Characteristic Properties of Polypropylene Cationic Fabrics and Their Derivatives

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ABSTRACT: Polypropylene fabrics were modified with 2*N*-morpholino ethyl methacrylate by electron beams and grafting. Then, the modified fabrics were quaternized with different alkylating agents, such as benzyl chloride, monochloroacetic acid, chlorosulfonic acid, and chloroethanol. The reaction completion was calculated from the increase in the fabric weight. The modified polypropylene fabrics were characterized by microanalysis and IR spectroscopy. The moisture regain was measured at 20°C and 65% relative humidity. The modified fabrics were sufficiently hydrophilic to adsorb the metal ion Cu^{2+} from a $CuSO_4$ solution. Their antimicrobial properties were evaluated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2917–2922, 2003

Key words: poly(propylene) (PP); ion exchangers

INTRODUCTION

Irradiation followed by grafting copolymerization has great advantages. It is a well-known method for the modification of the chemical and physical properties of polymers. Also, it provides some valuable and interesting materials, such as ion-exchange fibers,[1] antibacterial fabrics, and protein collection membranes.[2]

Ion-exchange chelating fibers have been obtained by the introduction of suitable functional groups onto various types of fibrous polymers, such as poly(ethylene tetraphthalate),[3] polyacrylonitrile,[4] and poly(vinyl alcohol).[5] The importance of chelating sorbents for chemical applications has been evident for a long period of time. Recently, there has been interest in the use of chelating sorbents in the fields of water treatment and pollution control.[6] Various forms of synthetic polymers containing complexes molecules are available on the market at low cost, and they have emerged as among the most important materials for the syntheses of new sorbents.[7,8]

The graft polymerization of glycidyl methacrylate to nonwoven polypropylene (PP) is interesting because of the high reactivity of its epoxy groups. Indeed, the use of chemical reactions such as amination, phosphorylation, sulfonation, and hydrolysis[9–11] leads to new materials that can be used for many other purposes, such as metal chelation.[10,12]

Nonwoven PP fabrics can be surface-modified to form linear, nonswellable cation exchangers through the introduction of chemically fixed sulfonic or phosphoric groups. When sulfonated and phosphonylated PP ion exchangers were compared, phosphonylated PP had a higher binding efficiency than sulfonated PP.[13] The new cation exchangers, particularly those carrying phosphonylate groups, are more effective in binding Pb^{+2} and Eu^{+3} ions than commercial sulfonic acid crosslinked ion exchange.

Gupta and Plessier[14] grafted acrylonitrile onto PP fibers with the preirradiation method. The influence of the reaction conditions on the degree of grafting was investigated. The same authors[15] studied the physical properties of modified fibers, such as the orientation, crystallinity, and moisture regain. The grafted fibers showed excellent dyeability with a disperse dye. Kaur and Basole[16] reported on the grafting of 4-vinyl pyridine and its mixture with acrylonitrile onto preirradiated PP fibers. The percentage of grafting was studied as a function of different reaction parameters, and the optimum conditions affording the maximum percentage of grafting were evaluated.

Antimicrobial textiles are modified textiles that kill or inhibit the growth of microorganisms such as bacteria, mold, and fungi. Antimicrobial textiles for medical, hygienic, and home usage are of great importance. Therefore, the demand for these textiles in the international market has increased.

Various antimicrobial agents are used for the modification of textiles, such as quaternary ammonium salts, quaternary ammonium silanes, halogenated phenolic derivatives, halogenated compounds, polybiguanidine, isothiazolinone, organometallic and

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metal salts, and organic and inorganic sulfur compounds.

In recent years, Park et al.[17] used a preirradiation grafting method to graft acrylic acid (AA) onto PP fabric. The antibacterial activity of metallic complexes of AA-grafted fabric was evaluated by viable cell counting. Ag-complexed fabric had a strong biocidal effect for all bacteria. The antibacterial activity of PP fabric grafted with sulfonated styrene and its metallic salt[18] was determined. The Ag complex of PP fabric grafted with sulfonated styrene had a biocidal effect and killed all bacteria within 30 min. The antibacterial activity of the metallic salts of sulfonated and grafted PP fabric showed that the complexed fabric had stronger biocidal effects for all bacteria than the other metal-complexed fabrics, which had different antibacterial activities depending on the bacterium species. Modified nonwoven PP cloth was prepared by radiation and the grafting of 4-vinyl pyridine onto the PP nonwoven cloth followed by quaternization. The results showed that the content and structure of the pyridinuim group of PP nonwoven cloth were important factors contributing to antibacterial effects.[19]

The aim of this investigation was the preirradiation and grafting of PP fabric with an electron-beam accelerator, followed by the grafting of an aqueous solution of 2*N*-morpholino ethyl methacrylate (MEMA). The tertiary amino groups of the grafted side chains were then quaternized with different alkylating agents to produce active biocidal fabric. The MEMA-grafted fabrics and their quaternary ammonium salts were treated with a $CuSO_4$ solution for complexation. The physical and antimicrobial properties of fabrics with MEMA quaternary ammonium salts and PP were evaluated.

EXPERIMENTAL

Materials

The PP fabric (100%) was obtained from Montedison Co. The PP was highly isotactic and had the following specifications: 238dtex warp and 251dtex fill. The monomer MEMA (purity = 97.85), stabilized by 50 ppm methyl hydroquinone, was supplied by German Rohm Co. and used without further purification. Alkylating agents were used, such as benzyl chloride, monochloroacetic acid, chlorosulfonic acid, and 2-chloroethanol.

Fabric washing

Before irradiation, the PP fabric was extracted for 1 week with acetone for the removal of the antioxidants and ultraviolet stabilizers, which were inhibitors for the grafting process, and then air-dried before irradiation.

Radiation source

The irradiation of samples was carried out in an electron-beam accelerator at the National Center for Radiation (Cairo, Egypt). A preirradiation method was adopted. The dry fabric was exposed to a 2-Mrad irradiation dose in the presence of air.

Grafting procedure

The electron-beam-irradiated PP fabric were grafted in a 15% aqueous MEMA solution at 100°C for 1 h. PP–MEMA was prepared according to a reported method.[20,21]

Quaternization of grafted tertiary amino groups

Quaternization was achieved by the immersion of a known weight of the grafted fabric in a specific solvent containing a threefold excess of the calculated weight of the alkylating agent (benzyl chloride, monochloroacetic acid, chlorosulfonic acid, or 2-chloroethanol). The sample was stirred at the reflux temperature for 1 h.

For example, the quaternization of grafted PP–MEMA fabric with chlorosulfonic acid was performed in chloroform. Chlorosulfonic acid was added dropwise to the previous solution with stirring. The reaction was continued at 50°C for 1 h, and the mixture was then removed and thoroughly washed with ethanol, warm water, and cold water. Finally, the sample was dried, and an increase in weight due to the quaternization reaction was noted. The completion of the quaternization reaction was calculated as follows:

$$\text{Percentage reaction completion} = \frac{W_1}{W_2} \times 100 \quad (1)$$

where W_1 is the actual weight increase due to the quaternization reaction and W_2 is the theoretical weight of the alkylating agent needed for complete quaternization of the grafted MEMA.

The weights of the grafted MEMA and the alkylating agent required were computed as follows:

$$\text{Weight of MEMA} = (\text{Graft yield} \times \text{Grafted sample weight})/100 \quad (2a)$$

$$\text{Weight of alkylating agent} = \frac{\text{Molecular weight of alkylating agent} \times \text{Weight of MEMA}}{\text{Molecular weight of MEMA}} \quad (2b)$$

Moisture regain

The samples were conditioned at room temperature for 4 days in a desiccator containing a saturated solution of sodium nitrite to achieve a relative humidity of 65%. The samples were weighed and dried. The moisture regain was calculated as follows:

TABLE I
Reaction Completion of PP Fabric Grafted with MEMA (Molecular Weight = 199) and Quaternized with Different Alkylating Agents

Alkylating agent	Solvent	Weight increase due to quaternization (40% grafted MEMA weight; %)	Quaternization reaction completion (%)
Benzyl chloride	None	10.3	67.5
Monochloroacetic acid	Ethanol	8.5	62.8
2-Chlorethanol	None	5.6	54
Chlorosulfonic acid	Chloroform	6.8	49.7

$$\text{Moisture regain (\%)} = \frac{W - W_0}{W_0} \times 100 \qquad (3)$$

where W and W_0 are the conditioned and dry weights of the sample, respectively.

IR spectroscopy

The IR analysis was carried out with an FTIR spectrophotometer (FTIR 300E, Jasco). The samples were ground to a very fine powder, mixed with highly dried KBr powder, and pressed into transparent disks.

Metal complexation of quaternized PP–MEMA grafts

Quaternized PP–MEMA fabrics with different alkylating agents were immersed into a solution of $CuSO_4 \cdot 5H_2O$ ($5 \times 10^{-2}M$) for 24 h at room temperature. The concentration of the metal-ion solution before and after exchange adsorption was determined by means of an atomic absorption method. The exchange adsorption amount (E) was calculated as follows:

$$E \text{ (mg/g)} = \frac{(M_0 - M) \times V}{W} \times W_m \qquad (4)$$

where M_0 and M are the concentrations of the metal-ion solution before and after exchange adsorption (mol/L), V is the volume of the solution used for exchange adsorption (mL), W is the weight of the exchange fabric, and W_m is the atomic weight of the metal.

Antimicrobial procedure

A modified form of AATCC Test Method 100 was adopted. One piece of the fabric was placed in a sterilized container. An *E. coli* suspension (100 μL) containing 10^6 to 10^7 CFU/mL of the bacteria was transferred onto the surface of the fabric. An identical piece of the fabric was then put onto the fabric with a 50-mL sterilized beaker. After a 3-h contact time, the fabric was transferred into 10 mL of sterilized distilled water, which was vigorously shaken for 5 min, and the solution was serially diluted and placed onto agar plates. After being incubated at 37°C for 24 h, bacteria on the agar plates were counted. A blank (untreated PP) was used as a control. Viable colonies of bacteria were counted by the spread plate method:

$$\text{Percentage reduction in numbers of bacteria growth} = \frac{A - B}{A} \times 100 \qquad (5)$$

where A is the number of bacteria counted for untreated fabrics (control) and B is the number of bacteria counted for treated modified PP fabrics

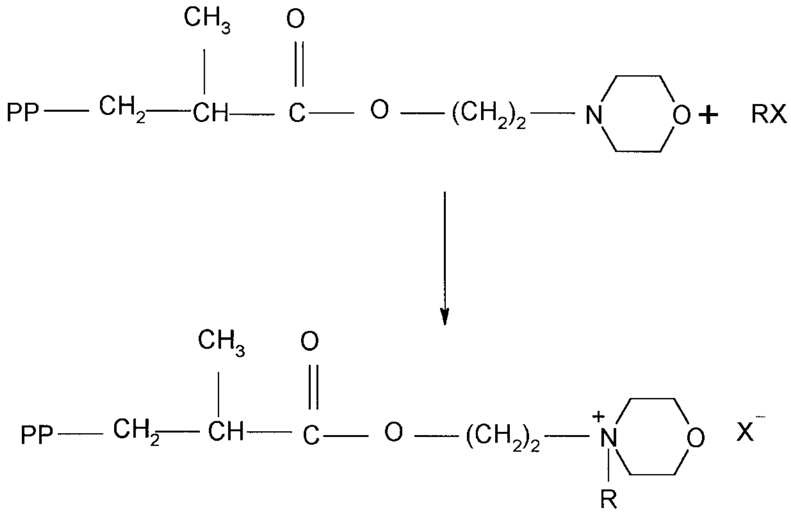
RESULTS AND DISCUSSION

Reaction of PP–MEMA grafts with the cationic agents

The quaternization reaction can be represented as follows:

TABLE II
Moisture Regain of PP Grafted with MEMA and Quaternized at 20°C and 65% Relative Humidity

Fabric sample	Graft yield (%)	Moisture regain of PP–MEMA fabric (%)	Moisture regain of quaternized ammonium fabric (%)	Moisture regain due to quaternized reaction only (%)
PP fabric	—	—		
PP–MEMA	40	2.3		
Quaternized PP–MEMA with benzyl chloride	40.5	2.3	5.6	3.3
Quaternized PP–MEMA with monochloroacetic acid	40	2.28	7.48	5.2
Quaternized PP–MEMA with 2-chloroethanol	40.5	2.34	6.93	4.59
Quaternized PP–MEMA with chlorosulfonic acid	41.5	2.33	6.94	4.61



(6)

quaternary ammonium salt PP- MEMA

where R is —CH$_2$—COOH, —SO$_3$H, —(CH$_2$)—OH, or benzyl and X is Cl. The quaternization reaction of PP grafted with MEMA with different alkylating agents is presented in (Table I). The most reactive reagent was benzyl chloride, with 67.5% reaction completion, and the least reactive was chlorosulfonic acid, with 49.7% reaction completion. The reactivity of the alkylating agents with MEMA was in the following order: benzyl chloride $>$ monochloroacetic acid $>$ 2-chloroethanol $>$ chlorosulfonic acid.

Moisture regain

The PP moisture regain was highly improved by the grafting of MEMA and subsequent quaternization. Therefore, the moisture regain increased with an increasing MEMA graft yield in comparison with the hydrophobic ungrafted fabric. In addition, the quaternization of MEMA leveled out the moisture regain of the fabrics (Table II) and rendered them more hydrophilic. As a result, there was an increase of 5.2% moisture regain because of the quaternization alone of PP–MEMA with monochloroacetic acid in comparison with the same grafted MEMA, which showed moisture regain values of 2.3 and 7.48% for the quaternized fabric. In general, the moisture regain varied with the type of alkylating agent used. The change of the hydrophobic character of PP to a more hydrophilic one by the incorporation of quaternary ammonium salt groups rendered the fibers more conductive, and the electrostatic changes that formed during processing were dissipated.[24]

Microanalysis

The analysis of the nitrogen, sulfur, and chlorine contents for PP–MEMA with quaternary ammonium salts confirmed the alkylating reaction completion of grafted MEMA (Table III).

IR microscopy

As shown in Table IV and Figure 1(A–F), the IR spectra[25] are given for PP, PP–MEMA, and PP–MEMA quaternized with chlorosulfonic acid, benzyl chloride, monochloroacetic acid, and 2-chloroethanol, respectively.

The spectrum of PP–MEMA [Fig. 1(B)], compared with that of PP fabrics [Fig. 1(A)], showed additional absorbance bands at the 1733-cm^{-1} C═O stretch of the carboxylic group, the 1150-cm^{-1} C—O stretch indicating the ester group of the MEMA.

As shown in Figure 1(C–F), different alkylating agents resulted in some major band changes and the appearance of new bands with respect to PP–MEMA. Figure 1(C–F) shows characteristic new absorption bands: 1400–1650 cm^{-1} due to the heterocyclic moi-

TABLE III
Elemental Microanalysis of PP Grafted with MEMA and Quaternized with Different Alkylating Agents

Fabric sample	Graft yield (%)	Elemental microanalysis found (%)		
		Nitrogen	Sulfur	Chlorine
PP fabric	—	—	—	—
PP–MEMA	40	1.64	—	—
Quaternized PP–MEMA with benzyl chloride	40.5	1.65	—	2.6
Quaternized PP–MEMA with chlorosulfonic acid	41.5	1.69	1.67	

TABLE IV
IR Analysis of PP Grafted with MEMA and Quaternized with Different Alkylating Agents

Fabric sample	Band position (cm^{-1})	Band
PP fabric	2700–3000	C—H stretch either as —CH, CH$_2$, or CH$_3$
PP–MEMA	1733	C═O stretch
	1150	C—O stretch
Quaternized PP–MEMA with different alkylating agents	1400–1650	Heterocyclic of quaternary salts
	800–900	Alkyl group or S—O stretch
Quaternized PP–MEMA with chlorosulfonic acid	1352	SO$_2$ asymmetry stretch
	1165	SO$_2$ symmetry stretch
	850	SO stretch
Quaternized PP–MEMA with benzyl chloride	2956	C—H stretch aromatic
	750	Out of plane (H wagging)
	700	Out of plane sextant ring
Quaternized PP–MEMA with monochloroacetic acid	3200–3440	O—H stretch
	1376	CH$_2$ wagging, OH bending, and C—O stretch in COOH
Quaternized PP–MEMA with 2-chloroethanol	3300	O—H stretch

eties of the quaternary salts and 800 cm^{-1} due to alkyl group or S—O stretch.

Figure 1(C) shows an absorption band due to SO$_2$ stretching of the sulfonic group appearing at the 1376-cm^{-1} asymmetric stretch and at the 1100-cm^{-1} symmetric stretch.

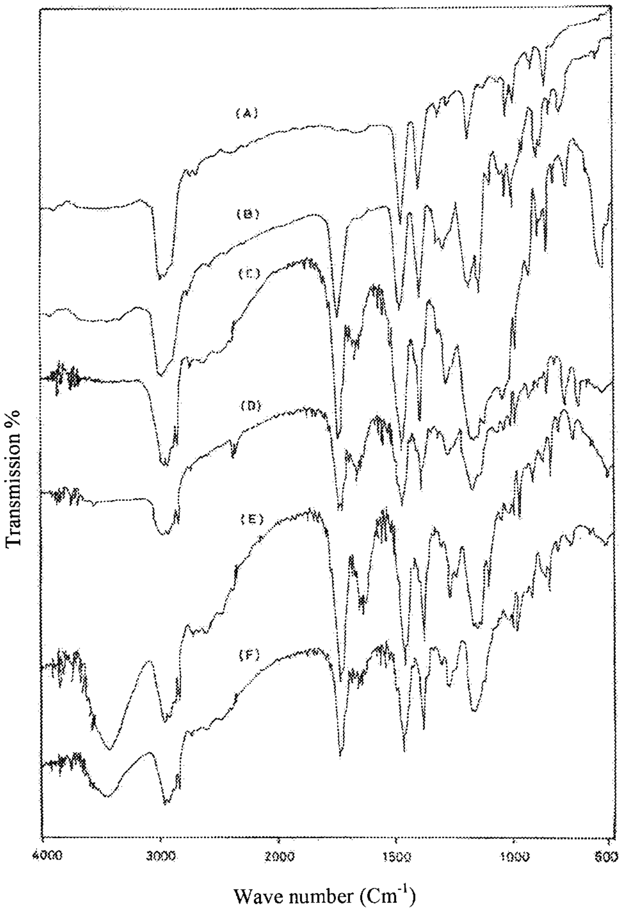


Figure 1 IR spectra of (A) PP, (B) PP–MEMA, (C) quaternized PP–MEMA with chlorosulfonic acid, (D) benzyl chloride, (E) monochloroacetic acid, and (F) 2-chloroethanol.

Figure 1(D) reveals a band at 2956 cm^{-1}, which is a multiple weak band due to aromatic C—H stretch vibrations. There is an absorption band at 750 cm^{-1} due to out-of-plane hydrogen wagging. There is another band at 700 cm^{-1} due to an out-of-plane sextant ring.

In Figure 1(E,F), a new band appears at 3200–3440 cm^{-1} due to the OH stretch for alcohol or acid.

The IR spectrum of quaternized PP–MEMA confirmed the presence of quaternary ammonium salt groups.

Antimicrobial efficacy of quaternized PP–MEMA fabrics

A PP control fabric and PP–MEMA fabrics (30–40% graft yields) had no antimicrobial effects.

However, the quaternization of PP–MEMA-grafted fabrics with a series of chosen alkylating agents was highly effective in producing biocidal fabrics. They had the structural configurations cited in eq. (6).

The majority of the quaternizing groups were hydrophilic in nature because of the presence of ionic quaternary ammonium salts, such as the carboxylic and sulfonic acid groups located in the R group, and the produced quaternized fabrics were highly effec-

TABLE V
Reduction of *E. coli* After 3 h of Contact Time

Fabric sample	Log reduction
PP–MEMA (30%)	No kill
PP–MEMA (40%)	No kill
Quaternized PP–MEMA with benzyl chloride	4 log reduction
Quaternized PP–MEMA with monochloroacetic acid	6 log reduction total kill
Quaternized PP–MEMA with chlorosulfonic acid	6 log reduction total kill
Quaternized PP–MEMA with 2-chloroethanol	6 log reduction total kill

TABLE VI
Adsorption and Antimicrobial Properties of PP–MEMA and Quaternized PP–MEMA with 0.05 M/L $CuSO_4 \cdot 5H_2O$

Fabric sample	Content of Cu^{2+} (mg/g)	Log reduction	Percentage reduction
PP–MEMA–Cu	0.091	6 log total kill	100
Quaternized PP–MEMA with benzyl chloride and Cu	0.094	6 log total kill	100
Quaternized PP–MEMA with monochloroacetic and Cu	0.114	6 log total kill	100
Quaternized PP–MEMA with chlorosulfonic and Cu	0.111	6 log total kill	100
Quaternized PP–MEMA with 2-chloroethanol	0.113	6 log total kill	100

tive as antimicrobial fabrics (Table V). They provided 100% reduction of *E. coli* because of the formation of both quaternary ammonium salts and acid salts with the metals present in the agar media, as explained in previous investigations.[17] These fabrics proved to be excellent biocidal fabrics against *E. coli*. In addition, the fabric quaternized with 2-chloroethanol gave the same result of 100% reduction of *E. coli*; this indicated that the antimicrobial functions of the fabrics were mostly attributable to the formed quaternary ammonium salt structures.

The quaternization of MEMA with the hydrophobic benzyl chloride agent produced a fabric that could provide a 4 log reduction against the bacterium.

The contact time for the PP control and PP modified fabrics with the bacterium was 3 h, which tool into consideration the hydrophobic nature of PP and allowed sufficient time for orientation of the anchored hydrophilic groups toward the surface and the aqueous agar media.

Also, the metallic adsorption of Cu^{2+} ions from a $CuSO_4$ solution onto the fabrics containing carboxylic or sulfonic groups formed salts that had an enhanced antimicrobial effect. The PP–MEMA–Cu fabric had an enhanced biocidal function and gave a 6 log reduction (100% reduction) against the bacterium with respect to the inactive PP–MEMA fabric (Table VI). This can be explained by the formation of the PP–MEMA–Cu complex due to the addition of Cu^{2+} ions to the free lone pair of electrons on the MEMA nitrogen and the constitution of a new complex bond. These antimicrobial fabrics can be used as water and ion-exchange filters.

In general, the quaternization reaction of PP–MEMA was less than 100% because the fabric contained unquaternized MEMA in addition to the quaternized groups. Therefore, for quaternization with benzyl chloride, the reaction completion was 67.5%, which meant that the fabric contained 32.5% unquaternized MEMA. The adsorption of Cu^{2+} was favored on the unquaternized MEMA portion, yielding a PP–MEMA–Cu complex fabric, which increased the reduction of bacteria to 100%. Therefore, the introduction and complexation of Cu with PP–MEMA have proven to also have a biocidal effect. This agreed with similar published articles.[17] The difference in the amount of Cu^{2+} adsorbed onto quaternized PP–MEMA (Table VI) can be explained by the difference in the chemical constitution of the alkylating agent itself.

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