Surface Characterization of 8-Quinolinyl Acrylate-Grafted Poly(ethylene terephthalate) Prepared by Plasma Glow Discharge and It's Antibacterial Activity

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ABSTRACT: Poly(ethylene terephthalate) (PET) film was exposed to oxygen plasma glow discharge to produce peroxides on its surface. These peroxides were then used as catalysts for the polymerization of 8-quinolinyl acrylate (QA) to prepare the PET grafted with QA (PET-Q). The surface-modified PET was characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The introduction of QA to the PET surface was confirmed by observing the presence of nitrogen in the XPS survey scan and high-resolution spectra. The amount of QA grafted on to the PET surface as measured by the gravimetric method was about $5.2 \ \mu g \ cm^{-2}$. The antibacterial activity of the surface-modified PET texture was investigated by using a shake-flask and an inhibition zone test method. After 6 h of shaking, the PET grafted with QA showed the inhibition (91%) of the growth of the gram-positive microorganism, *S. aureus*. Even after laundering ten times, an effectiveness of the inhibition was found. However, little inhibition was shown with the gram-negative microorganism, *K. pneumoniae*. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 863–868, 2006

Key words: poly(ethylene terephthalate); plasma glow discharge; 8-quinolinyl acrylate; antibacterial activity

INTRODUCTION

Surface modification has become increasingly important in various industrial and biomedical fields such as printing, biological coating,[1] fiber,[2] and membrane.[3] In particular, surface modification for antibacterial surface attains high functionality and high value products. Most of the surface modifications have been performed by a chemical reaction in a solution,[4] physical deposition or coating, γ-ray, ultraviolet light (UV),[5,6] plasma,[7] or ozone treatment.[3]
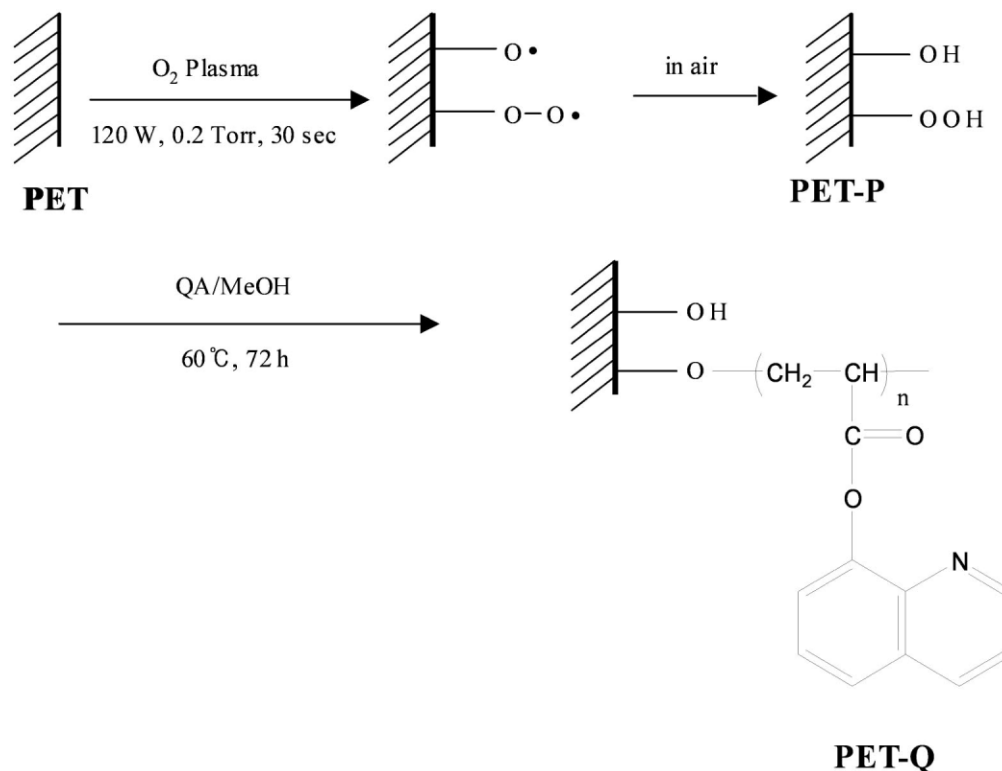
Poly(ethylene terephthalate) (PET) has been one of the most widely used polymers in various industries such as fiber, film, bottles, and plastics. PET, however, needs to be surface-modified for further application because of its low wettability and poor adhesion. Accordingly, many trials to modify the surface of PETs have been extensively reported.[4,5,7–9] Uchida et al.[5] immobilized poly(methacrylic acid) on to the surface of PET film by graft polymerization induced by light irradiation. They also grafted anionic and cationic polymers on to the surface of PET film by an UV irradiation.[8] Plasma glow discharge treatment is an effective method to introduce biological molecules to the surface of polymeric materials without causing any severe damage to their bulk properties. Sugiyama et al.[10] reported on the grafting of vinyl monomers on the surface of a PET film by using the Ar plasma post polymerization technique to increase the biocompatibility of PET. Kang et al.[11] prepared protein-immobilized PETs by the treatment of PETs with oxygen plasma glow discharge, followed by the graft polymerization of acrylic acid and subsequent reaction with proteins.

8-Hydroxyquinoline is known as an antimicrobial agent. Kenawy[12] prepared the polymers containing 8-hydroxyquinoline (HQ) moieties by reacting the chloromethyl groups-containing polymers with the potassium salt of HQ. He reported that the polymers proved to be effective against the tested microorganism. Kim et al.[13] prepared the hydrophilic copolymers, which consisted of 8-quinolinyl acrylate (QA) and acrylamide, and examined the release of HQ from them. In their results, the release of HQ increased with the increase in content of the hydrophilic acrylamide in the copolymers and with the increase in the pH of the release medium. Shen et al.[14] reported the synthesis and cytotoxicity of 7-morpholinomethyl-8-hydroxyquinoline as a derivative of HQ.

In this study, QA-grafted PET (PET-Q) was prepared by the treatment of PET with oxygen plasma

Scheme 1 Oxygen plasma treatment of PET and graft polymerization of 8-quinolinyl acrylate (QA) on PET.

glow discharge followed by the graft polymerization of QA. Surface characterization of PET-Q was carried out by using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and a contact angle goniometer. The growth inhibition of the bacteria on the surface-modified PET was also examined.

MATERIALS AND METHODS

Materials

The PET (woven texture and film) used in this study was kindly donated by the Kolon Company, Korea. Purification of the PET was carried out by soxhlet extraction with methyl alcohol for 24 h. Acryloyl chloride (Aldrich Chemical) and triethylamine (Yakuri Pure Chemical) were used without further purification. HQ as a reagent grade was recrystallized from acetone. Benzene as a reagent grade was dried with sodium wire for 1 day and purified by distillation. Methyl alcohol as a reagent grade was distilled under calcium sulfate. The bacteria used in this study were purchased from the Gene bank of the Institute of Life Sciences and Biotechnology in Korea (*S. aureus* ATCC 6538; *K. pneumoniae* ATCC 4352).

Synthesis of 8-quinolinyl acrylate

8-Quinolinyl acrylate (QA) was synthesized according to the literature.[13] Triethylamine (18.1 mL, 0.13 mol)

and HQ (14.5 g, 0.10 mol) dissolved in 150 mL of anhydrous benzene were placed in a round bottomed, three-necked flask equipped with a dropping funnel and a reflux condenser. Then AC (10.6 mL, 0.10 mol) diluted with 10 mL of benzene was added dropwise into the mixture under nitrogen with gentle stirring at 0°C. The reaction was allowed to proceed at room temperature for 12 h. The mixture was filtered and the filtrate was washed sequentially with 5% $NaHCO_3$ and pure water, and then the residual water was removed by using anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure. The resulting product was a viscous and brown-colored liquid. A crystallized product was obtained by placing the liquid in a refrigerator. The resulting solid was further recrystallized from a mixture of ether and *n*-hexane (v/v, 1 : 1). The final product was a yellowish and needlelike solid (yield 69%, m.p. 39–41°C).

Plasma glow discharge treatment and QA grafting

The oxygen plasma treatment of the PET texture (1×1 cm^2) was carried out in accordance with a previous report.[15] The oxygen plasma-treated PET (1×3 cm^2) film was immersed in methyl alcohol solution of QA (10%) and graft-polymerized at 60°C for 72 h, as outlined in Scheme 1. After the polymerization, the sample was taken and washed with methyl alcohol in an ultrasonic cleaner two times for 15 min so as to remove any free homopolymers together formed. The

sample was then rewashed using an ultrasonic cleaner filled with methyl alcohol and dried under reduced pressure for 24 h at room temperature. The amount of QA grafted on to the PET surface was calculated by measuring the weight of the PET film (1×3 cm^2) before and after the QA grafting with a microbalance (Sartorius XM 1000P).

Surface characterization

The surface-modified PET film was analyzed with X-ray photoelectron spectroscopy (XPS) equipment (ESCALAB MKII, V. G. Scientific, UK) equipped with Mg Kα at 1253.6 eV with a 100 W power at the anode. Spectra were taken at an angle of 55°. The sensitivity factors (S) for the C_{1s}, O_{1s}, and N_{1s} core-level peaks were $S (C_{1s}) = 0.205$, $S (O_{1s}) = 0.63$, and $S (N_{1s}) = 0.38$. For the evaluation of the surface wettability, the water contact angles of the surface-modified PET were measured at room temperature with a contact angle goniometer (Model G-I, Erma, Tokyo).

Bacterial strain and culture

The *S. aureus* (ATCC 6538) and *K. pneumoniae* (ATCC 4352) were maintained on nutrient agar plates consisting of peptone, beef extract, sodium chloride, and agar at 4°C. Single colonies were then transferred to a soy broth and incubated at 37°C for 10 h. The cell concentration was adjusted to 2×10^8 cells mL^{-1} by dilution with a phosphate-buffered solution (PBS). This was used as the preserving solution for all cell experiments.

Antibacterial activity test

The antibacterial activity of the PET-Q film was investigated by using a shake flask method.[7] Monopotassium phosphate (34 g) was dissolved in deionized water (500 mL), and the pH of the phosphate aqueous solution (PBS) was adjusted to 7.2 using a 4N NaOH aqueous solution. The PBS was sterilized using an autoclave at 120°C for 20 min, diluted 800 times with distilled water, and then used for the shaking flask culture test. The preserving solution was diluted 1000 times with the PBS. Next, 5 mL of the diluted cell solution was added to a flask (200 mL) and mixed with the PBS (70 mL). The final cell concentration was 1.5 $\times 10^4$ cells mL^{-1}. One milliliter of the diluted cell solution was then seeded on to an agar plate and incubated at 37°C for 24 h. The numbers in the colony (*A*) were counted by measuring the ones formed and compensating with the degree of cell dilution. The PET sample was added to the flask supplemented with the diluted cell solution and the mixture was incubated in a shaking incubator (150 rpm, KMC 8480S, Vision Scientific) for the requisite time. After

incubation, 1 mL of the cell solution was extracted, seeded on to an agar plate, and incubated at 37°C for 24 h. The numbers in the colony (*B*) were counted by measuring those formed and by compensating with the degree of cell dilution. The inhibition of cell growth was calculated using with the following equation:

$$\text{Growth inhibition of cells (\%)} = (A - B)/A \times 100$$

where *A* and *B* are the numbers in the colony before and after shaking, respectively. The experiment was repeated in quadruplicate and a mean value was calculated.

An inhibition zone test method is useful for measuring qualitative antibacterial activity.[16–18] The inhibition zone test toward bacterial species such as *S. aureus* (ATCC 6538) and *K. pneumoniae* (ATCC 4352) was carried out by using a modified procedure.[19] The tablets of QA (radius, 15.0 mm; weight, 20 mg) were placed on the center of every petri dish and pressed gently. The sizes of the inhibition zones (the distance between the edge of the tablet and the growth zone of the microorganism), observed for the active samples, were measured after subsequent incubation of the plates at 37°C for 24 h.

Effect of laundering on antibacterial activity[7]

The laundering of the QA-grafted PET textile was carried out using launder-o-meter (Matis Labomat Beaker Dyer BFA 9–16, Wener Matis AGCO) that contained eight stainless steel test bottles (450 mL bottle volume). Each bottle contained soaps (5 g L^{-1}), sodium carbonate (2 g L^{-1}), distilled water (100 mL), and 10 stainless steel beads. The PET textile (1×1 cm^2) was placed in a test bottle and the laundering was carried out at (70 ± 2)°C for 45 min. After laundering, the sample was washed twice with distilled water (100 mL) for 1 min to remove any remaining washing solution. The sample was then dried under a thermal convection oven at 60°C for 30 min. The antibacterial activity of the laundered sample was examined using the same inhibition zone test as described in the experiment with the QA-grafted PET texture.

RESULTS AND DISCUSSION

Graft polymerization

Plasma glow discharge has been frequently used to produce radicals on the polymer surface.[10] The surface radicals easily convert into peroxides when they come into contact with air. These peroxides are very useful initiators for the graft polymerization of vinyl monomers on the surface. In this study, HQ was reacted with AC to obtain 8-quinolinyl acrylate (QA). The QA
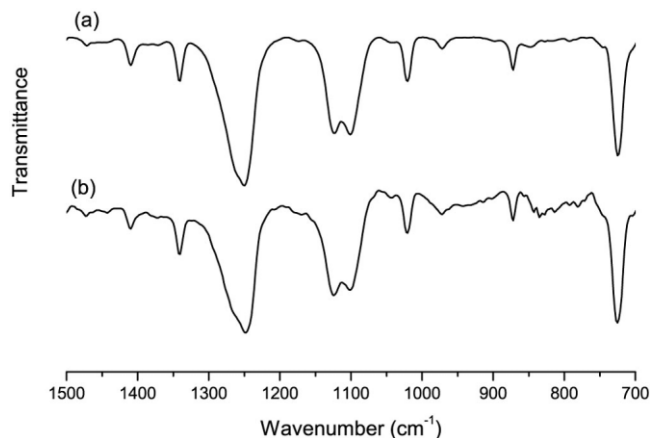
Figure 1 ATR-FTIR spectra of PET (a) and PET-Q (b).

Figure 2 XPS survey scan spectra of PET (a) and PET-Q (b).

was then polymerized by using the peroxides that formed on the PET surface by oxygen plasma treatment. For the purification of the grafted PET film (PET-Q), two kinds of rinsing methods, ultrasonicator and soxhlet, were employed. As a result, the amounts of grafted QA obtained after ultrasonic rinsing and after soxhlet extraction were 5.2 and 4.9 $\mu g \; cm^{-2}$, respectively.

Surface characterization

Figure 1 shows the ATR-FTIR spectra of PET and PET-Q. The assignment of the infrared peaks of PET has been discussed in various publications.[20–22] As shown in Figure 1, most peaks in their spectra overlapped because both PET and QA unit in PET-Q have benzene rings and ester group, respectively.[23] However, the weak peaks of the latter polymer at 780 and 814 cm^{-1} could be due to CH out-of-plane bend of the quinoline ring in the QA unit.[24,25]

Figure 2 shows XPS survey scan spectra of PET (a) and PET-Q (b). As expected, PET and PET-Q showed two peaks corresponding to C_{1s} (285-eV binding energy) and O_{1s} (532-eV binding energy).[26,27] In the spectrum of PET-Q, an additional weak peak at 400-eV binding energy corresponding to N_{1s} was found.

To discuss the formation of PET-Q in more detail, high-resolution XPS spectrum of PET-Q together with that of the PET was measured. Their spectra are given in Figure 3. As shown in this figure, the intensity of PET-Q in the range of 286–289 eV was different from that of PET. Thus, the curve fitting of their C_{1s} core-level scan spectra was made. The peak of the PET film appeared at 286 eV, whereas the peak of PET-Q appeared at 287 eV. The former peak was assigned to C_{1s} of CO bond in PET.[7] The latter peak was attributed to the mixed C_{1s} core-level of CO and CN bonds of quinoline ring in the QA unit grafted on PET.[28,29] The peak of N_{1s} core-level scan spectrum of PET-Q ap-
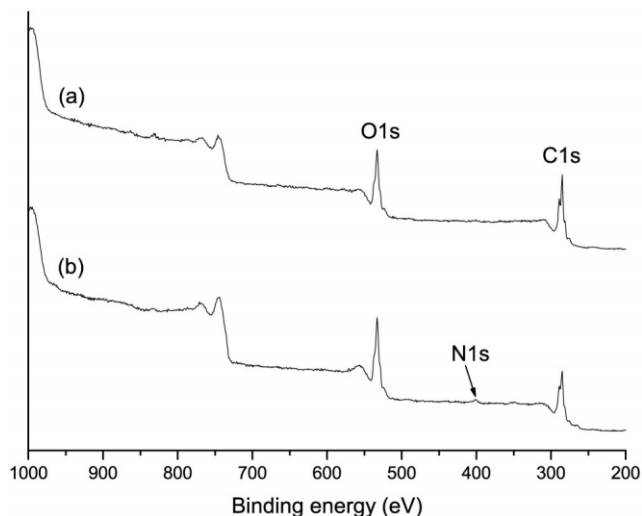
peared at 400 eV. On the other hand, PET showed a trace at the energy level, which might be attributed to nitrogen molecule adsorbed on the PET surface. Accordingly, these results indicate that QA was grafted on PET surface.

Based on the high-resolution XPS spectra of PET and PET-Q in Figure 3, the chemical compositions of the two polymers were calculated. Also, the compositions of plasma-treated PET film (PET-P) were calculated in the same manner. The compositions of the three polymers are given in Table I. The values of carbon and oxygen within a depth of the surface of PET agree with those of our previous report.[7,30] The oxygen content (35.8%) of PET-P was higher compared to that of PET because peroxides were formed on PET surface by plasma treatment.[7,30] The oxygen content (23.8%) of PET-Q was lower compared to that of PET because the QA unit of PET-Q has fewer oxy-
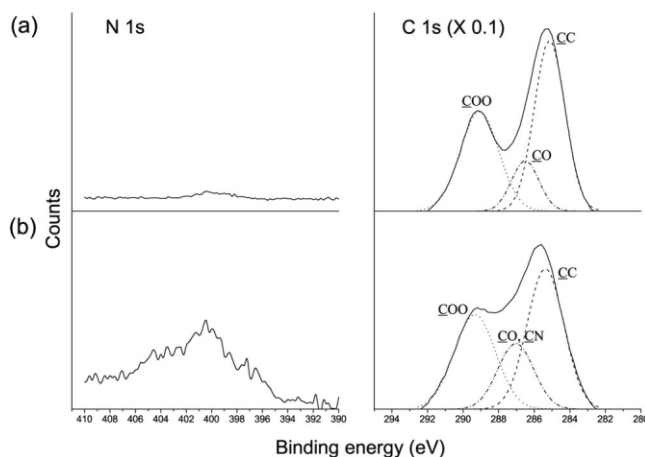

Figure 3 XPS high-resolution C_{1s}, O_{1s}, and N_{1s} spectra of PET (a) and PET-Q (b).

TABLE I
Chemical Compositions of PET and Surface-Modified
PET Films Calculated from High-Resolution XPS Spectra

Sample	Atomic percentage[a]			
	C	O	N	O/C
PET	74.0	26.0	–	0.35
PET-P[b]	64.2	35.8	–	0.56
PET-Q[c]	74.1	23.8	2.1	0.32

[a] Calculated using the atomic sensitivity factors of S (C_{1s}) = 0.205, S (O_{1s}) = 0.63, and S (N_{1s}) = 0.38.
[b] Plasma-treated PET.
[c] QA-grafted PET.

gen atoms than the repeating unit of PET. The nitrogen content of PET-Q was 2.1%. However, the values of the compositions of PET and PET-Q agree only qualitatively with the theoretical values of PET and the QA unit in PET-Q but not quantitatively. This could be related with surface analysis of XPS.[31,32]

Table II shows the water contact angles of PET film and the surface-modified PET films. The water contact angle (65°) of the PET film significantly decreased after plasma treatment (37°), indicating the hydrophilic surface because peroxides on the surface of the film were formed by treatment. The angle (70°) increased after QA grafting.

Antibacterial activity

Figure 4 shows the growth inhibition of bacteria on PET-Q. The growth inhibition of the PET control was almost zero, irrespective of the strain of bacteria. On the other hand, the growth of the gram-positive bacteria *S. aureus* was largely inhibited (91%) after contact with PET-Q. The gram-negative bacteria *K. paeumoniae*, however, showed little inhibition after contact with PET-Q. The reason why the growth inhibition of *S. aureus* by the PET-Q is different from that of *K. pneumoniae* by PET-Q is not clear.

Figure 5 shows the antibacterial activities of the QA monomer examined with the inhibition zone test toward *S. aureus* and *K. pneumoniae*. The QA monomer exhibited a large and a clear inhibition zone against *S. aureus*. However, it showed no inhibition zone against *K. pneumoniae*. Figure 6 shows the inhibition zones of

TABLE II
Water Contact Angles of PET and Surface-Modified PET
Films

Sample	Water contact angle (°)[a]
PET	65 ± 2
PET-P	37 ± 2
PET-Q	70 ± 2

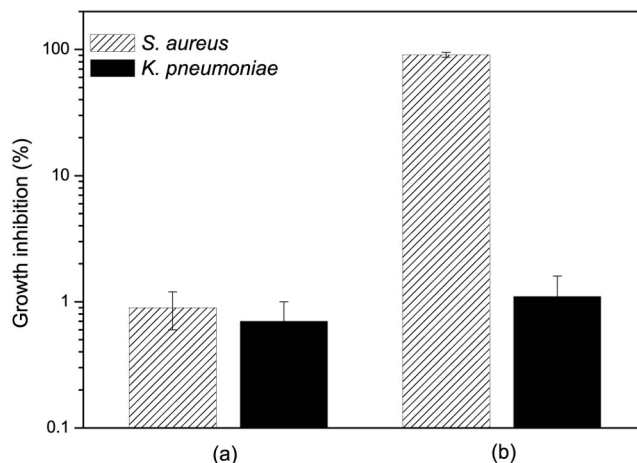[a] Measured by sessile droplet method.

Figure 4 Growth inhibition by PET (a) and PET-Q (b) against *S. aureus* and *K. pneumoniae*.

the PET and PET-Q textile against *S. aureus* and *K. pneumoniae*. No inhibition zones of PET and PET-Q textiles against *K. pneumoniae* were observed in Figure 6(B). Also, no inhibition zone of PET textile against *S. aureus* was displayed in Figure 6(A). This is consistent with the results observed by the shake-flask method. The origin of the inhibition of QA monomer and PET-Q for the gram-positive bacteria seems to be alkyl ester type of HQ. After laundering ten times, the inhibitory zone (c) exhibited a clear inhibition zone against *S. aureus*. These results mean that QA undertook a graft polymerization on the PET surface by the plasma treatment and QA unit in the grafted polymer had antibacterial activity against the gram-positive microorganism.

CONCLUSIONS

Bactericidal and fungicidal 8-hydroxyquinoline was reacted with acryloyl chloride to produce 8-quinolinyl acrylate (QA). QA was then graft-polymerized on to the plasma-treated PET surface to obtain the QA-
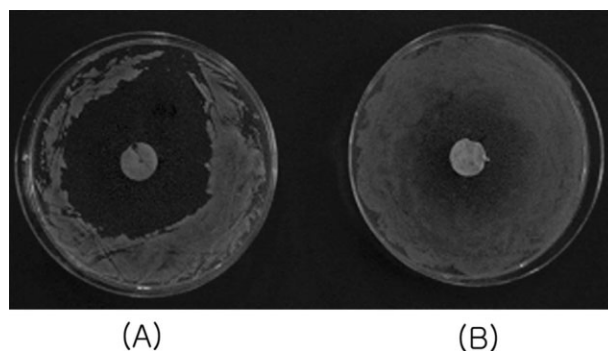

Figure 5 Inhibitory zones of the QA tablets on a medium seeded with *S. aureus* (A) and *K. pneumoniae* (B).
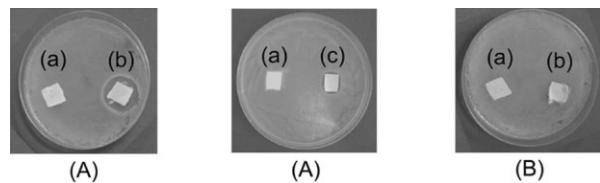
Figure 6 Inhibitory zones of PET before laundering (a), PET-Q before laundering (b), and PET-Q after laundering ten times (c) on a medium seeded with *S. aureus* (A) and *K. pneumoniae* (B).

grafted PET (PET-Q). The QA grafting on the PET surfaces was identified by using ATR-FTIR and XPS. In antibacterial activity experiments using *S. aureus* and *K. pneumoniae*, the QA-grafted PET film showed high-growth inhibition of 91% for *S. aureus*, but no growth inhibition for *K. paeumoniae*. Even after laundering ten times, the PET-Q textile showed an effectiveness of the antibacterial activity against *S. aureus*.

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