

Atmospheric Plasma-Aided Biocidal Finishes for Nonwoven Polypropylene Fabrics. I. Synthesis and Characterization

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ABSTRACT: Novel biocidal fabrics were synthesized by the graft copolymerization of glycidyl methacrylate (GMA) onto plasma-treated nonwoven polypropylene (PP) to produce PP/GMA grafts. Atmospheric oxygenated helium plasma was used to enhance the PP fabrics' initiation before GMA grafting. The grafted PP/GMA epoxide group was reacted with β -cyclodextrin, monochlorotrizynyl- β -cyclodextrins, or a quaternary ammonium chitosan derivative [*N*-(2 hydroxy propyl) 3-trimethylammonium chitosan chloride]. Some interesting biocidal agents were complexed into the cyclodextrin (CD)

cavity of PP/GMA/CD grafted fabrics. Fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and optical and scanning electron microscopies were used to characterize the grafted complexed fabrics. These synthesized biocidal fabrics proved to be antistatic, antimicrobial, and insect-repelling (see part II of this study). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1900–1910, 2007

Key words: cold plasma; graft copolymers; polypropylene; chitosan; inclusion chemistry

INTRODUCTION

Biocidal fabrics are more important nowadays to provide avoidance and safety against various microorganisms. Antimicrobial fabrics are synthesized to kill or inhibit the growth of microorganisms such as bacteria, molds, fungi, or insects (by repelling or killing). Diseases transmitted by insects, such as malaria and West Nile virus, are on the increase worldwide. These diseases and others are becoming more resilient to traditional forms of chemicals compared to 20–30 years ago. There is an increased demand for biocidal textiles for medical, hygienic, home, and deployed ground force use. The demand is increasing to protect the healthcare workers and armed personnel deployed in areas susceptible to disease-carrying insects. The appearance of fatal diseases has prompted the need for biocidal textiles. Biocidal textiles are composed of

natural, synthetic, or blended fibers manufactured from nonwoven or woven fabrics, and some are available in the international market under different brand names. They are generally based on some specific biocidal agents added during the melt spinning of the synthetic fibers or during the finishing process of the fabric. Although the addition of biocidal agents to the fibers during melt spinning appears to be a viable technique, the added agents have a low fastness to repeated washing. A high percentage (70%) of these biocidal products are nonwoven disposable fabrics.¹ Polypropylene (PP) has been used in various applications, such as general-purpose filters and wipers, because of its low cost and ease of manufacturing. The antimicrobial activity of nonwoven PP fabrics treated with chitosan derivatives was investigated against various strains of bacteria in part II of this study.²

In this study, the focus was on the synthesis of novel biocidal fabrics with permanent antistatic, antimicrobial, and insect-repelling activities. The graft copolymerization of bioactive monomers into fabric is traditionally initiated by chemical means (a wet process) or by irradiation techniques, such as high-energy electron beams and γ rays. Plasma aided grafting is a dry technique, as plasma is formed by ionized gaseous species. Furthermore, atmospheric

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plasma can be embedded online into the textile production line without changing the flow process.

The modification of textiles with plasma-aided grafting was investigated herein. Fabrics were exposed to an atmospheric dielectric barrier discharge for surface activation and were then grafted by selected hydrophilic monomers, such as 2-hydroxyethyl methacrylate (Hema).³ The grafting of acrylics, methacrylics, or mixtures of acrylics and acrylamides onto PP films with glow discharge plasmas have been investigated by other researchers.⁴⁻⁶ The modification of PP fabric was affected in cold plasma in both static and dynamic devices with several grafting agents to improve the hydrophilicity and dyeability of the fabrics.⁷

In this study, atmospheric plasma was used to pre-treat nonwoven PP fabric; then, glycidyl methacrylate (GMA), which is an interesting monomer because of the high reactivity of the epoxide group, was grafted onto the PP. Cyclodextrin (CD) derivatives were linked into the GMA grafted fabrics, without impairment of the original mechanical properties of the fabric. CD derivatives are, in particular, an interesting group of ligands without toxicological and ecological properties. CD derivatives are cyclic sugar molecules with a toroidal shape, in which the inner cavities of the molecules have hydrophobic characteristics, which allows nonpolar groups of organic compounds to be included inside.^{8,9} The CD derivatives could be perfumed extracts, odor, or pharmaceutically active agents of slow chemical-release action. Permanent fixation of CD adds new important functionality to fabrics.

The plasma treatment of fabrics was followed by the graft copolymerization of selected bioactive agents, including quaternary ammonium chitosan salts sites or CD derivatives [fixation of supermolecular compounds such as β -CD or monochlorotrizinyl- β -cyclodextrin (MCT- β -CD)]. The modification of the PP surface by the fixation of such supermolecular compounds, which contain some biocidal and reactive groups such as trizinyl rings in addition to the presence of the chlorine atom, is very interesting.^{8,9} The host inner cavities of CD compounds are able to form guest complexes with other chemical substances, and thus, treated fibers with CD achieve new functional properties by the selective inclusion of these chemical species in the fixed cavities. This modification finishing process is important for the production of medical, upholstery, and ground forces textiles^{10,11} Several articles and patents have reported relevant applications of cyclodextrin antimicrobial, insect-free, aroma finishing, and textile dyeing through the formation of physical bonds to different fibers.¹²⁻¹⁵

In this study, GMA was used to graft oxygenated helium plasma-treated PP; then, β -CD or MCT- β -CD or quaternary ammonium chitosan derivative was linked to the PP/GMA grafted fabric.

A series of successive reactions were used to produce biocidal textiles. Modifications of the PP fabrics, testing, and characterization were completed as follows:

1. PP fabric was initiated with a helium oxygenated atmospheric plasma treatment. The ionized gas and free electrons, on collision with the PP fabric, created free radicals on the fiber surface.
2. GMA monomer was graft polymerized onto the PP active sites to produce PP/GMA.
3. β -CD (or MCT- β -CD) or *N*-(2 hydroxy propyl) 3-trimethylammonium chitosan chloride (HTCC) were chemically bonded onto the grafted PP/GMA to produce PP/GMA/CD copolymers of different CD graft yields or to produce PP/GMA/HTCC.
4. Biocidal guests were introduced into the CD cavity, which included *p*-hydroxy benzoic acid, a AgNO₃-ethanolamine mixture,^{16,17} iodine, *N,N*-diethyl metatoluamide (DEET), and perfumed extracts, such as citronella, jasmine, and sweet basil.
5. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, optical microscopy, and scanning electron microscopy (SEM) were used to characterize the modified PP fabrics.
6. Antistatic, antimicrobial, and insect-repelling activities of the grafted fabrics were tested and evaluated (this is detailed in part II of this study²).

EXPERIMENTAL

Materials

Nonwoven PP fabrics were prepared in the Nonwoven Cooperative Center of North Carolina State University by a hydroentanglement spun bonding method, and the fiber had a linear density of 1.74 dtex, a fiber length of 38 mm, a 100-mesh forming wire, and a fabric basis weight of about 46.7 g/m². The samples were extracted with acetone before plasma exposure to remove the lubricant from the fabric. GMA containing 50 ppm methyl hydroquinone was purchased from Aldrich Co. (St. Louis, MO) and was used without further purification. Methacrylic acid containing 200–250 ppm methyl hydroquinone was purchased from Aldrich and was distilled before use. CDs (β -CD or MCT- β -CD, β W7WCT) were purchased from Wacker GmbH (Munich, Germany). Chitosan (type 652, density = 4–20 cps) was a gift from Chitine Co. (Marseille, France). Glycidyl trimethyl ammonium chloride was purchased from Dow Chemicals (Charlotte, NC).

Atmospheric plasma apparatus

The atmospheric plasma chamber had an active exposure area of approximately 60 cm × 60 cm and a 5-cm gap separation and was powered by a 4.8-kW audio-frequency power supply operating in the frequency range 5–10 kHz. The device had an inner plasma chamber installed inside an outer chamber, where the latter was equipped with a fabric roller system. The working gas was fed to the chamber through a gas flow controllers.^{18–22} Figure 1 shows a schematic drawing of the atmospheric plasma experimental facility. When helium or oxygenated helium flowed into the plasma chamber, there was always a slight amount of air due to the fact that the chamber was not pumped down and operated at atmospheric pressure. The apparatus was capable of the batch treatment of textiles with a test cell and continuous operation with the roller feeding system. For treatment of the PP samples (15 cm × 10 cm), oxygenated helium was used. The power supply frequency was kept constant, exposure time was varied between 1 and 5 min in 30 s intervals, and power, voltage, plate distance, and flow rate were held constant.

Plasma graft copolymerization reaction

After the exposure of PP fabrics to plasma, the fabrics were immediately graft copolymerized in a stoppered conical flask containing a solution of 50% aqueous methanol and 10–20% GMA with a liquor ratio of 1 : 30.¹⁵ The conical flask was placed in a shaking water bath at 80°C for 30–60 min. After grafting, the fabric was thoroughly washed with warm distilled water, ethanol, and acetone and then dried at 50°C. Scheme 1 shows the plasma graft copolymerization reaction of PP with GMA. The weight of the dried samples (W_2) were measured and compared to the original weight (W_1) to determine the percentage add-on, which represented the graft yield:

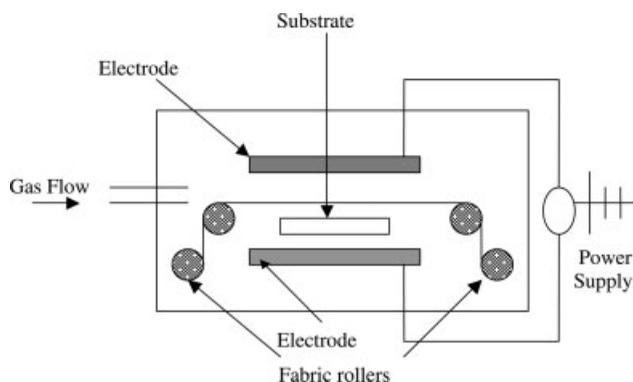


Figure 1 Schematic drawing of the inner chamber of the atmospheric plasma facility. Plasma was generated between two electrodes embedded in the dielectric material to form a dielectric barrier discharge.

$$\% \text{ Add-on} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Reaction of the quaternary ammonium chitosan derivative onto PP/GMA

The PP/GMA graft was further reacted with the antimicrobial agent HTCC, which was synthesized according to known procedures.²³ HTCC was used because it has better antimicrobial activity compared to pure chitosan.²⁴ This compound not only enhances the water solubility and antimicrobial activity of chitosan, but it can also be used as an antistatic finishing agent due to the presence of quaternary ammonium groups. The HTCC compound was synthesized with glycidyl trimethyl ammonium chloride and chitosan, as illustrated in Scheme 2.

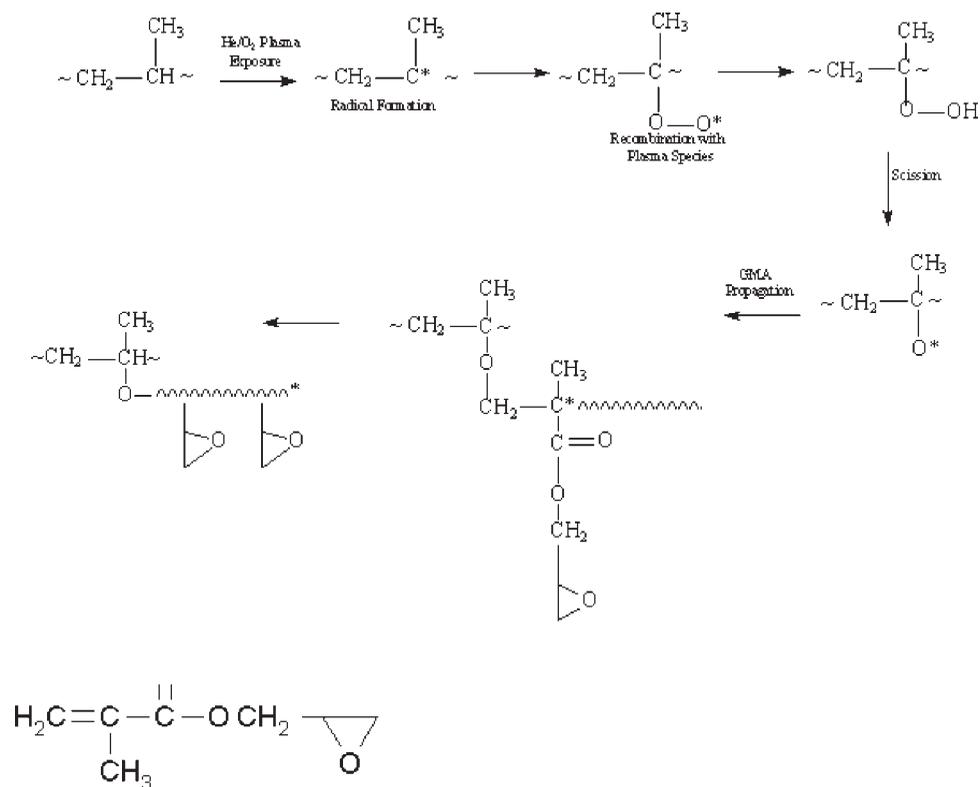
For this reaction, chitosan (1%, 4–20 cps) was dissolved in 1% acetic acid, precipitated with 0.1N NaOH, centrifuged at 0–4°C, and air-dried. Chitosan (2%) and glycidyl trimethylammonium chloride (8%) were dispersed in distilled water. The solution was stirred at 80°C for 24 h. After the reaction, the product was cooled and centrifuged, which separated the insoluble chitosan from the water-soluble chitosan fraction containing the quaternary ammonium chitosan. The soluble quaternary ammonium chitosan was then reprecipitated with a 50% ethanol/acetone mixture and air-dried under suction. After the synthesis of HTCC, a PP/GMA grafted fabric was allowed to react with 2 g of HTCC in the presence of 1% NaOH at a liquor ratio of 1 : 30. The reaction was held at 80°C for a specified time to produce the grafted PP/GMA/HTCC fabric according to the reaction shown in Scheme 3.

Reactions of CD onto PP/GMA

A second set of PP/GMA grafted fabrics were reacted with β -CD or MCT- β -CD. The fabric was added to a solution containing 2% β -CD, 1M NaCl, and 1% NaOH.²⁵ The solution was stirred at 80°C for the desired time. The grafted fabric was washed with warm distilled water and acetone, dried, and weighed, and the percentage add-on was calculated. The PP/GMA graft reaction with β -CD is illustrated in Scheme 4.

Biocidal treatment of grafted PP/GMA/CD with inclusion compounds

Once the β -CD or MCT- β -CD compound was grafted, additional biocidal agents were incorporated onto the CD cavity. The PP/GMA/ β -CD fabric (1 g) was immersed in a 25-mL mixture (10% distilled water and 90% ethanol) containing 1–2% of a guest molecule. These guest molecules included insect-



Glycidyl Methacrylate (GMA)

Scheme 1 Plasma graft copolymerization of PP/GMA.

repelling oils, such as DEET, citronella, jasmine, and sweet basil. The fabrics were soaked for 24 h in this solution at room temperature to form the inclusion complexes. The samples were then washed several times with cold distilled water and ethanol and were then air-dried. The chemical formulas for citronella and DEET are shown in Scheme 5.

Characterization techniques

Weight gains

Each sample was weighed before plasma treatment (W_0) and after grafting with an Explorer microbalance with an accuracy of $\pm 100 \mu\text{g}$ to determine the weight increase (W_1). The percentage weight gain for the PP fabric after grafting was calculated as follows:

$$\text{Weight add - on (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

DSC

Thermal analysis of the PP samples was conducted with a PerkinElmer 7 power-compensated differential scanning calorimeter.^{26,27} Each sample was scanned

at a rate of $20^\circ\text{C}/\text{min}$ over the range $25\text{--}300^\circ\text{C}$. The onset melting temperature was obtained from the intercept of the baseline and the maximum tangent of the corresponding exothermic and endothermic peaks.

TGA

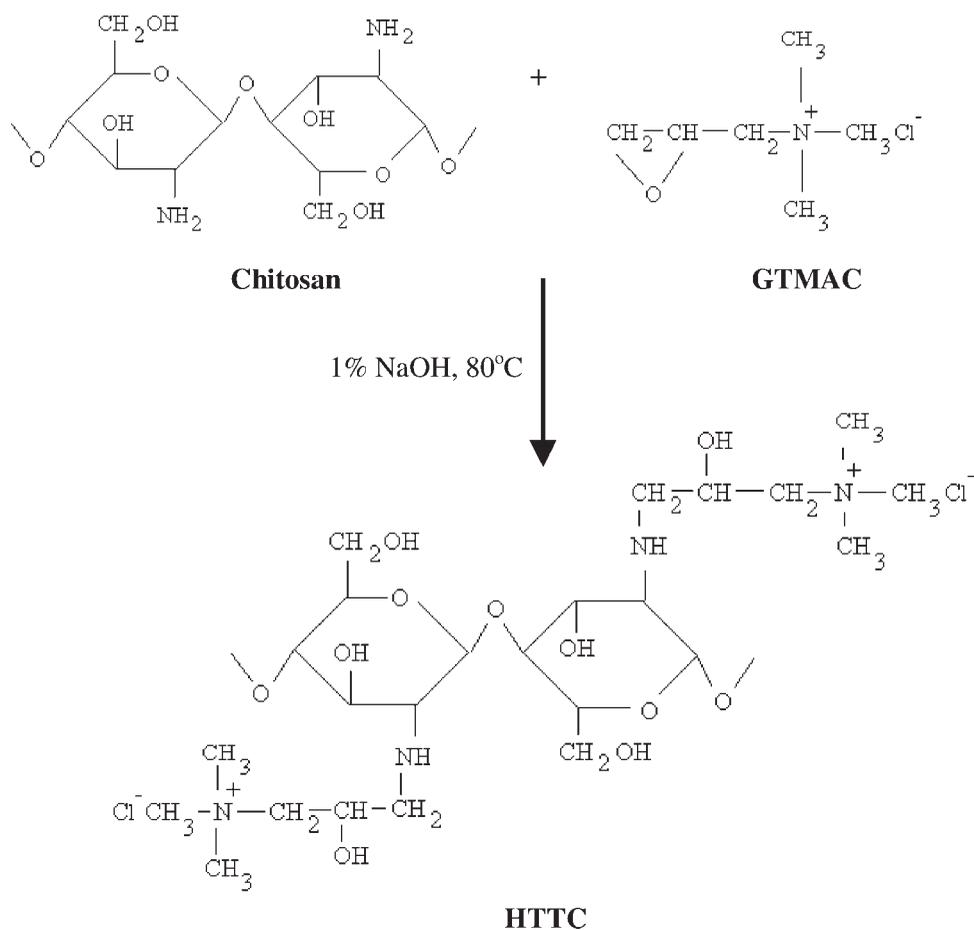
Thermal analysis was further conducted on the non-woven PP samples with a PerkinElmer TGA device. The percentage weight change versus temperature was evaluated at a scanning rate of $30^\circ\text{C}/\text{min}$ over a range of $25\text{--}700^\circ\text{C}$.

FTIR spectroscopy

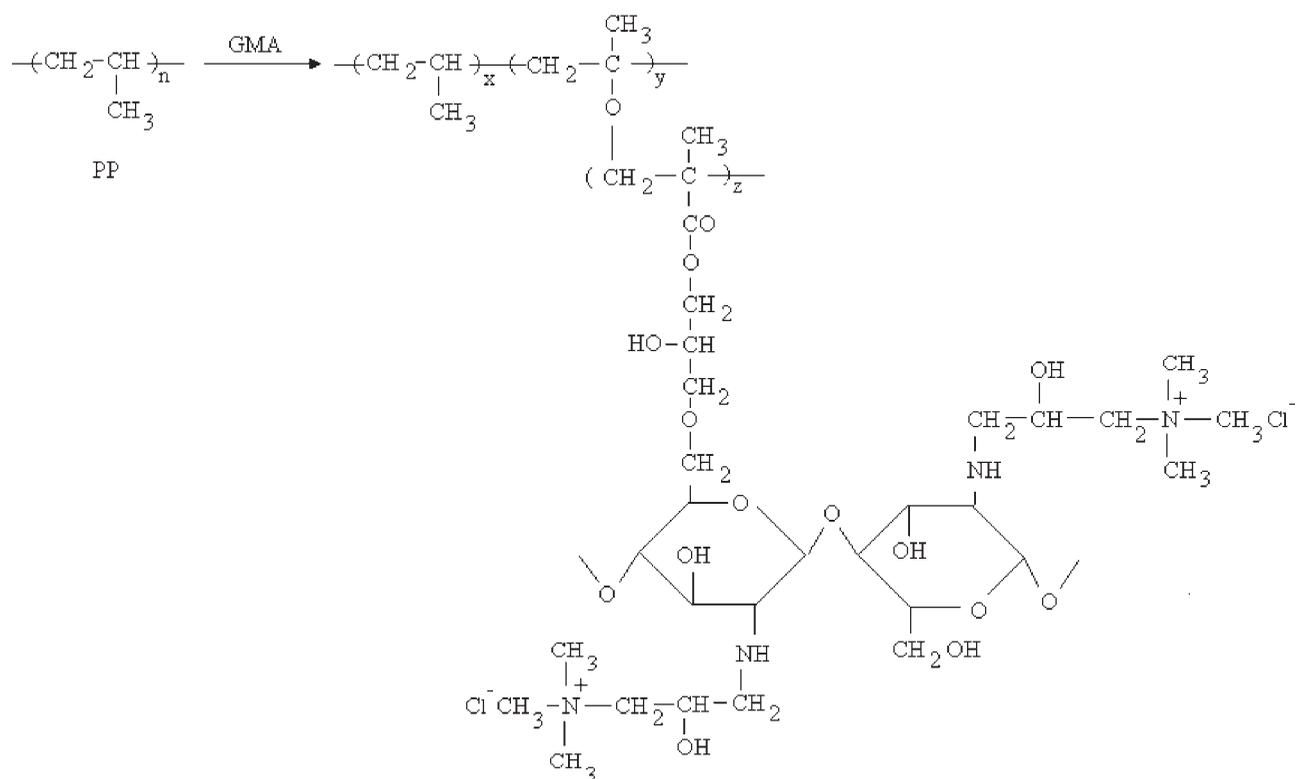
PP nonwoven fabric samples were evaluated with a Nexus 470 FTIR in conjunction with a Nicolet omni-sampler.

Optical microscopy

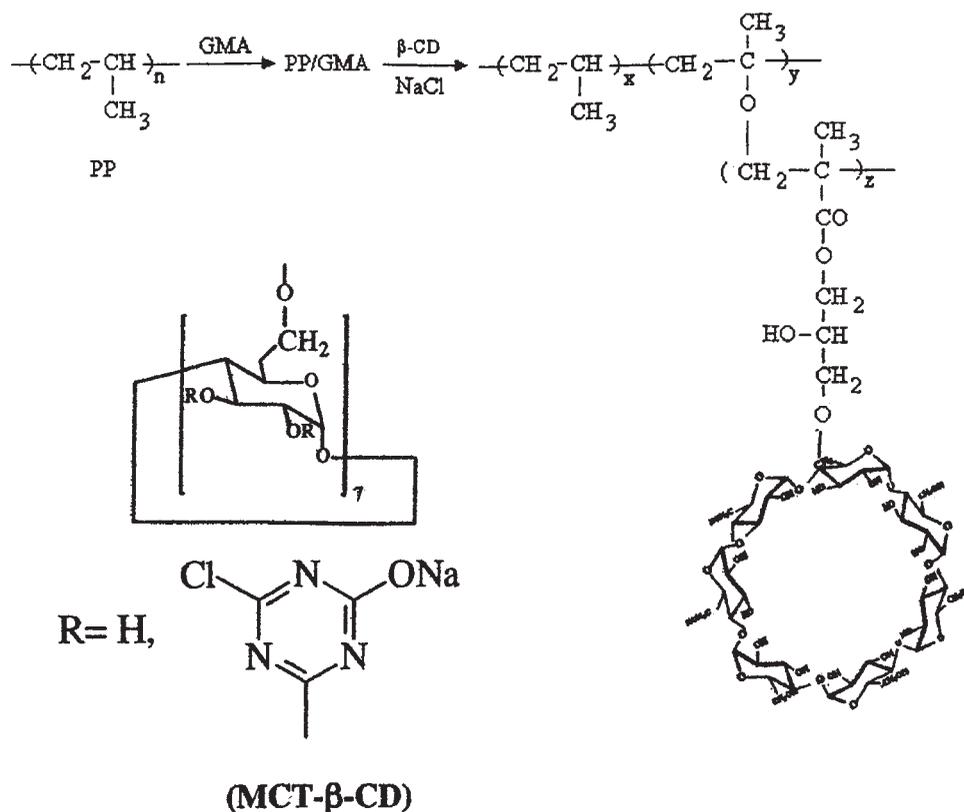
Optical pictures of the grafted samples were obtained with an Olympus optical microscope (model BH2-UMA) with magnification up to $1000\times$ and equipped with a digital camera.



Scheme 2 Reaction of HTCC synthesis.



Scheme 3 Synthesis of the grafted PP/GMA/HTCC fabric.



Scheme 4 Grafting of CD onto PP/GMA.

SEM

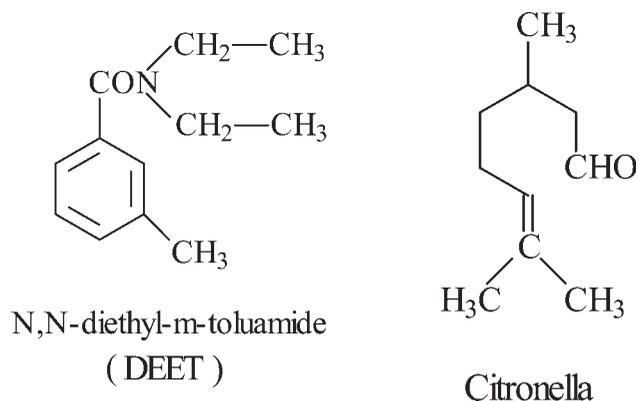
PP nonwoven fabric samples were evaluated with a Hitachi S-3200N variable-pressure scanning electron microscope. SEM micrographs were taken in magnification ranges of 100–1000×.

RESULTS AND DISCUSSION

Weight increase and graft yield

Fabric weights were measured before and after plasma treatment and after grafting with GMA to determine the percentage graft yield. On the basis of the plasma exposure time, the GMA solution dwell time, and the concentration of the GMA solution, the percentage GMA add-on varied from 3.9 to 38%, depending on graft time and temperature. Figure 2 shows the dependence of the percentage GMA add-on as a function of plasma exposure time for the grafting of 20% GMA at 80°C. It is clear that increased exposure to plasma allowed a higher percentage GMA add-on, which was attributed to enhanced plasma preactivation before grafting. The percentage GMA add-on dependence on the percentage GMA concentration is shown in Figure 3, and the effect of grafting time for 20% GMA concentration at 80°C is shown in Figure 4.

As seen from Figures 2 and 3, the percentage GMA add-on increased with extension of both the exposure time and the GMA solution concentration, which confirmed the ability of atmospheric plasma to activate PP for GMA grafting and, thus, the optimization of the percentage add-on. The effect of grafting time, as illustrated in Figure 4, indicated that extending grafting time allowed an increased percentage add-on; however, further extension of the grafting time beyond 45 min did not increase the add-on, as saturation was almost reached. Samples with the highest add-on were selected for further grafting reactions with quaternary ammonium chito-



Scheme 5 Chemical formulas of DEET and citronella.

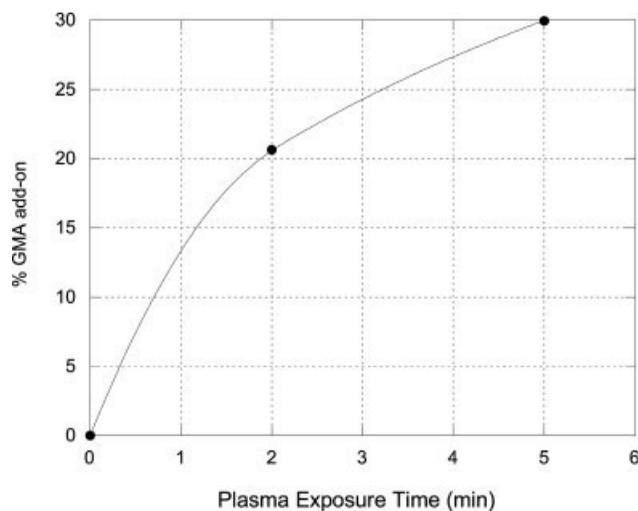


Figure 2 Percentage GMA add-on as a function of the exposure time to plasma. Fabrics were exposed to oxygenated helium plasma for activation (20% GMA at 80°C). Data are within 5% error.

san and β -CD for antimicrobial and insect-repelling functionality.

DSC

Thermal analysis was performed to confirm the grafting of the PP fabrics. Thermal analysis included DSC and TGA. The DSC profiles of samples of untreated and grafted PP fabrics are shown in Table I. The control PP fabric was characterized by a broad and large endothermic transition starting beyond 155°C, with a peak temperature of 158.84°C. The grafted PP fabrics showed a slight increase in melting

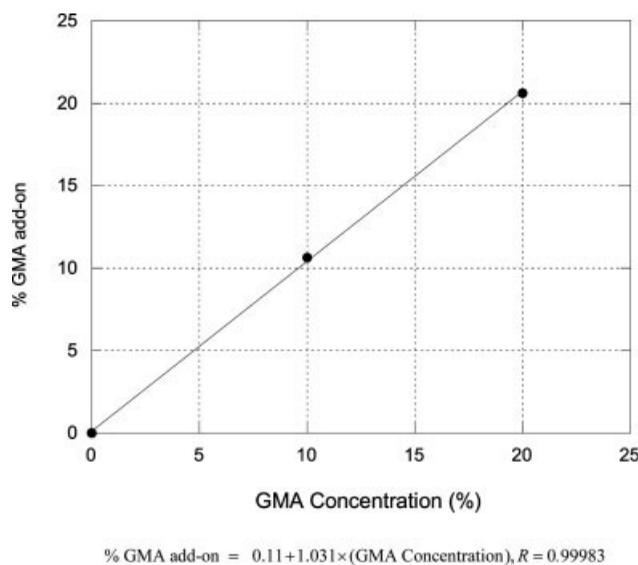


Figure 3 Percentage GMA add-on versus percentage GMA concentration at 80°C. Fabrics were exposed to oxygenated helium plasma for 2 min for activation. Data are within 5% error.

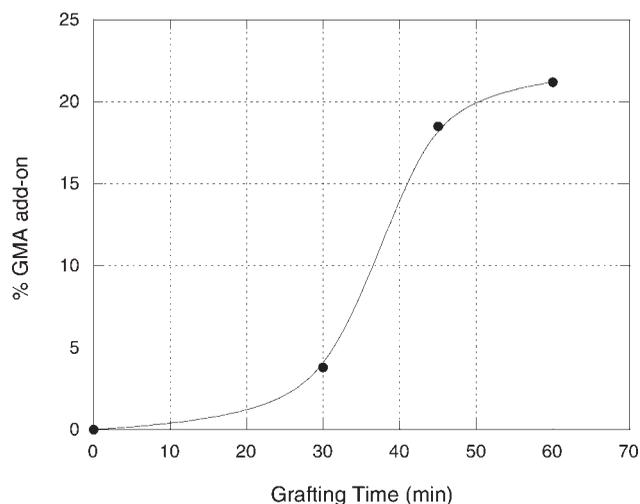


Figure 4 Effect of grafting time on the percentage GMA add-on for 20% GMA concentration at 80°C. Data are within 5% error.

point, and a decrease in both the melt endotherm and the crystallization exotherm. Specifically, the 8.7% GMA grafted fabric had a crystallinity of 56.4% (on the basis of $\Delta H_{\text{endotherm}}$), and the 18.08% GMA grafted fabric had a crystallinity of 54.14%. Both were at least 4% lower than the 60.5% crystallinity calculated for the control sample. Figure 5 further illustrates the effect of the percentage crystallinity versus the enthalpy (ΔH):

$$\% \text{crystallinity} = \frac{\Delta H_f \times 100}{\Delta H_{\text{cryst}}} \quad (3)$$

$$\Delta H_{\text{cryst}} = 149 \text{ J/g}$$

where ΔH_f and ΔH_{cryst} are the formation enthalpy and enthalpy of crystallinity, respectively.

In addition to the decrease in percentage crystallinity for the PP/GMA fabrics, the crystallinity of the multigrafted fabrics containing either CD or chitosan dropped even further. The percentage crystallinity of the PP/GMA/CD sample decreased to 50.96%, and the PP/GMA/HTCC fabric dropped to 49.16%. All values were consistent with the percentage add-on.

TGA

The increased thermal stability of the PP graft fibers was confirmed by TGA. The percentage residual weight versus temperature for the PP control and grafted fabrics is shown Figure 6.

These results show that plasma graft copolymerization of the fabric greatly increased the decomposition temperature. When GMA was grafted onto PP, the decomposition temperature shifted from 433 to

TABLE I
DSC of Grafted PP Nonwoven Samples Compared to the Control

| Sample | He/O ₂ plasma exposure time (min) | Melting temperature (°C) | ΔH_f (J/g) | Crystallinity (%) |
|------------------------------------|--|--------------------------|--------------------|-------------------|
| PP control | 2 | 158.84 | 90.131 | 60.5 |
| Fabric 10 (PP/29.7% GMA/2.6% HTCC) | 5 | 159.80 | 73.248 | 49.16 |
| Fabric 12 (PP/18.08% GMA) | 2 | 159.32 | 80.67 | 54.14 |
| Fabric 18 (PP/38% GMA/7.2% CD) | 2 | 159.27 | 68.413 | 45.9 |
| Fabric 19 (PP/20.6% GMA/1% CD) | 2 | 159.36 | 75.930 | 50.96 |
| Fabric 24 (PP/8.7% GMA) | 2 | 158.85 | 83.97 | 56.4 |
| Fabric 31 (PP/5% methacrylic acid) | 2 | 158.86 | 88.139 | 59.2 |

467°C and, thereby, created a more thermally stable fabric. Further grafting with quaternary ammonium chitosan revealed an even higher decomposition temperature, which correlated well with the additional grafted material.

In contrast to the PP/GMA/HTCC fabrics, PP/GMA/CD fabrics showed a lowering effect on the decomposition temperature to near 450°C (compared to PP/GMA at 467°C). This temperature correlated to the decomposition temperature of saccharides and confirmed the grafting of the CD compounds.²⁵ By comparing the residual weights at approximately 400°C, we also noted the effect of grafting; there was 47.55% remaining from the control, 98% remaining for the fabric containing HTCC, 72.08% remaining for the GMA fabric, and 55.44% remaining for the sample containing CD.

FTIR spectroscopy

The IR spectra of the plasma-grafted PP fabrics were obtained and compared to the control, as shown in

Figures 7 and 8. The spectrum for PP/18.08% GMA (PP fabric 12) showed additional absorbance bands compared to the PP control. These bands were attributed to the ester carbonyl group of GMA (1729 and 1151.54 cm⁻¹) and the epoxide group (at 1255.81 cm⁻¹), with a shoulder and an increase in the absorbance bands at 900 and 841 cm⁻¹. The stretching and increased peak intensity at 1151.5 cm⁻¹ further confirmed grafting with the formation of the -C-O-C- ether linkages of the grafted GMA. In contrast, the grafting of the quaternary ammonium chitosan showed characteristic bands of the quaternary chitosan itself but with lower absorbances at 1641 and 1480 cm⁻¹ for the methyl group and 1030 cm⁻¹.

The lower absorbance was due to its lower concentration. FTIR spectra were also useful in confirmation of the grafting of the CD onto the PP/GMA fabric. This was illustrated by a significant decrease in the epoxide peak and the appearance of intense absorbance bands at 1155.5 and 1030 cm⁻¹, which were characteristic absorbance bands of the CD itself. There

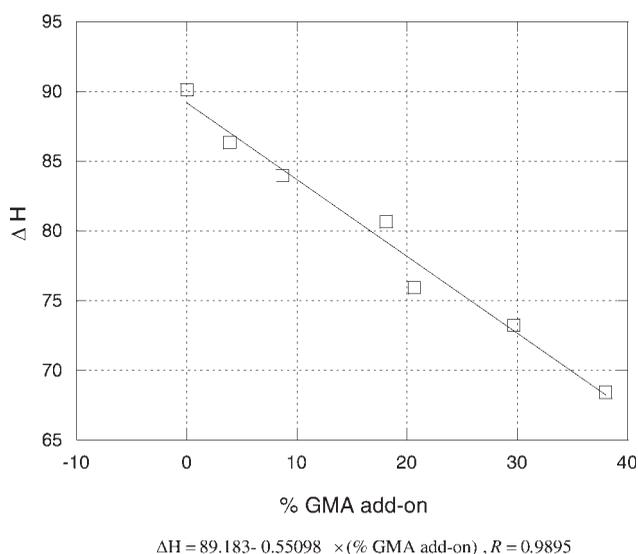


Figure 5 Dependence of ΔH on the percentage GMA add-on.

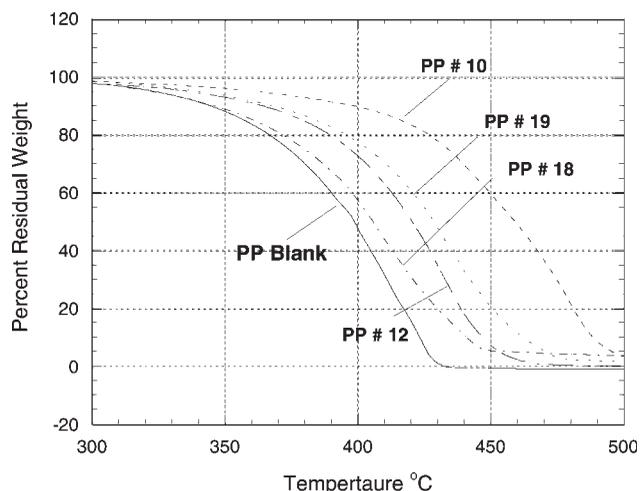


Figure 6 Percentage residual weights of the grafted PP nonwoven fabrics compared to that of the control.

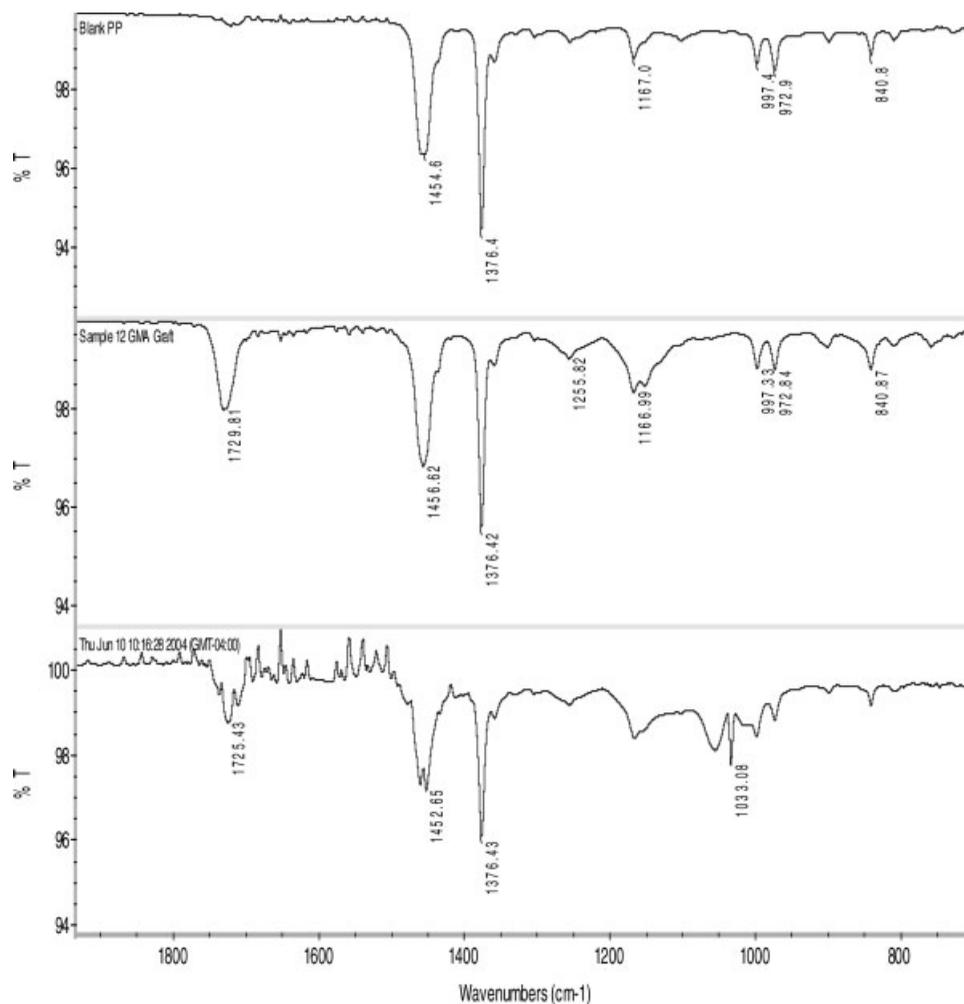


Figure 7 IR spectra of (a) nonwoven PP, (b) PP/18.08% GMA (PP fabric 12), and (c) PP/29.7% GMA/2.6% HTCC (PP fabric 10).

was also an additional absorbance band at 3348.7 cm^{-1} , which indicated the —OH group of the CD.

Optical microscopy and SEM

Digital pictures of samples taken by optical microscopy showed grafted agents on the PP fibers. For fabrics with the highest percentage GMA add-on (38%) and the inclusion of 7.2% CD, the additional inclusion of insect-repelling agents into the CD cavities was incorporated. For these samples, optical microscopy was performed and showed CD grafted onto the PP fibers. The inclusion of 1% DEET into the CD cavities allowed insect-repelling functionality. Optical microscopy photographs of the PP/38% GMA/7.2% CD/1% DEET and fabrics with 1% citronella and 1% sweet basil were obtained, and they clearly showed the CD clusters well grafted into PP/GMA. After optical microscopy analysis, samples were investigated by SEM to inspect the grafted

fibers in detail. Figure 9 shows a micrograph of the grafted fabric PP/38% GMA/7.2% CD at $1000\times$ magnification, in which CD was clearly attached to the fibers. Figure 10 is a $1000\times$ micrograph of grafted PP/29.7% GMA/2.6% HTCC, in which the HTCC is shown attached to the fibers. The SEM micrographs clearly showed the successful grafting of GMA onto PP and the further grafting of CD and HTCC. The higher magnification micrographs showed particulates attached to the fibers, which confirmed the grafting of GMA and additional chitosan and CD compounds.

CONCLUSIONS

Plasma-treated nonwoven PP fabrics were graft copolymerized with GMA, CD, and antimicrobial and insect-repelling inclusion agents. The weight increase data confirmed the grafting of GMA onto the nonwoven fabrics and revealed a dependence on the

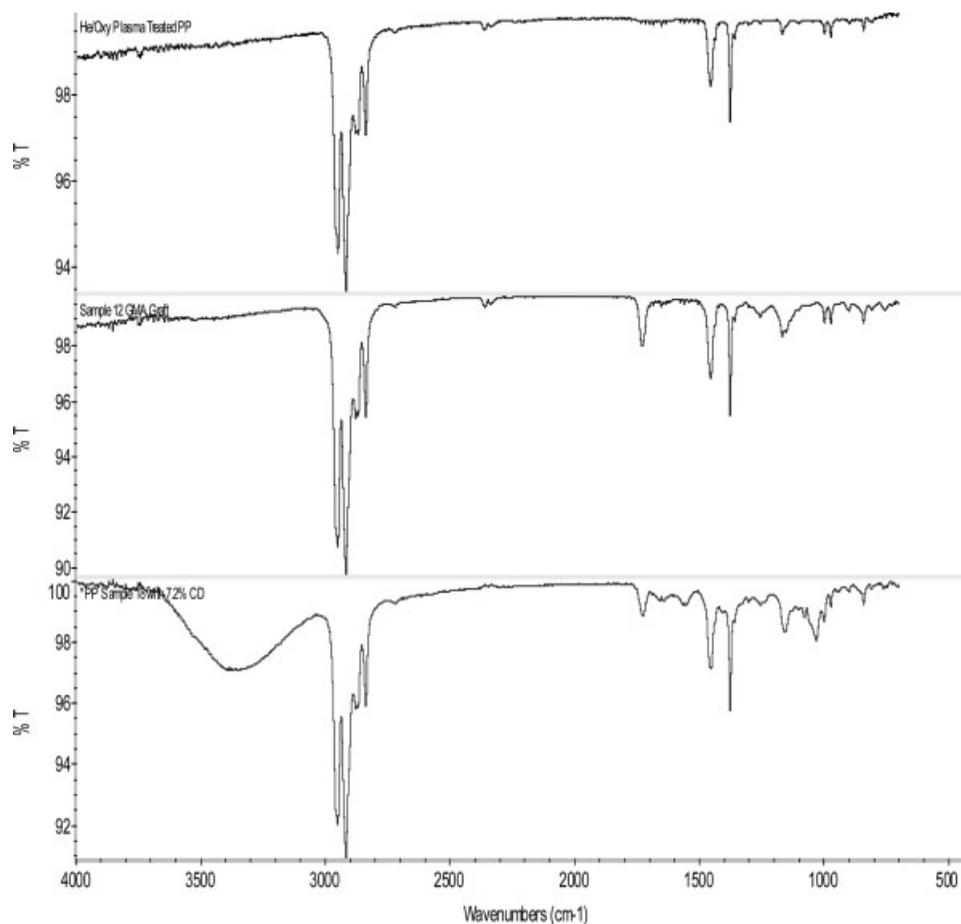


Figure 8 IR spectra of (a) nonwoven PP fabric with 2 min of He/O₂ plasma exposure, (b) PP/18.08% GMA (PP fabric 12), and (c) PP/38% GMA/7.2% β-CD (PP fabric 18). Arrows indicate the absorbance band of CD at 1030 cm⁻¹ and the -OH group of CD at 3348.7 cm⁻¹.

plasma exposure time. Thermal analysis and FTIR correlated well with the grafting of GMA, HTCC, and CD compounds. Further testing on the fabrics

revealed antimicrobial and insect-repelling actions and an antistatic effect. The antimicrobial assay is described in detail in part II of this study.²

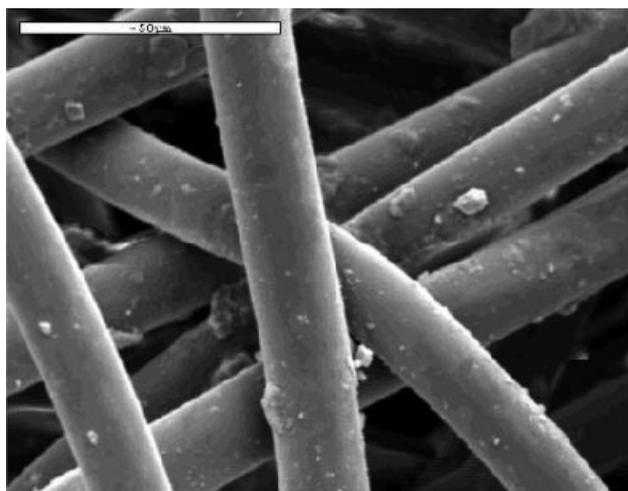


Figure 9 SEM micrograph of PP/38% GMA/7.2% CD (1000×).

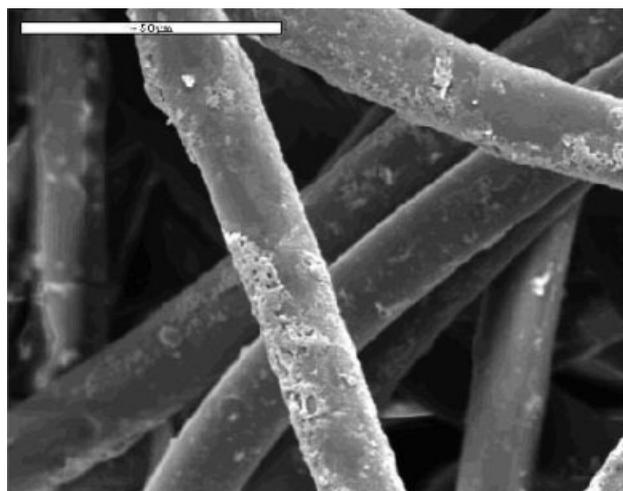


Figure 10 SEM micrograph of PP/29.7% GMA/2.6% HTCC (1000×).

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