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New Functionalities of PA6,6 Fabric Modified by Atmospheric Pressure Plasma and Grafted Glycidyl Methacrylate Derivatives

Abstract Oxidative atmospheric pressure plasma was utilized to activate surface of PA 6,6 fabrics followed by graft copolymerization of glycidyl methacrylate (GMA) and further reacted with triethylene tetramine (TETA), quaternary ammonium chitosan (HTCC) or β-cyclodextrin (β-CD). The inner CD cavity was complexed with some insecticidal perfumes. Modified PA6,6 fabrics were analyzed by differential scanning calorimetry, thermogravimetric analysis, Fourier transform infrared spectroscopy and scanning electron microscopy. Antimicrobial activity and insect repelling assay were conducted and showed efficient antimicrobial and insect repelling properties.

Key words PA6,6 fabrics, atmospheric plasma, inclusion compounds

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Atmospheric pressure plasmas have several advantages over vacuum plasma techniques since operation is at ambient conditions, can easily be adopted for continuous on-line surface modifications of textiles, and do not require vacuum equipment. Atmospheric pressure plasma has been applied for numerous functionalities such as increased hydrophilicity, antistatic and enhanced dyeing properties, fire retardant, and permanent fixation of biocidal agents into fibers. Biocidal fabrics kill or inhibit the growth of microorganisms such as bacteria, molds and fungi and repel or kill crawling and flying insects. An important feature of atmospheric plasma is its ability to modify the surface without affecting the bulk properties of the treated fabrics. Since 1978 and up to 2005 several studies have been conducted using plasmas either under vacuum or at atmospheric conditions for surface modification and graft copolymerization of textiles such as cotton, nylon, polypropylene, polyethylene terephthalate (PET) and polyvinyl alcohol (PVA) and their blends, in which surface modifications have successfully been achieved [1–22].

Glow discharge vacuum plasma was used in pre-treating nylon for surface activation followed by grafting 2-hydroxy ethyl methacrylate (HEMA) at 7.6% add-on to increase fibers hydrophilicity [23]. Graft polymerization of glycidyl methacrylate (GMA) onto nonwoven polypropylene was achieved by radiation-induced methods [24], and plasma-graft polymerization of Kevlar 49TM followed by reaction with triethylenetetramine (TETA) as a curing agent [25]. The tail portion of a glow discharge vacuum plasma was also used for surface activation of nylon 6,6 and grafting poly (acrylic acid, PAA) followed by grafting ethylene diamine and hexylamine to PAA [26]. The grafting of PAA to nylon reduced acid dye uptake by 20% on grafting ethylene diamine to PAA, and the dye uptake increased over that of native nylon by 11% [26]. Another grafting technique using ultraviolet radiation was achieved by grafting PP with HEMA in the presence of three different photo initiators; it has been shown that the moisture regain was increased in proportion to the graft add-on [27]. Dyeing with reactive dye gave only a color with the grafted fibers. Other studies using

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dichlorosilane vacuum RF plasma for surface functionalization of sisal fiber and finely powdered high-density polyethylene resulted in formation of C–O–SiH_yCl_x groups on the fiber surfaces, and have shown improved interfacial adhesion between the two dissimilar substrates with some improvements in mechanical properties of the composites [28].

The aim of the present work was to modify PA6,6 fabrics using oxidative atmospheric pressure plasma to generate active site radicals followed by grafting copolymerization of some selected active monomers, namely GMA, TETA, quaternary ammonium chitosan (HTCC) or β-cyclodextrin (β-CD), which are linked to PA/GMA grafted fabric. Cyclodextrin derivatives are cyclic sugar molecules with a toroidal shape in which the inner cavities of the molecules have hydrophobic character, which allows non-polar groups of organic compounds to be included inside the cavity [29, 30]. The inner CD cavity is complexed with some insecticidal perfumes and two proprietary formulations of BioUD30® (spray or silicon) (HOMS, LLC., Clayton, NC, USA), in which both formulations consist of 30% 2-undecanone by weight. Inclusion of BioUD30 onto β-CD cavity follows same procedure described in Gawish et al. [31].

Modified PA6,6 fabrics were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Antistatic, antimicrobial and insect repellency tests were performed and evaluated.

Experimental

Materials and Methods

Polyamide 6,6 was a plain light fabric 42/43 inches wide and weighing 124 g/m^2, obtained from NC State University College of Textiles. It is spun PA6,6 DuPont Type 200 Woven Fabric (ISO/F03). Glycidyl methacrylate containing 100 ppm methyl hydroquinone, TETA and β-cyclodextrin (β-CD) were purchased from Aldrich Co.; and were used without further purification. Low molecular weight de-acetylated 98% chitosan type 652 of density 4-20 cps was a gift form Chitine Co., Marseille, France. Proprietary BioUD30 spray and BioUD30 silicon were supplied by HOMS, LLC., Clayton, NC; USA. The formulations of BioUD30® (spray or silicon) consist of 30% 2-undecanone by weight.

Polyamide 6,6 fabric was scoured in 2 g/L nonionic detergent for 30 minutes at 45°C. After drying and weighing, the samples were exposed to oxygenated atmospheric pressure plasma (99% He and 1or 2% O_2) for 5–15 minutes. These samples were grafted with 20% GMA solution (50% water/methanol) at 80°C for 1 hour, and then washed in warm water and acetone. Plasma treatment of PA 6,6 allows for radical formation followed by recombination with plasma species and chain scission after which GMA propagation takes place [31, 32]. The percentage add-on GMA was determined based on the dry weight of fabric. Synthesis of HTCC or TETA or β-CD follows where GMA serves as a linking agent [31, 32] The reacted PA6,6/GMA with either β-CD or HTCC or TETA produces antimicrobial fabrics.

Table 1 Composition of plasma exposed and grafted PA6,6/GMA and derivatives.

Sample number	Sample composition
F2	PA6,6/9.00% GMA
F6	PA6,6/19.80% GMA
F29	PA6,6/24.50% GMA
F3	PA6,6/35.40% GMA
F21	PA6,6/81.85% GMA
3aF	PA6,6/35.40% GMA/2.5% TETA
F28A	PA6,6/24.50% GMA/1.62 % TETA
F28B	PA6,6/24.50% GMA/1.02% HTCC
3F	PA6,6/35.40% GMA/1.33 β-CD
F21A	PA6,6/81.85% GMA/1% β-CD/0.477 % BioUD30 spray®
F21B	PA6,6/81.85% GMA/1% β-CD/0.84% BioUD30 silicon®
F3B	PA6,6/35.40% GMA/1.35% β-CD/3.13 BioUD30 silicon®

Biocidal guests, such as BioUD30, which is water soluble, were introduced onto the β-CD cavity. It is important to note that the active ingredient in both formulations of BioUD30 against ticks is 2-undecanone, which is 30% by weight, therefore the sample containing 3.13% BioUD30 consists of 0.939% 2-undecanone. Samples with inclusion of BioUD30, containing 0.477% (spray formulation) and 0.84% (silicon formulation), consisted of 0.143 and 0.25% 2-undecanone, respectively.

Cross-linking of TETA or HTCC to GMA was done at a liquor ratio 1 : 20. Thus a sample of PA/GMA (1.5 g) was added to 30 mL distilled water, 1 g NaOH and 3.0 ml TETA (or 1.5 g HTCC), heated at 80°C for 1 hour in a shaking water bath and the percentage add-on TETA or HTCC was calculated based on the fabric dry weight. The composition of the synthesized PA6,6/GMA samples and their derivatives are shown in Table 1. Synthesized PA6,6 fabrics were tested for static decay (with positive 5 kV and specified negative charges), antimicrobial and insect repellent assays. Figure 1 shows a schematic representation of the plasma-aided graft copolymerization and the process sequence to produce antibacterial and insect repellent fabrics. Scheme 1 shows the plasma graft copolymerization reactions to produce PA6,6/GMA/HTCC or PA6,6/GMA/β-CD. Figure 2 shows the chemical structure of biocidal grafted PA6,6 fabrics.

As shown in Figure 2 the GMA grafted nylon has a free epoxy group, which can react with either the –COOH or –NH_2 groups in the surface regions of nylon depending on the level of penetration of the monomer molecules. Such reaction is possible especially at high temperatures.

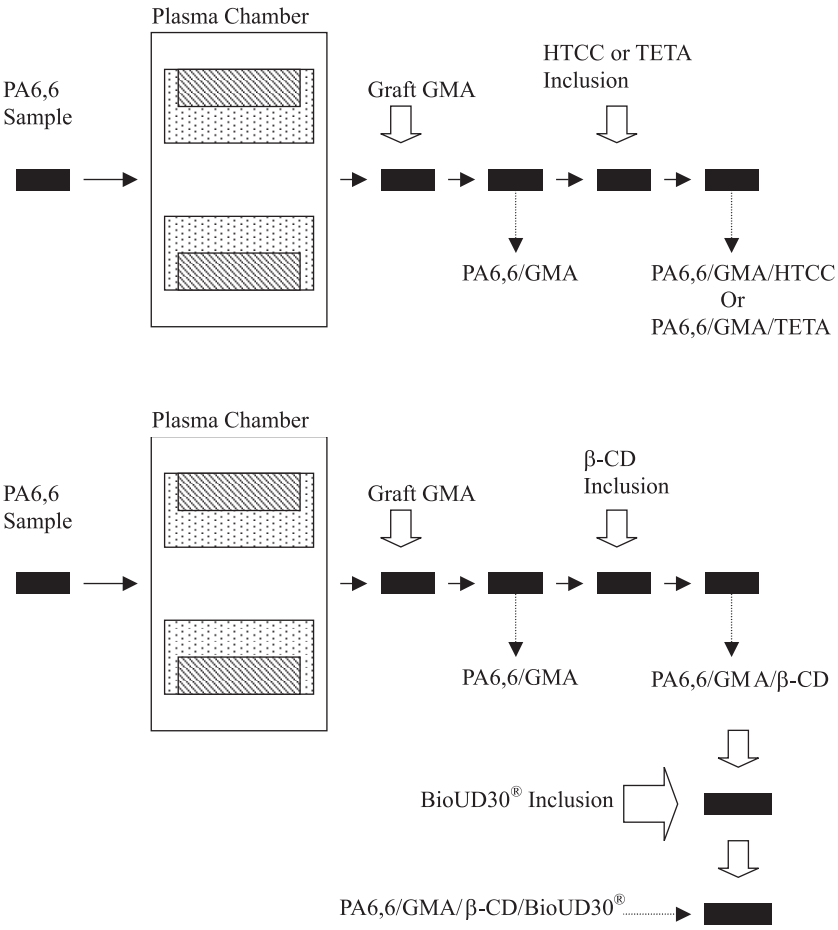


Figure 1 Schematic representation of the plasma-aided graft copolymerization process. Path one (top) shows PA6,6/GMA/HTCC or PA6,6/GMA/TETA production. Path two (bottom) shows PA6,6/GMA/β-CD production followed by inclusion of insect repelling agent (such as BioUD30® spray or silicon) to produce PA6,6/GMA/β-CD/BioUD30.

Atmospheric Pressure Plasma Device

The device is a capacitively coupled dielectric barrier discharge (DBD) operated by a 4.8 kW audio frequency power supply at 4–10 kHz. It has a 60 cm × 60 cm active exposure area between two copper electrodes with a fixed 5.0 cm gap separation. Helium is the seed gas to initiate the discharge at a constant flow rate of ~ 10 L/m and 1 or 2% oxygen was added to the gas flow. The discharge generates low-temperature (1–2 eV), low electron number density (10^{14}–10^{16} /m^3) glow discharge at ambient conditions. The discharge generates electrons, ions, excited atoms and molecules, and UV radiation. Batch or continuous on-line treatments can be performed in this device. All samples were batch-treated in the plasma using a test cell. Input power, operating voltage, frequency and plate separation were all held constant. The device details could be found elsewhere [15, 16, 20].

Characterization Techniques

Weight Change

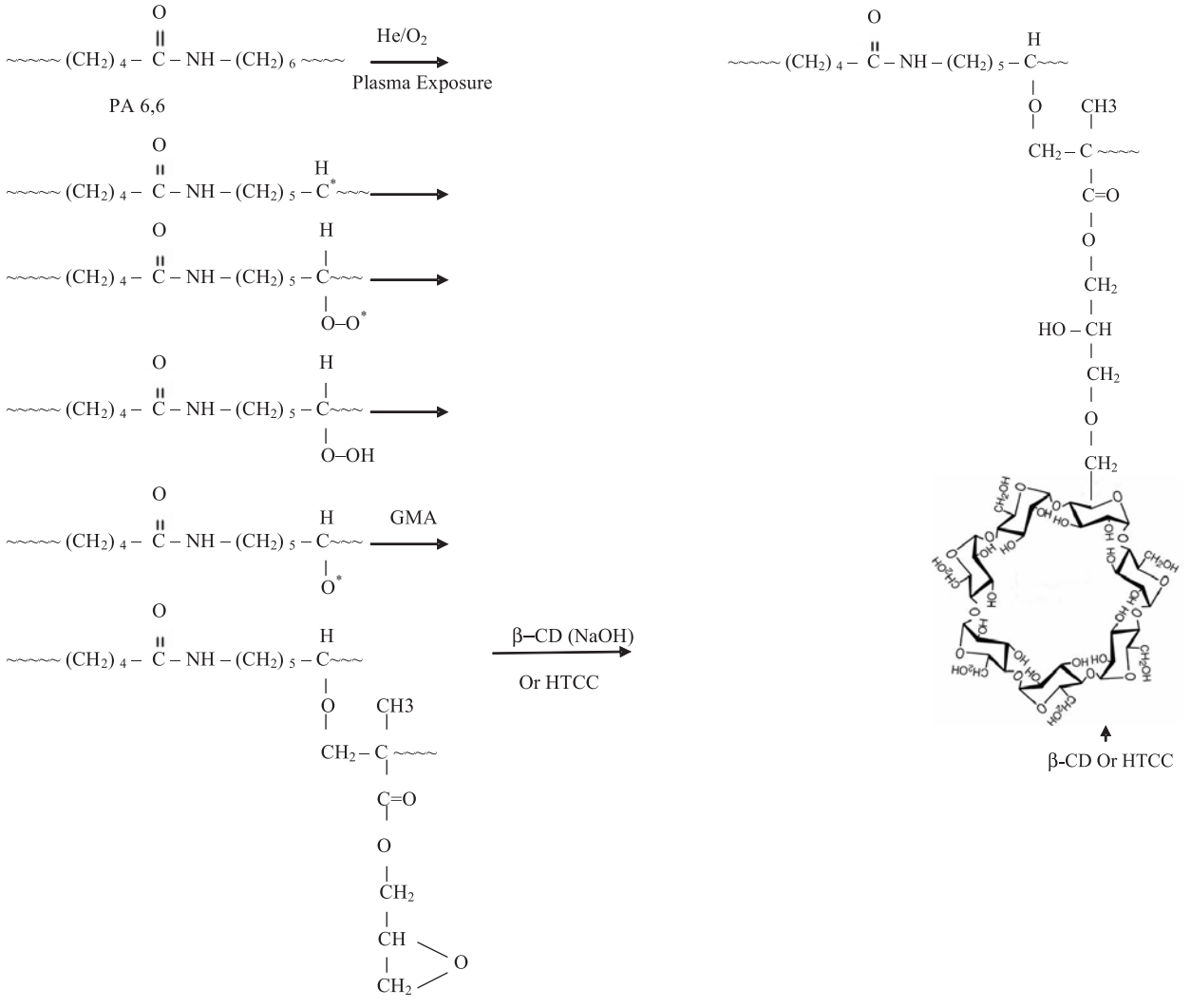
Each sample was weighed prior to plasma treatment and after grafting using an Explorer microbalance with an accuracy of ± 100 μg to determine the percentage weight change.

Differential Scanning Calorimetry

Thermal analysis of the PA6,6 samples was conducted using a Perkin-Elmer 7 Power Compensated differential scanning calorimeter. Each sample was scanned at a rate of 20°C/minute over the range of 25–300°C. The onset melting temperature was obtained from the intercept of the baseline and the maximum tangent of the corresponding exothermic and endothermic peaks.

Thermogravimetric Analysis

Thermogravimetric analysis was further conducted on the nonwoven PA6,6 samples using a Perkin Elmer thermogravimetric analysis device. Percentage weight change ver-



Scheme 1 Plasma graft copolymerization of PA6,6/GMA/HTCC or PA6,6/GMA/β-CD.

sus temperature was evaluated at a scan rate of 30°C/min over a range of 25–550°C.

Fourier Transform Infrared Spectroscopy

Grafted and un-grafted PA6,6 fabric samples were evaluated using a Nexus® 470 FTIR in conjunction with a Nicolet® Omnisampler.

Antistatic Test Method

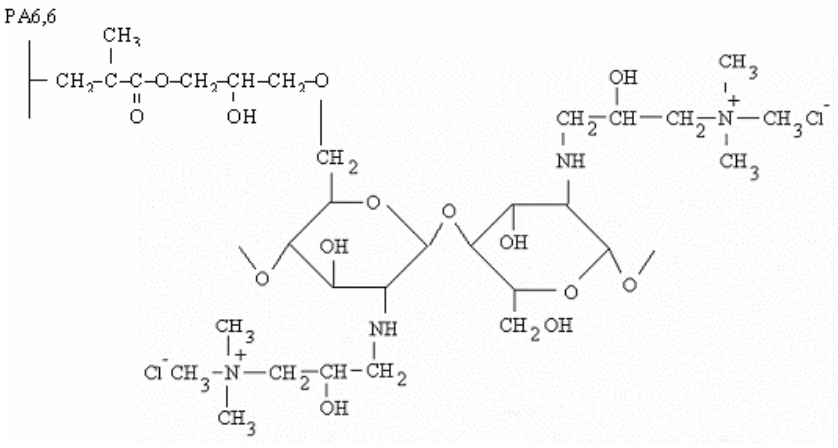
Nondestructive static decay was conducted using Electrotech systems (ETS) Model 806A test fixture with ETS Model 406 static decay meter inside Model 518 automatically controlled environmental chamber, at 5 kV charging voltage with both positive and negative polarity tests. Static decay was measured at 10 and 50% cut-offs.

Scanning Electron Microscopy

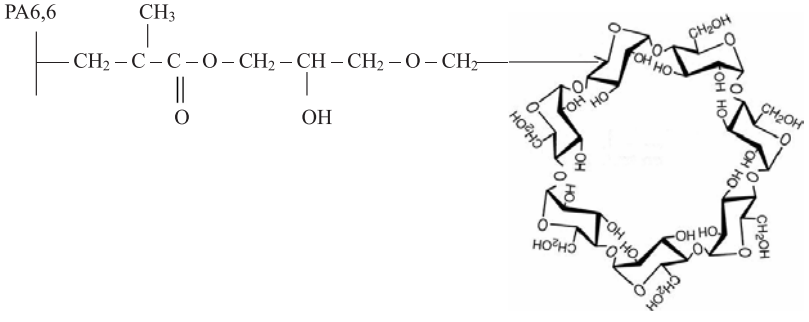
PA6,6 fabric samples were evaluated using a Hitachi S-3200N Variable Pressure scanning electro microscopy. The SEM micrographs were taken with magnification ranges of 100–1500×.

Antibacterial Activity Test Method

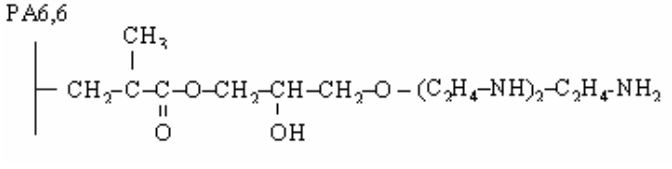
Escherichia coli k.12 (*E. coli* k.12) and *Staphylococcus aureus* (*S. aureus*) were obtained from the U.S. Food Fermentation Laboratory Culture Collection (USDA-ARS, Raleigh,



PA6,6/GMA/HTCC



PA6,6/GMA/β-CD



PA6,6/GMA/TETA

Figure 2 Chemical structure of biocidal grafted PA6.6 fabrics.

NC). Bacterial strains were grown overnight on tryptic soy broth or agar (Difco Laboratories, Detroit MI) for 14 hours. A modified form of AATCC (American Association of Textile Chemist and Colorist) test Method 100 was adopted [33]. The reduction in numbers of bacteria was calculated and expressed in terms of "Log Reduction", where one log reduction indicates that finished fabrics were able to kill 90% of the bacteria.

One piece of fabric (1 inch × 1 inch) was transferred to a sterilized plate. A 100 µL containing 10^7 CFU/mL of organism was transferred onto the surface of the fabric, which was placed in a Petri plate (100 mm × 15 mm in diameter; Fisher Scientific, Pittsburgh, PA). The plate was covered and transferred to 100 mm × 15 mm in diameter Petri plate (Fisher), 1 mL sterilized dH_2O was added to the large plate outside the smaller Petri plate containing the fabric sample, to protect the fabric from dryness. The plates were covered and incubated for 3 hours at 37°C. After 3 hours the fabrics were transferred into stomacher bags (Spiral Biotech, Inc., Norwood, MA) with 10 mL sterilized 8.5g/L NaCl (saline), which were treated for 1 min on high in the stomacher (Model TR5T, Tamar Co. Cincinnati, OH). The supernatant was diluted and plated on nutrient agar plates using a spiral platter (Model 4000, Spiral Biotech). Bacterial colonies, following 24–48 hours of incubation at 30°C, were counted by an automated spiral plate reader (QCount, Spiral Biotech).

Tick Repellency Test Method

The testing arena was constructed of an upside-down, 60-mm-diameter Petri dish lid (Becton Dickinson, Franklin Lakes, NJ) with a plastic ring glued to the outside top rim to allow approximately 2 mm of space between the dish and the bottom of the arena. The ticks had enough room to freely move about the arena, but could not flip over or completely avoid the testing surface. American dog ticks, *Dermacentor variabilis* (Say), were obtained from a lab-reared strain maintained on New Zealand White Rabbits, *Oryctolagus cuniculus* L., in the Department of Biological Sciences at Old Dominion University, Virginia, and reared as described in Sonenshine, 1993 [34]. Rearing conditions were 26 ± 1°C, 92 ± 6% relative humidity and 14 : 10 (light : dark). Two equal-size half-circle pieces of fabric (1.4 cm^2) were placed on a plastic surface; six unfed male ticks were placed in the center of the arena on top of the fabrics and the Petri dish lid covered the fabrics and ticks. The fabrics were positioned so that each fabric covered exactly half of the 60 mm diameter arena, thereby forcing the ticks make a choice about which type of fabric on which to reside. All tests were conducted in total darkness at 26 ± 2°C, 80 ± 3% relative humidity. In addition, each arena was separately covered with a lid wrapped with aluminum foil to limit the entrance of light into the arena during the recording of the results. Distribution of the ticks in the arena was recorded at 0.5, 1, 2, and 3 hours.

Results and Discussion

Percentage Graft Yield GMA onto PA 6,6

PA 6,6 fabric weights were measured prior to and after plasma treatment and after grafting with GMA to determine the percentage add-on. Figure 3 shows the graft yield (% add-on) dependence on plasma exposure time for grafting 20% GMA solution at 80°C, for two different oxygen contents in the helium plasma stream (1 and 2% O_2). It is clear that the percentage add-on increased with increased exposure time as a result of increased surface activation, however, the 1% oxygen in the plasma flow stream was better than the higher 2% case. The GMA graft yield varied from 2.4% at 5.0 minutes exposure to 35% GMA at 15 minutes exposure for the 1% O_2 case. For the 2% O_2 case these numbers were 0.9 and 19.8%, respectively. The oxygenation of the helium plasma enhanced the formation of active free radicals, such as hydroperoxides or other oxides, which are essential for the copolymerization reaction of GMA. Plasma formation is followed by recombination with other plasma species, chain scission and GMA propagation. Pure helium plasma does not form radicals but helium is a necessary seed gas to induce plasma formation at reasonable applied voltage. The observed decrease in the percentage graft yield for increased oxygen content in the plasma

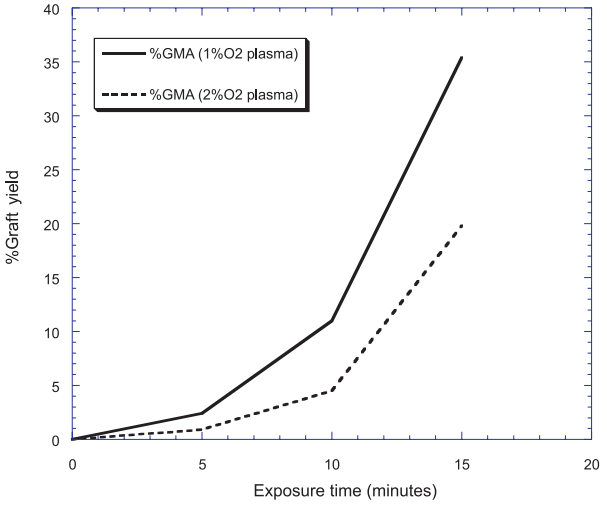


Figure 3 Percentage graft yield GMA onto PA6,6 samples exposed to 1% and 2% oxygen content in the helium plasma. Grafting conditions: 20%GMA (50% water/methanol mixture) at 80°C, for 1 hour.

stream was possibly due to higher recombination rates with increased oxygen content. Oxygen can produce a series of reactions in the plasma as a result of collisional processes with plasma electrons. It can produce positive oxygen (O^+), molecular oxygen (O_2^+) ions, excited atoms (O^*) or negative oxygen ions (O^-). The increased oxygen concentration would increase recombination rates and hence reductions in the effectiveness of graft yield. Similar results were obtained by others, for vacuum plasma treatment, where polyester was treated in varying contents of oxygen in argon vacuum plasma, then grafted with acrylic acid in vapor phase [22].

Differential Scanning Calorimetry

Thermal analysis was performed to confirm the grafting of the PA6,6 fabrics. Thermal analysis included DSC and TGA. The DSC profiles of samples of untreated and grafted PA6,6 fabrics are shown in Table 2. The control PA6,6 fabric is characterized by a sharp and intense endothermic transition starting beyond 253°C, with a peak temperature of 259.40°C. The grafted PA6,6 fabrics show a slight decrease in melting point, and a decrease in both the melt endotherm and the crystallization exotherm. Specifically, the 9.0% GMA grafted fabric has a crystallinity of 38.78% (based on $\Delta H_{endotherm}$), and the 19.8% GMA grafted fabric has a crystallinity of 29.5%, which is over 25% lower than the 40% crystallinity calculated for the control sample. Figure 4 further illustrates the effect of the percentage crystallinity versus the enthalpy. The relation between ΔH and percentage

Table 2 DSC of grafted PA6,6 grafted samples compared to the control.

Sample	Melting onset (°C)	ΔH (J/g)	Crystallinity (%)
PA6,6 Control	253.99	82.020	40.01
F2: PA6,6/9%GMA	248.46	79.505	38.78
F6: PA6,6/19.8%GMA	243.94	60.480	29.50
3F: PA6,6/35.4%GMA/1.33% β-CD	244.76	52.534	25.63
3aF: PA6,6/35.4%GMA/2.5%TETA	247.29	49.948	24.36

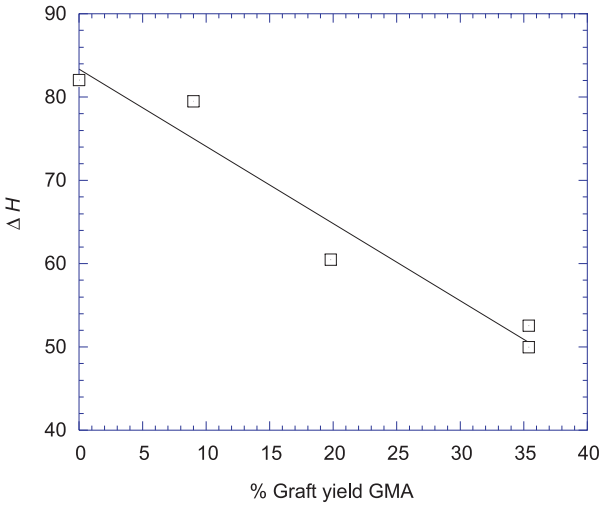


Figure 4 Dependence of ΔH on percentage graft yield GMA.

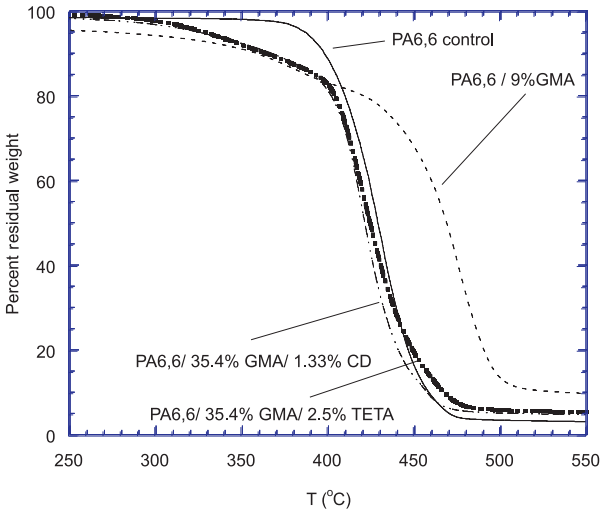


Figure 5 Percentage residual weight of grafted PA6,6 as compared to the control.

$$\Delta H_f^{\circ} = 205 \text{ J/g}, \qquad \%\text{Crystallinity} = \frac{\Delta H_f}{\Delta H_{Cryst}} \times 100$$

$$\Delta H = 83.367 - 0.9272 \times (\%Graft\ Yield\ GMA), R = 0.97376$$

graft yield is linear and takes the form $\Delta H = 83.367 - 0.9272 \times (\%Graft\ Yield\ GMA)$ with $R = 0.97376$ accuracy. In addition to the decrease in percentage crystallinity for PA6,6/GMA fabrics, the multi-grafted fabrics containing either cyclodextrin or TETA dropped even further. The percentage crystallinity of the PA6,6/GMA/β-CD sample decreased to 25.63%, and the PA6,6/GMA/TETA fabric dropped to 24.36%. All values are consistent with the percentage graft yield. Although plasma acts on the surface and on subsequent grafting GMA and GMA derivatives, it gave new modified PA6,6 fabrics with different T_m and ΔH values than the un-grafted fabric. Therefore, T_m and ΔH decreased with increased %GMA. Plasma treatment is essentially a surface phenomenon; however, the plasma sheath around immersed object accelerates the ions towards the substrate, which results in interaction into the bulk. This is obvious from the DSC and TGA analyses where changes in both the melt endotherm and the crystallization exotherm were observed. Thus, oxygenated helium plasma would induce some alterations in the bulk property.

Thermal Gravimetric Analysis

The increased thermal stability of PA6,6 grafted fibers is confirmed by TGA. This, essentially, is due to the excellent properties of GMA, which contains both acrylic and epoxy groups. It is a high purity dual functionality monomer for coatings and resins. It has excellent weathering, acid and impact resistance; improves water, heat and adhesive strength; and improves thermoplastic polymer blend compatibility. The decomposition temperatures and the percent residual weights of the PA 6,6 control and grafted fabrics are shown in Table 3, and the percentage residual weight graphs are illustrated in Figure 5. On grafting GMA onto PA6,6 the decomposition temperature was shifted from 475°C (4.53% residual PA6,6) to 550°C (9.7% resid-

Table 3 TGA for PA6,6 grafted fabrics showing temperature versus residual weight percentage.

Temperature (°C)	PA6,6 blank (control sample)	PA6,6/9%GMA	PA6,6/35.4%GMA/ 1.33%β-CD	PA6,6/35.4%GMA/ 2.5%TETA
250	98.78	95.41	98.23	99.19
300	98.61	94.16	96.73	97.55
350	98.33	90.96	92.28	91.91
400	89.29	82.97	80.98	82.42
425	59.16	78.93	41.79	48.43
450	17.13	67.74	13.34	19.15
475	4.53	40.39	5.77	7.43
500	3.75	13.26	5.11	5.81
550	3.41	9.69	4.73	5.33

ual PA6,6/9%GMA) creating a more thermally stable fabric. In contrast to PA6,6/GMA fabric, PA6,6/GMA/β-CD and PA6,6/GMA/TETA were without effect on the decomposition temperature of PA6,6, both having a decomposition temperature of 475°C, which is the same temperature as that of PA6,6.

Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of the plasma-grafted PA6,6 fabrics were obtained and compared with the control and the GMA-only grafted sample F6 (PA6,6/19.8% GMA) as shown in Figure 6. The FTIR of sample 3aF (PA6,6/PA/35.4%GMA/2.5%TETA) and sample 3F (PA6,6/35.4% GMA/1.33%CD) are also shown. The infrared spectra of the PA6,6 control and plasma-grafted PA6,6/9%GMA fabrics and its derivatives with HTCC, β-CD and TETA showed additional peaks at 1723, 1727 and 1180 cm^{-1} attributed to the ester carbonyl group.

Antistatic Test Results

The PA 6,6/GMA grafted fabrics showed an improved antistatic property for 50% positive polarity cut off since it was decreased to 0.01 seconds for all GMA grafted samples in

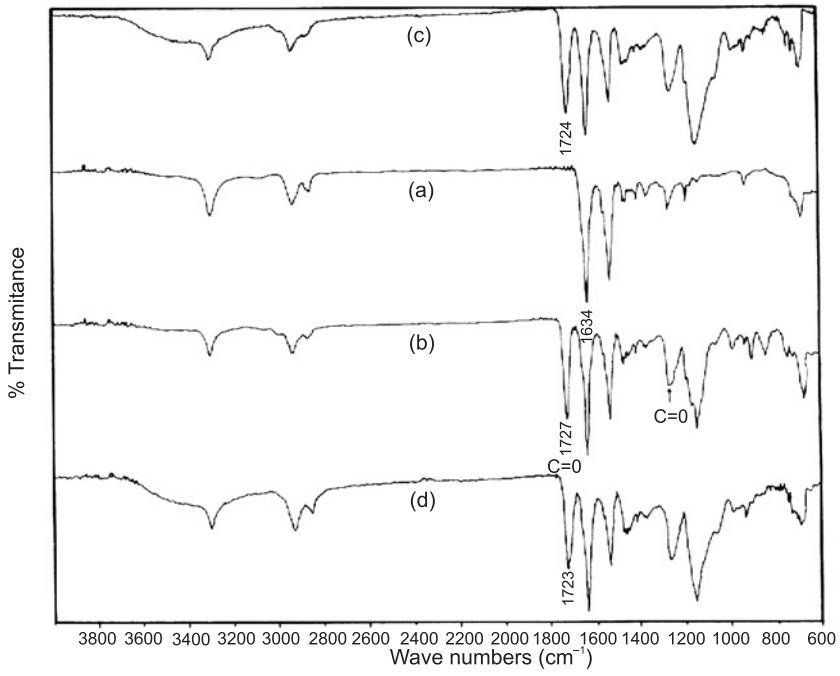
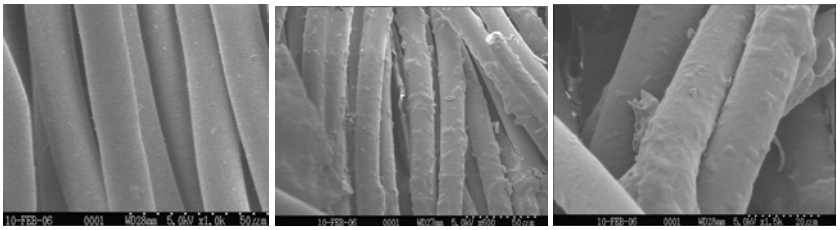


Figure 6 Infrared spectra (a) PA6,6 control, (b) PA6,6/19.8%GMA, (c) PA6,6/35.4%GMA/1.33%CD and (d) PA6,6/PA/35.4%GMA/2.5%TETA.



(a) (b) (c)

Figure 7 SEM micrographs of PA6,6 control (a) at 1000×, and grafted PA6,6 (b) at 600× and (c) at 1500× showing homogeneously grafted GMA.

Table 4 Antistatic properties of grafted PA6,6 fabrics.

Cut off	Control	PA6,6/19.8%GMA	PA6,6/81%GMA
10% negative	> 90 poor	0.01 excellent	0.01 excellent
50% negative	0.01excellent	0.01 excellent	0.01 excellent
10%positive	> 90 poor	> 90 poor	> 90 poor
50% positive	> 90 poor	> 90 poor	0.01 excellent
Cut off	**Control**	**PA6,6/24.5%GMA/1.6%TETA**	**PA6,6/24.5% GMA/1%HTCC**
10% negative	> 90 poor	78.13 poor	53.16 poor
50% negative	0.01 excellent	2.73 excellent	6.09 good
10%positive	> 90 poor	> 90 poor	> 90 poor
50% positive	> 90 poor	9.20 moderate	9.30 moderate

comparison with > 90 seconds for all the control samples, and no change for 10% positive polarity. Samples grafted with GMA/TETA (PA6,6/24.5%GMA/1.6%TETA) or GMA/HTCC (PA6,6/24.5% GMA/1%HTCC) improved the 50% positive polarity in comparison with the control PA6,6 fabric. The upgrade of the antistatic property is determined by the static decay measured at 10 and 50% cut-offs. Excellent antistatic property is when the decay time is between 0–3 seconds, 4–6 seconds is good, 7–9 seconds is moderate and greater than 9 seconds is considered poor [35]. Table 4 shows the antistatic test results. These results may also indicate cross-linking between GMA and nylon via removal of the hydrophilic groups, which would increase the static resistance. Control nylon shows poor static resistance because the surface is hydrophilic. When grafting TETA or HTCC new hydrophilic groups are created, which result in a decreasing of the static resistance. However, a large enough amount of GMA will dominate the small amounts of TETA and HTCC and thus the static resistance is retained. This correlates to the possibility of having a free epoxy group on GMA grafted nylon, which can react with either the –COOH or $–NH_2$ groups in the surface regions of nylon, as shown in Figure 2.

Scanning Electron Microscopy

Scanning electron microscopy was conducted to view the contents of grafting on PA6,6 fabrics. Figure 7 shows SEM micrographs of un-grafted and GMA-grafted PA6,6, The micrographs clearly show GMA on PA6,6 fibers. It is important to notice the smoothness and uniformity of grafting when using oxygenated helium plasma. This confirms that the technique of plasma-aided grafting provides homogeneous and uniform grafting, which is highly competitive to chemical wet techniques.

Antimicrobial Assay Results

Two sets of samples were tested for antimicrobial activity, Control, intermediate fabric PA6,6 grafted with 19.8%GMA (sample F6), and samples further cross-linked with TETA, HTCC or CD. The cross-linked fabrics were PA6,6/24.5% GMA/1.62%TETA (F28A), PA6,6/24.5% GMA/1.06% HTCC (F28B), PA6,6/35.4% GMA/1.33%CD (3F) and PA6,6/35.4% GMA/2.5% TETA (3aF).

Escherichia coli k12 Test Results

Test results using *E. coli* k12 showed that fabric 3F (PA6,6/35.4% GMA/1.33%CD) had the highest antimicrobial activity, greater than 3 Log reduction (99.96% kill), which correlates well to similar results obtained on PP at the same graft condition and same concentrations [31, 32]. Sample F28B (PA6,6/24.5% GMA/1.06% HTCC), which contained quaternary ammonium groups and secondary amino groups in the side chains of HTCC, was the second in high antimicrobial activity, about 2.32 Log reduction (99.52% kill). The antibacterial activity of the fabrics is due to the synergistic

Table 5 Reduction in viable cells of *E. coli* k12 on PA6,6 grafted fabrics.

Sample	CFU/mL	Log CFU/mL	Log reduction	% Kill
Control set 1	6.00E+06	6.78	0	0
F6 (PA6,6/19.8%GMA) Intermediate fabric	4.00E+06	6.6	0.18	33.33
F28A (PA6,6/24.5% GMA/1.62%TETA)	2.76E+06	6.44	0.34	54
F28B (PA6,6/24.5% GMA/1.06% HTCC)	2.86E+04	4.46	2.32	99.52
Control set 2	6.04E+06	6.78	0	0
3F (PA6,6/35.4% GMA/1.33%CD)	2.20E+03	3.34	3.44	99.96
3aF (PA6,6/35.4% GMA/2.5% TETA)	4.94E+04	4.69	2.09	99.18

effects of the secondary amino groups and quaternary ammonium groups in HTCC side chains, which is in agreement with previous results obtained using PP with similar graft yield and concentrations [31, 32]. In addition, the cations of the quaternary ammonium groups and secondary amines content in HTCC fabrics interact to the negatively charged cell bacteria surface destroying the cell membrane of the bacteria with leakage of the interior contents and causing bacteria killing [36]. Inclusion of TETA, sample 3aF (PA6,6/35.4% GMA/2.5% TETA), has shown antimicrobial activity with about 2 Log reduction (99.18% kill), this is also because the cations of the secondary amines content in TETA fabrics interact to the negatively charged cell bacteria surface, similar to HTCC, and destroying the cell membrane. Less inclusion of TETA, sample F28A (PA6,6/24.5% GMA/1.62% TETA), dramatically reduces antimicrobial activity. Control or GMA only (intermediate fabric) have shown no antimicrobial. The test results are shown in Table 5 and Log reduction is shown graphically in Figure 8.

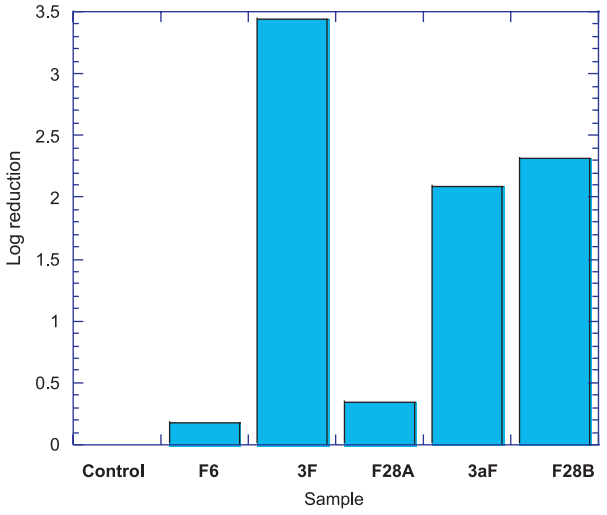


Figure 8 Reduction in viable cells of *E. coli* k12 on PA6,6 grafted fabrics. The log reduction in cell numbers after 3 hours incubation at 37°C is shown. Control (blank PA 6,6), F6: PA6,6/19.8% GMA, 3F: PA6,6/35.4% GMA/1.33%CD, F28A: PA6,6/24.5% GMA/1.62% TETA, 3aF: PA6,6/PA/35.4% GMA/2.5% TETA, F28B: PA6,6/24.5% GMA/1.06% HTCC.

Staphylococcus aureus Test Results

Test results using *S. aureus* show that the highest log reduction was for the sample grafted with HTTC, F28B (PA6,6/24.5% GMA/1.06% HTCC), which showed 2.4 Log reduction (99.61% kill). This is also in good correlation with results obtained for PP using a similar graft yield and concentrations [31, 32]. Samples with TETA inclusion show that the higher percentage of TETA produced better results, which is in correlation to results obtained using *E. coli* k12. This is obvious when comparing sample 3aF (PA6,6/35.4% GMA/2.5% TETA) that showed 1.65 Log reduction (97.77% kill) versus F28A (PA6,6/24.5% GMA/1.62% TETA) with only about 1.0 Log reduction (89.63% kill). Sample 3F (PA6,6/35.4% GMA/1.33%CD) had only about 1.0 Log reduction (90.56% kill) in this case. Control or GMA only (intermediate fabric) showed no antimicrobial effect indicating that un-grafted samples do not incorporate antimicrobial activity. As previously mentioned in the *E. coli* test results, the antibacterial activity of the fabrics is due to the synergistic effects of the secondary amino groups and quaternary ammonium groups in HTCC side chains, as well as the cations of the quaternary ammonium groups and secondary amines content in HTCC and TETA fabrics. Test results are shown in Table 6 and Log reduction is shown graphically in Figure 9.

Comparison between *E. coli* and *S. aureus* Test Results

A comparison between the antimicrobial effectiveness of grafted PA6,6 samples for the two different microorganisms (gram-negative *E. coli* and gram-positive *S. aureus*) is shown

Table 6 Reduction in viable cells of *S. aureus* on PA6,6 grafted fabrics.

Sample	CFU/mL	Log CFU/mL	Log reduction	% Kill
Control set 1	2.68E+05	5.43	0	0
F6 (PA6,6/19.8%GMA) Intermediate fabric	1.38E+05	5.14	0.29	48.51
F28A (PA6,6/24.5% GMA/1.62%TETA)	2.78E+04	4.44	0.98	89.63
F28B (PA6,6/24.5% GMA/1.06% HTCC)	1.04E+03	3.02	2.4	99.61
Control set 2	2.88E+05	5.46	0	0
3F (PA6,6/35.4% GMA/1.33%CD)	2.72E+04	4.43	1.02	90.56
3aF (PA6,6/35.4% GMA/2.5% TETA)	6.41E+03	3.81	1.65	97.77

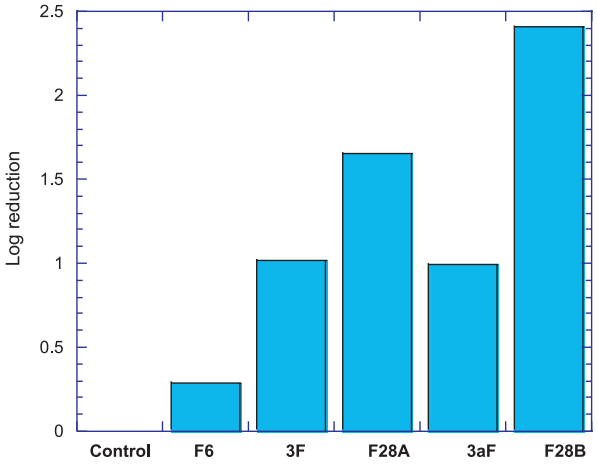


Figure 9 Reduction in viable cells of *S. aureus* on PA6,6 grafted fabrics. The log reduction in cell numbers after 3 hours incubation at 37°C is shown. Control (blank PA 6,6), F6: PA6,6/19.8% GMA, 3F: PA6,6/35.4% GMA/1.33%CD, F28A: PA6,6/24.5% GMA/1.62% TETA, 3aF: PA6,6/PA/35.4% GMA/2.5% TETA, F28B: PA6,6/24.5% GMA/1.06% HTCC.

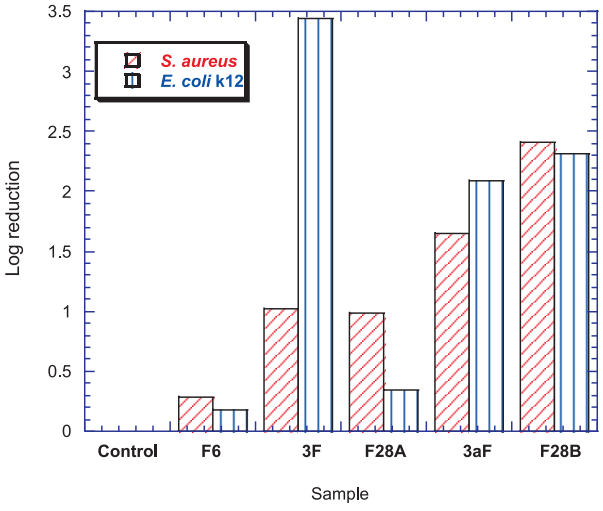


Figure 10 Comparison between experiments with *E. coli* k12 and *S. aureus*. Control (blank PA 6,6), F6: PA6,6/19.8% GMA, 3F: PA6,6/35.4% GMA/1.33%CD, F28A: PA6,6/24.5% GMA/1.62% TETA, 3aF: PA6,6/PA/35.4% GMA/2.5% TETA, F28B: PA6,6/24.5% GMA/1.06% HTCC.

in Figure 10. This is an important comparison in which the effectiveness of certain antimicrobial agent may not be the same on different microorganisms. Samples grafted with higher concentration of TETA, 3aF (PA6,6/PA/35.4% GMA/2.5% TETA) had effectiveness on both microorganisms with higher effect on *E. coli* k12. The sample with CD grafting, sample 3F (PA6,6/35.4% GMA/1.33%CD), had higher effectiveness on *E. coli* k12 and less effectiveness on *S. aureus*. It appears that HTTC and TETA can produce antimicrobial effectiveness on both gram negative and gram-positive bacteria, while cyclodextrin is more efficient on gram-negative bacteria. However, cyclodextrin has another advantage over HTTC and TETA in that it allows for further inclusion of other agents inside the CD cavities, such as additional antimicrobial agents or insect repelling compounds. It is obvious that sample F28B (PA6,6/24.5% GMA/1.06% HTCC) grafted with quaternary ammonium chitosan has similar antimicrobial activity on both gram-negative and gram-positive bacteria, with Log reduction greater than 2.0 in both cases.

Insect Repellent Test Results

The percentage of ticks on either the untreated control fabric or the treated fabric was arcsine transformed using the formula of Freeman and Tukey [37], and the transformed data were analyzed using the general linear model (PROC GLM, SAS Institute Inc.) [38]. Ticks that were

Table 7 Response of *D. variabilis*, American dog tick, 3 hours after exposure to a choice test of untreated and treated fabrics containing BioUD30[a] (spray or silicon formulation). A comparison to grafted PP with inclusion of other insect repelling agents could be found in Refs 31 and 32.

Treated fabric	% Choosing control ± 1 SEM
F3B: 35.4 % GMA, 1.33% CD, 3.13%BioUD30 silicon	100.00 ± 0.00
F21A: 81.85 % GMA, 1.0% CD, 0.477% BioUD30 spray	38.89 ± 24.22
F21B: 81.85 % GMA, 1.0% CD, 0.84% BioUD30 silicon	33.33 ± 25.46

touching both the control and treated fabric were removed from the analysis. Test results are tabulated in Table 7. Ticks that were subjected to a choice test of two untreated identical fabric samples (controls) did not significantly choose either sample. The samples with the inclusion of 3.13% BioUD30 silicon formulation significantly repelled the ticks with 100% repellency. Samples with less BioUD30 percentage (0.477% BioUD spray or 0.84% BioUD silicon) repeeled ticks but were less efficient (38.89 and 33.33% repellency, respectively).

It is important to note that the active ingredient in both formulations of BioUD30 against ticks is 2-undecanone, which is 30% by weight, and therefore the sample containing 3.13% BioUD30 consists of 0.939% 2-undecanone. Two other samples with the inclusion of BioUD30 contained 0.477% (spray formulation) and 0.84% (silicon formulation), consisted of 0.143% and 0.25% 2-undecanone, respectively, and did not effectively repel ticks significantly. BioUD30 consists of 30% 2-undecanone by weight [39]. Comparisons to grafted PP with different grafting chemicals and inclusion of other insect-repelling agents can be found in recent publications [31, 32].

Conclusions

Atmospheric pressure plasma-aided graft copolymerization of PA 6,6 fabrics was successful. The GMA was grafted to PA6,6 followed by further reactions of HTCC, TETA and β-CD. Inclusion of the insect repelling agent (BioUD30) into the cavity of cyclodextrin added insect repellency action to the grafted fabrics. Static decay testing has shown that these modified fabrics are antistatic. Grafted PA6,6 fabrics have shown antimicrobial activity and tick-repellent efficiency. SEM micrographs of PA6,6/GMA fabric have shown homogeneous grafts onto the fabric. TGA results indicate that GMA grafting increases the thermal stability of PA6,6.

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