Atomic Force Microscopy Analysis of Cellulose Triacetate Surface Modified In Low Temperature Argon Plasma and Its Adhesion Behavior

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ABSTRACT: The surface of cellulose triacetate (CTA) film was modified with gaseous plasma of several discharge power in the presence of Argon (Ar) gas at 0.5 torr pressure. After gas plasma etching, the surface structure of the films is analyzed by atomic force microscopy (AFM) and measured with peel strength. Furthermore, the wetting properties of the CTA film treated with Ar plasma are studied by contact angle measurement. Peel strength after plasma treatment was increased with increasing plasma treatment time. However, treatments of plasma greater than 7 min did not find an additional increase in peel strength, similarly to roughness and morphological changes of AFM. The water contact angle decreased for an initial treatment time due to the improved wettability of the film, but showed an increasing trend for a higher treatment time (7 min). These results show that Ar plasma treatment is a convenient tool for improving the adhesive properties of CTA film. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3963–3971, 2006

Key words: CTA film; argon plasma; adhesive property

INTRODUCTION

The industrial use of low plasma treatment was developed by the micro electronic industry for the deposition of thin films.[1] The more extensive application of plasma is due to its ability to enhance the surface adhesion properties of many materials, without producing any modification of the bulk properties.[2,3] Besides chemical modification of polymer surfaces, gas plasma etching was also widely used as a tool to obtain more information about the polymer structure. Ordinarily, plasma surface treatment also offers the advantage of greater chemical flexibility. The use of radio frequency (RF) plasma for surface modification of polymeric surfaces has been well documented over the past 60 years.[1] The most significant effect of plasma treatment is surface chemistry modification of polymeric surfaces. The utilization of CTA membrane material was recommended by Kesting.[4] To date, cellulose triacetate (CTA) has been the polymer of choice for polymer inclusion membranes, because it is easily workable and readily available as a component of food packing, films, molding, surface coatings, lacquers, fibers, reverse osmosis materials, and filtration systems.[5–11] However, hardly any research was aimed at improving the adhesion properties of CTA film by Ar plasma treatment. Nowadays, Liquid crystal displays (LCDs) are being widely used in notebook computer, mobile telephone display, 3D display, micro display, car navigation system, and so on. Polarizing film is indispensable for LCD.

Polarized film can be achieved by taking the following two steps, soaking oriented poly(vinyl alcohol) (PVA) film in iodine (I_2) and dichromatic dye solution and then disposing the iodine molecules and the dye molecules in the stretching direction of the PVA film.[12–14] Iodine molecules and dye molecules, which are dichromatic, absorb optical waves oscillating in the stretching direction of a PVA film and transmit optical waves normal to the stretching direction. Iodine-polarized film is a polarized film for high quality LCD, which require high transmissivity and excellent polarization property. This polarized film uses iodine, which is highly dichromatic, to allow the transparent PVA film to absorb a visible ray.[15–17] Most of polarized films used in LCD are iodine-polarized films. But polarizing films have a serious problem of iodine sublimation under high temperature and humidity. Thus, for improving adhesive ability of the CTA film attached to the PVA film, we considered the effect on durability improvement of the CTA film by Ar low temperature plasma

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treatment. CTA films were prepared by market product. These films are treated with RF plasma. Ar is used as discharge gas, since it was widely used nowadays. After gas plasma etching, the surface structure of the films is analyzed by ESCA, atomic force microscopy (AFM), peel strength test, and surface roughness. Furthermore, the wetting properties of the CTA film treated with Ar plasma are studied by water contact angle measurement.

EXPERIMENT

Materials

Cellulose triacetate (CTA; containing 43.8 wt % of acetyl) films were provided from ACE Degitech, Korea. The number average degree of polymerization and saponification value was 1700 and 99.9%, respectively. The thickness of the films was found to be 80 μm. Ethanol was purchased from Duksan Pure Chemical, Korea. These chemicals were used without further purification. For rinsing and contact angle measurements, deionized water was used. Ar gas of purity higher than 99.99% was used as the processing carrier gas.

Preparations of the CTA

The samples used in this study were CTA films, whose sizes were 10 cm × 25 cm. For plasma treatment, the CTA film was conditioned in a desiccator, vacuum compression in which the silica gel is, for 24 h or more after dried in vacuum of 40°C for 12 h. Before the plasma treatment, these samples were washed by cleaner with ethanol, and thoroughly dried in air.

The gas pressure was 0.5 torr and etching was conducted in RF generator with variable generating power from 50 to 200 W. The films were exposed to the plasma for various treating times ranging from 3 to 11 min (3, 5, 7, 9, and 11 min) while maintaining a constant gas flow through the reactor.

Plasma treatment of the CTA

The apparatus used for plasma treatment is glow-discharge etching system and coupled with RF-generator (Max. Power; 650 W) of 13.56 MHz. The capacitively coupled chamber used for the plasma treatment is shown in Figure 1. The characteristics of the plasma devices are given as follows:

Reactor capacity: 0.3 m^3 (130 L)
Electrode mode: Parallel-plate internal electrode
Reactor type: Cylindrical chamber
Electrode size: 175 mm × 550 mm × 3 mm
Vacuum pump: 200 L/min

Surface characterization of the film by ESCA

The plasma-chemically etched structure of the CTA films was analyzed by ESCA. The measurements

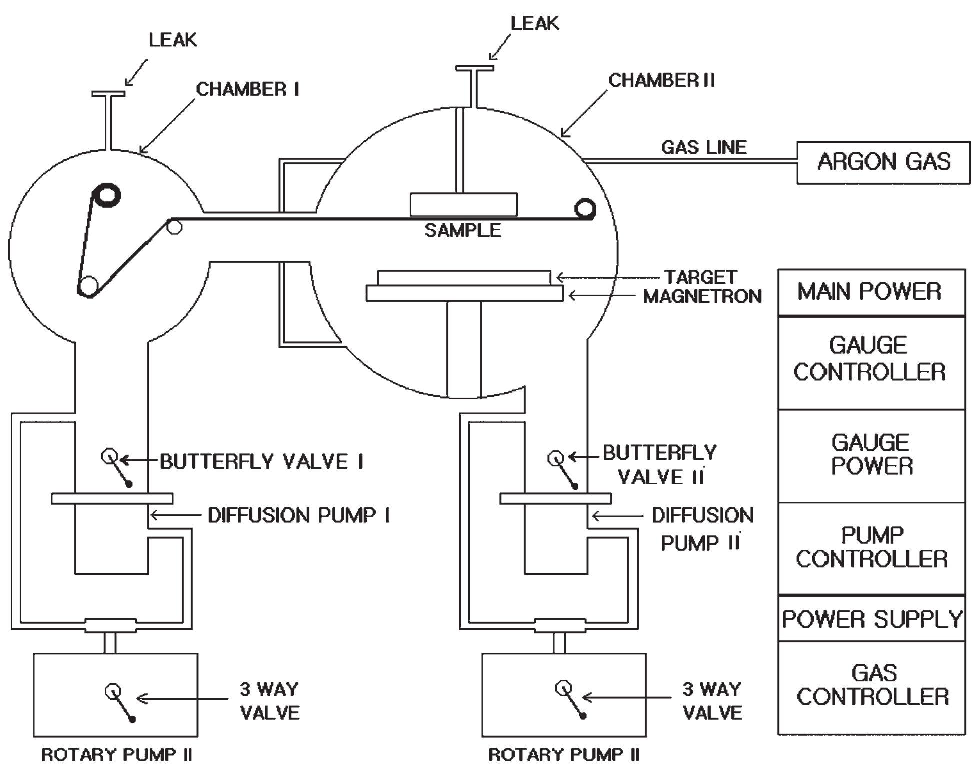

Figure 1 Schematic draws of plasma devices.

were performed with a MultiLab2000, THERMO VG SCIENTIFIC (UK) using an Mg/Al Twin X-ray source. A spot size of 1 mm was analyzed. The pressure was 5×10^{-10} mbar. From the wide scanning ESCA spectra, intensities of the C_{1S}, O_{1S}, and N_{1S} were determined.

Atomic force microscopy

To investigate the surface morphology of the CTA films by the plasma treatment, AFM observations were done using a Digital Instruments AFM with a nanoscope IIIa controller (Digital instruments, USA). The conditions are shown in as follows:

Data scale: 50.00 nm
Scan size: 1.000 μm
Scan rate: 0.4002 Hz, 0.5003 Hz
Mode: tapping AFM

Roughness

The surface roughness of the CTA films was observed using an atomic force microscope analysis. Roughness (R_{rms}, root-mean-square) average of height deviations, taken from the mean data plane, was calculated from the equation as follows:

$$R_{rms} = \sqrt{\frac{Z_1{}^2 + Z_2{}^2 + Z_3{}^2 + \cdots + Z_n{}^2}{N}}$$

where Z is the height of each peak.

Peel strength

The adhesion was determined by a peel test. Peel strength of the plasma-treated films was measured with using Universal testing machine Z-005, Zwick, Germany, and the method was processed by the following equipment shown in Figure 2. The films for the peel strength test were prepared in the following way. In the first step, CTA film was attached with an insulating tape and cut by 3.2 cm × 15 cm size. After that, the film was put between the glass plates (3 mm of thickness) and kept loading 3 kg for 2 h.

Contact angle measurement

Contact angle analysis was performed on OCA 20 system (DataPhysics Instruments GmbH, Filderstadt, Germany). Prior to plasma treatment, CTA films were preserved in a vacuum desiccator and characterized by static water contact angle measurements using the sessile drop method. Ten different spots for each new fresh water single drops (1 μL) of deionized water were dropped onto the surface of the same CTA film with an electronically regulated pipette and measurements were determined 10 min after drop deposition, to give the average value of contact angle with an error less than ±2° at 25°C.

RESULTS AND DISCUSSION

ESCA analysis

The chemical surface composition of plasma-treated CTA films was investigated by ESCA that could contribute to any increased adhesion. The results are presented in Table I. The experimentally calculated O_{1S}/C_{1S} of untreated CTA film is 0.69, which agrees quite similar with the theoretical value of 0.7. Furthermore, by increasing the plasma treating time, it confirmed that the CTA surface was slightly oxidized during continuous Ar plasma treatment, which CTA film decreases the carbon contents while increasing the oxygen content, it indicative O_{1S}/C_{1S} increased up to 96.2% (5 min) from 68.9%. Moreover, from these chemically reasonable contribution, it makes clear that the CTA films were obviously etched, which is in agreement with the result from next roughness val-

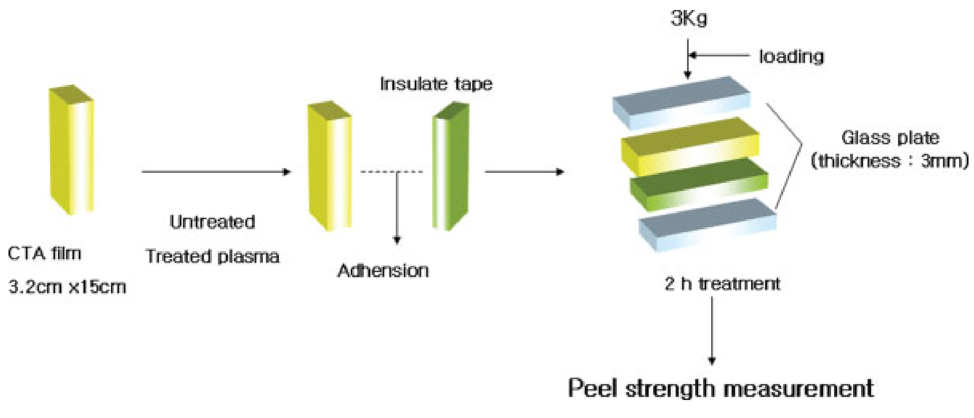

Figure 2 Skim of peel strength measurement. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
ESCA Data of Untreated and Plasma-Treated CTA Films at 100 W power

Treated time (min)	Relative peak area (at %)			
	C_{1S}	O_{1S}	N_{1S}	O_{1S}/C_{1S}
0	59.1	40.7	0.2	68.9
1	59.3	40.1	0.6	67.6
5	50.0	48.1	1.9	96.2
9	51.8	46.2	2.0	89.2

ues, but prolonged treatment times did not increase O_{1S}/C_{1S}.

Surface analysis of the CTA films by AFM

Figures 3–6 show the effects of RF power; these results indicated that the CTA film was certainly etched in Ar plasma. Each surface etched rate increased with an increase in RF power. The untreated, CTA films have smooth and flat structure. The surface of the film gradually changes into an irregularity structure. Unevenness could not be observed in the surface, which is normal for this kind of untreated film. Furthermore, the surface of untreated CTA films is quite rough, which is caused by the presence of plasma in the film. When CTA surfaces were treated by Ar plasma with 50 W RF power, as shown in Figure 3, no surface structural change could yet be observed during 5 min. During longer plasma treatments, the surface roughness of the film slightly increased as a result of etching. The plasma was further exposed at the surface and some unevenness started to appear and become large more than the first. Figure 4 shows that the changes of surface structure of CTA films during Ar plasma treat-

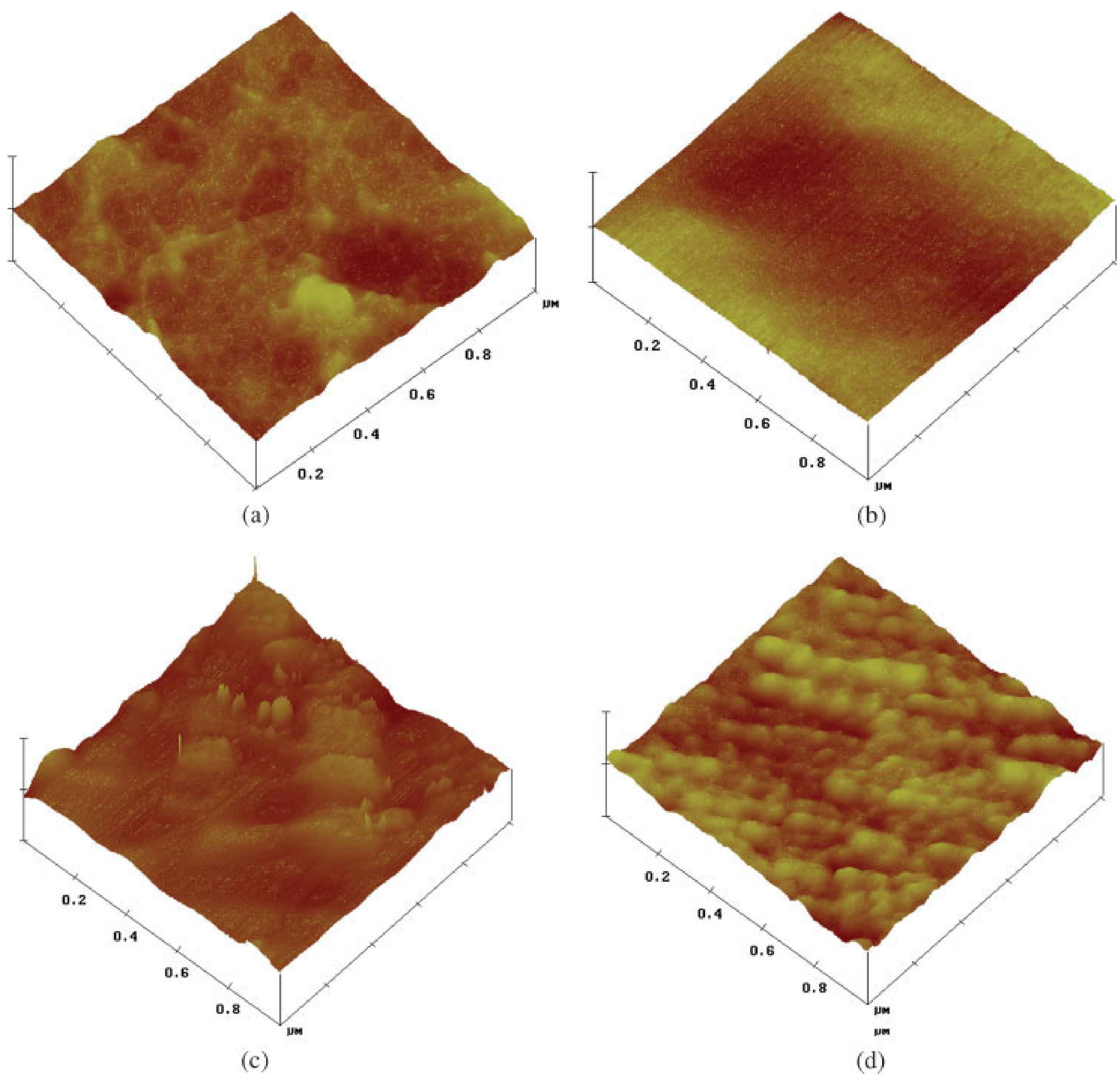

Figure 3 AFM images of CTA film untreated and treated with Ar low temperature plasma at 50 W: (a) untreated, (b) 5 min, (c) 7 min, (d) 9 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

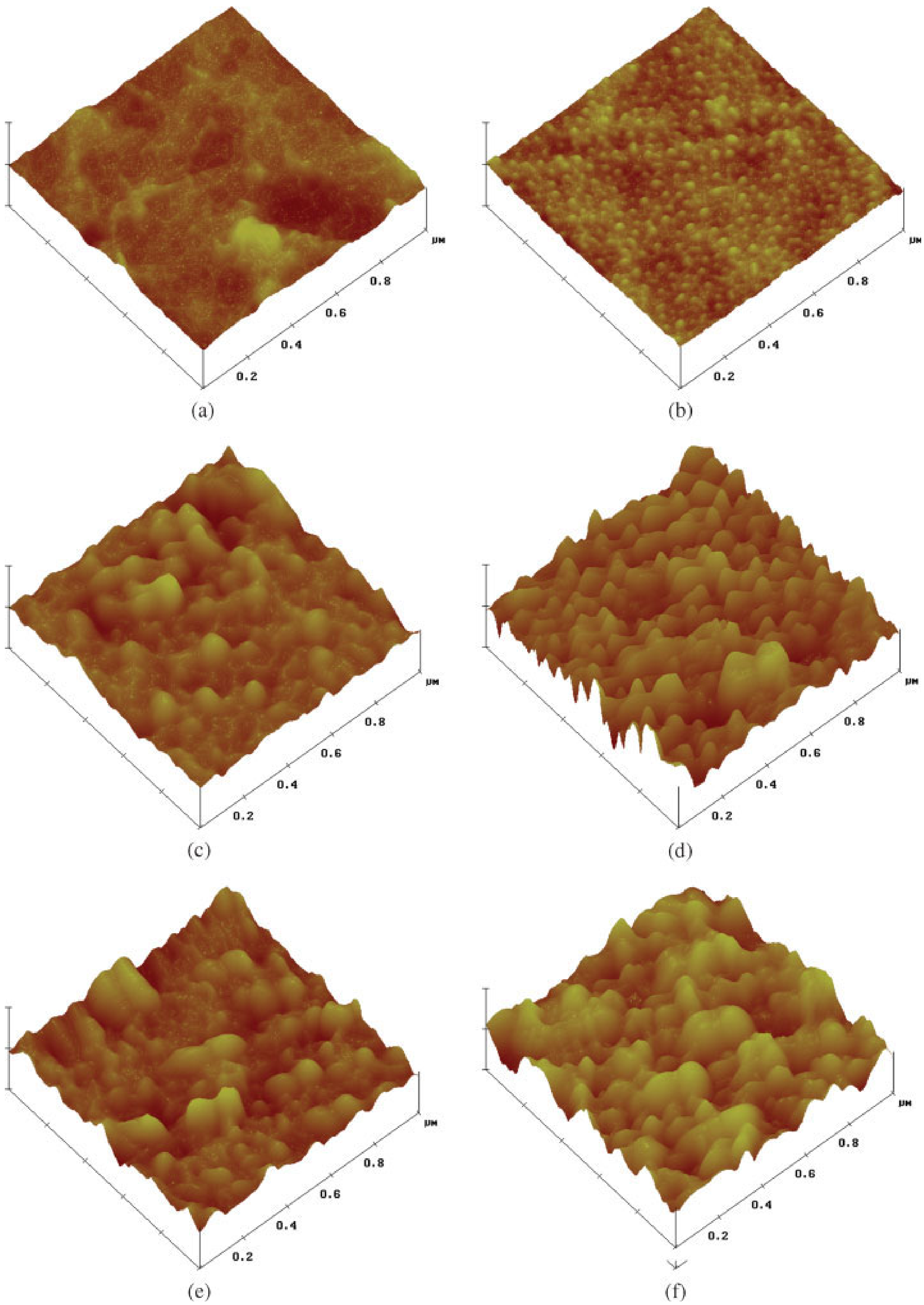

Figure 4 AFM images of CTA film untreated and treated with Ar low temperature plasma at 100 W: (a) untreated, (b) 3 min, (c) 5 min, (d) 7 min, (e) 9 min, (f) 11 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

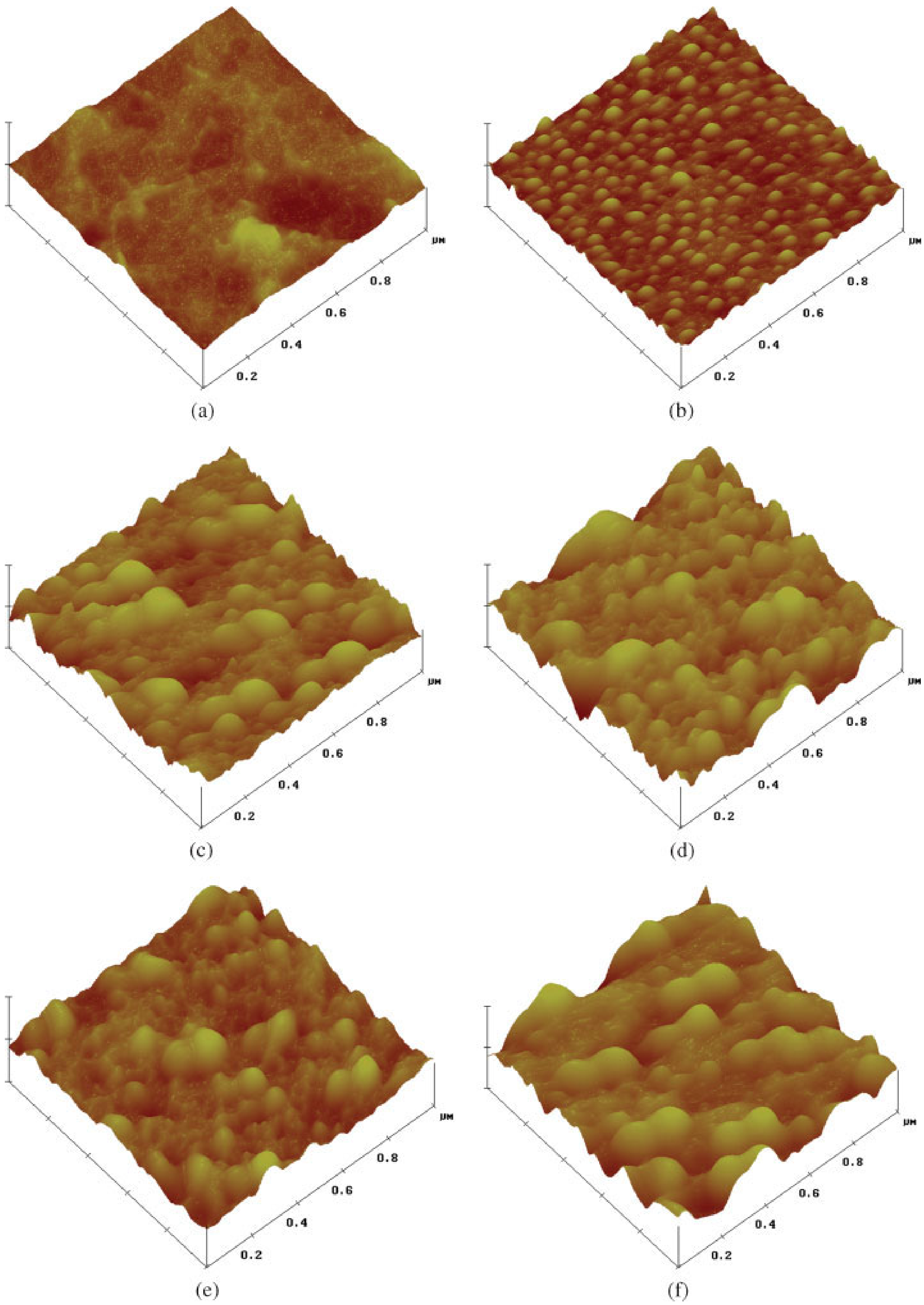

Figure 5 AFM images of CTA film untreated and treated with Ar low temperature plasma at 150 W: (a) untreated, (b) 3 min, (c) 5 min, (d) 7 min, (e) 9 min, (f) 11 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

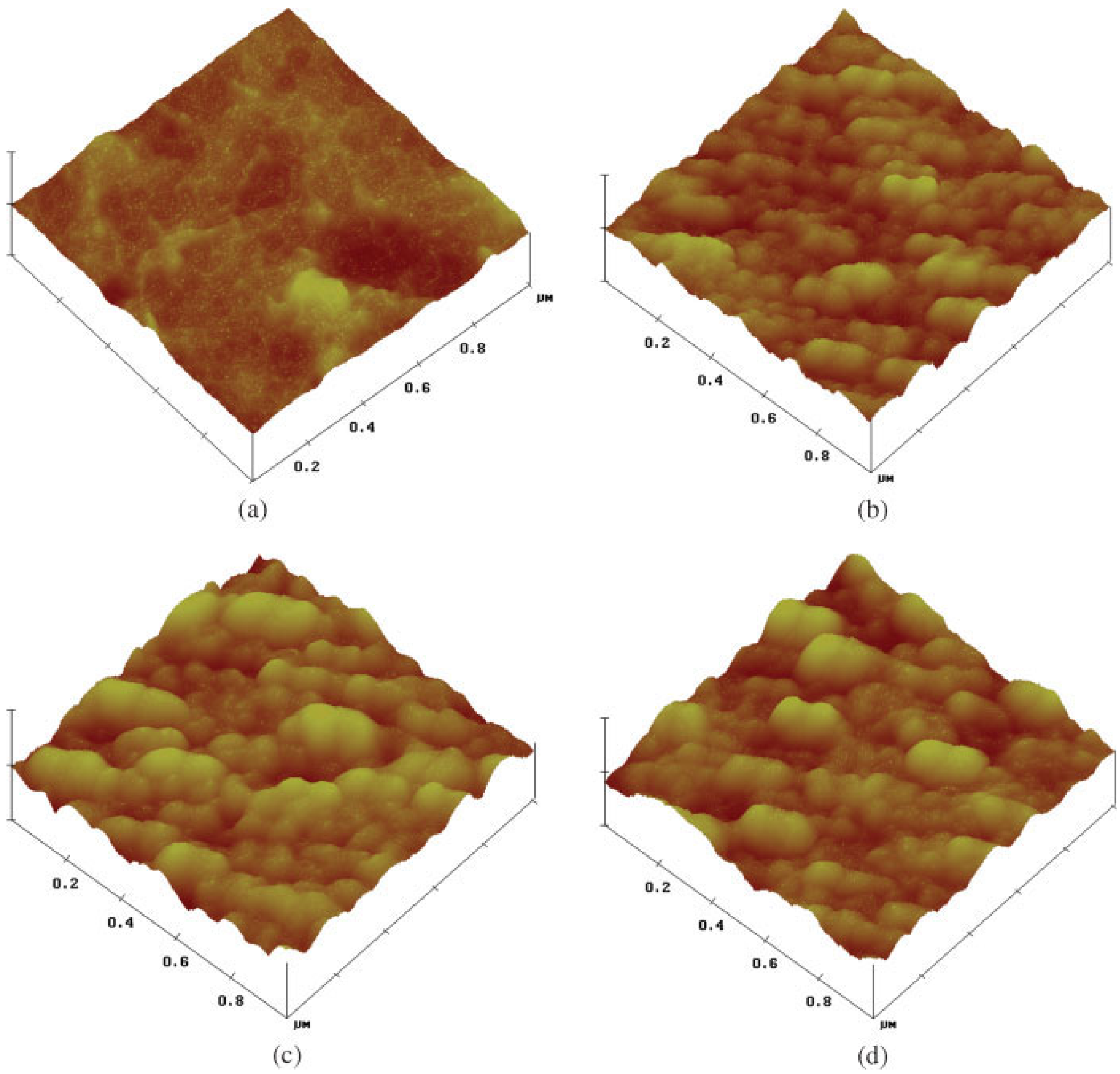

Figure 6 AFM images of CTA film untreated and treated with Ar low temperature plasma at 200 W: (a) untreated, (b) 5 min, (c) 7 min, (d) 9 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ment were quite similar from those of Figure 5 (150 W). Unevenness is heavy in 5 min than in 3 min, generally small and close unevenness occurs until 3 min. There was considerable surface structural changes that took place between 5 and 9 min of treatment time, due to gradual etching of the surface. But no significant differences of surface structure could be found in continuously treated (9 min) CTA films. It was seemed because the re-deposition occurs. That is to say, etched CTA films can be reactivated in plasma and re-deposition took place.[18,19] Figure 5 shows the images obtained from CTA film treated at 150 W power. As time goes by, the size of unevenness became large. After 7 min, there is no big change. When it is the same treatment time, if we compare with Figures 3 and 4, the size of unevenness changes according to output power. As shown in Figure 6, CTA film shows the strongly increased unevenness induced by the Ar even after such short treatment times. This behavior can be attributed to strong surface activation. If we compare 100 W with 150 W, clear difference is seen in which the output is confirmed by the image in first 3 min. But, we know that change of the surface-treated long time plasma is no clear change (see after 7 min). AFM studies indicate that no considerable change of surface morphology occurred up to 3 min of Ar treatment time, but a considerable unevenness of surface structure resulted from treating time after 7 min.

Peel strength

The peel test was usually used for assessing the extent of adhesion ability between two materials.[20] Peel strength measurement was used to study the adhesion properties of the surface of plasma-treated CTA film. Namely, the adhesion ability was deter-

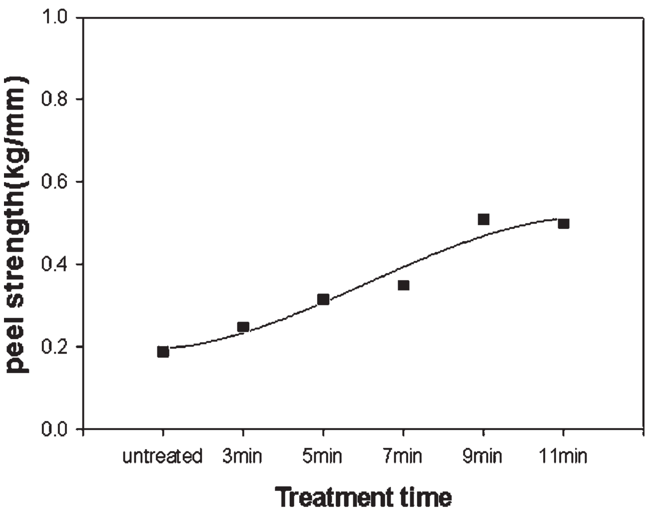

Figure 7 Changes of peel strength of plasma-treated CTA films.

mined by peel strength test. Figure 7 shows the results of peel tests of plasma-treated and untreated CTA films (150 W of power). Since the adhesive strength is commonly influenced by the physicochemical structure, as expected, an Ar plasma treatment initially slightly increased peel strength of CTA films against the surface, but after 9 min, the peel strength decreased below that of the maximum (100 W). The results suggested that the polar component parts of the CTA surface decreased considerably. Peel test indicates that the plasma-induced changes increases adhesion. Adhesive strength does not increase in proportion of plasma treatment time.

Surface roughness (R_{rms})

Plasma treatment is effective to change the polymeric materials. It is expected that the plasma treatment causes roughness of the film surface and leads to the modification of the film. The surface roughness can enhance the anchor effect, and this has relatively a strong influence on the adhesive property.[21] Table II shows the root-mean-square roughness values of plasma-treated CTA films calculated by eq. (1). The surface of Ar-treated CTA film samples became rougher than those of untreated films under 100 and 150 W RF power, especially. The roughness values increased with treatment time, but after 7 and 9 min, it decreased at 100 and 150 W RF power, respectively, such as peel strength values and AFM images. Therefore, it was noted that the higher roughness of the films was also a reason for their higher peel strength.

It is evident that the plasma treatment of CTA films actually changes their surface structure. The extent of surface structural changes can be prepared by varying the plasma treatment conditions, such as the control of RF power and the treatment time.

Contact angle

The wettability of the surfaces of the CTA film was determined by measuring the contact angle between water droplets and the plasma-treated surfaces. Figure 8 shows the results of water contact angle by sessile and captive drop methods, when treated in Ar plasma for various duration of time at different output power. As shown in figure, the contact angle was found to decrease from 66.7° for untreated surfaces to 37.2° for treated surface with 100 W RF power. It is seen from the figure that there is a decrease from the start to 7 min (both power), due to an improvement in wettability in the CTA surface, but increased after 7 min. It is pointed out that the etching reaction is not so much closely remarkable in the crystalline region as in the amorphous region from the CTA surfaces. When CTA films surfaces were treated with low temperature plasma, their surface free energy increased and wettability improved. It is obvious from the results that the improved wettability may be due to cohesion of the making of hydrophilic groups, molecular changes, morphological changes, and increased roughness of the CTA surface.

CONCLUSIONS

CTA films were treated with Ar low temperature plasma and the effect of the treatment on the functional property of the films was investigated. Through the plasma treatment, we tried to improvement iodine-sublimation inhibition and the adhesive property of the CTA film, which is attached to PVA film using polarizing film. The surface roughness value by AFM analysis increased with treating time until 7 min but decreased thereafter. The adhesive property by peel strength increased especially for 7 min after plasma treatment. To assess the wettability at the surface of the plasma-treated CTA film, the water contact angle

TABLE II
Roughness Values (R_{rms}) of the Plasma-Treated CTA Films

	R_{rms}			
Time (min)	50 W	100 W	150 W	200 W
Untreated	1.279	1.279	1.279	1.279
3	–	2.517	2.347	–
5	2.451	4.812	6.404	3.994
7	2.794	8.871	6.759	5.163
9	2.658	7.372	7.993	4.955
11	–	5.420	5.095	–

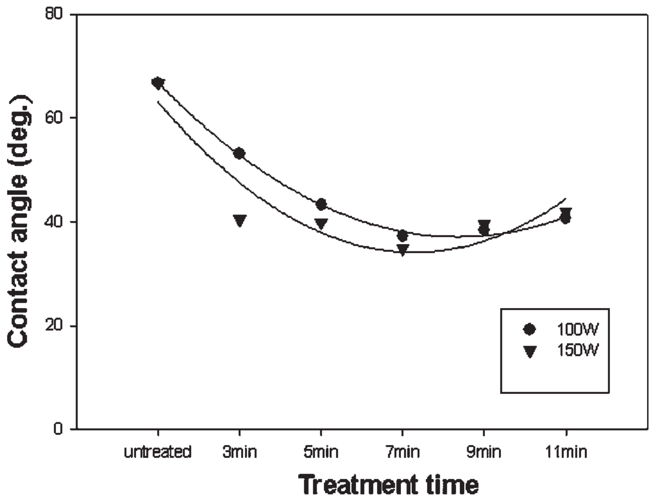

Figure 8 Changes of contact angle of plasma-treated CTA films.

measurement was determined. Treatment with plasmas from Ar gas enhanced the wettability, introduced roughness effect, and decreased the water contact angle at the surface of the CTA film. From these results, it seems that the Ar plasma treatment causes a change in the CTA surface. Thus, by controlling the plasma treatment conditions like RF power and treatment time, these films could be of great use for not only in the adhesion improvement but also in the industrial applications.

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