

Polymer Surface Modification: Relevance to Adhesion,

> *Volume 5* Edited by K.L. Mittal

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Polymer Surface Modification: Relevance to Adhesion

Volume 5

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# Polymer Surface Modification: Relevance to Adhesion Volume 5

Edited by K. L. Mittal



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# Preface

This book documents the proceedings of the Sixth International Symposium on Polymer Surface Modification: Relevance to Adhesion held under the aegis of MST Conferences at the University of Cincinnati, Cincinnati, OH, June 11–13, 2007. The premier symposium on this topic was held in Las Vegas, Nevada, November 3–5, 1993, the proceedings of which were properly chronicled [1]. The second symposium in this series was held under the auspices of MST Conferences in Newark, NJ, May 22–26, 1999 which was also documented in a book form [2]. Apropos, it should be recorded that the third symposium in this vein was organized also by MST Conferences in Newark, NJ, May 21–23, 2001 but, for a variety of reasons, the proceedings of this event were not documented in the form of a book. The fourth symposium on this topic was also organized by MST Conferences in Orlando, FL, June 9–11, 2003 the proceedings of which were documented in a hard-bound book [3]. The fifth symposium in this series was also held under the auspices of MST Conferences in Toronto, Canada, June 20–22, 2005 which was also incarnated in a hard-bound book [4].

Even a cursory look at the literature will evince that recently there has been a burgeoning interest in the topic of polymer surface modification. This is ascribed to the fact that polymers are used in a wide variety of technologies for a myriad of purposes and whenever a polymer comes in contact with other materials, its surface characteristics become of paramount importance. By suitably modifying polymer surfaces, one can obtain the desired surface traits without tempering with the innate bulk properties.

There are many aspects to polymer surface modification, viz., technique to modify, monitoring of surface chemical and morphological features, and life of treatment. There has always been a keen interest in devising new, improved and quicker ways to modify polymer surfaces and in inventing methods to prolong the life of surface treatment as the limited life of a surface treatment is a drawback and poses limitations in the use of surface modified polymers. Also it should be stressed that currently there is tremendous interest in the use of atmospheric pressure plasma (APP) treatment and all signals indicate that further developments in this particular technique will take place at an accelerated pace. The technical program for this symposium contained 40 papers reflecting both overviews and original research contributions. The presenters represented many and varied disciplines and organizations and hailed from many corners of the globe. The various aspects (as mentioned above) of polymer surface modification were accorded due coverage.

Now turning to this volume, it contains 22 papers, others are not included for a variety of reasons, which were rigorously peer-reviewed, revised (some twice or thrice) and edited before acceptance and inclusion in this volume. So it should be recorded that this book is not a mere collection of papers — which is normally the case with many proceedings volumes - rather it represents the highest standard of publication and is of archival value. The book is divided into three parts as follows: Part 1: Surface Modification Techniques; Part 2: Interfacial Aspects and Adhesion; and Part 3: General Papers. The topics covered include: various techniques for surface modification including plasma (both vacuum and atmospheric pressure), ozone, photografting, UV photo-oxidation, laser, use of charged particles, and others for a variety of polymers; longevity of surface treatment; hydrophobic recovery; fabrication of high-density polymer nano-dots; immobilization of organometallic catalysts on textile carrier materials; polymer membranes and their antifouling properties; electroless metallization of polymers; effects of surface modification on interfacial shear strength of composites, cord/rubber adhesion, adhesion of UV-curable coatings, and attachment of hyperbranched polymers; plasma polymerization; block copolymers; and application of plasma technology in decontamination of heat-sensitive polymer surfaces.

This volume and its predecessors [1–4], containing about 2300 pages, provide a repository of current information and reflect the cumulative wisdom of a legion of researchers in this exciting and technologically highly important arena. As new and improved ways to modify polymer surfaces are developed, more new and exciting application vistas will emerge. Also the information covered in this set of five volumes should help spur further activity in this field. In essence, this book and previous volumes in this series should be of interest and value to anyone with a desire or need to learn the latest R&D activity in this domain, and the information contained here should be very valuable in deciding the optimum surface modification technique for his/her particular requirements.

### Acknowledgements

Now comes the pleasant task of thanking all those who helped in this endeavor. First of all, I (on behalf of MST Conferences) would like to express my sincere gratitude to Prof. Wim J. van Ooij of the University of Cincinnati for sponsoring this symposium as well as for his generous support. Prof. van Ooij and his colleagues were extremely helpful during the course of this symposium and we appreciated it very much. Then, as usual, it is a pleasure to express my thanks to my colleague and friend, Dr. Robert H. Lacombe, for taking care of the requisite details entailed in organizing this symposium. Thanks for extended to all the contributors to this book for their interest, enthusiasm, patience and cooperation without which this book would not have been in the hands of the readers. The unsung heroes (reviewers) are profusely thanked for their time and efforts in providing many valuable comments which contributed significantly towards improving the quality of manuscripts. Finally, my appreciation goes to the staff of VSP/Brill (publisher) for giving this book a body form.

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# Part 1

# **Surface Modification Techniques**

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# Plasma Bromination — A Selective Way to Monotype Functionalized Polymer Surfaces

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#### Abstract

In contrast to other plasma processes, the bromoform plasma functionalizes polymer surfaces very selectively with C–Br groups in high yield. Other brominating plasmas such as the use of elemental bromine and *tert*-butyl bromide or the deposition of Br-bearing plasma polymers from allyl bromide and vinyl bromide show much lower selectivity and yield. The bromoform process gives yields in C–Br in the range of 20–100 C–Br groups per 100 C accompanied by only 1–3 post-plasma introduced O-functionalities per 100 C. Br-containing thin films deposited from the allyl bromide plasma exhibit about 20–24 C–Br groups/100 C and more than 10 oxygen-containing groups per 100 C.

C–Br groups serve as anchoring points for chemical grafting of OH and NH<sub>2</sub> groups terminated molecules, oligomers and pre-polymers used as spacers between deposited metal layers and polymer.

#### Keywords

Functional groups, polymer surfaces, plasma bromination, grafting, spacer, selective plasma process

### 1. Introduction

The lack of selectivity of plasma processes for the introduction of monotype functional groups of sufficient density onto polymer surfaces is a strong limitation for the broader application of all plasma processes. In particular, the broad variety of plasma products and the post-plasma oxygen attachment are strong hindrances for specific graft reactions with plasma-introduced functional groups at the polymer surface. For grafting of molecules and oligomers onto the polymer surface, monotype functional groups are needed as anchoring points for their covalent grafting. Convenient monotype functional groups for grafting are amino, aldehyde, epoxy, carboxylic acid, sulfonic acid, double bonds, or other groups.

Selective plasma processes should dominantly or exclusively produce only one type of functional groups accompanied by only very low concentrations of other

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types of functional groups derived from the plasma gas or by post-plasma reaction of oxygen with the plasma-produced trapped radical sites over long durations such as weeks or months [1, 4].

Such selective plasma processes occur very seldom using the plasma technique. One reason is the high energy level of electrons in the plasma with several tens of electron volts in the high-energy tail of the electron energy distribution. These high energies may exceed the C-C and C-H bond energies in polymers by tenfold [5]. Therefore, controlled and selective functionalization reactions are not possible. Moreover, the high numbers of different atoms and fragments in the plasma and their attachment onto the polymer surface is also responsible for the detected broad variety of different types of functional groups. Additionally, the plasma vacuum UV irradiation of the polymer surface produces further changes in functional groups and structure of the polymer. Therefore, the polymer surface functionalization in any gas plasma results most often in the formation of a broad number of different functional groups (non-specific functionalization) (cf. Fig. 1). Nearly all plasmaactivated processes are radical reactions and the additional plasma UV radiation further produces radicals at the surface, in near-surface layers, or even in the bulk of polymers [6]. Thus, the remaining unsaturated and metastable trapped radicals are the reason for post-plasma oxidation by molecular oxygen from the ambient air. This oxidation is self-accelerating, known as auto-oxidation, which is strongly nonselective and leads to the appearance of a broad spectrum of O-functional groups.



Figure 1. Schematics of polymer surface functionalization.

Therefore, the need for a selective and specific surface functionalization is evident (Fig. 1).

The non-specific (non-selective) surface functionalization is the normal occurrence, for example, using the oxygen, ammonia, carbon dioxide plasmas. Any optimization of the plasma parameters does not make sense because the selectivity of the functionalization and, therefore, the production of monotype functionalized polymer surfaces can only be marginally improved. There is the general contradiction between high energy introduced from the plasma on the one hand and the low energies necessary to dissociate chemical bonds or to make them reactive on the other hand. Particularly, the high-energy tail of the electron energy distribution function in the plasma exceeds the binding energies in polymers significantly. The ionization energies and also the corresponding energies of other plasma-relevant features such as metastables, the short wavelength of radiation, the continuous delivering of energy into the plasma by the electromagnetic field make it difficult to adjust the two opposite energy requirements, that of sustaining the plasma and that of activating polymer bonds. Moreover, the continuous energy input into the electrical discharge plasma produces a high energy flow to each gas molecule in the plasma (10–1000 eV as calorimetrically measured [6]). Using the pulsed or remote plasmas as well as lowering the wattage may limit the energy transfer to the molecules, but only marginally.

On the other hand, both the chemistry and the thermodynamics also play important roles. Thus, the dissociation energy, chain propagation energy, or heat of formation of the new products formed must be balanced. The dissociation energies of C–H bonds and C–C backbone bonds are very similar (385–411 kJ/mol and ca. 370 kJ/mol). The heat of HBr formation is 363 kJ/mol and, therefore, the bromination is chemically endothermic [7]. Moreover, the disruption of C–H and C–C bonds needs nearly the same energy (cf. equations (1) and (2)):

$$\cdot Br + R - H \to R \cdot + H - Br \tag{1}$$

$$\cdot Br + -CH_2 - CH_2 - \rightarrow -CH_2 \cdot + Br - CH_2$$
<sup>(2)</sup>

Thus, the H substitution by Br is always accompanied by the backbone scission with nearly the same probability.

Generally, polymer surface modifications with halogens are possible by exposure to halogen-atoms producing plasmas such as  $CF_4$ ,  $CHF_3$ ,  $CCl_4$ ,  $CHCl_3$ ,  $CHBr_3$ ,  $CH_2I_2$ , etc. Because of the significantly lower ionization potentials of bromine and iodine precursor molecules ( $CH_2I_2$ ,  $CHBr_3$ ) in comparison to those of fluorine or chlorine precursor molecules ( $CF_4$ ,  $CHF_3$ ,  $CCl_4$ ,  $CHCl_3$ ) the bromine and iodine producing plasmas should possess a lower electron energy level. Therefore, the plasma-induced degradation of polymer surface layers associated with auto-oxidation for weeks or months should be minimized using  $CH_2I_2$  or  $CHBr_3$ containing plasmas [8, 9]. Bromoform (HCBr<sub>3</sub>) has a sufficient vapour pressure for using it in plasma processing. Under plasma conditions the bromoform molecule should dissociate as proposed:

$$HCBr_3 \to Br \cdot + \cdot CHBr_2 \tag{3}$$

$$\cdot \text{CHBr}_2 \to \cdot \text{CHBr} + \cdot \text{Br} \tag{4}$$

$$HCBr_3 \to H \cdot + \cdot CBr_3 \tag{5}$$

The dissociation energy of the C–H bond is higher than that of C–Br. Therefore, equations (3) and (4) are more probable.

A few plasma-initiated functionalization reactions are relatively selective because of the absence of a chemically exothermic reaction. The liberation of an excess of reaction enthalpy leads to thermal bond scissions in polymers, the formation of radicals and the post-plasma addition of oxygen onto these radicals. The chemical fluorination of polymers is exothermic and is, therefore, accompanied by radical formation and oxygen introduction [9]. The chemical bromination of aliphatics is usually endothermic. Therefore, the polymer bromination is exclusively initiated by plasma-produced bromine atoms. Bromine atoms are suitable radical scavengers. Thus, any possibility for side-reactions with oxygen is suppressed. Bromoform (CHBr<sub>3</sub>) is a well-suited precursor for the production of free bromine atoms in the plasma. This bromination is a one-way reaction leading to bromine monotype surface functionalization with a covalent C–Br bond.

All halogen elements want to complete their outer electronic shell by capturing one electron. Thus, they can reach the same energetically stable electron shell as the noble gases. Therefore, the most favourable reactions are only the formation of C–X or X<sup>-</sup>. Halogen anions X<sup>-</sup> are most often not present at polymer surfaces. Another side reaction is the trapping of radicals and their slow auto-oxidation as explained before [10].

Br-functionalized polypropylene surfaces were used for a number of wetchemical graft reactions following synthesis routes introduced by Williamson or following Gabriel to modify polymer surfaces [7]:

$$\equiv C-Br + HO-[CH_2]_n - OH \rightarrow \equiv C-O-[CH_2]_n - OH \quad \text{Williamson}, \qquad (6)$$

$$\equiv C-Br + H_2N-[CH_2]_n - NH_2 \rightarrow \equiv C-NH-[CH_2]_n - NH_2 \quad \text{Gabriel.}$$
(7)

The grafted spacer molecules possess hydroxyl or primary amino end groups capable to react with (deposited) metal atoms or chemical reagents. The chain length of grafted molecules can be varied from  $[CH_2]_2$  to  $[CH_2]_{>100}$ . However, in the case of higher chain lengths (may be  $[CH_2]_{>6}$ ) the graft density is limited. If the chain length grows, the chain begins to coil along the surface. Therefore, most of anchoring points at the polymer surface are blocked by the voluminous coiled spacer molecule. Such modified surfaces should improve the adhesion to deposited metals or the compatibility to biological systems by covalent linking *via* flexible longchain spacer molecules, which should be able to overcome any mechanical stress along the metal–polymer interface. These aliphatic or siloxane-like spacer molecules should also repel water molecules from the interface and avoid any hydrolysis of the covalent metal–polymer bonds.

High bromine concentrations can also be achieved by depositing brominecontaining plasma polymers [1, 17]. Vinyl bromide and allyl bromide are suitable precursors for bromine-rich thin film deposition. This process was also investigated in this study (cf. Fig. 1).

### 2. Experimental

Polypropylene foils of different thicknesses (10 and 1500  $\mu$ m) were used as substrates (Goodfellow). To remove residual slip agents, light stabilizers, antioxidants etc. the polymer samples as received were intensively washed in an ultrasonic bath with diethyl ether for 15 min.

To avoid problems during graft-chemical processing of the plasma brominated polymer substrates, loosely bonded bromine-containing fragments at the brominated surfaces were removed by applying a second intense wash process in tetrahydrofuran (THF) for 2 h (cf. Fig. 1).

The plasma bromination was performed in a glass bell jar reactor with internal electrodes working with 13.56 MHz frequency in the pulsed (duty cycle 0.1) or in the continuous-wave (c.w.) mode. The plasma equipment is shown schematically in Fig. 2.

The pressure within the plasma reactor was varied between 2 and 25 Pa, the power input in the range of 10–300 W and the treatment time between 2 and 600 s. The plasma gases (vapours) used were bromoform (CHBr<sub>3</sub>), *tert*-butyl bromide



Figure 2. Plasma equipment used.

 $((CH_3)_3C-Br)$  and bromine (Br<sub>2</sub>). Allyl bromide (CH<sub>2</sub>=CH-CH<sub>2</sub>Br) and vinyl bromide (CH<sub>2</sub>=CH-Br) were used as plasma polymer layer-forming monomers. All liquids were evaporated and fed to the plasma reactor through heated tubes. The polymer substrate was mounted on a stainless steel plate or onto a rotating steel cylinder that rotated in the plasma zone.

The introduction of bromine onto the polymer substrate surface was controlled by monitoring C<sub>1s</sub>, O<sub>1s</sub>, Br<sub>3d5/2</sub> or Br<sub>3p3/2</sub> XPS peaks (XPS: X-ray Photoelectron Spectroscopy). The spacer-grafted polymer surfaces were also characterized using XPS. The spectrometer used was a SAGE150 (Specs, Berlin, Germany) equipped with channeltrons and using non-monochromatic Mg K<sub> $\alpha$ </sub> radiation with 11 kV and 250 W settings at a pressure  $\approx 1 \times 10^{-7}$  Pa in the analysis chamber. XPS spectra were acquired in the constant analyzer energy (CAE) mode at a 90° take-off angle.

The grafting onto brominated polypropylene foils was carried out by immersing the foil in liquid phase using tetrahydrofuran (THF) as solvent, diols, glycols or diamines and sodium metal (0.5 mol) [7]. Grafted molecules were aliphatic diols of different chain lengths ( $[CH_2]_2-[CH_2]_{12}$ ) and glycols ( $[CH_2]_2-[CH_2]_{100}$ ) as well as aliphatic diamines ( $[CH_2]_2-[CH_2]_6$ ). The addition of sodium to diols forms mono sodium alcoholates. Amines reacted without addition of sodium because of their high reactivity caused by their high nucleophilicity.

The usual processing consisted of immersing the plasma brominated polypropylene foils ( $10 \times 14$  cm) in equimolar quantities of diols or glycols and sodium in anhydrous THF. Thus, mono sodium alcoholates or glycolates were formed. NaI was added as catalyst. Sodium glycolates and sodium alcoholates reacted 48 h with the brominated polypropylene surface, amines 8 h. After finishing the chemical process, the grafted polymer samples were submerged successively for 10 min in THF, 10 min in HCl/water, 10 min in pure water,  $2 \times 10$  min MeOH/water, and  $2 \times 10$  min in methanol.

For unambiguous identification and quantification using XPS, the OH end groups of grafted spacers were derivatized with trifluoroacetic anhydride (TFAA) (additionally checked using m-trifluoromethylphenylisocyanate (TMPI) and amino end groups with pentafluorobenzaldehyde (PFBA) or 4-trifluoromethylbenzaldehyde (TFMBA) [11, 12, 18]. The samples were exposed to the derivatizing reagent in vapour-saturated atmosphere for 15 min or in the case of isocyanate for 3 h. The number of functional groups was calculated from the percentage of the introduced fluorine ( $F_{1s}$  peak) and the theoretical stoichiometry of the derivatized polymer. It was assumed that the XPS-analyzed outermost layer ( $\approx$ 3 nm) was uniformly derivatized. This was confirmed using FT-IR–ATR spectroscopy. Moreover, the completeness of the derivatization and the absence of non-consumed functional groups in the deposited polymer layer were also estimated using the ATR technique. The C<sub>1s</sub> peak fitting (293.6 eV –CF<sub>3</sub>, 289.2 –COOR, 286.6 eV –C–O– and 285.0 eV –CH<sub>x</sub>) was performed using the peak fit routine from Specs.

It was assumed that the calculated concentrations of functional groups and grafted spacer molecules were homogeneously distributed within the XPS sampling

depth. This is surely a rough approximation but it provides a basis for comparing the efficiency and yield of different bromination and graft processes.

### 3. Results and Discussion

### 3.1. Bromination With Bromoform

The attachment of bromine onto the polymer backbone dominates using elemental bromine, bromoform and *tert*-butyl bromide plasmas. Plasma polymer deposition as the origin for Br-containing polymer surfaces was negligible under the plasma conditions used as measured with a quartz microbalance detector. The bromoform plasma was most efficient in introducing bromine onto the polypropylene surface in comparison to plasmas with elemental bromine or *tert*-butyl bromide as well as polymer forming plasmas (Fig. 3).

The unavoidable post-plasma oxygen introduction amounted to only 1-3 O/ 100 C, whereas 20–100 Br per 100 C could be introduced onto the polypropylene surface. The bromine and *tert*-butyl bromide plasmas did not produce comparable yield in C–Br.

The XPS spectra show a weak broadening of the  $C_{1s}$  signal in the region of higher binding energy and the appearance of the  $Br_{3s}$ ,  $Br_{3p}$  and  $Br_{3d}$  peaks known from C– Br-containing polymers (Figs 4 and 5). The  $O_{1s}$  peak rises only slightly above the noise level. The existence of exclusively one kind of bromine species in the  $Br_{3p_{1/2}}$ and  $Br_{3p_{3/2}}$  as well as in  $Br_{3d_{3/2}}$  and  $Br_{3d_{5/2}}$  signals indicates an exclusive presence of C–Br species at the surface of the brominated polypropylene. The measured binding energy in the  $Br_{3d_{5/2}}$  signal was 70.5 eV, characteristic of C–Br groups.



**Figure 3.** Efficiency of different bromination processes before ('plasma') and after 8 h extraction in tetrahydrofuran (THF) ('plasma + extraction') as well as O introduction by the post-plasma oxidation.



**Figure 4.**  $C_{1s}$  peaks of PP before and after bromination with bromoform using the pulsed RF plasma (100 W, 30 s, 6 Pa, duty cycle 0.1).



**Figure 5.**  $Br_{3p_{1/2}}$  and  $Br_{3p_{3/2}}$  peaks of PP before and after bromination with bromoform using the pulsed RF plasma (100 W, 30 s, 6 Pa, duty cycle 0.1).

Br<sup>-</sup> anions appearing at 69 eV were absent. The above mentioned unwanted sidereaction of the post-plasma addition of traces of oxygen excludes any significant formation of Br–O<sub>x</sub> components.

The rate of bromination was found to depend on the plasma parameters. The introduction of bromine atoms onto the polypropylene surface increased with time (Fig. 6). Thus, the bromine concentration at the polymer surface could be easily adjusted by varying the plasma exposure time and the power.

The oxygen content did not exceed 3 O/100 C after intense extraction with THF (4 h) followed by exposure to the ambient air for 4 months.

### 3.2. Allyl Bromide Plasma

Another good possibility for producing bromine-rich surfaces is the deposition of thin bromine-containing plasma polymers (cf. Fig. 1). Vinyl bromide and allyl bro-



**Figure 6.** Bromination of polypropylene surfaces using bromoform (CHBr<sub>3</sub>) or bromine (Br<sub>2</sub>) plasmas before and after extraction with THF (CHBr<sub>3</sub>, remaining bromine after 24 h rinsing in THF) and the unwanted oxygen co-introduction using the CHBr<sub>3</sub> plasma.

mide are suitable monomers for such polymer thin film deposition. The highest yield in bromine concentration was achieved by depositing allyl bromide plasma polymers (cf. Fig. 3).

The bromine concentration in the deposited polymer films is limited by the stoichiometry of the allyl bromide molecule, i.e. the resulting bromine concentration at the polymer surface correlates with the C/Br ratio in the precursor molecule (CH<sub>2</sub>=CH–CH<sub>2</sub>Br). This threshold Br/C ratio is 33 Br per 100 C. In contrast to this, only 23–27 Br/100 C were measured in the deposited 100 nm thick plasma polymer films depending on the conditions of plasma polymer deposition, i.e. 20% of the original bromine atoms in the precursor molecules were not retained in the plasma polymer (Fig. 7).

However, two points must be mentioned using this process: the adhesion of the plasma polymer to the polymer substrate and the high concentration of trapped radical sites. Although, the adhesion of the allyl bromide plasma polymer film to the polymer substrate was sufficient in the case of polypropylene, but the concentration of trapped radicals within this layer was very high. These radicals are generally responsible for the pick-up of oxygen from the air and the initiation of the auto-oxidation. Thus, 10–20 unwanted oxygen functionalities per 100 C were introduced, thus increasing the quantity of by-products.

The maximum Br introduction (100 Br/100 C and, after washing the sample, 27 Br/100 C) was obtained at about 100 W RF power input using the continuouswave (c.w.) mode (Fig. 7). However, this maximum was accompanied by the unwanted post-plasma introduction of 17 O species per 100 C. The optimum pressure ranged from 4 to 6 Pa under the given conditions (c.w. mode, 100 W).



**Figure 7.** Bromine introduction (Br) to the polypropylene surface by deposition of allyl bromide plasma polymer layers and unwanted co-introduction of oxygen (O) in dependence on power input.

### 3.3. Grafting Onto Bromine Groups

Using the bromoform plasma and brominated polypropylene surfaces with 20 Br per 100 C different amounts of Na-glycolates and amines could be grafted in dependence on the length of grafted chains (2–15 glycolates and 3–15 amines per 100 C) (Fig. 8).

Starting from allyl bromide layers with ca. 24 Br/100 C but with the relatively high percentage of 17 post-plasma introduced oxygen per 100 C, from 3.7 to 15 OH-terminated spacer molecules per 100 C-atoms could be chemically grafted onto the brominated surface (Fig. 8). The excessive oxygen introduction into the poly(allyl bromide) anchoring layer in comparison to the bromoform plasma treated polypropylene is exemplified for the grafting of triethyleneglycol presented in Fig. 9.

Similar yields were realized using aliphatic diols (dialcohols) of different chain lengths (Fig. 8). 2–12 alcoholic spacers per 100 C could be grafted depending on the chain length. As expected, the graft yield depends on the chain length of the grafted molecule as shown in Fig. 10.

### 3.4. Changing the Surface Functionality From C-Br to C-NH<sub>2</sub>

Starting from the allyl bromide plasma polymer coated surfaces another interesting feature, i.e. the substitution of C–Br by C–NH<sub>2</sub> was established as follows:

$$\equiv -Br + NH_3 \rightarrow \equiv -NH_2 + HBr \tag{8}$$



**Figure 8.** Graft yields of diols, glycols and amines onto bromoform with 20 Br per 100 C atoms or allyl bromide with 24 Br per 100 C atoms modified polypropylene surfaces.



**Figure 9.** Comparison of bromination methods (bromoform plasma or allyl bromide plasma polymer layer deposition) with respect to the Br introduction onto polypropylene surfaces, the produced OH concentration after grafting of triethylene glycol (TEG) onto C–Br groups and the oxygen introduction by the grafting process or by the unwanted post-plasma reactions of radical sites with oxygen from air.

The substitution  $Br \rightarrow NH_2$  had an yield of more than 80% and thus about 15 NH<sub>2</sub> groups per 100 C-atoms were detected by XPS after derivatization of the amino groups with PFBA.



**Figure 10.** Maximal graft yields onto brominated polypropylene surfaces after bromination of the polypropylene surface using the bromoform plasma for different chain-length (*x*) of grafted molecules (x = 2-12) and different types of grafted molecules (diols = '-(CH<sub>2</sub>)<sub>x</sub>-OH'; glycols = -(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>x</sub>-OH, and diamines = -(CH<sub>2</sub>)<sub>x</sub>-NH<sub>2</sub>).

The idea was to produce a stable  $NH_2$  functionalization of polymer surfaces in an indirect way. For this purpose, a bromoform plasma treated polymer surface was used. The thus produced C–Br groups were chemically converted into amino groups (equation (8)). It was expected that such an amino-group containing surface layer would be much more stable than that produced by plasma deposition of allylamine. The chemical exchange of Br by  $NH_2$  offers a new approach for obtaining stable amino-group bearing polymer surfaces because the deposition of the allylamine plasma polymers has an yield of only 12–18  $NH_2$  groups per 100 C (e.g. 40–55% of the introduced amino groups remain in the respective allylamine plasma polymer), and there is an unwanted post-plasma introduction of oxygen (10–20 O per 100 C) [11–14]. The amino group introduction *via* the ammonia plasma has yield only in the range of 1–3 amino groups per 100 C atoms [13, 19]. Thus, chemically produced  $NH_2$  group-containing polypropylene surface did not show any indication of postplasma oxidation during its exposure to the ambient air for 4 months. The reason is the absence of significant concentration of C-radical sites.

Other reactions tested for changing the Br-substitution to primary amino groups gave much less success such as using NaNO<sub>2</sub> for introducing NO<sub>2</sub> groups:

$$\equiv C - Br + NaNO_2 \rightarrow \equiv C - NO_2 + NaBr$$
(9)

and its subsequent reduction to amino groups:

$$\equiv C-NO_2(Fe, FeSO_4, H^+) \rightarrow \equiv C-NH_2$$
(10)

The yield of amino groups was about 4 NH<sub>2</sub> per 100 C.

Table 1	Т	ab	le	1
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Ionization potentials of halogen-containing plasma gases and methane

Halogen precursor	Ionization potential (eV)
CF <sub>4</sub>	17.8
CCl <sub>4</sub>	11.5
HCCl <sub>3</sub>	11.4
HCBr <sub>3</sub>	10.5
CH <sub>2</sub> I <sub>2</sub>	9.3
CH <sub>4</sub>	13.0

Another way for introducing a new type of functional group consisted in the reaction with potassium cyanide:

$$\equiv C - Br + KCN \rightarrow \equiv C - C \equiv N + KBr$$
(11)

It follows the reduction of the nitrile formed with  $LiAlH_4$ . A yield of 3  $NH_2/100$  C was measured:

$$\equiv C - C \equiv N \rightarrow \equiv C - CH_2 - NH_2 \tag{12}$$

The same result (3  $NH_2$  per 100 C) was obtained by coupling the bromine with sodium azide:

$$\equiv C - Br + NaN_3 \rightarrow \equiv C - N_3 + NaBr$$
(13)

and exposing it to low pH:

$$\equiv C - N_3(+H^+) \rightarrow \equiv C - NH_2 \tag{14}$$

As mentioned in the Introduction Section the average electron energy is dependent on the ionization energy of the plasma gas molecules. The lower the ionization energy the lower is the electron energy in the plasma. Ionization energies of the halogen-containing precursors decrease from fluorine to iodine (Table 1) [14].

In the same manner as the ionization energy decreases from fluorine to bromine the average electron energy also decreases following the Schottky theory of the positive column of a direct-current low-pressure glow discharge under the condition of ambipolar diffusion [15]. Therefore, the bromine and iodine plasmas should possess an energy level which is much lower than that of F-containing plasmas. Consequently, the damage to the structure of the polymer substrate should be less. Moreover, also the radical formation and, therefore, the auto-oxidation over weeks or months should be reduced (cf. [9, 16]).

Additionally, Br atoms are good radical scavengers. Thus, they can hinder the post-plasma auto-oxidation. The radical–radical recombination introduces bromine atoms onto the polymer chain:

$$\mathbf{R} \cdot + \mathbf{\cdot} \mathbf{B} \mathbf{r} \to \mathbf{R} - \mathbf{B} \mathbf{r} \tag{15}$$

This quenching reaction is also a reason for the low-percentage of post-plasma introduced O functional groups.

The reactivity of radicals has the following order [7]:

$$F \cdot > HO \cdot > CI \cdot > CH_3 \cdot > Br \cdot > R - O - O \cdot$$
(16)

Thus, bromine atoms (and also CBr<sub>3</sub> radicals) show the highest specificity in reaction with different activated carbon C–H features. Tertiary C–H bonds react 1600 times faster, secondary C–H bonds 32 times faster than primary C–H bonds (=1) (cf. equation (17)) [7]:

$$\cdot Br + R - H \to R \cdot + H - Br \tag{17}$$

Olefinic double bonds were easily brominated and aromatic rings were brominated under vigorous conditions.

It must be mentioned that chemically neutral halogen precursors are preferred because elemental halogens are chemically very aggressive. Especially, the fluorination is thermodynamically preferred but is strongly exothermic so that it is nearly uncontrollable and unselective using gas phase processing [17]. The chemical fluorination proceeds with the same mechanism as shown for the bromination:

$$\cdot \mathbf{F} + \mathbf{R} - \mathbf{H} \to \mathbf{R} \cdot + \mathbf{H} - \mathbf{F} \tag{18}$$

The standard reaction enthalpy can be derived from the R–H dissociation energy and the heat of HF formation [7]:

$$\Delta_{\rm R} {\rm H}_{298}^{\ominus} = \Delta_{\rm R} {\rm H}_{\rm R-H}^{\ominus} - \Delta_{\rm R} {\rm H}_{\rm H-F}^{\ominus} = (396-566) \text{ kJ/mol} = -170 \text{ kJ/mol}, \quad (19)$$

 $\Delta_{\rm R} {\rm H}^{\ominus}_{298} =$  standard reaction enthalpy at 298 K,

 $\Delta_R H_{R-H}^{\ominus}$  = standard dissociation energy at 298 K,

 $\Delta_{\rm R} {\rm H}_{{\rm H}-{\rm F}}^{\ominus}$  = standard heat of formation at 298 K.

As shown in Table 2 the bromination and also the iodination are endothermic, i.e. there is no possibility to start a chemical bromination or iodination chain reaction

Standard reaction enthalpies for chemical halogena reactions			
Reaction	Standard reaction enthalpy (kJ/mol)		

....

Reaction	Standard reaction enthalpy (kJ/mol
Fluorination	-170
Chlorination	-32
Bromination	33
Iodination	101

of aliphatics or aliphatic polymers by bromine or iodine atoms. Therefore, no additional chemical contribution to the plasma bromination process need be considered. Thus, the selectivity of the plasma bromination process is not decreased by exothermic chemical processes.

Hence, it is not very surprising that under the relatively moderate plasma conditions employed (power input  $\leq 100$  W) the bromination of aliphatic polymers with bromoform is a nearly selective reaction. Among all plasma functionalization processes, only the bromination is a specific and selective process which results in chemically useful reactive C–Br groups.

### 4. Summary

The bromination is a selective plasma chemical way for the production of monotype functionalized polymer surfaces using a one-step plasma process with bromoform as precursor. Up to 100 C–Br groups per 100 carbon atoms were introduced, of which at least 20 C–Br per 100 C were permanently bonded to the polymer substrate. The low ionization potential of bromoform was responsible for the 'soft' plasma conditions during the bromination. Chemical contributions to the bromination of aliphatic polymer moelcules should be absent because of the endothermic character of this reaction.

The alternative process, the deposition of thin plasma polymer top coatings made of allyl or vinyl bromide, resulted also in 20–25 Br/100 C but this process was accompanied by a very high post-plasma introduction of oxygen as unwanted side-reaction.

Up to 80% of all C–Br groups could be used for grafting reactions of diols, glycols and diamines. The larger the grafted molecule the lower was the graft density at the polymer surface. Nevertheless, it was possible to graft also polymer chains onto the bromine sites in respectable yields.

Another application of the highly selective plasma bromination is the change from the bromine functionalization to the amino functionalization using ammonia. This process opens an avenue to a stable and dense amino-functionalized polymer surface which promises more stable amino surfaces with a minimum of by-products.

The grafted spacer molecules were introduced into the metal–polymer interface as a flexible element to compensate for the different thermal expansion coefficients of metals and polymers. Another application is the use of grafted polymer surfaces in biochips or for biocompatible material surfaces.

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# Plasma Surface Modification of Aromatic Polyester (Vecstar OC<sup>®</sup>) Films for Copper Metallization — Dynamic Surface Properties of Plasma-Modified Vecstar OC Films

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#### Abstract

Vecstar OC films were modified by Ar,  $O_2$ ,  $N_2$  and  $NH_3$  plasmas and further heat-treated in order to improve their adhesion to deposited copper metal. Effects of these plasma modifications and heat treatment were evaluated from water contact angle measurements, surface roughness measurements with a scanning probe microscope and chemical composition measured with XPS. The plasma modification alone is not efficient, but the combination of plasma modification and heat treatment is effective in improvement of adhesion between copper metal and the Vecstar OC films. Furthermore, O=C groups and amino groups formed by the plasma modification contribute to adhesion improvement. In order to achieve an effective improvement, the O=C and amino groups should be present in the topmost layer (within 3 nm depth from the film surface) of the Vecstar OC films. The O=C and amino groups not available in the topmost layer do not contribute to adhesion improvement. The heat treatment on a glass plate helps migration of the O=C and amino groups from the inner layer to the topmost layer of the plasma-modified Vecstar OC films.

#### Keywords

Aromatic polyester, Vecstar OC<sup>®</sup>, plasma modification, water contact angle, surface roughness, copper metallization, peel strength, XPS, polymer chain ends

### 1. Introduction

An aromatic polyester is often called one of the third-generation engineering plastics because of its excellent electrical and thermal properties as well as mechanical properties [1]. Vecstar which is a trade name of Kuray Company, Ltd., Japan is an aromatic polyester made from acetoxy benzoic acid and acetoxy naphthoic acid (Fig. 1). Vecstar is fabricated into a sheet form by a blow molding technique, and is commercially available in the form of a film (25 and 50  $\mu$ m thickness). In the fabrication process, polymer chains near the film surface are oriented in the machine

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Figure 1. Polymerization of Vecstar, copolymer of oxybenzoate-co-oxynaphthoate.

### Table 1.

Essential properties of Vecstar FA and OC and polyimide films

Property	Vecstar film	Polyimide	
	Vecstar FA	Vecstar OC	Kapton H
Tensile strength (MPa) <sup>1)</sup>	333/304	196/196	340
Tensile modulus (GPa) <sup>1)</sup>	7.0/6.7	3.9/3.8	3.4
Elongation at fracture $(\%)^{1}$	16/14	30/28	80
Melting point (°C)	280	325	_
Glass transition temperature (°C)	205	285	_
Thermal expansion coefficient (ppm)	$-20 \sim 0$	$-10 \sim 10$	27
Water absorption (%)	0.04	0.04	2.9
Resistivity ( $\Omega$ cm)	$7.7 \times 10^{-15}$	$7.7 \times 10^{-15}$	$1 \times 10^{-15}$
Dielectric constant at 1 MHz	3.0	3.0	3.1
Dissipation factor at 1 MHz	0.022	0.022	0.089

<sup>1)</sup> Machine direction/transverse direction.

direction due to its highly crystalline nature and thermotropic liquid–crystalline behavior. As a result, Vecstar film is not homogeneous but has a heterogeneous structure (skin–core structure). The skin–core structure leads to troublesome problems such as fracture from the skin–core interface, curling of the film, etc. when shear stress or heat shock is applied to the films. In order to eliminate the skin–core structure, Vecstar films are subjected to heat treatment for converting into a homogeneous structure. Two types of Vecstar films, Vecstar FA and Vecstar OC, are available in the market. Vecstar FA is a film without the heat treatment, and Vecstar OC is a film which has been subjected to the heat treatment. Essential properties of the Vecstar FA and OC and polyimide are compared in Table 1.

Table 1 shows excellent electrical properties as well as mechanical and thermal properties of Vecstar OC [2, 3]. Vecstar OC film is superior in dielectric constant and dissipation factor compared to polyimide film (Kapton H). The dielectric con-

stant at 1 MHz and dissipation factor at 1 MHz are 3.0 and 0.022 for Vecstar OC film, compared to 3.1 and 0.089 for Kapton H film, respectively. Furthermore, the water absorption for Vecstar OC film (0.04%) is much lower than that for Kapton H film (2.9%). Therefore, Vecstar OC film offers much promise as a new material for microelectronics. Flexible printed circuit board (FPCB) is an example of promising applications of Vecstar OC films. An FPCB is a composite of polymer film and copper metal, which is deposited directly on the surface of the polymer film by conventional techniques such as electroless plating, vacuum deposition, sputtering, ion plating, etc. How strongly the deposited copper metal adheres to Vecstar OC film surface is an important factor in the FPCB performance. Surface modification of Vecstar OC films is indispensable for good adhesion between copper metal and Vecstar OC film. Many attempts have been made [4–11], but so far there has not been much success in obtaining good adhesion between copper metal and Vecstar OC film.

We have investigated the effects of plasma modification on the adhesion between copper metal and Vecstar OC film. Even though Vecstar OC films were successfully modified by Ar, O<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub> plasmas, the plasma-modified Vecstar OC films showed no improvement in adhesion with copper metal. On the other hand, Vecstar FA films showed remarkable improvement in adhesion by Ar, O<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub> plasmas. We believe that this difference in plasma susceptibility between Vecstar OC and FA films may be due to the end groups of polymer chains which exist near the film surfaces. Details of the difference will be shown in the next section on theoretical background on interactions operating at the copper metal/Vecstar film interface. In this study, we have focused on dynamic surface properties of plasma-modified Vecstar OC film. Following topics, (1) How is Vecstar OC film modified by plasma?, (2) Is there any difference in chemical composition between plasma-modified Vecstar OC and FA film surfaces? and (3) How to improve the adhesion between copper metal and Vecstar OC film? were investigated.

### 2. Theoretical Background

Polymer surface is different in physical properties from the polymer bulk. Figure 2 represents the glass transition temperature  $(T_g)$  for surface and bulk of polystyrene films as a function of molecular weight, as observed by Tanaka and coworkers [12–14]. The  $T_g$  for the film surface is lower by a few tens of degrees than that for the film bulk. This difference may be due to larger free volume of polystyrene chains at the film surface than in the film bulk. This indicates that polymer chains distribute randomly in the polymer bulk, but the ends of the polymer chains tend to aggregate at the surface rather than in the polymer bulk. Such aggregation of chain end groups has been observed by means of dynamic secondary ion mass spectrometry, neutron reflectivity, angular XPS and Monte Carlo simulations [15–21]. Figure 3 shows the SIMS depth profiles for thin film cast from chloroform solution of deuterated polystyrene ( $M_n = 15000$ ;  $M_w/M_n = 1.09$ ). The polystyrene used



Figure 2. Glass transition temperatures for surface and bulk of polystyrene films as a function of molecular weight.



Figure 3. SIMS depth profiles for thin film cast from chloroform solution of deuterated polystyrene.

for SIMS measurement is composed of deuterated styrene unit as the main chain and un-deuterated  $C_4H_9$ - and  $(Ph)_2CH$ -groups as chain end groups (Fig. 3) [1]. The chain end groups are distinguished from the main chain of styrene component. As shown in Fig. 3, <sup>1</sup>H atoms aggregate near the surface and then the <sup>1</sup>H atom concentration decreases with increasing depth from the surface and becomes constant at about 10 nm depth from the surface. From the  $T_g$  results and the SIMS measurements, we can expect that chain end groups in Vecstar OC film also aggregate near the film surface. These chain end groups aggregated near the film surface will be more mobile than the main chains, and will be able to interact strongly with the copper metal deposited directly on Vecstar OC film surfaces. From this viewpoint we are interested in (1) What chain end groups are present at Vecstar OC film surface?, (2) What is the concentration of the chain end groups located at Vecstar OC film surface?, (3) How do the chain end groups orient when they contact other materials? and (4) How the chain end groups contribute to adhesion with copper metal?

# 3. Experimental

# 3.1. Materials

Two types of Vecstar films (50  $\mu$ m thick), Vecstar OC and Vecstar FA, were received from Kuraray Company, Ltd., Japan. The sheet was cut to dimensions of 12 mm  $\times$  90 mm, and used as specimens for surface modification experiments. Prior to surface modification experiments, the Vecstar films were washed with acetone in an ultrasonic washer and dried at room temperature under vacuum. Argon (Ar), oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>) and ammonia (NH<sub>3</sub>) (purity 99.995%) were purchased from Teikoku Sanso Co., Japan, and were used as plasma gases without further purification.

# 3.2. Modifications of Vecstar Film Surfaces by Plasmas

A special reactor was used for the modification by plasmas. The reactor was a tubular one made of Pyrex. The reactor was 50 mm in diameter and 1000 mm in length. At an end of the tubular reactor, an inlet for plasma gases was set up, and the other end was connected to a vacuum system (a combination of a rotary pump and a diffusion pump). RF power at 13.56 MHz frequency for glow discharge was inputted into the reactor by a capacitive-coupling system. The details of the reactor have been described elsewhere [4].

Vecstar film specimens ( $12 \text{ mm} \times 90 \text{ mm}$ ) were positioned in the plasma reactor. The air in the reactor was displaced with argon, and the reactor was evacuated to a pressure of approximately  $1.3 \times 10^{-2}$  Pa. Afterwards, Ar, O<sub>2</sub>, N<sub>2</sub> or NH<sub>3</sub> gas was introduced into the plasma reactor from the inlet at a flow rate of 10 cm<sup>3</sup> (STP)/min adjusted by a mass flow controller. The system was maintained at a pressure of 13.3 Pa by adjusting the vacuum valve. The plasma for the Vecstar film surface modification was operated at an rf power of 25–100 W at 13.56 MHz frequency for 10–180 s.

# 3.3. Copper Metallization of Vecstar Films

A combination of two processes, evaporation and electroplating, was employed for copper metallization of Vecstar film surfaces. The total thickness of the copper metal layer deposited by evaporation and electroplating was about 30  $\mu$ m. First a copper layer of about 100 nm thick was thermally evaporated onto the Vecstar films in a ULVAC Model LEE-400 vacuum evaporator. The copper deposition process was carried out at a pressure of 10<sup>-6</sup> Torr or less and at a deposition rate of about 0.5 nm/s. The metallized Vecstar films were electroplated further with copper to

a thickness of 30  $\mu$ m. The electroplating procedure was carried out at a constant current of 10 A (current density of 300 A/m<sup>2</sup>) and a constant voltage of 8 V at 24°C for 1 h in a sulfuric acid bath (190 g/l) containing copper sulfate (75 g/l), hydrogen chloride (50 ppm) and a glossy reagent (5 ml) (Nippon Rironal Co., Japan, trade name Copper Gleam PCM). Finally, the metallized Vecstar film surfaces were washed with distilled water and dried at 80°C for 12 h under vacuum.

# 3.4. Contact Angle of Water on the Plasma-Modified Vecstar Films

Contact angles of water on the plasma-modified Vecstar films were measured at 20°C using the sessile drop method [12]. A contact angle meter (Erma Co. Ltd., Japan, model G-1) was used for the measurements.

# 3.5. XPS Analysis of the Surface-Modified Vecstar Films

XPS spectra for the surface-modified Vecstar films were obtained on an Ulvac-Phi Quantera SXM spectrometer using a monochromatic Al  $K_{\alpha}$  photon source at 400 W. XPS measurements were carried out at a pressure of  $3.2 \times 10^{-8}$  Pa. To avoid charging of the specimen surface, a neutralizer was operated during the XPS measurements. XPS spectra were recorded at take-off angles of 20 and 45° against the sample surface. The O/C and N/C atom ratios were calculated from the C<sub>1s</sub>, O<sub>1s</sub> and N<sub>1s</sub> peak intensities and the sensitivity factors, with an experimental error less than 0.03. Sensitivity factors (S) for the C<sub>1s</sub>, O<sub>1s</sub> and N<sub>1s</sub> core level peaks were S(C<sub>1s</sub>) = 1.00, S(O<sub>1s</sub>) = 2.85, S(N<sub>1s</sub>) = 1.61. The C<sub>1s</sub>, O<sub>1s</sub> and N<sub>1s</sub> spectra were decomposed using the curve-fitting program (PeakFit) supplied by Sea Solve Software Inc., Framingham, MA, USA.

# 3.6. Surface Topography of Plasma-Modified Vecstar Films

The plasma-modified Vecstar film surfaces were scanned with a scanning probe microscope, SPM, (Shimadzu SPM-9500) to evaluate changes in surface topography. Using Olympus OMCL-AC160TS cantilever (160  $\mu$ m long and 50  $\mu$ m wide, spring constant of 42 N/m), SPM images were acquired in air using the dynamic mode at a scanning speed of 1 Hz, and the scanning area was 1  $\times$  1  $\mu$ m.

# 4. Results and Discussion

# 4.1. Polymer Chain Ends of Vecstar OC Films

Vecstar OC or FA film, poly (oxybenzoate-co-oxynaphthoate), which is made from a mixture of acetoxy benzoic acid and acetoxy naphthoic acid by polycondensation reaction (Fig. 1) [2] has two types of chain end groups, acetoxy (CH<sub>3</sub>–C(O)–O) and carboxylic acid (HO–C(O)–O) groups. Carbons of these chain ends can be distinguished in XPS (C<sub>1s</sub>) spectra from aromatic carbons which are composed of polymer main chains. Aromatic carbons (C<sub>1s</sub>) appear at 284.7 eV in XPS spectra, and aliphatic carbons appear at 285.0 eV [24]. The C<sub>1s</sub> spectrum for Vecstar FA at a take-off angle of 20° is shown in Fig. 4.



**Figure 4.** XPS ( $C_{1s}$ ) spectrum at a take-off angle of 20° for the pristine Vecstar FA film.



Figure 5. Chain end structures of the Vecstar films.

The analysis depth (d) at a take-off angle ( $\theta$ ) is given by the following equation:

$$d = 3\lambda \sin\theta,\tag{1}$$

where  $\lambda$  is the inelastic mean free path of the photoelectrons ( $\lambda = 3$  nm for organic polymers). For a take-off angle ( $\theta$ ) of 20° using equation (1), the analysis depth (*d*) is 3 nm. The C<sub>1s</sub> spectrum at a take-off angle of 20° represents polymer chains which exist within 3 nm from the film surface. An analysis depth of 3 nm is much less than the radius of gyration (8 nm) of unperturbed chains ( $M_n = 15000$ ). Therefore, the C<sub>1s</sub> spectrum at a take-off angle of 20° emphasizes the chemical composition in the topmost layer of Vecstar films. The C<sub>1s</sub> spectrum in Fig. 4 can be decomposed into five components, Comp. C#1 at 284.7 eV, Comp. C#2 at 285.6 eV, Comp. C#3 at 286.2 eV, Comp. #4 at 288.7 eV and Comp. C#5 at 291.0 eV, which were assigned to <u>C</u>H in aromatic groups, <u>C</u>–C(O) groups, <u>C</u>–O groups, <u>C</u>(O)–O groups, and  $\pi$ – $\pi$ \* shake-up satellite, respectively [24]. These assignments are shown in Fig. 5. Therefore, two chain end groups, acetoxy end groups and carboxylic acid end groups, of Vecstar films can be estimated.

Similarly, the chain end groups for Vecstar OC film were analyzed by XPS, and the concentration of the chain end groups was compared with that for Vecstar FA. Vecstar FA film is fabricated from molten Vecstar by a blow molding technique, and the fabricated films have skin–core structure [1, 2] in which polymer chains near film surfaces are oriented in the direction of expansion of the films in the blow



(leads to decrease in chain end groups)

Scheme 1.

### Table 2.

Concentration of chain end groups for Vecstar OC and FA films

Film	Polymer chain end group (%)			
	Acetoxy group	Carboxylic acid group		
Vecstar FA	45	2		
Vecstar OC	40	0		

molding process, but the polymer chains in inner layers of the films are distributed randamly. The fabricated film is annealed at elevated temperature of about 230°C to eliminate the skin–core structure (see Scheme 1). This annealed film is Vecstar OC film. In the heat treatment process, the orientation of polymer chains near film surfaces (skin–core structure) is destroyed and the polymer chains are randomly distributed. At the same time, the condensation of carboxylic acid and acetoxy groups occurs at polymer chain ends.

As a result, the concentration of chain end groups is reduced. Table 2 shows the concentration of the end groups estimated from XPS spectra for Vecstar FA and OC films. The chain end group for Vecstar films is predominantly acetoxy group rather than carboxylic acid group. The concentration of the chain end groups (acetoxy and carboxylic acid groups) for Vecstar OC films (40%) is lower than that for Vecstar FA films (47%).

### 4.2. Effects of Plasma Modification on Adhesion With Copper Metal

Vecstar OC films were modified by Ar,  $O_2$ ,  $N_2$  and  $NH_3$  plasmas and the effects of the plasma modification on adhesion to copper metal were evaluated. On the plasma-modified Vecstar film surfaces, copper metal (30 µm thick) was deposited by a combination of vacuum deposition and electroplating processes. Copper metal–Vecstar film systems were peeled off at 90° at a peel rate of 10 mm/min,



**Figure 6.** Peel strength of copper metal/plasma-modified Vecstar OC film system and copper metal/plasma-modified Vecstar FA film system for different plasma treatments.

and the peel strength was determined as functions of the plasma used for the modification and the plasma exposure time. Figure 6 shows typical peel strength results for copper/plasma-modified Vecstar film systems as a function of the plasma gas used for the two Vecstar films used. There are large differences in the adhesion improvement among the plasmas used for the modification. The N<sub>2</sub> and NH<sub>3</sub> plasmas were effective in adhesion improvement, and the peel strength for Vecstar OC film increased from 0.007 to 0.70 N/5 mm. However, the Ar plasma was not effective, and the peel strength (0.33 N/5 mm) for the Ar plasma-modified Vecstar OC film/copper metal system was about half of that for the N<sub>2</sub> and NH<sub>3</sub> plasma-modified Vecstar OC film/copper metal systems. Furthermore, there were large differences in adhesion improvement by the plasmas between Vecstar OC and FA films. For example, the N<sub>2</sub> plasma-modified Vecstar OC film showed a peel strength of 0.70 N/5 mm; on the other hand, the N<sub>2</sub> plasma-modified Vecstar FA film showed peel strength of 1.3 N/5 mm, which was 1.9 times larger than that for the N<sub>2</sub> plasma-modified Vecstar OC film. Similarly, the Ar plasma-modified Vecstar FA film showed peel strength of 0.45 N/5 mm, which was 1.4 times larger than that for the Ar plasma-modified Vecstar OC film. The O2 plasma also showed similar effects on the adhesion improvement of Vecstar FA and OC films. These comparisons indicate that Vecstar OC films may be difficult to be modified by plasma. Was there any difference in the plasma modification reactions between Vecstar OC film and Vecstar FA film?

In order to elucidate what factor brought about large differences in peel strength between the plasma-modified Vecstar OC and FA films, contact angle of water, atomic composition, and surface roughness were investigated. Figure 7 shows the contact angles of water on the plasma-modified Vecstar OC films as a function of the plasma exposure time for different plasmas used for the modification. The water contact angle decreased with increasing plasma exposure time, and then leveled



Figure 7. Contact angle of water on plasma-modified Vecstar OC films as functions of the plasma exposure time and plasma gas.



**Figure 8.** Contact angle of water on plasma-modified Vecstar OC films as a function of the plasma discharge power for different plasmas.

off after a plasma exposure time of 60 s. The water contact angle for the plasmamodified Vecstar OC films was also influenced by the magnitude of the plasma discharge power. The water contact angle was independent of the magnitude of the plasma discharge power, when the plasma modification was carried out at plasma discharge powers of more than 50 W (Fig. 8). Therefore, we believe that Ar, O<sub>2</sub>,

Plasma			Atomic comp	position <sup>b</sup>		
	Contact angle (°) <sup>a</sup>		O/C atomic ratio		N/C atomic ratio	
	Vecstar OC	Vecstar FA	Vecstar OC	Vecstar FA	Vecstar OC	Vecstar FA
Ar plasma	36	41	0.32	0.23	0	0
O <sub>2</sub> plasma	23	50	0.33	0.33	0	0
N <sub>2</sub> plasma	30	63	0.35	0.25	0.09	0.07
NH <sub>3</sub> plasma	66	73	_	0.22	_	0.13
None	84	85	0.18	0.19	0	0

#### Table 3.

Water contact angles and	atomic com	positions of	plasma-modified	Vecstar films
		0 0 0 0 0 0 0 0 0 0 0 0 0		

<sup>a</sup> Modified at a plasma discharge power of 100 W for 60 s.

<sup>b</sup> Estimated from XPS at a take-off angle of 45°.

 $N_2$  and  $NH_3$  plasmas can modify Vecstar OC film surfaces, and their modification reactions occurring on the Vecstar OC film surfaces were in a steady-state when the plasma modification was carried out at an rf power of 100 W for 60 s.

So both Vecstar OC and FA films were plasma-modified at an rf power of 100 W for 60 s, and water contact angles on these plasma-modified Vecstar films are summarized in Table 3. Comparison of water contact angles between the plasmamodified Vecstar OC and FA films shows that (1) Both Vecstar OC and FA film surfaces could be modified by Ar, O<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub> plasmas, and as a result, their water contact angle decreased. (2) Decrease in the water contact angle for the plasma-modified Vecstar OC films was in the order O<sub>2</sub> plasma > N<sub>2</sub> plasma > Ar  $plasma > NH_3 plasma.$  (3) There was a difference in contact angles between the plasma-modified Vecstar OC and FA films even when the same plasma was used for the treatment. For example, the water contact angle on the N<sub>2</sub> plasma-modified Vecstar OC film surface was 30°, and that on the N2 plasma-modified Vecstar FA film surface was 63°. Similarly, the Vecstar OC film modified by Ar plasma showed a contact angle of 36°, and the Ar plasma-modified Vecstar FA film showed a contact angle of 41°. Such difference in water contact angle indicates that modification reactions occurring on the two Vecstar film surfaces were not identical but somewhat different between Vecstar OC and FA films. The difference in the modification reactions was investigated by XPS.

Table 3 shows the atomic composition of the plasma-modified Vecstar OC and FA films, which were analyzed by XPS at a take-off angle of 45°. The specimens used for XPS analyses were the same as those used for water contact angle measurements. Therefore, the same film surfaces could be inspected by two different techniques, water contact angle measurement and XPS. The plasma modification, as shown in Table 3, led to large increase in O/C atomic ratio from 0.18 to 0.35 for Vecstar OC films and from 0.19 to 0.33 for Vecstar FA films, due to formation of oxygen functional groups on their film surfaces. Furthermore, nitrogen functional



Figure 9. Etched film thickness as a function of the plasma exposure time for different plasmas.

groups were formed in the plasma modification by both  $N_2$  and  $NH_3$  plasmas, and the N/C atomic ratios were 0.09 and 0.07 for the  $N_2$  plasma-modified Vecstar OC and FA films, respectively. From XPS results, it is reasonable to conclude that both Vecstar OC film and Vecstar FA film surfaces were successfully modified by Ar,  $O_2$ ,  $N_2$  and  $NH_3$  plasmas to form oxygen functional groups on the film surface. Nitrogen functional groups also were formed on the film surface in both  $N_2$  and  $NH_3$ plasma modifications. We believe that such oxygen and nitrogen functional groups contribute to decrease in water contact angle.

Plasma exposure of Vecstar film surfaces initiated etching reactions as well as formation reactions of oxygen functional groups onto the film surfaces. In the etching reactions, small fragments are stripped off from the film surface and, as a result, weight loss occurs. Figure 9 shows typical results of weight loss from Vecstar OC films as a function of the plasma exposure time for different plasmas. In this figure, the weight loss by etching reactions is converted into the etched film thickness using a density (1.61 g/cm<sup>3</sup>) of Vecstar OC film. From a linear relationship between etched film thickness and plasma exposure time, the etch rates (nm/s) were calculated, and are summarized in Table 4. The etch rate is not the same among the plasmas used for etching reactions, but strongly depends on the plasma used. The etch rate for Vecstar OC films was in the order O<sub>2</sub> plasma > NH<sub>3</sub> plasma > Ar plasma  $> N_2$  plasma. The etch rate for Vecstar FA film was not equal to that for Vecstar OC film even though the same plasma was used for etching reactions. The etch rate for Vecstar FA films by Ar and O<sub>2</sub> plasmas, as shown in Table 4, was lower than that for Vecstar OC films, but the etch rate for Vecstar FA films by N<sub>2</sub> and NH<sub>3</sub> plasmas was higher than that for Vecstar OC films. Such differences in etch rate indicate that chemistry of plasmas is an important factor in etching reactions.