

# Wettable Films Plasma-Polymerized From Nitroethane

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## Synopsis

Plasma polymerization of nitroethane provided highly wettable films whose surface energy was  $66 \times 10^{-3}$  N/m. The contact angle of water was  $7 \pm 2^\circ$  at  $20^\circ\text{C}$  in air. This high wettability was maintained for a long duration of at least 2 months. Infrared and ESCA spectra showed that the plasma polymers contained no nitro groups and were composed of dehydrogenated carbon chains with a large amount of amido groups. The amido groups whose concentration reaches approximately 40% of the total carbon units may contribute to the high wettability.

## INTRODUCTION

Wettable surfaces are of interest in improving adhesion, biocompatibility, membranes for reverse osmosis and pervaporation, and handling of fabrics.<sup>1-18</sup> Many techniques involving coating, grafting, polymer blending, and surface oxidation have been applied for these improvements. Plasma treatment or plasma coating is one of them. First, Schonhorn et al.,<sup>1,2</sup> demonstrated a significant improvement of the adhesion strength between olefin polymers and glue by the plasma treatment technique. By exposure to argon, helium, oxygen, or nitrogen plasma for a few seconds, unsaturated and polar groups, such as carbonyl groups, are generated at the surface of the polymer, and the adhesion strength increases significantly (approximately 10 times). This technique is called CASING (cross-linking of activated species of inert gases). The wettable properties generated by the exposure to these plasmas, however, do not maintain themselves for long periods of time but decrease rapidly within 1-2 days after plasma exposure. This rapid decrease in the wettability is due to rotation of the polar groups from the surface side to the inner side around the axis of the polymer chains. Therefore, durable wettability should be attained by restricting the rotation of the polar groups. Cross-linked polymer surfaces would provide the durable improvement due to the restricted rotation of the polar groups.

Plasma polymers are generally insoluble in ordinary organic solvents and their polymer chains are cross-linked, which stresses the importance of the modification with plasma polymers (plasma coating). In many cases, starting materials used for the wettable plasma coating are nitrogen-containing compounds.<sup>19-23</sup> The saturated compounds are more suitable than unsaturated to yield highly cross-linked polymer chains. There has been less attention to oxygen-containing compounds as starting materials because of their high plasma susceptibility.<sup>24,25</sup> Yasuda et al.<sup>26-28</sup> pointed out the possibility of

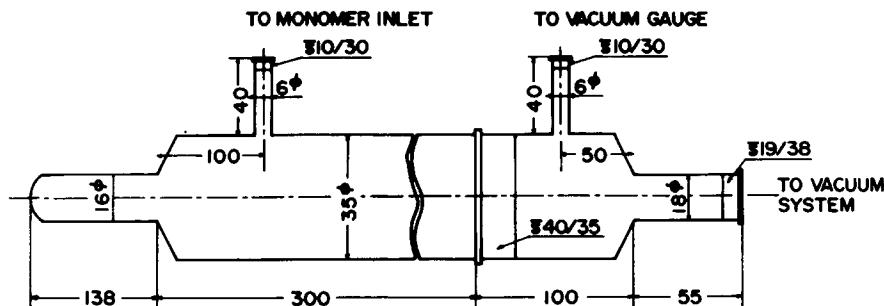


Fig. 1. Schema of reaction chamber for plasma polymerization.

using oxygen-containing compounds in wettable plasma coating. They used the nitrogen-water-acetylene gaseous mixture as starting material.

This study is focused on the plasma polymerization of a compound containing both nitrogen and oxygen elements. Nitroethane is thus chosen as starting material, and the wettability of the plasma polymers formed is investigated.

## EXPERIMENTAL

### Plasma Polymerization

The reaction chamber (35 mm inner diameter and 400 mm long) made of Pyrex glass for plasma polymerization is fitted with a monomer inlet, pressure gauge, vacuum system, and matching network for inductive coupling of a 13.56 MHz radio frequency (RF) source (Fig. 1). The experimental procedures of the plasma polymerization were essentially the same as reported previously.<sup>29</sup> The reaction system was evacuated to about 0.13 Pa using the combination of a diffusion and a rotary pump. Argon gas was introduced into the reaction chamber, and the surfaces were exposed to argon plasma for 10 min to eliminate the water adsorbed on substrate surfaces. The system was again evacuated to 0.13 Pa, and the monomer gas, adjusted at a given flow rate of 0.5–5 cm<sup>3</sup> (STP) per minute at 1.3 Pa, was introduced into the reaction chamber. The RF power was turned on, and the plasma polymerization was conducted at a constant level of 25 W RF power for 0.5–3 h.

Nitroethane, triethylamine (analytic grade), and methane (99.99% purity) were purchased from Wako Pure Chemical Industries, Ltd., and Matheson, respectively, and used without further purification.

### Elemental Analysis

The plasma polymers deposited on the glass plate were analyzed for C, H, N, and O determination. The C, H, and N content of the plasma polymers was determined with a Yanagimoto CHN analyzer MT-2. The O content was found as the difference between the sample weight and the sum of the determined C, H, and N contents.

### Infrared and ESCA Spectra

The plasma polymer flakes scraped from the glass plates were provided for preparation of KBr disks. Infrared spectra of the polymers were recorded with a Nihon Bunko Fourier transform infrared spectrophotometer FT/IR-3.

The plasma polymer films (approximately 100 nm thick, determined by interferometry) deposited on silicon wafers were provided for the measurement of ESCA spectra. The ESCA spectra were recorded with a Shimadzu electron spectrometer ESCA 750 employing a  $MgK_{\alpha}$  exciting radiation at 8 kV and 30 mA in  $6.5 \times 10^{-6}$  Pa. An Au core level at 84.0 eV was temporarily used for the calibration of the energy scale. The complex spectra of the  $C_{1s}$  core level were resolved using a Shimadzu ESCAPAC 760 data system under the assumption of gaussian distribution. Three parameters, the position and the height of the peak and the full width at half-maximum (FWHM), were varied to correspond roughly to the observed spectra.

### Surface Energy

Contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate on the plasma polymer films deposited on the glass plates were measured at 20 °C using an Erma contact anglemeter G-I with a goniometer. The contact angle data were analyzed to estimate the surface energy according to Kaelble's method.<sup>30</sup>

## RESULTS AND DISCUSSION

### Wettability

Nitroethane was plasma polymerized to yield light-yellow films. Figure 2 shows the polymer deposition rate as a function of the  $W/FM$  value, where  $W$ ,  $F$ , and  $M$  are the RF input power, the flow rate of the monomer, and the molecular weight of the monomer, respectively. The  $W/FM$  value means an apparent input energy per mass of the monomer, a parameter of controlling the plasma polymerization process.<sup>24, 25</sup> The polymer deposition rate, as shown

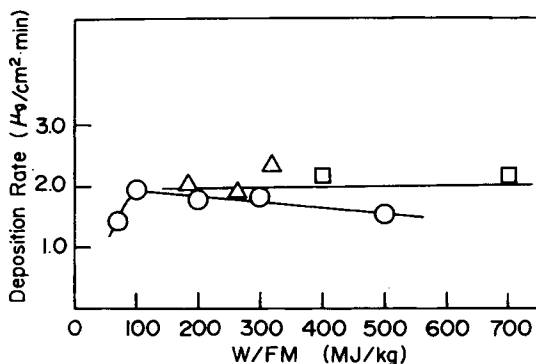


Fig. 2. Polymer deposition rate as a function of  $W/FM$  value; ○, in nitroethane system; △, in triethylamine system; □, in methane system.

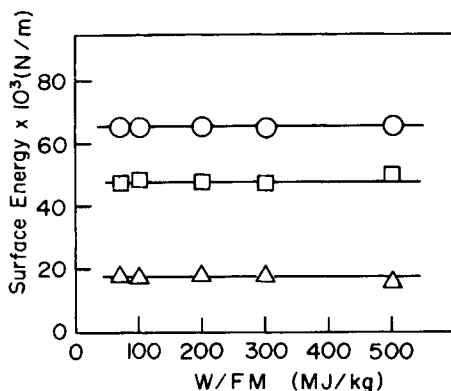


Fig. 3. Surface energy of plasma polymers from nitroethane as a function of  $W/FM$  value; ○,  $\gamma_s$ ; △,  $\gamma_s^d$ ; □,  $\gamma_s^p$ .

in Figure 2, increases with increasing  $W/FM$  values up to 100 MJ/kg and then slightly decreases. Polymer deposition in the plasma polymerization of nitroethane was in the range of 1.5–2.0  $\mu\text{g}/\text{cm}^2\text{-min}$ , which is comparable to that of plasma polymerization of methane (2.1  $\mu\text{g}/\text{cm}^2\text{-min}$  at a  $W/FM$  value of 400 MJ/kg) and of triethylamine (2.3  $\mu\text{g}/\text{cm}^2\text{-min}$  at 320 MJ/kg). This result indicates that the nitro substituent is not an obstacle in the polymer-forming process during plasma polymerization.

The plasma polymers from nitroethane were deposited on slide glass surfaces, and their surface energy was estimated as a function of the  $W/FM$  value. The contact angle measurements to estimate the surface energy were carried out within 30 min immediately after completing the plasma polymerization process, considering our misgivings about the deterioration of the surface properties of the deposited plasma polymers. Figure 3 shows the surface energy for the plasma polymers from nitroethane as a function of the  $W/FM$  value. Their surface energy was an almost constant value ( $66 \times 10^{-3}$  N/m) independent of the  $W/FM$  ratio. This value is larger than that for the plasma polymers from methane ( $30 \times 10^{-3}$  N/m) and triethylamine ( $38 \times 10^{-3}$  N/m). This comparison indicates that the nitro substituent plays an important role in the enhancement of the surface energy for the plasma polymers.

Successive changes in the surface properties for the plasma polymers were monitored over a period of 2 months. The specimens were films that were plasma polymerized from nitroethane (at a  $W/FM$  value of 100 MJ/kg), triethylamine (at 100 MJ/kg), and methane (at 400 MJ/kg), deposited on slide glass surfaces. Figure 4 shows the contact angles of water against these plasma polymer surfaces as a function of the preservation time at room temperature, in air. No change in the contact angle for the three plasma polymers was observed during at least 2 months. The contact angles were  $7 \pm 2^\circ$ ,  $70 \pm 2^\circ$ , and  $96 \pm 2^\circ$  for the plasma polymers from nitroethane, triethylamine, and methane, respectively. From this result one can conclude that these plasma polymers have stable surfaces and that the polar groups generated at the polymer surface are tightly fixed without their rotation. Yasuda et al.<sup>31</sup> have measured the forward and backward contact angles of water

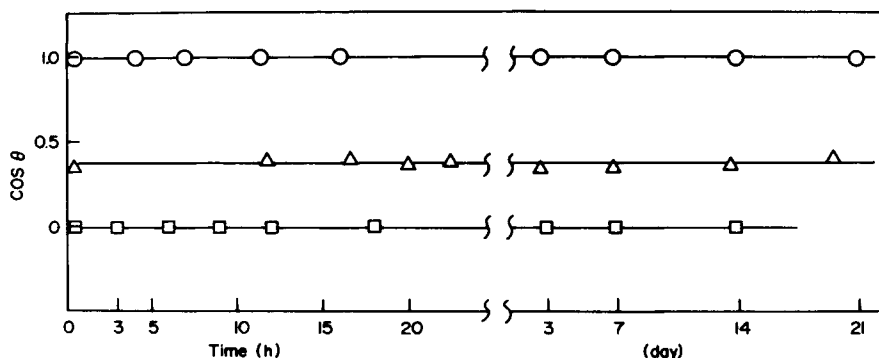


Fig. 4. Contact angle of water against plasma polymers from nitroethane (at 100 MJ/kg) as a function of standing time; ○, polymers from nitroethane; △, from triethylamine; □, from methane.

against the polymer surface and suggested that the polar groups at the surface of the polymer obtained by plasma polymerization of saturated compounds, such as methane, do not rotate around the axis of polymer chains.

### Chemical Composition of the Plasma Polymers

From the investigation in the previous section there is no doubt that plasma polymers from nitroethane provide significant wettable surfaces. What polar groups contribute to this high wettability? Table I shows the elemental composition of the plasma polymers from nitroethane as a function of the  $W/FM$  value. Plasma polymers were composed of large amounts of nitrogen and oxygen atoms, as well as carbon and hydrogen atoms, possessing almost the same elemental composition of  $C_{2.0}H_{2.6}N_{1.0}O_{1.4}$  when plasma polymerizations were performed at  $W/FM$  values from 70 to 500 MJ/kg. In many cases, the elemental composition of plasma polymers strongly depends on the  $W/FM$  value. For example, in the plasma polymerization of trimethylsilyldimethylamine, the H/Si atomic ratio for the plasma polymers formed decreases from 11.9 to 6.9 with increasing the  $W/FM$  value from 143 to 571 MJ/kg, and the N/Si atomic ratio increases from 0.8 to 1.1.<sup>29</sup> It is worth noting that the plasma polymerization of nitroethane does not depend on the elemental composition of the  $W/FM$  value. Furthermore, the H/C atomic ratio of the plasma polymers from nitroethane (1.3) is lower than that of

TABLE I  
Elemental Composition of Plasma Polymers from Nitroethane.

$W/FM$ (mJ/kg)	Empirical formula of polymers	H/C	N/C	O/C
70	$C_{2.0}H_{2.7}N_{1.0}O_{1.5}$	1.3	0.5	0.8
100	$C_{2.0}H_{2.3}N_{1.1}O_{1.5}$	1.2	0.6	0.7
200	$C_{2.0}H_{2.7}N_{1.2}O_{1.5}$	1.4	0.6	0.7
300	$C_{2.0}H_{2.7}N_{1.1}O_{1.4}$	1.4	0.6	0.7
500	$C_{2.0}H_{2.7}N_{1.0}O_{1.1}$	1.4	0.5	0.6
AV.	$C_{2.0}H_{2.6}N_{1.0}O_{1.4}$	1.3	0.5	0.7

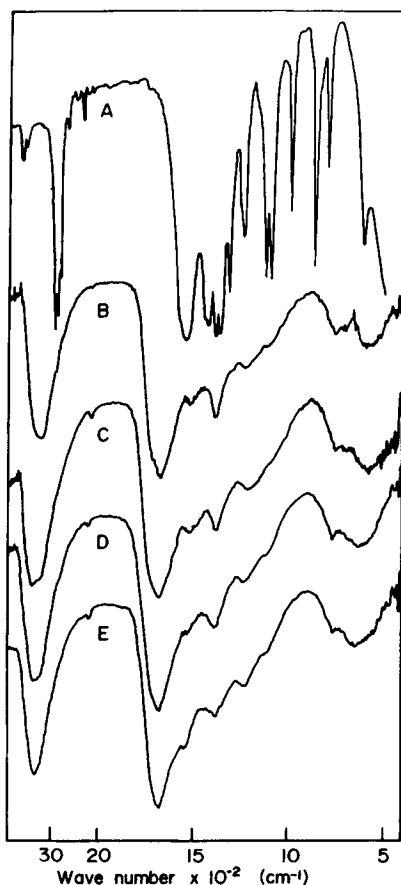


Fig. 5. IR spectra for plasma polymers from nitroethane as a function of  $W/FM$  value; (A) monomer; (B) at a  $W/FM$  value of 70 MJ/kg; (C) at 100 MJ/kg; (D) at 200 MJ/kg; (E) at 500 MJ/kg.

starting nitroethane (2.5), indicating that the dehydrogenation from nitroethane occurs in the discharge state to yield polymers.

The plasma polymers from nitroethane showed simple infrared spectra. Typical spectra are illustrated in Figure 5. On their infrared spectra there are strong absorptions at 3341 (adsorbed water and NH), 1679 (NC(O)), 1399, and 1386  $\text{cm}^{-1}$  (CH), and weak absorptions at 1549 ( $\text{NO}_2$ ), 1531 (NH), 1233 (C—N), and 768  $\text{cm}^{-1}$  (unknown). Characteristic absorptions due to  $\text{NO}_2$  groups (1335, 880, and 815  $\text{cm}^{-1}$ ) could not be observed on these spectra. Furthermore, the stretching absorptions due to  $\text{CH}_2$  and  $\text{CH}_3$  groups (2960 and 2925  $\text{cm}^{-1}$ ) were not intense. From these spectral results one can assume that the plasma polymers from nitroethane may be composed of dehydrogenated carbon chains containing amide but no nitro groups.

This assumption has been supported by ESCA measurements. Typical ESCA spectra are illustrated in Figure 6. The  $\text{C}_{1s}$  complex, as shown in Figure 6, could be resolved into three components ( $\text{C}_{1s}$  components 1, 2, and 3) which were positioned at 285.0 (C—C), 286.6–287.0 (C—O and C—N), and

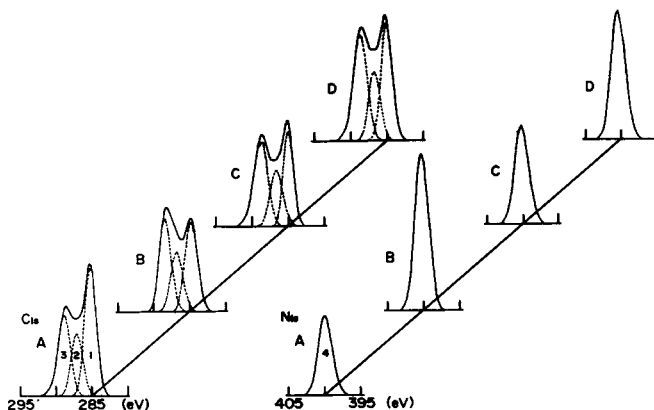


Fig. 6. ESCA spectra for plasma polymers from nitroethane as a function of  $W/FM$  value; (A) at a  $W/FM$  value of 70 MJ/kg; (B) at 100 MJ/kg; (C) at 200 MJ/kg; (D) at 300 MJ/kg.

288.5–288.7 eV (C=O), respectively. The relative concentration of the respective  $C_{1s}$  components was less changeable with increasing the  $W/FM$  value, reaching about 38, 23, and 39%. The  $N_{1s}$  spectra were symmetrical peaks having a FWHM value of approximately 2.3 eV and positioned at 400.3–400.9 eV, which could be assigned to NC(O) groups. These  $N_{1s}$  spectra suggest that plasma polymers contain no nitro groups, those expected to give a  $N_{1s}$  spectrum appearing at near 405 eV.<sup>32</sup>

From these spectral results one can conclude that plasma polymers from nitroethane are composed of dehydrogenated carbon chains with a large number of amide groups. The groups contributing to the high wettability of these plasma polymers may be amide groups whose concentration reaches about 40% of the total carbon units.

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