was attributed to the O—H stretching vibration of HEMA grafted onto the nylon. New absorption peaks observed in the spectrum of nylon-*g*-HEMA–VBTAC at 605, 655, 680, 890, and near 1470 cm^{-1} probably corresponded to chloroalkane and aromatic C—H groups of the VBTAC cografted with HEMA onto nylon. These results were also verified by the examination of the solid ^{13}C-NMR spectra. As shown in Figure 11, the peak at 62 ppm, corresponding to the N—CH of nylon, was split into doublets at 60 and 67 ppm in the spectrum of nylon-*g*-HEMA. The peak at 67 ppm probably corresponded to CH$_2$—OH groups of HEMA grafted onto nylon. Furthermore, the C=O peak, which appeared at about 173 ppm in the
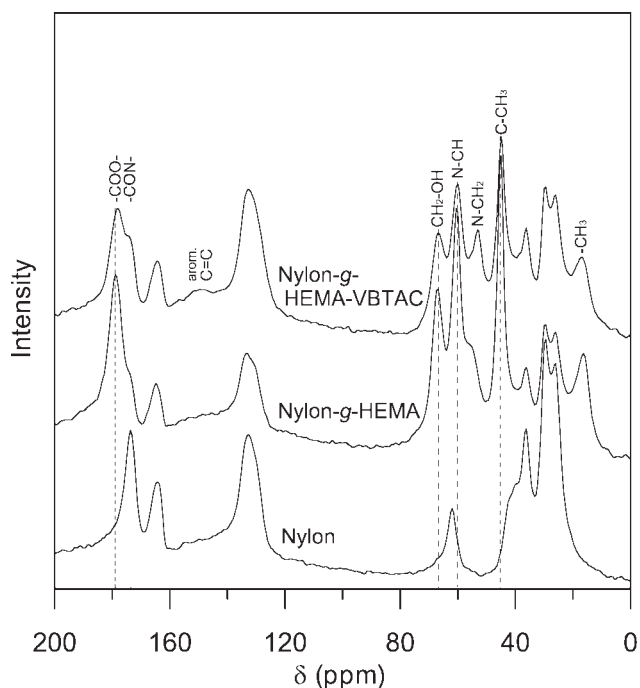
Figure 11 Solid ^{13}C-NMR spectra of the nylon substrate, nylon-*g*-HEMA, and nylon-*g*-HEMA–VBTAC.
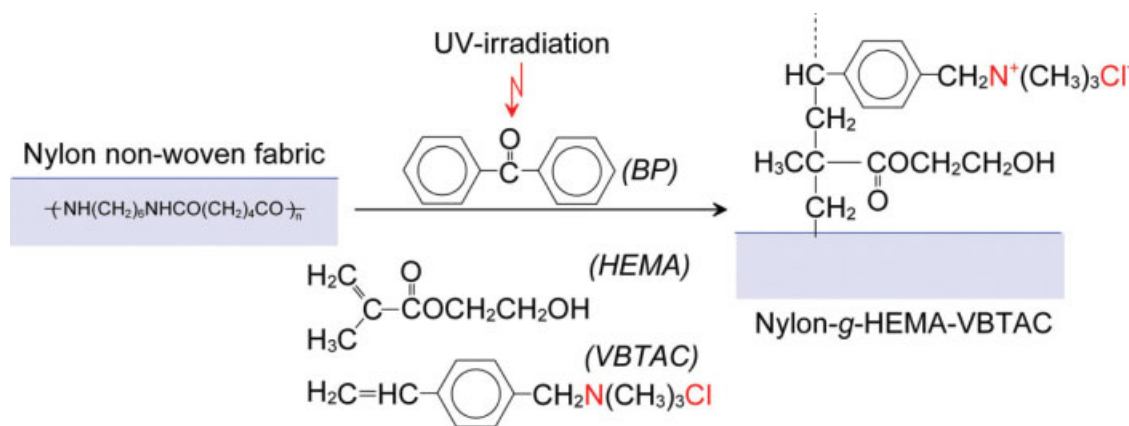
Figure 12 Preparation and chemical structure of nylon-*g*-HEMA–VBTAC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nylon spectrum, was shifted significantly to 179 ppm in the nylon-*g*-HEMA spectrum. The peak at 173 ppm was indicative of the amide (—CON—) groups in nylon, and the peak at 179 ppm was attributed to an ester (—COO—) group in the grafted HEMA. A strong peak at 45 ppm, probably corresponding to C—CH$_3$ groups, was also characteristic of poly(2-hydroxyethyl methacrylate). New peaks were also observed in the nylon-*g*-HEMA–VBTAC spectrum at about 150 and 53 ppm, which probably corresponded to aromatic C=C and N—CH$_2$ groups in the cografted VBTAC, respectively. On the basis of these results, the most probable structure of ny-

lon-*g*-HEMA–VBTAC was deduced and is shown in Figure 12.

Scanning electron microscopy (SEM) observation, analysis of the surface area and porosity, and surface charge density studies were used to investigate the effect of grafting on the surface properties of the substrate fibers. Figure 13(a–c) shows the SEM images of the substrate nylon, nylon-*g*-HEMA, and nylon-*g*-HEMA–VBTAC, respectively. The nylon fiber swelled as a result of the grafting of HEMA and the cografting of VBTAC with HEMA. At a degree of grafting of 175%, the swelling ratio, defined by division of the diameter of the grafted
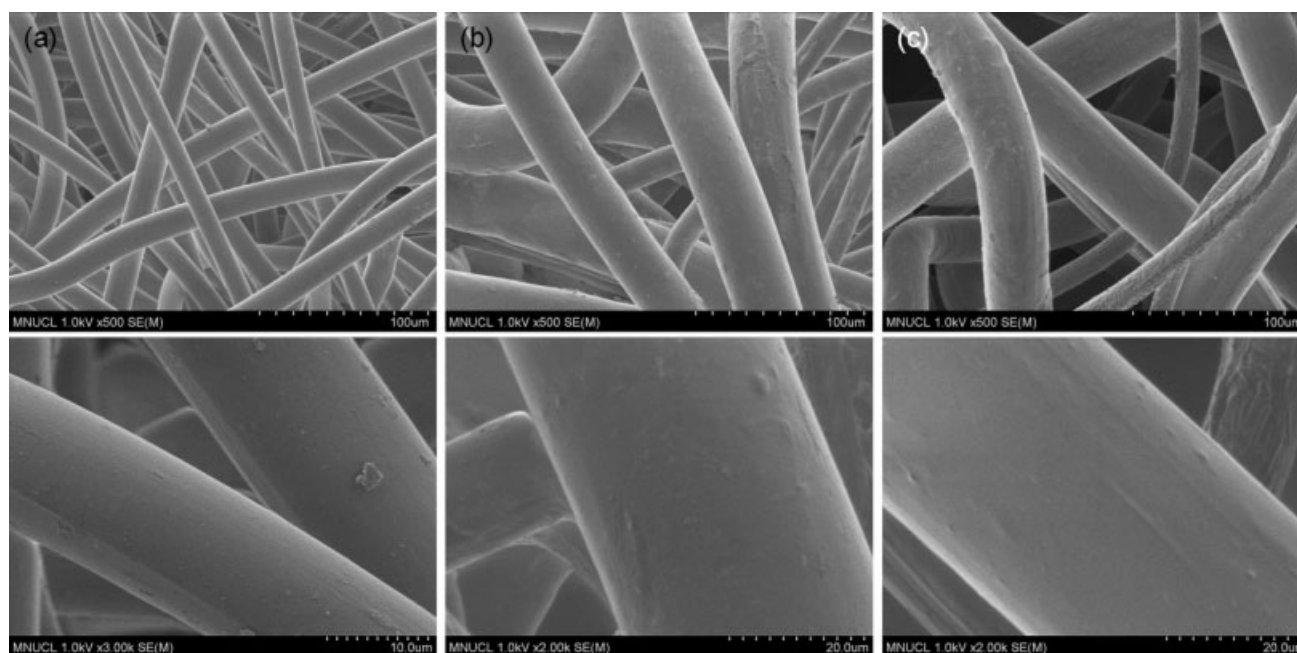
Figure 13 SEM images of (a) the nylon substrate fabric, (b) nylon-*g*-HEMA, and (c) nylon-*g*-HEMA–VBTAC.

TABLE II
Results of the Surface Area and Porosity Analysis for the Substrate and Grafted Nylon Fabric

|	BET surface area (m^2/g)	BJH pore volume (cm^3/g)	Average pore size (nm)
Nylon	2.95	0.0019	4.27
Nylon-g-HEMA (172%)	2.66	0.0017	4.53
Nylon-g-HEMA–VBTAC (163%)	1.83	0.0012	4.36
Nylon-g-HEMA–VBTAC (245%)	0.88	0.0004	4.19
Nylon-g-HEMA–VBTAC (346%)	0.55	0.0002	4.09

BET = Brunauer–Emmett–Teller; BJH = Barrett–Joyner–Halendar.

fiber by that of the substrate nylon fiber, was 2.7 ± 0.1 and tended to be slightly higher for nylon-g-HEMA–VBTAC than for nylon-g-HEMA. In contrast to the nylon fiber, the PE fiber that was mixed with the nylon fiber to improve the manufacturing process and the physical properties of the nonwoven fabric showed a nearly constant diameter regardless of the graft polymerization; this indicated that no grafting occurred on its surface, even though a surface deformation was observed in nylon-g-HEMA–VBTAC, as shown in Figure 13(c). The swelling of the nylon fiber after grafting led to a decrease in the surface area and pore volume of the grafted fabric, as shown in Table II. The surface area and the pore volume of nylon-g-HEMA–VBTAC decreased with the degree of grafting and were much lower than those of nylon-g-HEMA, even with a higher degree of grafting; this indicated that a more swollen and denser graft layer was formed on the surface of the substrate nylon fiber when VBTAC was cografted with HEMA. On the other hand, the average pore sizes of the grafted fabric depended on the degree of grafting. The effect of grafting on the surface charge density of the nylon fiber was investigated. As shown in Figure 14, the surface charge density for both the substrate nylon fabric and nylon-g-HEMA were very similar and were nearly constant over a pH range of 4–9, whereas the surface charge of nylon-g-HEMA–VBTAC became more positive with decreasing pH. This result indicates that the cografting of VBTAC with HEMA led to a positive potential on the surface of the nylon fiber, which facilitated the electrostatic interaction with anions. The pH_{pzc} values, determined from the point of intersection of the surface charge density with the pH curves, were 7.7, 8.2, and 8.8 for the substrate nylon, nylon-g-HEMA, and nylon-g-HEMA–VBTAC, respectively.

Regeneration characteristics

The important characteristics of a sorbent are the sorption capacity and the regeneration efficiency because it is mainly these parameters that determine the efficiency and the cost of the sorption process.

The regeneration efficiency of a sorbent is a very important component in cost reduction. To evaluate the regeneration efficiency of nylon-g-HEMA–VBTAC, repeated sorption–desorption experiments were done with nylon-g-HEMA–VBTAC with a degree of grafting of 160% and prepared with a monomer mixture of 10% (v/v) HEMA and 7% (w/v) VBTAC. Nylon-g-HEMA–VBTAC was immersed in 0.1N NaCl and shaken for 1 h at room temperature. After complete desorption, the nylon-g-HEMA–VBTAC was regenerated by repeated washing with deionized water and air drying at 60°C. This sorption–desorption cycle was done five times, and the AEC and weight loss of the fabric were measured after each cycle. As shown in Figure 15, although the weight of nylon-g-HEMA–VBTAC decreased in each regeneration cycle, the total loss range was less than or equal to 4%, even after five regeneration cycles. On the other hand, the AEC of the regenerated fabric increased to about 5% more than that of the new
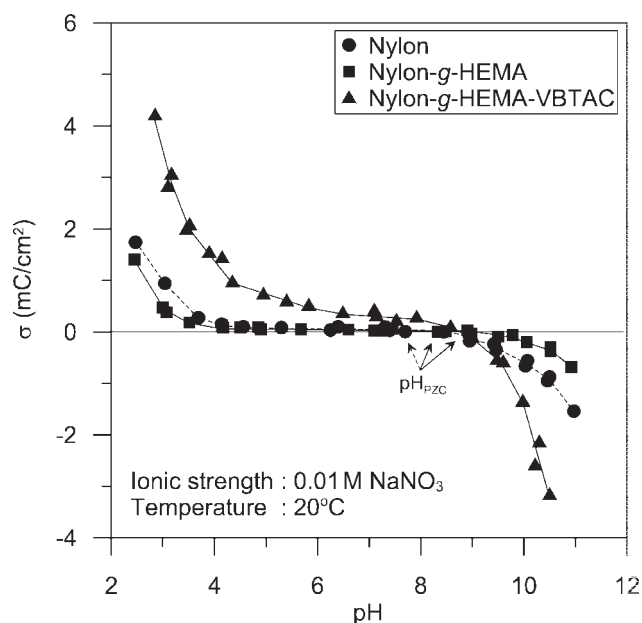
Figure 14 Surface charge density (σ_0) of the nylon substrate fabric, nylon-g-HEMA, and nylon-g-HEMA–VBTAC as a function of pH.
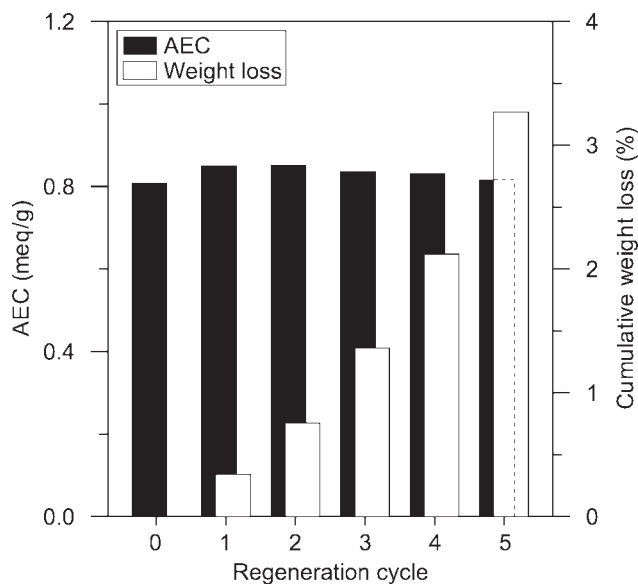
Figure 15 Regeneration efficiency of nylon-*g*-HEMA–VBTAC via washing with 0.1*M* NaCl.

fabric after the first regeneration cycle and, thereafter, decreased with each regeneration cycle and was nearly equal to that of the new fabric after five regeneration cycles. The sorption–desorption results demonstrate that nylon-*g*-HEMA–VBTAC could be regenerated by a simple wash with 0.1*M* NaCl without a significant reduction in the AEC or physical durability and, thus, could be used more than five times with the retention of an AEC value very similar to that of the new fabric.

CONCLUSIONS

VBTAC was cografted with HEMA onto nylon by photoirradiation-induced graft polymerization with BP as the photoinitiator. The cografted VBTAC afforded an anion-exchange functionality to the resulting polymer, nylon-*g*-HEMA–VBTAC, without any further modification. Together with the anion-exchange functionality, the nitrogen content, FTIR and ^{13}C-NMR spectra, SEM morphology, surface area, porosity, and charge density of the grafted fabrics further confirmed the cografting of VBTAC with HEMA. The HEMA/VBTAC ratio in the monomer solution was an important factor determining the degree of grafting and the molar fraction of VBTAC units in the grafted polymer and, ultimately, the AEC of the resulting nylon-*g*-HEMA–VBTAC. On the basis of the AEC of the grafted fabric, the optimal HEMA/VBTAC ratio was shown to be 10 : 7 (v/w); this corresponded to a molar fraction of VBTAC of 0.286 in the mixed monomer solution. Under these conditions, the molar fraction of VBTAC units in the polymer chain cografted onto nylon along with HEMA was in the range 0.15–0.20;

this indicated different grafting rates for the two monomers. Other parameters, including the photoirradiation time, reaction temperature, and concentrations of BP and MeOH, affected the cografting of VBTAC and HEMA onto nylon. The AEC value of nylon-*g*-HEMA–VBTAC was governed directly by the density of VBTAC units rather than by the degree of grafting. The maximum AEC was obtained for nylon-*g*-HEMA–VBTAC prepared at 60°C with an HEMA/VBTAC ratio of 10 : 7 (v/w) and with 0.2% (w/v) BP and 5% (v/v) MeOH for a photoirradiation time of 2 h. Nylon-*g*-HEMA–VBTAC was regenerated by washing with 0.1*M* NaCl and could be reused more than five times without a significant reduction in the AEC or physical durability.

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