

Surface Grafting Polymerization of *N*-Vinyl-2-pyrrolidone onto a Poly(ethylene terephthalate) Nonwoven by Plasma Pretreatment and Its Antibacterial Activities

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ABSTRACT: The objective of this research was the surface grafting polymerization of biocompatible monomer *N*-vinyl-2-pyrrolidone (NVP) onto a plasma-treated nonwoven poly(ethylene terephthalate) (PET) substrate with ultraviolet (UV)-induced methods. The effects of various parameters, such as the monomer concentration, reaction time, initiator (ammonium peroxodisulfate) concentration, and crosslinking agent (*N,N'*-methylene bisacrylamide) concentration, on the grafting percentage were studied. The grafting efficiency of the modified nonwoven PET surfaces reached a maximum at 50 min of UV irradiation and with a 30 wt % aqueous NVP solution. After the plasma activation and/or grafting, the hydrophobic surface of the nonwoven was modified into a hydrophilic surface. NVP was success-

fully grafted onto nonwoven PET surfaces. The surface wettability showed that the water absorption of NVP-grafted nonwoven PET (NVP-g-nonwoven PET) increased with increasing grafting time. NVP-g-nonwoven PET was verified by Fourier transform infrared spectra and scanning electron microscopy measurements. An antibacterial assessment using an anti-*Staphylococcus aureus* test indicated that *S. aureus* was restrained from growing in NVP-g-nonwoven PET. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 803–809, 2006

Key words: graft; *N*-vinyl-2-pyrrolidone; plasma; UV-induced

INTRODUCTION

Medical materials are usually sterilized with dry/wet heat or ionizing radiation. The technique to change and improve the antibacterial activities is an important factor in this process. Materials can be impregnated with antimicrobial agents, such as antibiotics, quaternary ammonium compounds, silver ions, or iodine, which are released gradually into the surrounding solution over time and kill microorganisms therein.^{1–4} Poly(4-vinyl-*N*-alkylpyridinium bromide) was covalently attached to glass slides to create a surface that killed airborne bacteria on contact.⁵ An easy and simple method is to provide adequate biocides.^{6,7} However, to introduce biocides, some pretreatment must be conducted to activate the material surface. The general methods are radiation, ultraviolet (UV), chemical, and plasma activation.^{8–10} Plasma irradiation, which can enhance wettability and adhesion,

causes a wide range of reactions, such as crosslinking, etching, and cleaning on the polymer surface.¹¹ Radicals can be formed in these plasma reactions. Peroxides and some other polar groups are also created when plasma-treated polymers are exposed to air. The improved affinity of the surface of a plasma-treated polymer has been attributed to the induced polar groups, surface oxidation, and surface roughness.¹² However, the surface of a modified polymer is etched because of the reorientation of the hydrophilic group toward the bulk of the polymer.¹³

Grafting polymerization is a well-known method for the modification of the chemical and physical properties of polymeric materials; various commercial polymers can be used as the grafting substrate. Various kinds of grafting polymerization techniques have been developed in the past few decades. The most common methods for grafting are carried out with ion-radiation-induced grafting polymerization, photo-induced grafting polymerization (e.g., UV and chemical initiator), plasma-induced grafting polymerization, and plasma polymerization.^{9,10,17} Functional groups, such as maleic anhydride,^{14–16} acrylic acid,^{17–19} styrene,²⁰ and

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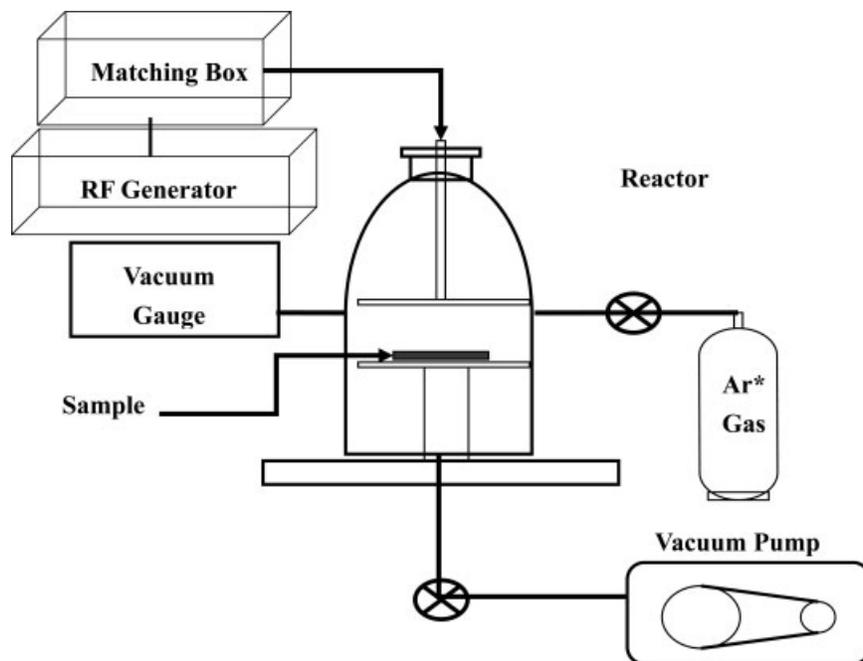


Figure 1 Schematic diagram of a bell-jar-type plasma equipment system.

methyl methacrylate,²¹ are usually grafted onto matrix polymers. Moreover, some of the radicals on a polymer surface produced by plasma treatment can initiate vinyl monomer grafting polymerization.

In this study, a hydrophobic poly(ethylene terephthalate) (PET) nonwoven was treated with plasma activation and the subsequent UV-induced grafting polymerization of *N*-vinyl-2-pyrrolidone (NVP) to modify its surface hydrophilicity (NVP-*g*-PET nonwoven). The effects of various parameters, such as the NVP concentration, reaction time, initiator [ammonium peroxodisulfate (AP)] concentration, and crosslinking agent [*N,N'*-methylene bisacrylamide (MBAAm)] concentration, on the grafting percentage were determined. The antibacterial properties of the modified NVP-*g*-PET nonwoven were evaluated.

EXPERIMENTAL

Materials

The commercial PET nonwoven (1.5 × 1.5 cm) was a product of Nissho Co., Ltd. (Tokyo, Japan). The reaction monomer of NVP was purchased from Acros Organics Co. (New Jersey, USA). AP (Wako Pure Chemical Industries, Ltd.) as an initiator (concentration = 0.3 mol % monomer) and MBAAm (Sigma Chemical Co., Steinheim, Germany) as a crosslinking agent (concentration = 1 mol % monomer) were used as received. Vitamin B₂ (Sigma Chemical) was used to prevent oxidation.

Argon-plasma treatment

The PET nonwoven was individually placed inside a bell-jar-type plasma reactor with a parallel electrode, as schematically shown in Figure 1. The plasma reactor (model PD-2S, Samco, Tokyo, Japan) was pumped to a base pressure of 40 mTorr before the plasma pretreatment. A radio frequency of 13.6 MHz was used in this study, and an impedance matching unit was required. After the pressure was adjusted to the stable desired working pressure (200 mTorr) by a continuous flow of argon gas, the plasma pretreatment was initiated at 50 W for 10 min.²² The substrate temperature was kept at room temperature during the process.²³

Uv-induced grafting polymerization

UV-induced grafting polymerization on the substrate was carried out in a Pyrex glass container (8-cm i.d.) with a 30 wt % aqueous NVP solution, in which the given concentrations of the additives were dissolved. Then, 0.01 g/L riboflavin (B₂; C₁₇H₂₀N₄O₆) was added in a ratio of NVP solution/riboflavin = 4:1. The grafting polymerization was carried out by the irradiation of the substrate with 1000-W UV light (wavelength = 365 nm; Henchman, Taipei, Taiwan) for 30–60 min. The apparatus is schematically shown in Figure 2. After the grafting polymerization reaction, the unreacted monomers and homopolymer were removed by

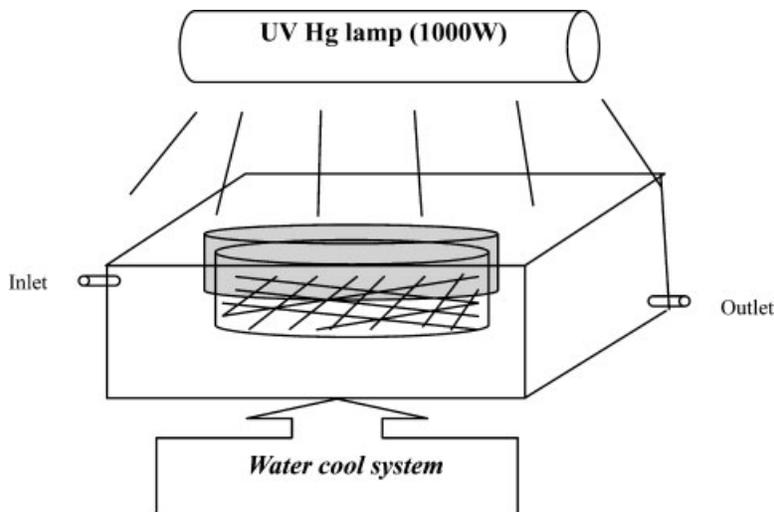


Figure 2 Schematic diagram of UV-induced grafting equipment.

the washing of the substrate in distilled water for 24 h with continuous stirring. The grafting percentage (% G) was determined by gravity metrically with the following equation:

$$\%G = [(W_1 - W_0)/W_0] \times 100 \quad (1)$$

where W_0 is the weight of the original nonwoven PET and W_1 is the weight of the grafted PET nonwoven after the complete removal of the unreacted NVP.

Characterization of the NVP-g-PET nonwoven

A clean and dried grafted PET nonwoven with a known weight was immersed in distilled water at 25°C until equilibrium was reached (24 h in most cases). The NVP-g-PET nonwoven was then removed, and the excess water that was deposited on the surface was quickly taken up with filter paper and weighed. The degree of water absorption was calculated as follows:

$$\text{Water absorption (\%)} = [(W_s - W_g)/W_g] \times 100 \quad (2)$$

where W_g and W_s represent the weights of the dry and wet NVP-g-PET nonwoven, respectively.

The chemical structure of the NVP-g-PET nonwoven was determined with Fourier transform infrared (FTIR) spectroscopy (FT/IR-300E spectrometer, Jasco, Tokyo, Japan) with the attenuated total reflectance (ATR) method (germanium, refractive angle = 60°; ATR-500/V, Jasco).

To observe the true morphology structure of NVP grafted onto the plasma-treated PET nonwoven, the specimens were coated with a thin layer of gold (coating for 5 min) before investigation. Scanning electron

microscopy (SEM; JSM-6300, JEQL, Tokyo, Japan) was used to observe the morphologies of the specimens.

The antibacterial NVP-g-PET nonwoven was fabricated with the following method. The antibacterial PET nonwoven was created by the immersion of the untreated PET nonwoven and NVP-g-PET nonwoven substrate in an iodine solution for 1 h (concentration = 10 wt %); after the immersion reaction, the substrate was washed in distilled water for 12 h with continuous stirring and dried *in vacuo*. The biocidal properties of the various substrates in the study were assessed with the bacterial (*S. aureus*) population after 24 h of inoculation. *S. aureus* was cultured in a nutrient broth (1% glucose, 0.3% malt extract, 0.3% yeast extract, 0.5% pepton, and 0.8% agar). The nutrient medium was sterilized in an autoclave at 120°C for 15 min. The surface morphologies of the antibacterial modified PET nonwoven fabric were observed with a digital camera.

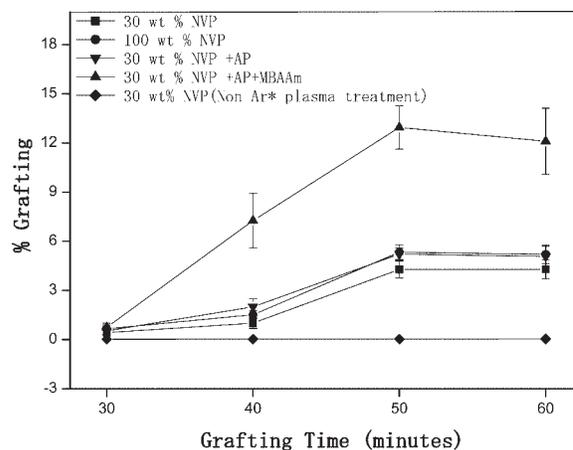


Figure 3 Grafting percentage versus the UV-induced grafting time for NVP-g-PET nonwovens (Ar* plasma at 50 W for 10 min).

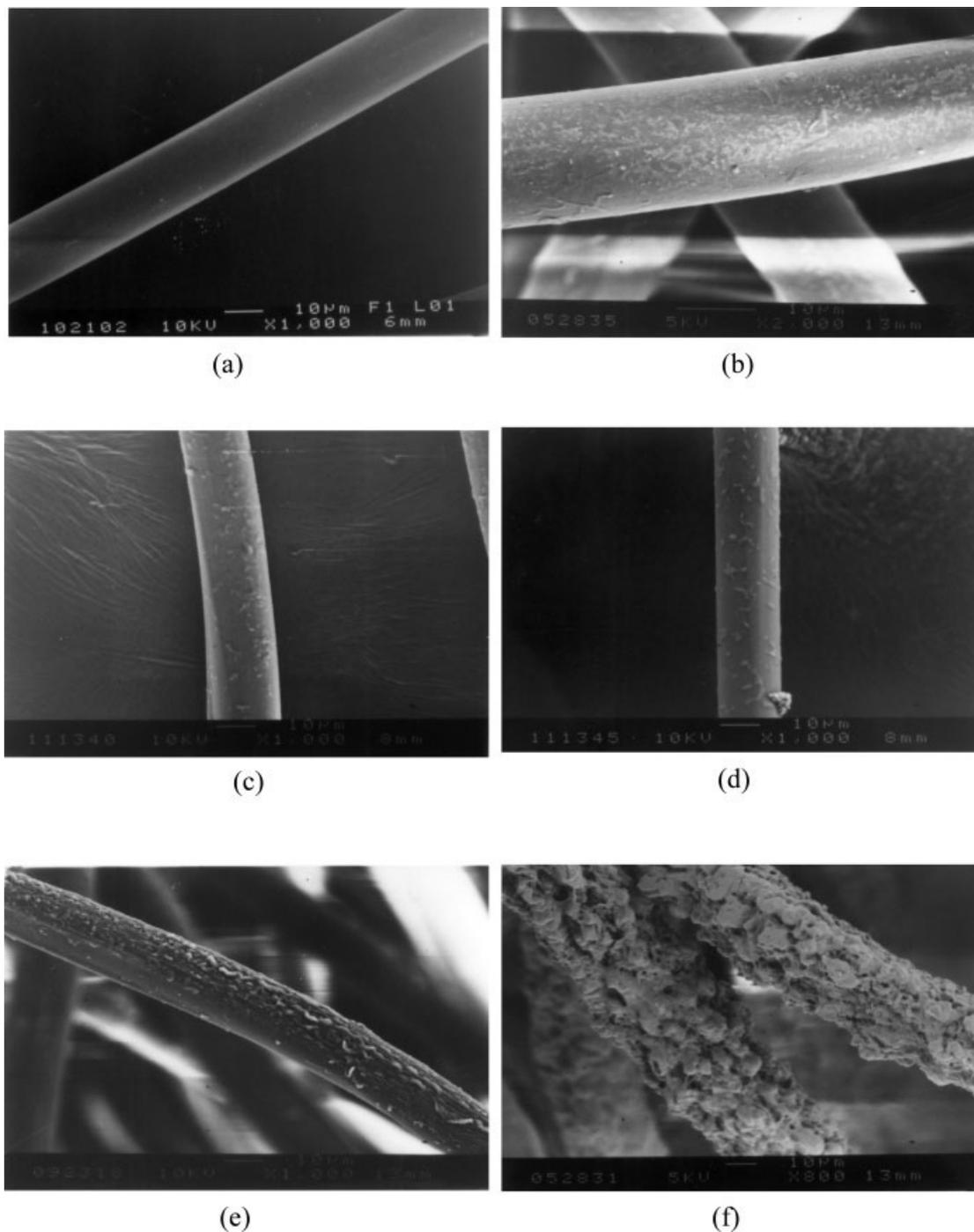


Figure 4 SEM micrographs (bar = 10 μm) of (a) a PET nonwoven (original magnification = 1000 \times), (b) an Ar-plasma-treated PET nonwoven (original magnification = 2000 \times), (c) a 30 wt % NVP-g-PET nonwoven (original magnification = 1000 \times), (d) a 100 wt % NVP-g-PET nonwoven (original magnification = 1000 \times), (e) a 30 wt % NVP-g-PET nonwoven (additive AP; original magnification = 1000 \times), and (f) a 30 wt % NVP-g-PET nonwoven (additives AP and MBAAm; original magnification = 1000 \times).

RESULTS AND DISCUSSION

Influence of the grafting time and additives on the grafting percentage

Figure 3 shows the grafting percentage results for various grafting times for NVP-g-PET nonwovens.

The grafting percentage increased initially. When the grafting time became greater than 50 min, UV caused the grafted NVP to degrade and made NVP homopolymers. For this reason, the NVP grafting percentage decreased when the grafting period was greater than 50 min.¹⁶

The effects of the additives (AP and MBAAm) of UV-induced grafting polymerization on the NVP-g-PET nonwovens are shown in Figure 3. Plasma activation promoted the grafting because the more active sites of the plasma-treated surface were created. The additives could also play a critical role for the grafting of NVP onto the PET nonwoven substrates. When the surface was not pretreated with Ar* plasma, grafting polymerization was not easy, and mainly homopolymers were produced in the reaction. The plasma pretreatment created lots of active surface on the PET nonwovens; these abundant active sites provided favorite sites for initiating the polymerization. The presence of AP and MBAAm could be beneficial for accelerating this process.

SEM morphological observations

SEM photography is shown in Figure 4; the PET nonwoven surface appears in Figure 4(a). The surface of the PET nonwoven treated with Ar* at 50 W for 10 min became rougher, as shown in Figure 4(b). NVP was evenly distributed on the surface, as shown in Figure 4(c,d). Figure 4(e) shows the surface of the NVP-g-PET nonwoven (additive AP), which was rough and corrugated in comparison with Figure 4(a). Figure 4(f) shows the surface of the NVP-g-PET nonwoven (additives AP and MBAAm), which appeared as a rather thick and bundle-grafted fiber on the PET nonwoven surface.

FTIR characterization of the NVP-g-PET nonwoven

The ATR-FTIR spectra of the untreated PET nonwoven and plasma-treated PET nonwoven are shown in Figure 5(a,b). The presence of the PET nonwoven was verified by the characteristic absorption peaks at 1712 cm^{-1} , which could be associated with the C=O group in the PET nonwoven. As shown in Figure 5(c), the absorption peak around 3384 cm^{-1} could be ascribed to the C—N absorption band, and the absorption peak at 1712 cm^{-1} could be associated with the C=O absorption band. In Figure 5(c), the absorption peak around 3262 cm^{-1} could be ascribed to —C=O—N, and the absorption peak at 1712 cm^{-1} could be associated with the C=O absorption band. The absorption peaks at 3384 cm^{-1} for the C—N group and at 1712 cm^{-1} for C=O of the NVP-g-PET nonwoven demonstrated that the grafting and polymerization reactions were successfully achieved in the PET nonwoven. The schematic diagram for the grafting polymerization is shown in Figure 6.

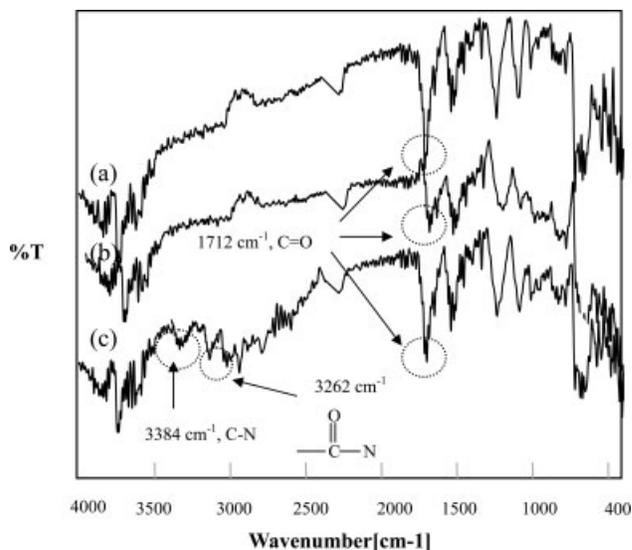


Figure 5 FTIR spectra of (a) a PET nonwoven, (b) an Ar*-plasma-treated PET nonwoven, and (c) a 30 wt % NVP-g-PET nonwoven.

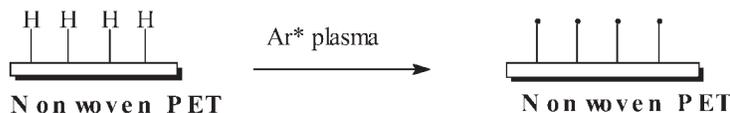
Surface wettability

The intrinsically hydrophobic PET nonwoven could be modified into a hydrophilic surface after Ar-plasma activation or UV-induced polymerization of a hydrophilic monomer, such as NVP. The hydrophilic modification was verified by the capacity for water absorption, as shown in Table I. All swelling behaviors were the averages of three trials. The improvement in the surface tension could substantially facilitate the capacity for water absorption. Hence, the highly hydrophilic surface and hydrophilic monomer NVP could improve the absorption of the solution in the application of dressing clothes. Among these specimens, the most optimal treatment, from the viewpoint of surface wettability, was the NVP-g-PET nonwoven.

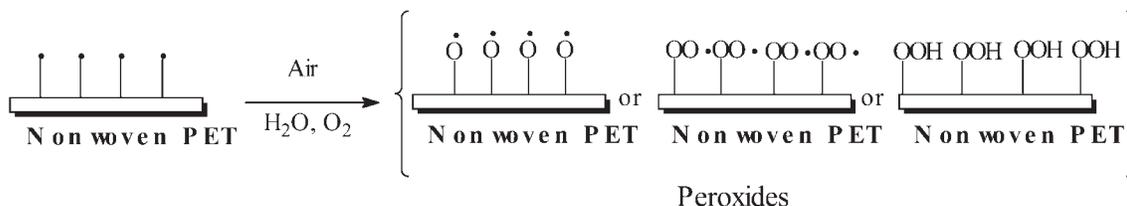
Antibacterial assessment

The preliminary antibacterial assessment was determined qualitatively from the area from which *S. aureus* had been eradicated, as shown in Figure 7. The eradicated area was transparent. In comparison with the as-received nonwoven cloth, these three additive factor treatments improved the antibacterial properties of the PET nonwoven. Figure 7(a) shows that the untreated PET nonwoven could not be anti-*S. aureus* growth; Figure 7(b–d) could be anti-*S. aureus* growth because NVP integrating an iodine molecule acted as a biocidal agent. The improvement increased with an increase in the grafted amount of NVP on the surface of the PET nonwoven. It is apparent that NVP (additive AP and/or MBAAm) gave the best biocidal results.

1. Plasma pretreatment (radical formation)



2. Oxidation of radical



3. Surface Graft polymerization

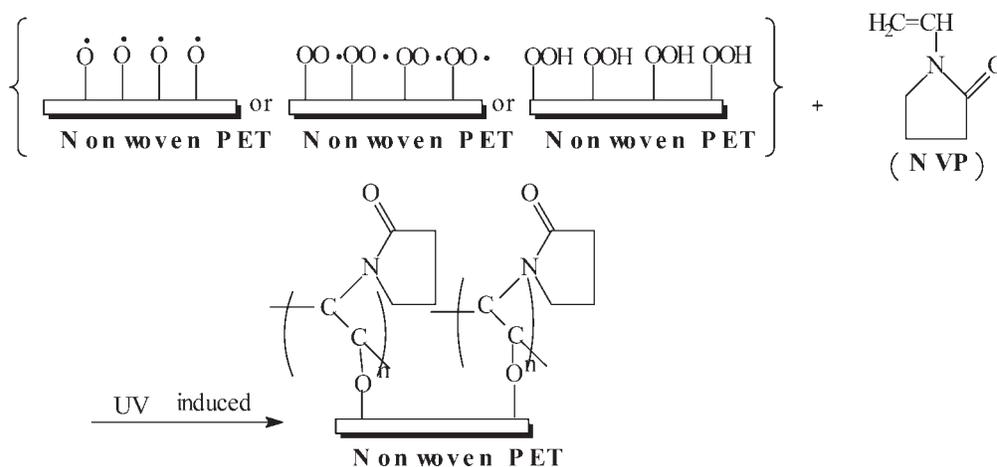


Figure 6 Schematic diagram of the chemical reaction of UV-induced grafting polymerizations.

CONCLUSIONS

An Ar*-plasma activation pretreatment and UV-induced grafting polymerization modified a hydrophobic PET nonwoven into a hydrophilic one.

NVP monomer was grafted onto the PET nonwoven with the addition of AP and/or MBAAm, and this resulted in a large grafting percentage and better water absorption.

TABLE I
Wettability of Surface-Treated PET Nonwovens with the Grafting Time

Treatment	Grafting time (min)			
	30	40	50	60
Control			414 ± 35	
Ar plasma			637 ± 75	
100 wt % NVP-grafted	856 ± 23	883 ± 19	899 ± 12	890 ± 17
30 wt % NVP-grafted	824 ± 19	840 ± 13	868 ± 25	870 ± 31
30 wt % NVP-grafted (additive AP)	838 ± 28	863 ± 22	874 ± 31	886 ± 27
30 wt % NVP-grafted (additives AP and MBAAm)	1190 ± 32	1257 ± 37	1389 ± 34	1377 ± 21

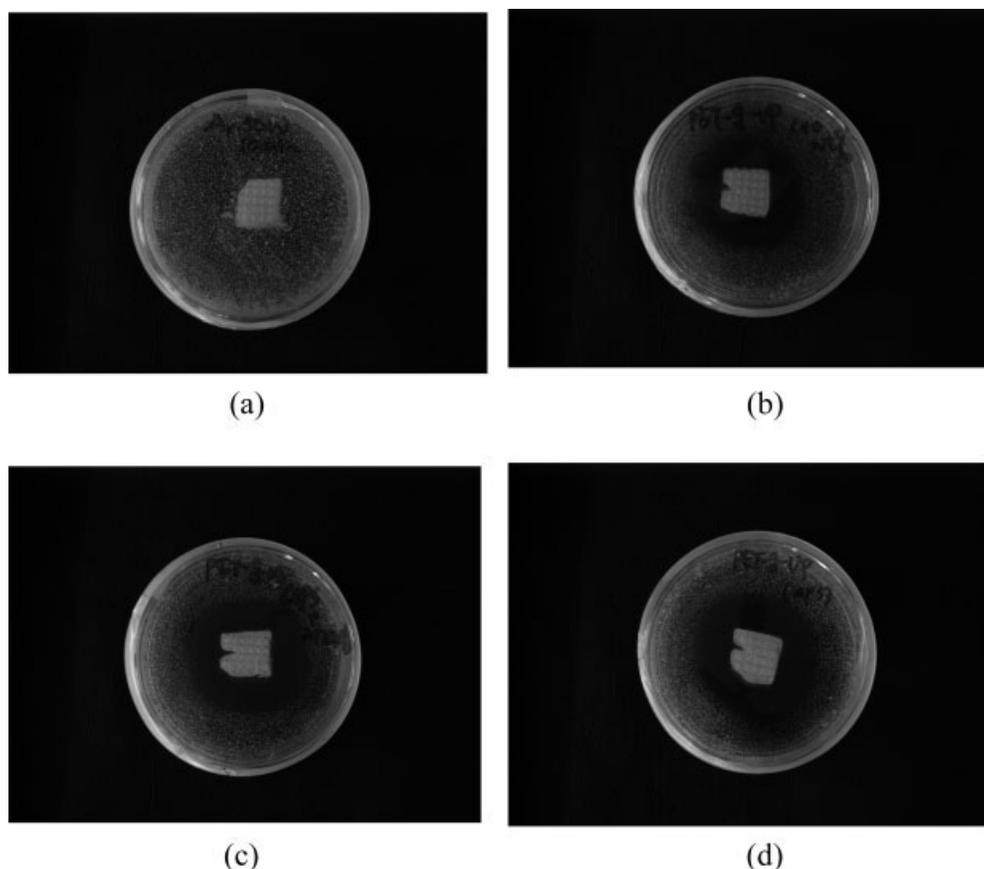


Figure 7 Antibacterial results of (a) an Ar-plasma-treated PET nonwoven, (b) a 100 wt % NVP-g-PET nonwoven, (c) a 30 wt % NVP-g-PET nonwoven (additive AP), and (d) a 30 wt % NVP-g-PET nonwoven (additives AP and MBAAm).

The ATR-FTIR characteristic absorption peak indicated that NVP was successfully grafted onto the PET nonwoven.

A preliminary test of antibacterial assessment showed that *S. aureus* was restrained from growing in the NVP-g-PET nonwoven.

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