**Wei-Hua Yao[1], *Chi-Hui Tsou[1,2,3,4], Jui-Chin Chen[1]**

[1]Department of Materials and Textiles, Oriental Institute of Technology, Pan-Chiao District, New Taipei City, Taiwan, 22061, R. O. C.

[2]Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan, R. O. C.
*E-mail: mayko0301@hotmail.com

[3]R&D Center for Membrane Technology, Chung Yuan University, Jongli, Taoyuan, Taiwan 32023, R. O. C.

[4]Center for Thin Film Technologies and Applications, Department of Materials Engineering, Ming Chi University of Technology, New Taipei City, Taiwan, 24301, R. O. C.

# Plasma Grafting with Methyl Di-Ally Ammonium Salt to Impart Anti-Bacterial Properties to Polypropylene

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**Abstract**
*Quaternary methyl di-ally ammonium salt (MDAA) was grafted on the surface of a polypropylene (PP) nonwoven using a low-temperature radio frequency discharge plasma. The graft ratio of MDAA to PP increased with the grafting temperature; at low grafting temperatures (30 or 60 °C), the graft ratio increased with the H2SO4 catalyst concentration, but at a high grafting temperature (80 °C), it was not affected, even without the use of an acid catalyst. The finished PP nonwoven exhibited excellent antibacterial activities toward Staphylococcus aureus, suggesting that plasma grafting is an effective method.*

**Key words:** *low-temperature plasma, polypropylene nonwoven, methyl di-ally ammonium salt, quaternary ammonium salt, graft, antibacterial property, hydrophilicity.*

## Introduction

Polypropylene (PP) is cheap and has good mechanical properties. However, antimicrobial agents do not easily adhere to PP because it is hydrophobic and lacks functional groups. Its surface needs to be modified to make it antibacterial; it can then be used in various applications: packaging, textiles, and general-purpose filtration.

Many techniques for surface modification have been reported: plasma, chemical, flame, corona, Co-γ-ray, and UV treatment [1 - 8]. Plasma is known to be the most efficient technique to enhance the adhesive [16] and hydrophilic [9] properties of polymers. Plasma modification causes physical and chemical changes on the polymer surface, but it is limited to a depth of a few microns [17]. In general, plasma treatments using either oxygen or argon as a carrier gas result in the production of oxygen-containing groups, whereas those using a nitrogen or ammonia carrier gas produce both nitrogen- and oxygen-containing groups [10 - 14]. Chemical changes that occur during plasma treatment lead to the formation of reactive species that will readily bond on the polymer surface [11 - 15].

The graft polymerisation of a monomer onto PP is significant for its modification [18 - 24]. Although plasma is an excellent polymer processing technique, the steps of grafting and binding require a long time to impart antibacterial [27] or biocompatible properties [27, 28]. In this study, methyl di-ally ammonium (MDAA) was synthesised as a grafting agent. It already has functional groups (oxirane group and π bond), and hence binding or coordination reaction is no longer required. Thus MDAA can readily impart functional properties to a PP nonwoven by plasma grafting. Furthermore it has quaternary ammonium groups that can provide antibacterial activity. The effects of the following on the graft ratio were determined: plasma discharge time, concentration of MDAA, grafting temperature, and grafting time. After the grafting, the hydrophilic and antibacterial properties of the finished PP fabric were evaluated as a function of the graft ratio.

## Exprimental

### Materials and synthesis of methyl di-ally ammonium salt

Polypropylene (PP) nonwoven fabric with an average of 50 g/m$^2$ and 0.15 mm thickness was used, supplied by Industrial Technology Research Institute, Taipei, Taiwan. MDAA was synthesised as in our previous study [28], following the method described by Topfl [27]. Its chemical structure is shown in ***Figure 1***. Argon and oxygen gases (purity = 99.99%) were obtained from San Fu Gas Co., Ltd., Taiwan. Hydrochloric acid (37%, 1.2 g/ml) was a product of Sigma-Aldrich, Steinheim, Germany. Sulfuric acid (98.08%, 1.834 g/ml) and nitric acid

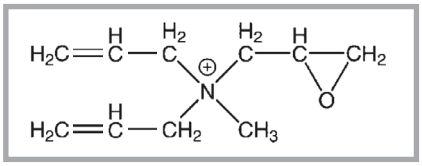

***Figure 1.*** *Methyl di-ally ammonium salt.*

***Table 1.*** *Quantitative nitrogen determination for grafted PP nonwoven at different plasma power and discharge times. MDAA = 4%, $H_2SO_4$ = 0.03 M, grafting temperature - 30 °C for 3 h.*

| Power, W | Time, min | Nitrogen, % × $10^2$ |
|---|---|---|
| 50 | 1 | 0.17 ± 0.01 |
| 100 | | 0.25 ± 0.02 |
| 150 | | 0.23 ± 0.02 |
| 200 | | 0.22 ± 0.01 |
| 250 | | 0.20 ± 0.02 |
| 300 | | 0.19 ± 0.02 |
| 400 | | 0.17 ± 0.03 |
| 100 | 0.5 | 0.18 ± 0.04 |
| | 1.0 | 0.25 ± 0.03 |
| | 2.5 | 0.35 ± 0.02 |
| | 5.0 | 0.32 ± 0.02 |
| | 7.5 | 0.31 ± 0.03 |
| | 10.0 | 0.30 ± 0.02 |

(≥ 90.09%, 1.48 g/ml) were supplied by Nihon Shiyaku Industries, Ltd., Osaka, Japan. All other chemical reagents were of technical grade.

### Plasma treatment

Plasma treatments were conducted using Ar or $O_2$ as a carrier gas with a flow rate of 50 ml/min. To treat the PP surface, we used a radio frequency (RF) plasma machine (Plasma Treatment System RF-O-001, Helix Technology, Inc., Ltd., Taiwan), which involved a glow discharge with direct cold plasma (low temperature) [29]. Aluminum plates measuring 22 × 38 $cm^2$ were used as electrodes. The plasma power and discharge time ranged from 0 W to 400 W and from 0.5 min to 10 min, respectively. The PP nonwoven was first treated with plasma. Then, for the grafting procedure, it was immediately placed in a three-necked flask containing a solution of MDAA (4 wt% or 10 wt%) and a catalyst (0 to 0.5 M). The weight ratio of the PP nonwoven and the solution was 1:50. After that, the nonwoven was washed with a 0.1 wt% aqueous soap solution in a high-frequency ultrasonic tank for 4 min, which was followed by rinsing with water and drying at 80 °C.

### Graft ratio determination

The graft ratio, the amount of MDAA grafted onto the PP nonwoven, was determined indirectly, which was based on the quantitative amount of nitrogen in % present in the sample, determined using conventional Kjeldahl analysis [30]. About 0.5 g of the sample was digested with $H_2S0_4$, together with a catalyst containing 2.8% $TiO_2$, 3.0% $CuS0_4{\cdot}5H_2O$, and 94.2 % $K_2SO_4$. The residue was treated with NaOH to liberate $NH_3$, which was subsequently absorbed in boric acid and titrated with HCl. The total nitrogen bound was determined by oxidising and thermally decomposing it into $NO_2$, which was then detected using an electrochemical detector. $NO_2$ underwent oxidation at the anode, causing a change in the current between the electrodes proportional to the $NO_2$ concentration. Analyses were made using at least triplicate samples to ensure reproducibility and exclude statistical errors.

***Table 2.*** *Comparison between Ar and $O_2$ carrier gas during plasma treatment. Conditions: 100 W for 2.5 min, grafting temperature - 80 °C for 3 h. ($H_2SO_4$ = 0.2 M).*

| MDAA, % | Carrier gas | Nitrogen, % × $10^2$ |
|---|---|---|
| 4 | $O_2$ | 0.61 ± 0.03 |
| | Ar | 0.53 ± 0.01 |
| 10 | $O_2$ | 0.86 ± 0.04 |
| | Ar | 0.81 ± 0.02 |

### Chemical structure analysis

The chemical structure of MDAA, pristine PP, and grafted PP nonwoven at 80 °C for 3 h with Ar and $O_2$ as carrier gas during plasma treatment (MDAA = 10%, $H_2SO_4$ = 0.2 M) was determined with Fourier transform infrared (FT-IR Spectrum One Perkin–Elmer, PerkinElmer, Co., Ltd., Shelton, CT). During each FT-IR measurement, 32 scans were made at a resolution of 1 $cm^{-1}$.

### Chemical composition analysis

Electron spectroscopy for chemical analysis (ESCA) system (VG Scientific, ESCALAB 250, England) was employed to obtain the spectra of pristine PP, plasma-treated PP, and MDAA-grafted PP nonwoven. A magnesium twin anode X-ray at a power of 300 W (15 kV) was used. The scan mode was for an area of

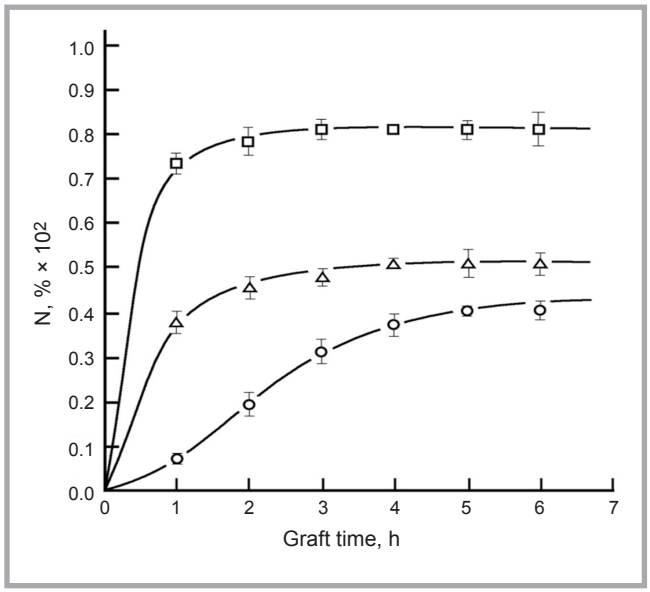


***Figure 2.*** *Effect of grafting time on nitrogen content (graft ratio) for PP nonwoven treated at different grafting temperatures: -○- 30 °C; -Δ- 60 °C; -□- 80 °C. Error bars are based on standard deviation for three replicated measurements. Ar was used as a carrier gas during the plasma treatment; 100 W for 2.5 min. MDAA = 10%, without $H_2SO_4$.*

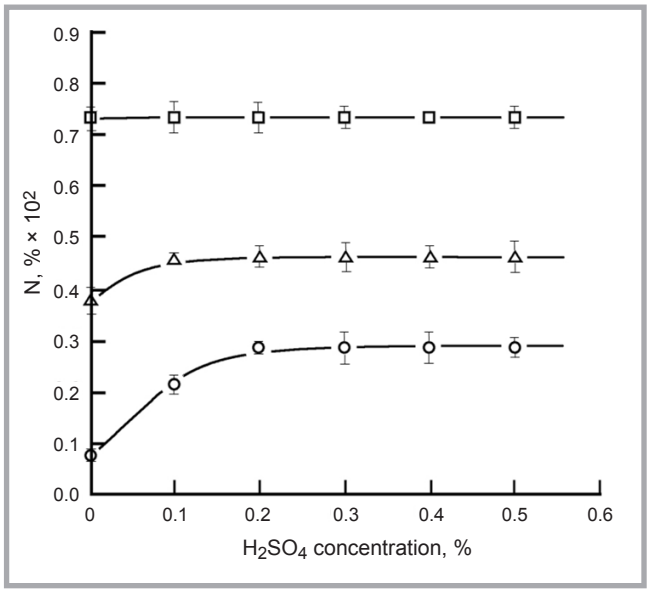


*Figure 3. Nitrogen content (graft ratio) vs. $H_2SO_4$ concentration for PP nonwoven treated for a grafting time of 1 h at different grafting temperatures: -○- 30 °C; -Δ- 60 °C; -□- 80 °C. Error bars are based on standard deviation for three replicated measurements. Ar was used as carrier gas during plasma treatment; 100 W for 2.5 min. (MDAA = 10%).*

150 mm, and the PP nonwoven size was 0.50 × 5 cm$^2$. C1s, N1s, and O1s spectra were deconvoluted by fitting a Gaussian function to an experimental curve using a nonlinear, least-squares curve-fitting program, Origin Pro 7.5 (OriginLab Corporation, Massachusetts, USA).

### Test for anti-bacterial properties

A PP nonwoven with a surface area of 6.25 cm$^2$ was placed on sterile Petri dishes. Inoculum suspensions with 5.0 × 10$^7$ CFU/ml *Staphylococcus aureus* were prepared. The culture method was based on AATCC 100-1998 methodology, a procedure for the qualitative determination of the antibacterial activity of a textile material. All textile samples were inoculated with 0.1 ml suspension at 30 °C for different periods of time. The samples were collected after 0, 1, 3, 5, and 7 h of PP nonwoven inoculation. Then the PP nonwoven was transferred to a sterile physiological saline solution, and the microorganisms were shaken and washed for 15 minutes in an aqueous bath. After that, the suspension of bacteria was diluted with a sterile physiological saline solution and inoculated on a sterile Petri plate. Each PP nonwoven was immersed and mixed in a semi-liquid culture medium. This mixture was allowed to stand for equilibration. The inoculated plates were then incubated at 30 °C for 24 h. Finall, all the colonies grown were counted. The antibacterial ratio is defined as [(Ma - Mb)/Ma] × 100%, where Ma is the original number of bacteria on the PP nonwoven and Mb is the number of bacteria after nourishment for a specific time.

### Contact angle measurement

Contact angles (CAs) were measured with a FACE instrument (model CA-VP150) using deionised water at room temperature. The CA for each PP nonwoven was the average values from 3 to 4 water drops.

## Results and discussion

### Optimum plasma power and discharge time

***Table 1*** indicates that the optimum plasma power is 100 W, at which the optimum plasma treatment time is 2.5 min; these values are based on the highest nitrogen content while keeping the other plasma and grafting conditions constant. When the plasma power is higher than 100 W, the high energy during the plasma treatment may cause the MDAA to decompose or the PP surface structure to be damaged.

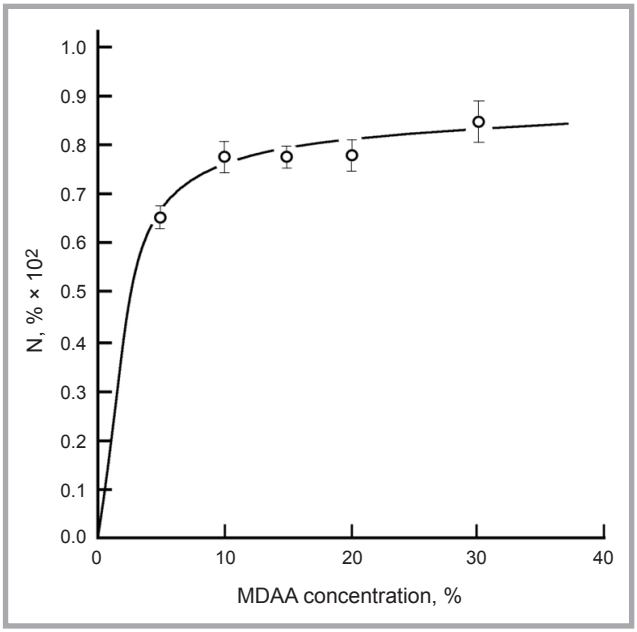


***Figure 4.*** *Effect of MDAA concentration on nitrogen content (graft ratio) for PP nonwoven at a grafting temperature of 80 °C for 2 h. Error bars are based on standard deviation for three replicated measurements. Ar was used as carrier gas during plasma treatment; 100 W for 2.5 min. $H_2SO_4$ = 0.2 M.*

### Use of carrier gas

Data in ***Table 2*** establish that $O_2$ is a better carrier gas than Ar during the PP plasma treatment. The nitrogen content is higher when $O_2$ rather than Ar was used as the carrier gas, with the other plasma and grafting conditions the same. During the plasma treatment, the peroxides formed are mainly responsible for initiating the grafting. With $O_2$ as the carrier gas, more peroxides or carboxylic acid groups are introduced [31], and the higher nitrogen content is attributed to the presence of these.

### Plasma grafting conditions

***Figure 2*** indicates data on the effect of grafting temperature and grafting time during the plasma grafting process. At 80 °C and 3 h, the nitrogen content (0.0081%) is highest, because MDAA easily diffuses into the PP nonwoven and grafts onto it at high temperatures and longer periods of time. During grafting,

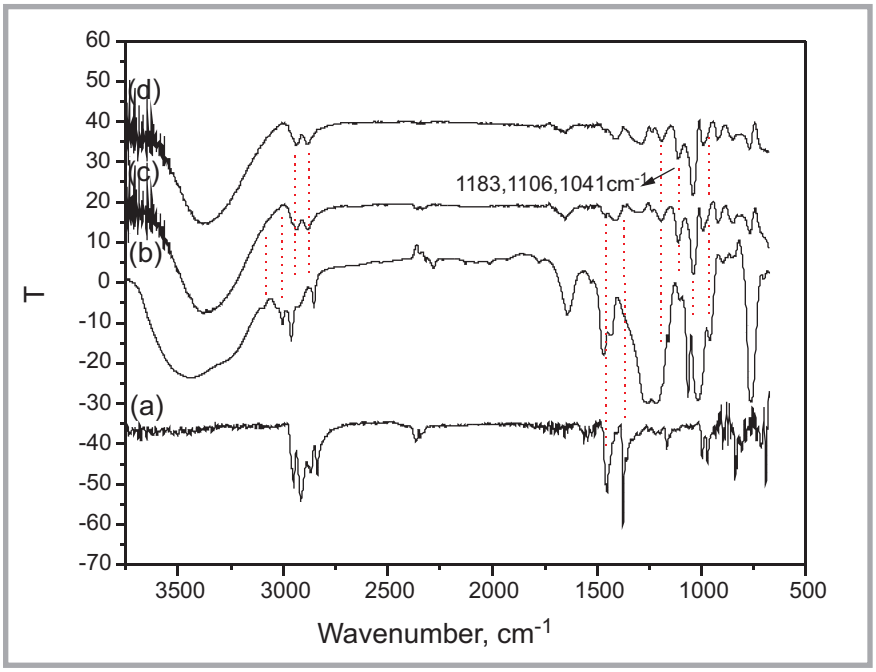


***Figure 5.*** *FT-IR spectra of (a) pristine PP, (b) MDAA, (c) grafted PP with Ar as carrier gas during plasma treatment, and (d) grafted PP with $O_2$ as carrier gas during plasma treatment. MDAA=10%, $H_2SO_4$ = 0.2 M, grafting temperature - 80 °C for 3 h.*

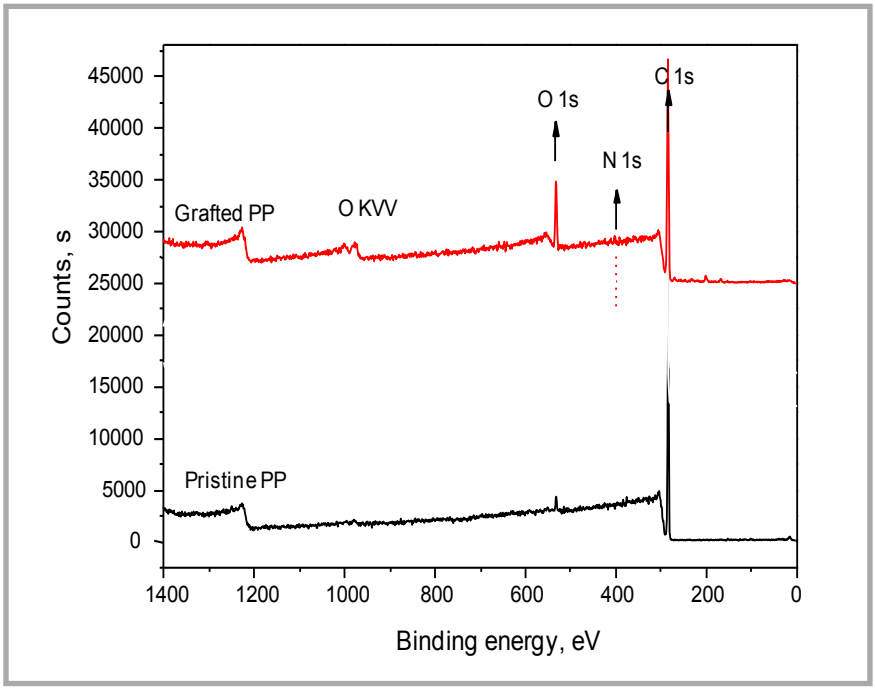


***Figure 6.*** *ESCA analysis of surface properties for pristine PP and grafted PP with Ar as carrier gas during plasma treatment. MDAA = 10%, $H_2SO_4$ = 0.2 M, grafting temperature - 80 °C for 3 h.*

the chain mobility of the PP matrix increases with the temperature. Therefore MDAA reacts with PP more effectively at 80 °C than at 60 °C or 30 °C.

***Figure 3*** shows the effect of the grafting temperature and $H_2SO_4$ catalyst concentration on the graft ratio. At lower temperatures of 30 °C and 60 °C, varying the catalyst concentration tends to affect the nitrogen content; but at a higher temperature of 80 °C, even without using a catalyst, the nitrogen content is not affected. This result is caused by the oxidation/degradation of the PP polymer chain after the plasma treatment [32]. Therefore MDAA is possible to be grafted onto the PP nonwoven even without the $H_2SO_4$ catalyst, especially at a high temperature; the same is true at low temperatures, although the graft ratio is very low.

### MDAA concentration during plasma grafting

***Figure 4*** shows the effect of MDAA concentration during plasma grafting at 80 °C. The graft ratio is 0.64 when the MDAA concentration is 5%, but it becomes nearly constant at 0.81 for MDAA concentrations higher than 10%.

### Chemical structure analysis

***Figure 5*** shows the spectra of pristine PP nonwoven, MDAA, and grafted PP nonwoven during the plasma treatment using $O_2$ or Ar as the carrier gas. For pristine PP, two distinguished absorption bands at 2918/2833 and 1453 $cm^{-1}$ correspond to C-H aliphatic stretching and C-H aliphatic bending. The MDAA spectrum indicates interesting and important absorption bands at 3440, 1062, and 961 $cm^{-1}$, corresponding to O-H stretching vibrations, oxirane ring C-O-H stretching vibrations, and C-O-C asymmetrical deformation bands. Similar characteristic absorption peaks are indicated for PP fabrics grafted with $O_2$ or Ar as the carrier gas; the absorption bands centered at 3372, 2934, 1451, and 1183 $cm^{-1}$ correspond to O-H stretching vibrations, C-H stretching vibrations, C-H bending vibrations, and aliphatic ether (C-O-C), respectively. These characteristic peaks were also observed by other studies [29, 34 - 36].

The absorption bands of C-H aliphatic stretching and aliphatic bending shown in the pristine PP spectrum all disappeared after the grafting process. The following disappeared as well: absorption bands at 3092 and 3005 $cm^{-1}$, corresponding to C-H stretching vibration for olefinic C-H stretching vibrations of MDAA. The peak at 1644 $cm^{-1}$ for C=C stretching vibrations is weak. The absorption bands at 256 and 961 $cm^{-1}$ for oxirane ring disappeared. Those peaks that disappeared were replaced by new absorption bands at 2934, 1451, and 1183 $cm^{-1}$, corresponding to C-H stretching vibration, aliphatic ether, and aliphatic alcohol, respectively.

After the plasma grafting at a high temperature of 80 °C, some characteristic absorption peaks (2918 and 2833 $cm^{-1}$) of the PP nonwoven disappeared, dem-

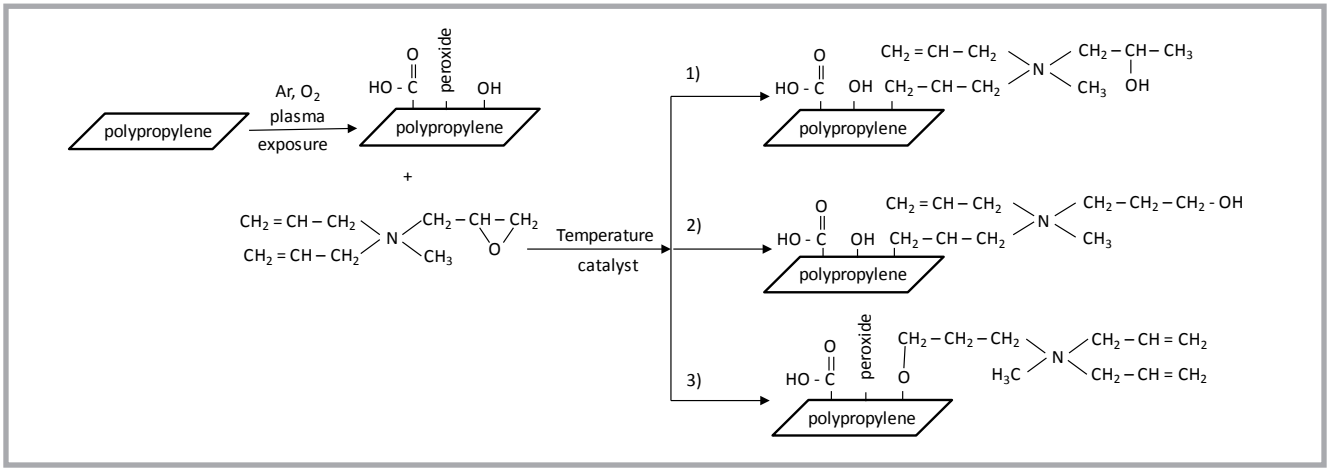


***Figure 7.*** *Possible mechanisms of plasma grafting.*

***Table 3.*** *Antibacterial properties of pristine PP and grafted PP. $H_2SO_4$ = 0.2 M, grafting temperature - 80 °C for 3 h.*

| Process | MDAA, % | Carrier gas | CFU/ml × $10^{-4}$ | | | | | | Antibacterial ratio (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Exposure time (h) | | | | | | Exposure time (h) | | | | | |
| | | | 0 | 1 | 3 | 5 | 7 | 9 | 0 | 1 | 3 | 5 | 7 | 9 |
| Without treatment | - | - | 330 | 365 | 384 | 402 | 425 | 441 | -- | -- | -- | -- | -- | -- |
| Plasma grafting | 4 | Ar | -- | 251 | 226 | 178 | 158 | 144 | -- | 23.9 | 31.5 | 46.1 | 52.1 | 67.3 |
| | | $O_2$ | -- | 196 | 178 | 110 | 92 | 64 | -- | 40.6 | 46.1 | 66.7 | 72.1 | 85.5 |
| | 10 | Ar | -- | 185 | 120 | 96 | 65 | 21 | -- | 43.9 | 63.6 | 70.9 | 80.3 | 95.2 |
| | | $O_2$ | -- | 95 | 72 | 32 | 8 | 0 | -- | 71.2 | 78.2 | 90.3 | 97.6 | 100 |

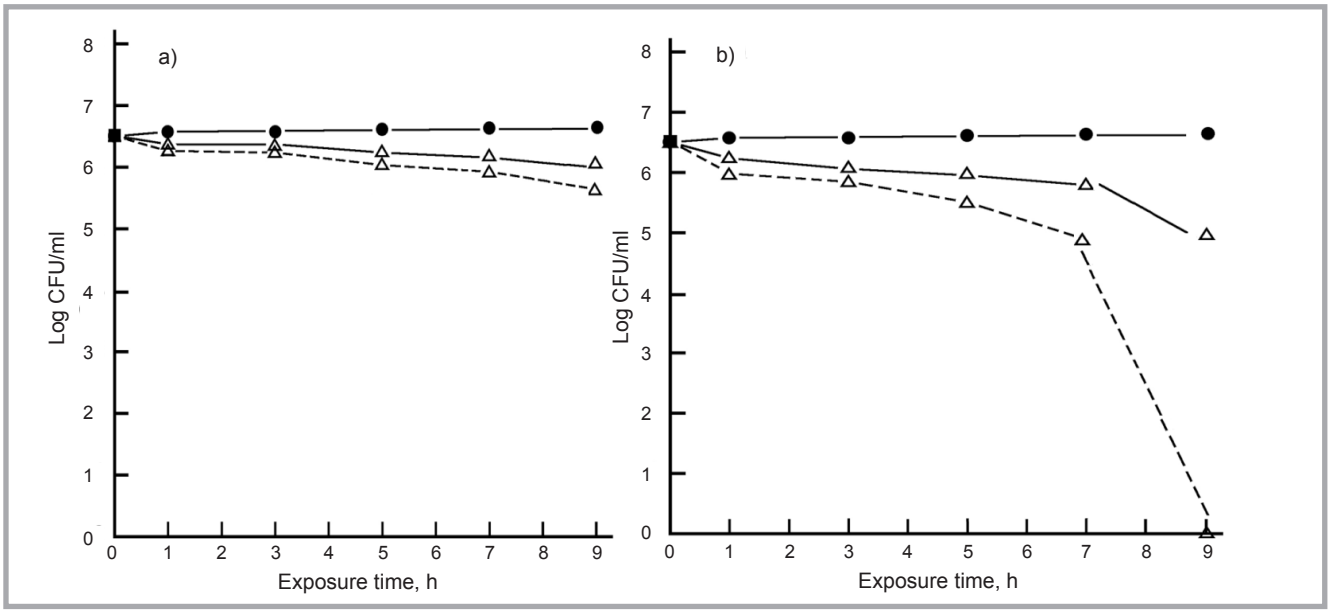


***Figure 8.*** *Antibacterial activity for PP nonwoven: (a) grafting with 4% MDAA, (b) grafting with 10% MDAA. (-●- without treatment; -Δ- grafted PP with Ar as carrier gas during plasma treatment; ---Δ--- grafted PP with $O_2$ as carrier gas during plasma treatment). ($H_2SO_4$ = 0.2 M, grafting temperature - 80 °C for 3 h)*

onstrating that PP was decomposed by the $H_2SO_4$ catalyst. The oxirane ring of MDAA was opened to aliphatic secondary or primary alcohol, and then it reacted with PP to produce C-O-C aliphatic ether (1183 $cm^{-1}$).

After the plasma treatment, the PP surface was activated, and C-O-O-H and O-H polar groups were produced [38, 39]. During plasma grafting, ether and alcohol groups were formed, which is consistent with that of the FT-IR analysis. In the structure of the grafted PP, the C-H stretching vibration disappeared. In the MDAA structure, olefinic C-H stretching vibrations (3092 $cm^{-1}$) and C=C stretching vibrations (1644 $cm^{-1}$) disappeared as well. These peaks that disappeared were replaced by new ones of aliphatic ether (2934 $cm^{-1}$) and aliphatic secondary or primary alcohol (1183 $cm^{-1}$), which is due to the degradation of the PP nonwoven caused by the $H_2SO_4$ catalyst during the plasma grafting process at 80 °C. The oxirane ring of MDAA was opened to produce aliphatic secondary or primary alcohol, and then it reacted with the O-H group of PP to produce C-O-C aliphatic ether (1183 $cm^{-1}$).

***Figure 6*** shows ESCA analysis at higher binding energies for pristine PP and grafted PP. It illustrates the $-CH_2-N^+$ structure at 402.2 eV, a finding similar to that in [40, 41]. On the basis of the discussion of FTIR and ESCA results above, we proposed mechanisms of plasma grafting (***Figure 7***). Three possible grafting reactions from the functional groups of vinyl and epoxy are indicated.

**Test for antibacterial properties**

***Table 3*** shows the antibacterial properties of pristine PP and plasma-treated PP nonwoven. ***Figure 8*** shows the antibacterial activity for the PP nonwoven; data on grafting with 4% and 10% MDAA are given in ***Figures 8.a*** and ***8.b***, respectively. From the antibacterial properties in ***Table 4***, it is indicated that the use of $O_2$ as a carrier gas for the plasma treatment is better than Ar. Results in ***Tables 3*** and ***4*** illustrate that with a higher graft ratio, the PP nonwoven demonstrates good antimicrobial properties, as the colony forming units decrease significantly.

**Contact angle measurement**

Contact angle data for the PP nonwoven are shown in ***Figure 9*** (see page 122). The pristine PP's contact angle ranges from 87.7° to 89.4°. For the PP nonwoven treated by $O_2$ plasma, the contact angle is 90° to 71.3°. Generally $O_2$ plasma treatment initially brings the contact angle to hydrophilic values (≤ 80°). Vesel and Mozetic [42] reported on the surface modification of various polymers with $O_2$ plasma. $O_2$ was detected on the polymer surface, associated with C-O, C=O and O=C-O groups on the surface. For the PP nonwoven treated by Ar plasma, the contact angle is 89.8° to 78.7°, which is a bit higher compared with $O_2$ plasma treatment, but lower compared with the pristine PP nonwoven. Jong-Il Weon [43] indicated that PP grafted using Ar plasma presents new functional

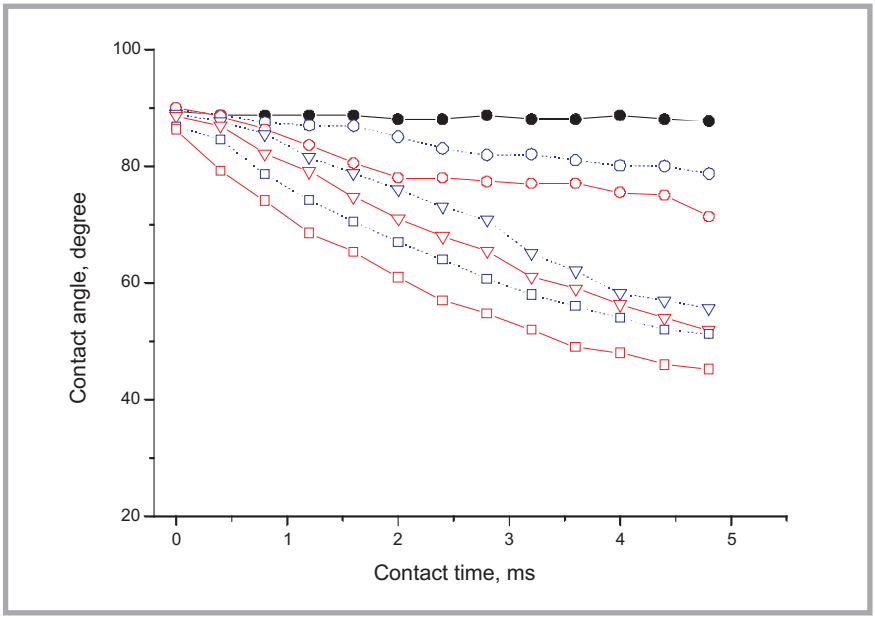


***Figure 9.*** *Contact angle data for PP nonwoven: (···●··· ) neat PP; (···○···) PP treated with Ar plasma; (-○-) PP treated with $O_2$ plasma; (···Δ···) grafted PP with 4% MDAA using Ar as carrier gas during plasma treatment; (-Δ-) grafted PP with 4% MDAA using $O_2$ as carrier gas during plasma treatment; (···□···) grafted PP with 10% MDAA using Ar as carrier gas during plasma treatment; (-□-) grafted PP with 10% MDAA using $O_2$ as carrier gas during plasma treatment. ($H_2SO_4$ = 0.2 M, grafting temperature -f 80 °C for 3 h).*

groups such as O-C=O, which might be related to the esterification of the OH group generated during the plasma treatment [44,45]. Based on the contact angle data, $O_2$ is a better carrier gas than Ar in conducting plasma grafting, which is attributed to the hydrophilic MDAA material. Therefore the contact angle is lower when the grafting rate is higher.

## Conclusions

As indicated by FT-IR and SEM, MDAA was successfully grafted onto a PP nonwoven. Optimum conditions were found as follows: plasma power = 100 W for a gas flow rate of 50 ml/min, and plasma treatment time = 2.5 min. $O_2$ was found to be a better carrier gas than Ar. On the basis of FT-IR, some of the peaks for the PP nonwoven disappeared when grafting temperature is 80 °C with Ar or $O_2$ as the carrier gas, which was due to the decomposition caused by the $H_2SO_4$ catalyst at a high grafting temperature. Results of the antibacterial ratio and contact angle were related to the graft ratio for the finished PP nonwoven: higher graft ratios led to higher hydrophilic and antibacterial properties. Overall the synthesised MDAA grafted onto the polymer surface had the potential for applications in functional fabrics.


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