

Properties of Amine-Containing Coatings Prepared by Plasma Polymerization

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ABSTRACT: Two monomers, ethylenediamine (EDA) and diaminocyclohexane (DACH), were plasma-polymerized in continuous-wave (CW) and pulse modes. The influence of different plasma parameters on the deposition rate and film composition were investigated in detail and the changes in aminofunctionalization with varying pulse parameters were examined by FTIR, ESCA, and chemical-derivatization techniques. It was shown that a varying duty cycle does not

produce a considerable effect on the retention of amine groups into the film, while power and t_{on} play a significant role in the polymerization process. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 979–990, 2004

Key words: plasma polymerization; thin films; functionalization of polymers

INTRODUCTION

Recently, many attempts have been made to achieve surfaces enriched by a certain kind of functional groups. These so-called tailored surfaces are essential in various biomedical applications. Active functionalities dispersed over surfaces are used as bonding agents for specific molecules. As usual, one aims to increase the surface concentration of active groups, although it should be taken into account that the highest possible concentration is not always needed. The great quantity of bonding agents may be ineffective considering the spatial dimensions of species to be linked. In any case, there must exist a reliable way to control the surface concentration of active functionalities. One of the approaches for that is plasma polymerization. Precursor molecules getting into the reactor undergo interactions with energetic electrons, producing a great number of active species. Among them, free radicals and positive ions are of particular importance. The former take part in film formation while the latter, accelerated in the sheath, mostly play a destructive role. To reduce ion bombardment, the experiments are performed at lower discharge powers or pulsing is applied. In pulsed plasma, the fraction of low-energy ions in the ion energy distribution function increases, which leads to significant changes in the plasma chemistry.

Many works have been devoted to the analysis of the influence of pulsed plasma on the polymerization

processes for different types of monomers.^{1–8} The duty cycle and average power characterize the pulsing process. The former parameter is determined as $D = t_{\text{on}}/(t_{\text{on}} + t_{\text{off}})$, where t_{on} and t_{off} are the duration of periods when the discharge is turned on and off, respectively. The average power is then expressed as $P_{\text{av}} = P_{\text{peak}}D$, where P_{peak} is the power put into the discharge during t_{on} .

Amine-rich coatings have a wide range of applications, mainly for biomedical purposes. They are used in the development of acoustic wave sensors,⁹ microfiltration membranes,¹⁰ or enzyme electrodes,¹¹ in which primary amines serve as linking agents for other species. The aim of this work was to investigate, in detail, the influence of pulse parameters on the properties of resulting amine-rich films prepared by the plasma polymerization of ethylenediamine (EDA) and diaminocyclohexane (DACH).

EXPERIMENTAL

A tubular reactor with an external rf (13.56 MHz) excitation was used (Fig. 1). This was pumped out by a rotary and diffusion pump protected by a liquid nitrogen trap. The exchange of the substrates was provided by use of a load-lock. Surface modification was performed at various powers ranging from 2 to 30 W (at a 5-Pa working gas pressure) for various time periods ranging from 5 to 50 min. *In situ* diagnostics was performed by optical emission spectroscopy (OES). The self-built OES apparatus consists of an optical fiber, an ARC SpectraPro-300i monochromator with a grid, and a Hamamatsu photomultiplier R928.

A pulsed plasma polymerization mode was performed in the same experimental setup using a power

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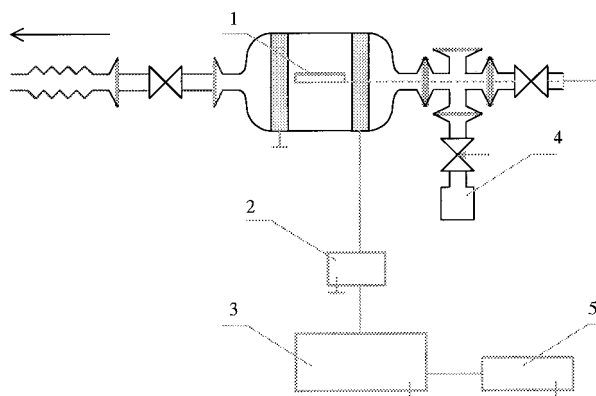


Figure 1 Experimental setup: (1) loadlock with substrate holder; (2) matching unit; (3) rf power supply; (4) monomer tank; (5) pulse generator.

supply (ENI AGC-6B) connected with a pulse generator (Hung Chang PG1000). The ENI power supply output was checked with an oscilloscope (Good Will Instrument, GOS-620). Polysulfone (PS) membranes (Osmonics Inc., S02SP04700), aluminum foil, and glass were chosen as substrates for plasma treatment.

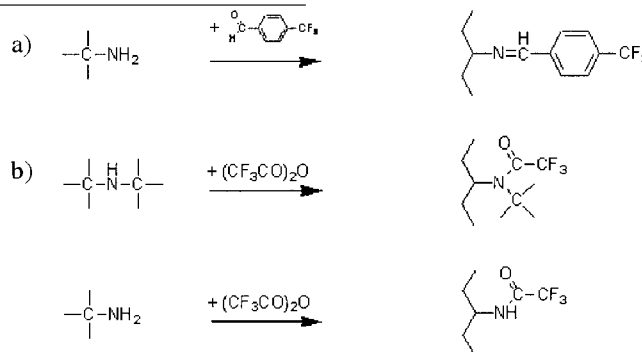
Infrared measurements were performed in the attenuated total reflection (ATR) mode using a Nicolet Impact 400 Fourier transform infrared (FTIR) spectrophotometer. An ambient-temperature deuterated trig-

lycine sulfate (DTGS) detector was used for the wavelength range from 400 to 4000 cm^{-1} . A Happ-Genzel apodization function was used in all regions and the spectral resolution was 2 cm^{-1} . Approximately 300 scans were coadded to achieve the acceptable signal-to-noise ratio.

A baseline horizontal ATR accessory with ZnSe crystal ($n = 2.4$ at 1000 cm^{-1}) was used for measurements of the infrared spectra of the thin films on PS membranes. In our experiments, the effective pathlength was approximately a few micrometers (angle of incident, 60°; number of reflections: 7). The ATR correction was made to eliminate the dependence of the effective pathlength on the wavelength.

ESCA measurements were performed on a Kratos-165 apparatus with monochromatic $\text{AlK}\alpha$ radiation. Wide- and high-resolution spectra were read at 80 or 20 eV pass energy, respectively. A hybrid lens mode was applied, which means that both electrostatic and magnetic lenses were used. All spectra were charge-corrected with respect to the hydrocarbon component of the C 1s peak at 285.0 eV and processed with a linear baseline.

The surface concentration of primary and secondary amine groups was determined by the derivatization technique using (a) trifluoromethyl benzaldehyde (TFBA) and (b) trifluoroacetic anhydride (TFAA):



The reactions were performed in the gas phase. The preliminary experiments were done to establish the time necessary for the processes to be entirely completed. According to this, the samples were treated for 30 and 10 min with TFBA and TFAA, respectively. XPS was applied afterward to determine the fluorine and carbon concentrations, and the primary and secondary amine concentrations were derived as follows:

Primary amines $[\text{NH}_2]$

$$= \left[\frac{[\text{F}]}{3} / ([\text{C}] - 8[\text{F}]/3) \right] \times 100\%$$

where $[\text{F}]$ and $[\text{C}]$ are the fluorine and carbon concentrations, respectively, determined by XPS after the reaction with TFBA. Because TFAA reacts both with NH_2

and NH , the secondary amine concentration is calculated as

$$[\text{NH}] = \left[\frac{[\text{F}']}{3} / \left([\text{C}'] - \frac{2[\text{F}']}{3} \right) \right] \times 100\% - [\text{NH}_2]$$

where $[\text{F}']$ and $[\text{C}']$ are the fluorine and carbon concentrations, respectively, determined by XPS after the reaction with TFAA. $[\text{NH}_2]$ and $[\text{NH}]$ are the percents of carbon atoms carrying this type of group.

RESULTS AND DISCUSSION

Influence of duty cycle and average power on film composition

Figure 2 shows the results of FTIR-ATR measurements of liquid EDA and DACH and the plasma poly-

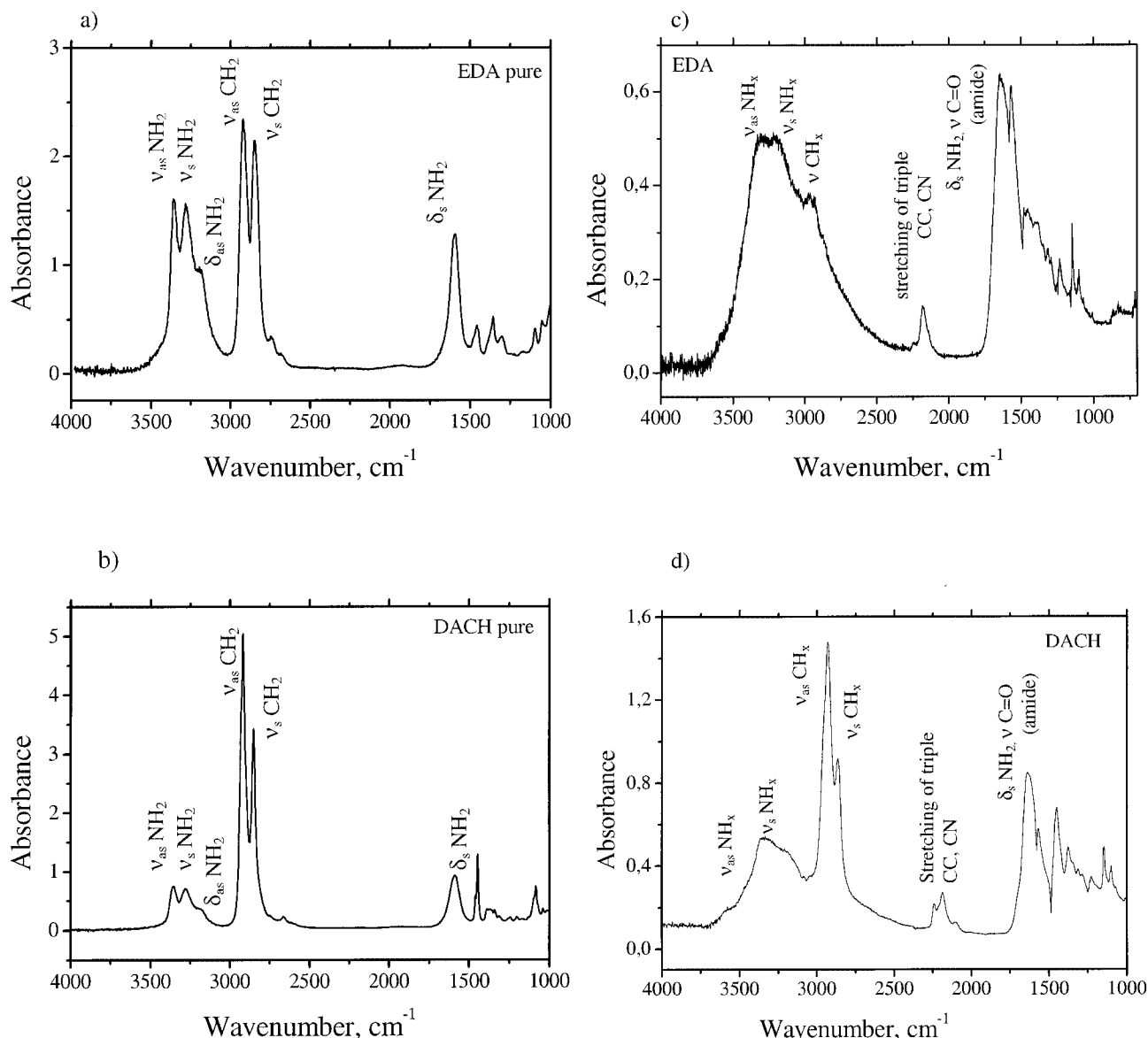


Figure 2 FTIR-ATR spectra of liquid monomers EDA and DACH and of plasma polymers prepared from the same monomers: (a) liquid EDA; (b) liquid DACH; (c) plasma-polymerized EDA on PS membrane (15 W, CW); (d) plasma-polymerized DACH on PS membrane (15 W, CW).

mers prepared from these monomers. The spectra of plasma polymers were obtained by subtraction of the untreated PS membrane spectrum from the spectra of the modified membranes. It is apparent that absorption peaks of the plasma polymers have a broad, poorly resolved character compared to those of the liquid monomers. Glow discharge, being an effective source of reactive species, supplies a great variety of oligomers for polymer growth. Thus, the deposited film is a complex carbon matrix with chaotically dispersed multiple functionalities. As a consequence, there exists a number of close absorption bands, which overlap to result in a broad final envelope. For instance, the spectrum in the absorption region from 3700 to 2700 cm^{-1} is a very broad superposition of different contributions. Primary and secondary

amines (R-NH_2 , $\text{R-NH-R}'$) give rise to asymmetric ($\nu_{\text{as}} \sim 3300 \text{ cm}^{-1}$) and symmetric ($\nu_{\text{s}} \sim 3200 \text{ cm}^{-1}$) stretching and asymmetric ($\delta_{\text{as}} \sim 3190 \text{ cm}^{-1}$) and symmetric ($\delta_{\text{s}} \sim 1590 \text{ cm}^{-1}$) deformation vibrations. The presence of oxygen in a local amine environment (e.g., amide group O=C-N) slightly shifts the absorption to lower wavelengths and this is another reason for the broadening. It should be mentioned also that plasma-deposited films after extraction from the experimental chamber inevitably absorb water vapor from the air, which may get into the matrix either as molecular inclusions or react with radicals to form R-OH bonds. As usual, in plasma polymers, hydroxyl groups are responsible for a very broad band at about 3300–3200 cm^{-1} . It cannot be detected in our spectra, but one should bear in mind that it may contribute

into the spectrum. It is impossible to determine the concentration of OH groups even approximately and another technique is needed.

Next to amine/amide absorption bands at the lower wavenumber side are CH_x peaks. Again, they are distinctly resolved in the case of the liquid monomers. The symmetric and asymmetric stretching vibration peaks of the CH₂ group are positioned exactly at ν_{as} -2921 cm⁻¹ and ν_s -2850 cm⁻¹ for both EDA and DACH. The same peaks are discernible in the DACH plasma polymer spectrum; but they are broader. (We marked them as CH_x on the pictures, meaning that CH and CH₃ functionalities can also contribute to the resulting band). In the case of EDA, the hydrocarbon stretching vibrations are nearly fully absorbed by the amine/amide band. EDA (C₂H₈N₂) initially has a bigger N/C ratio compared to DACH (C₆H₁₄N₂) and plasma polymers prepared by EDA are richer with nitrogen components. The intensity of the amine/amide band exceeds that of CH_x, which is not the case for liquid EDA and both liquid and plasma-polymerized DACH. This might mean that EDA is the better choice for the production of amine-rich coatings.

Another confirmation of the very complex film composition is that a new multiple peak develops not present in the liquid monomer spectra. The region at ~2100–2300 cm⁻¹ is assigned to a number of functional groups, mainly to triple CC and CN stretching vibrations. The possible assignment in our case is as follows: 2240 cm⁻¹ (R—C≡N), 2182 cm⁻¹ (C=C=O, —N=C=N—), and 2100 cm⁻¹ (R—C≡C—R). This peak is more developed for the DACH plasma polymer. The opening of the heterocycle ring by electron impact in the discharge probably produces biradicals, which might form double and triple bonds more easily.

As was pointed out previously, the existence of a number of closely positioned bands imposes a certain limitation on the quantitative evaluation of the different functional group concentrations. In fact, only qualitative estimation by different peak ratios is more or less reliable. Of course, the peak intensity does not correlate directly with the concentration but the peak ratio can provide approximate yet useful information about changes in the film composition. The intensities of several FTIR-ATR peaks were taken with respect to the linear baseline and the results are plotted in Figure 3.

The changes in the duty cycle or discharge power do not have any effect on the $\nu_{as}NH_x/\nu CH_x$ ratio. This value stays nearly constant through the whole range of duty cycles and powers. On the other hand, the concentration of triple- and double-bonded groups significantly falls down as the duty cycle or power decreases. This results in an abrupt increase of the $\nu_{as}NH_x/\nu CN$ ratio at low D and P_{av}. The higher power input is responsible for an increase in the concentra-

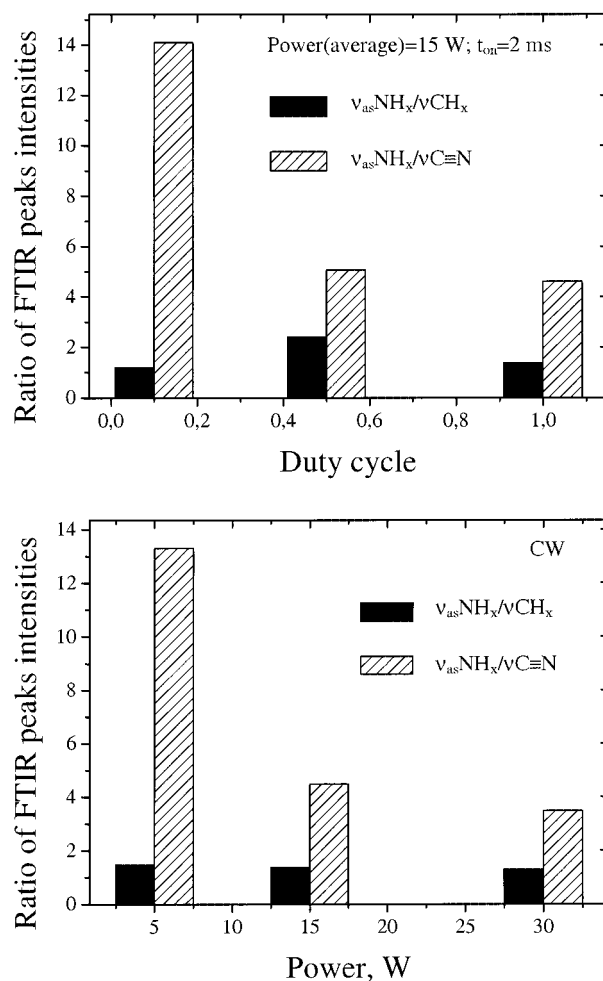


Figure 3 Changes in composition of EDA plasma polymers prepared under different conditions.

tion of the high-energy electrons, which might be the cause of creating the variety of complex excited species in the discharge. As a consequence, the atoms with double and triple bonds are abundant in the films prepared at higher powers. The influence of the duty cycle on the film composition is not so straightforward. In our experiments, the average power was held constant, that is, the lower values of the duty cycle correspond to the higher peak powers during the same t_{on} with the following longer t_{off} time. The mentioned effect of the duty cycle implies that it is ion bombardment that plays a crucial role in the film structure creation. Probably, the polymerization process during the t_{off} time runs predominantly through the formation of ordinary bonds, while intensive ion bombardment during t_{on} facilitates the creation of double- and triple-bonded networks.

The presence of CN particles in the discharge volume is confirmed by a strong $B^2\Sigma-X^2\Sigma$ emission band belonging to the CN group detected by OES (Fig. 4). Emission of that band reduces with a decreasing duty cycle, which results in a decrease of the CN concentration in the film.

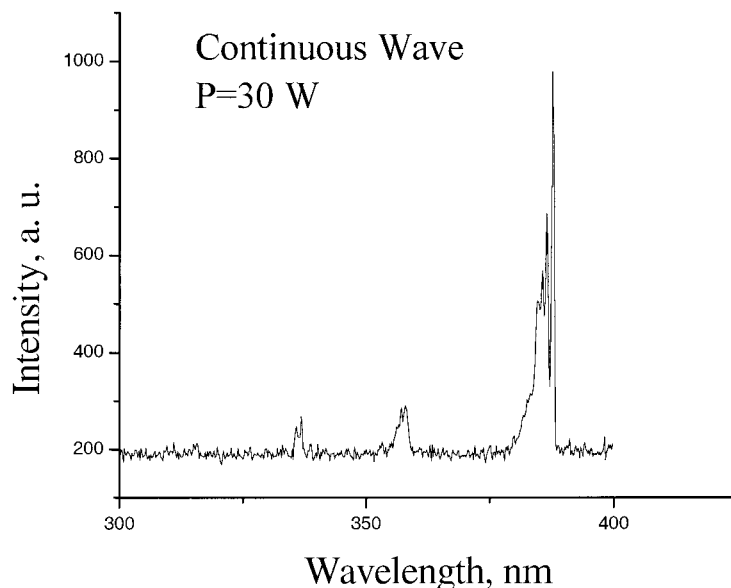


Figure 4 EDA optical emission spectrum for CW (power 30 W). CN violet system $B^2\Sigma-X^2\Sigma$ (ref. 12) is shown.

To find more information about film composition, it is necessary to apply another method. X-ray photoelectron spectroscopy has become a powerful technique in polymer surface research.

The results of element analysis are gathered in Table I. The N/C \approx 0.5 ratio for the EDA plasma polymer, as expected, is larger than that of DACH (N/C \approx 0.2) and the concentration of nitrogen is twice higher for the former coating. A certain amount of oxygen is incorporated into the films. The original monomers do not contain oxygen, so it may appear during the deposition process or due to aging after it. As leakage from outer atmosphere into the chamber cannot be excluded totally, the precursor monomer becomes slightly diluted by the air, and extremely reactive oxygen is involved in the film formation.

Another route for oxygen to get into the polymer is film aging after the deposition has been done. The spectra acquired at longer intervals after the deposition reveal an increase of oxygen concentration. It is known that plasma polymers are rich with radicals captured during film growth in a nonreactive environment. The rotational movement of polymer chains enables part of the radicals to react with each other

and their concentration decreases with time. All samples were left in the chamber after the experiment for 30 min to reduce the concentration of the radicals. Nevertheless, a certain amount of radicals are still not deactivated when the sample is exposed to the atmosphere. Exposed coatings readily react with oxygen. The further increase in oxygen concentration is supposed to be due to absorption of water vapor and air molecules.

DACH plasma polymers contain more oxygen than do plasma-polymerized EDA. This fact may indicate that the cyclic molecules of DACH getting into the discharge transform into species, which more readily react with oxygen.

High-resolution spectra were obtained for C, N, and O (Fig. 5). Although the shift in the core-level binding energy is not very big, sometimes it is possible to identify certain functionalities and reveal the chemical composition of the substance. In the case of plasma polymers, the main problem again is in the existence of a great variety of functional groups produced by carbon, nitrogen, and oxygen, the differences in binding energies being so small that the separate peaks overlap to give a broad unresolved structure. The C 1s

TABLE I
Element Composition of Plasma-polymerized Amine-rich Coatings

Type of monomer	Element concentration (at %)			Interval between deposition and acquiring spectra
	C	N	O	
EDA 15 W, CW	60.46	33.79	5.76	49 days
	60.6	29.6	9.8	68 days
DACH 15 W, CW	75.78	16.18	8.04	48 days
	71.19	15.45	13.36	163 days

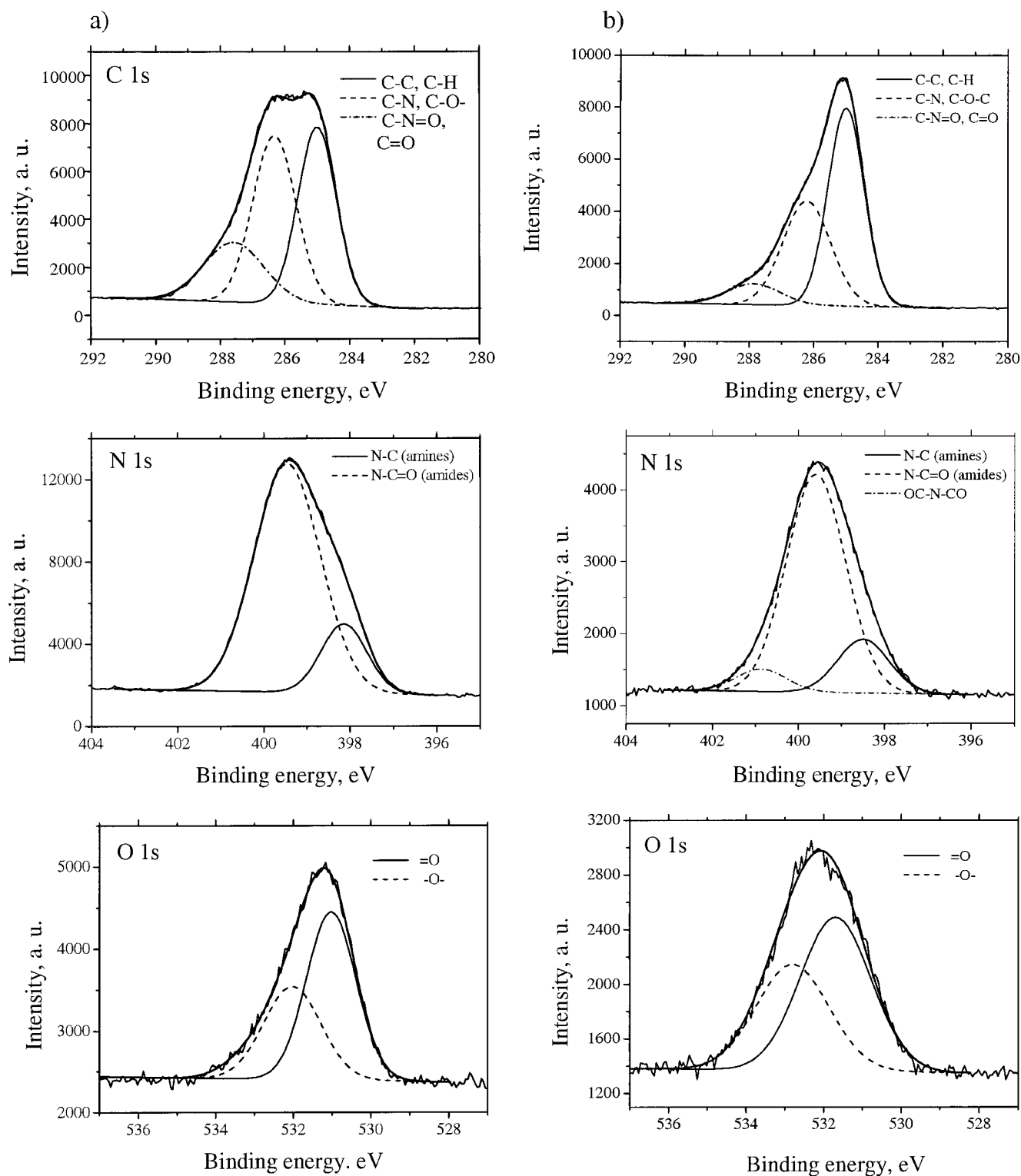


Figure 5 High-resolution XPS spectra of plasma-polymerized amine-rich coatings: (a) EDA (15 W; CW); (b) DACH (15 W; CW).

peak is the most informative. It reveals at least three overlapped peaks. The peak at 285 eV is assigned to C—C and C—H bonds. This is a reference point that all the spectra are shifted with respect to. Of course, one should make sure that an investigated substance has

enough C—C and C—H bonds without alien atoms in the local environment. Fortunately, most of the polymers meet this requirement. In our case, plasma-polymerized EDA has 60% of carbon and DACH has even more. This makes the above-said spectra shift justified.

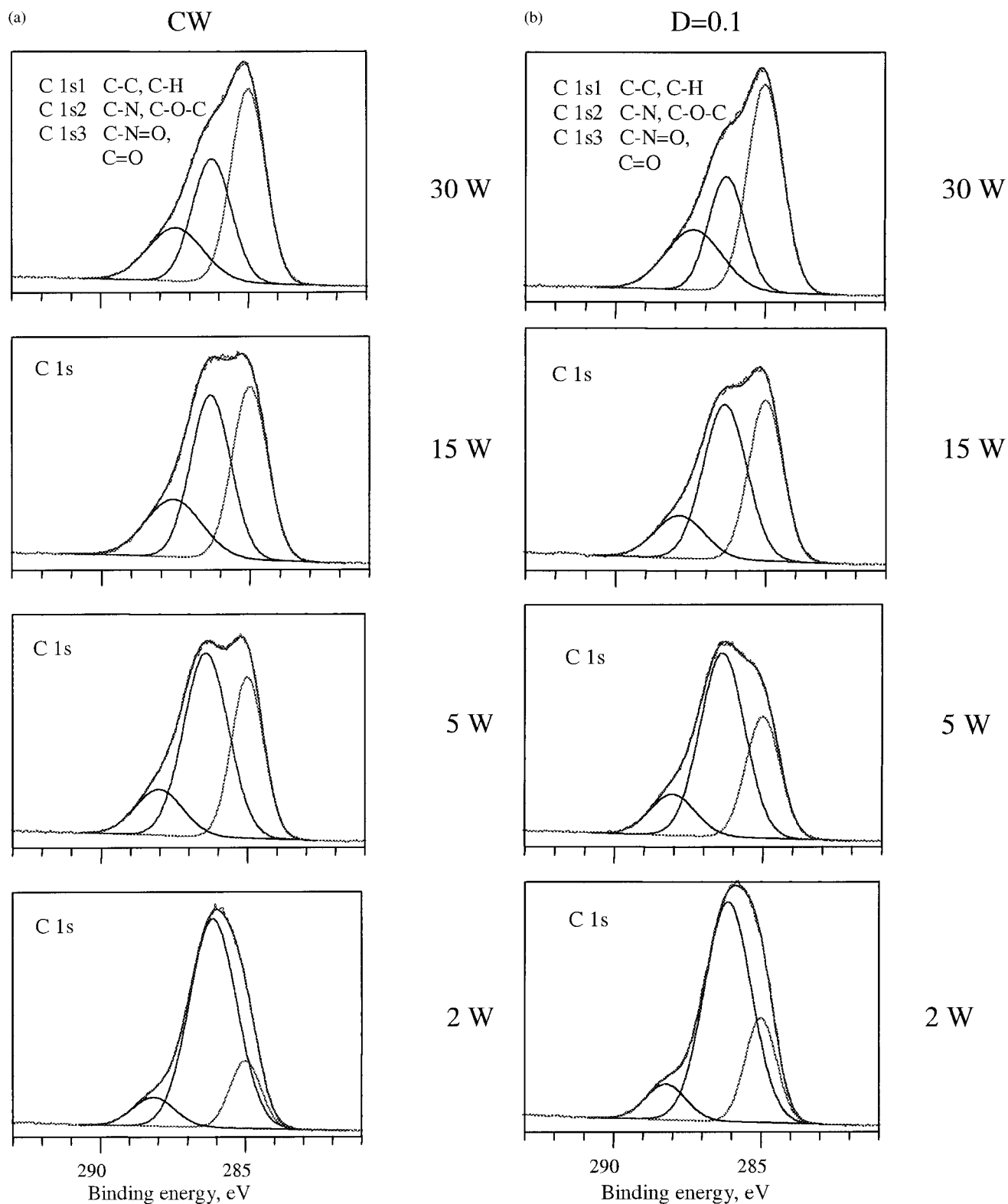


Figure 6 C 1s XPS spectra of EDA plasma polymer: (a) CW; (b) D = 0.1.

The other two components in the carbon spectra are broad (especially the third one) and cannot be exactly assigned to certain groups. The full-width-at-half-maximum parameter (fwhm) of the second compo-

nent is about 1.6–1.7 eV for both EDA and DACH. Its shift of 1.2 eV with respect to the C—C peak allows assigning it to C—N bonds, perhaps with a contribution from C—O—C groups. The third component of

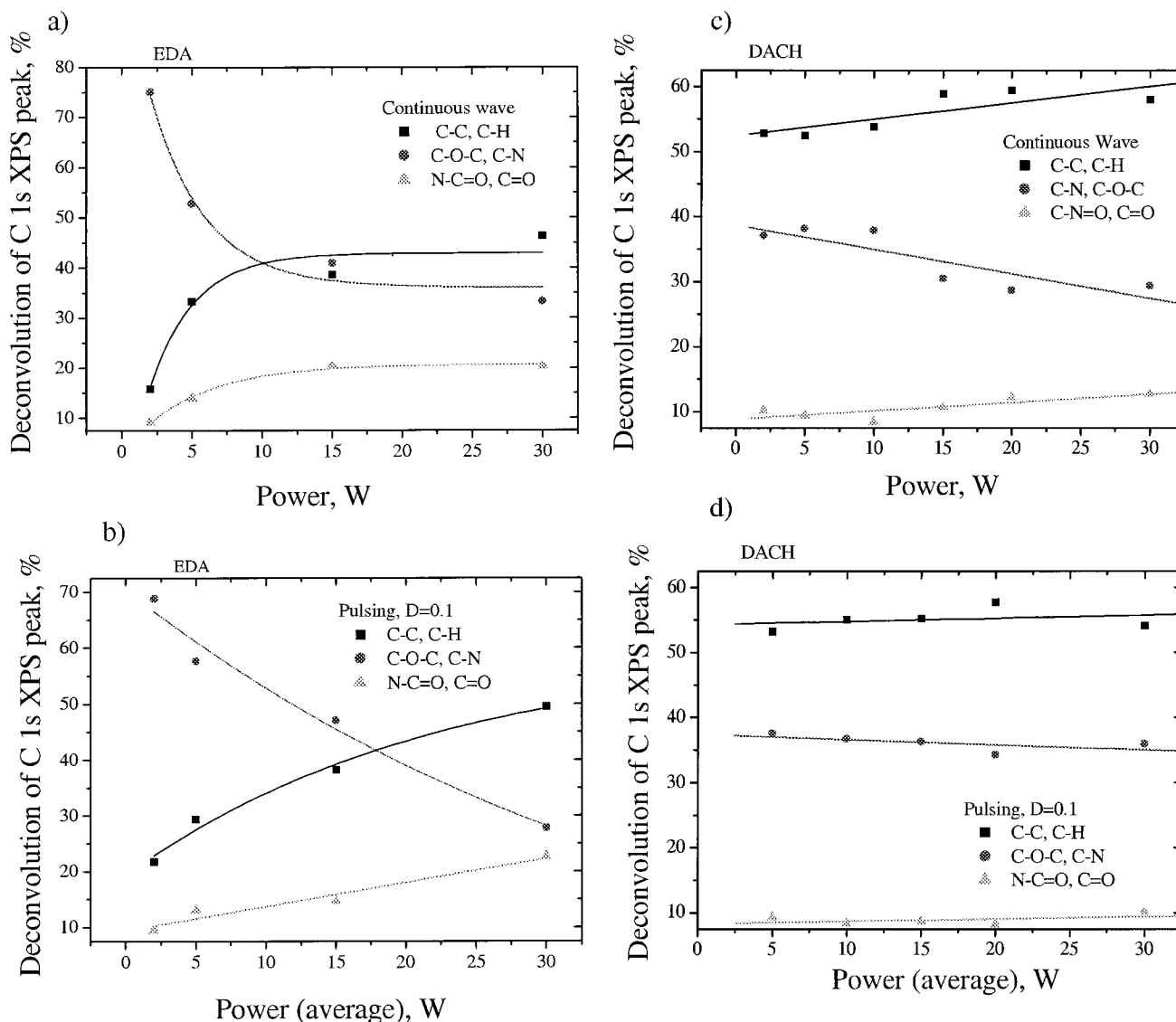


Figure 7 Changes in film composition of plasma polymer with dependence on power and duty cycle: (a) EDA plasma polymer, CW; (b) EDA plasma polymer, $D = 0.1$, $t_{\text{on}} = 0.05$ ms; (c) DACH plasma polymer, CW; (d) DACH plasma polymer, $D = 0.1$, $t_{\text{on}} = 0.05$ ms.

the carbon peak is shifted by approximately 2.8 eV. The big value of fwhm (2.2 eV) indicates that a number of functionalities contribute to that peak. We assign it mainly to N—C=O and C=O groups.

It may be seen that the carbon spectra for EDA and DACH plasma polymers are different. The second component in the EDA C 1s peak is very strong and almost equal to the C—C component, while in DACH spectrum, it is nearly twice less. The fact is explained by taking into account that C—N groups are the main constituents of that peak and that EDA plasma polymers have twice as much nitrogen in their composition than has DACH. The third component makes up ~20% in a total carbon peak for EDA and ~8% for DACH, being of a different character in both of these. In the DACH spectrum, it is lower and broader. That

might mean that different constituents make nearly equal contributions to that peak. This seems not to be the case, however, for EDA. Here, one functionality (probably N—C=O) likely plays a dominant role. This correlates with the FTIR results for 2100–2300 cm^{-1} , where the more expressed diversity of the species was established in the case of the DACH plasma polymers.

The peaks of nitrogen and oxygen are not structured that well, although some useful information can be derived from them. Two components, which are assigned to amine (398.1 eV) and amide (399.5 eV) groups, fit the N 1s EDA plasma polymer spectrum. In the case of DACH, a third component at 400.8 eV was added to maintain a satisfactory fitting and this fact again confirms the assumption that this film is more diverse with various functionalities. It is impossible to

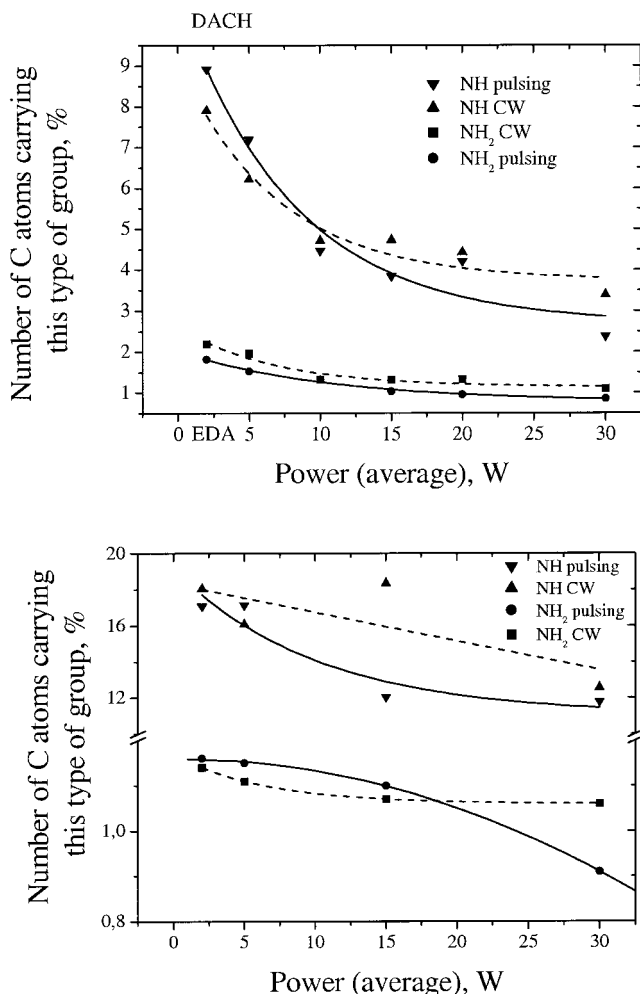


Figure 8 Dependence of NH and NH₂ groups' concentration on deposition conditions.

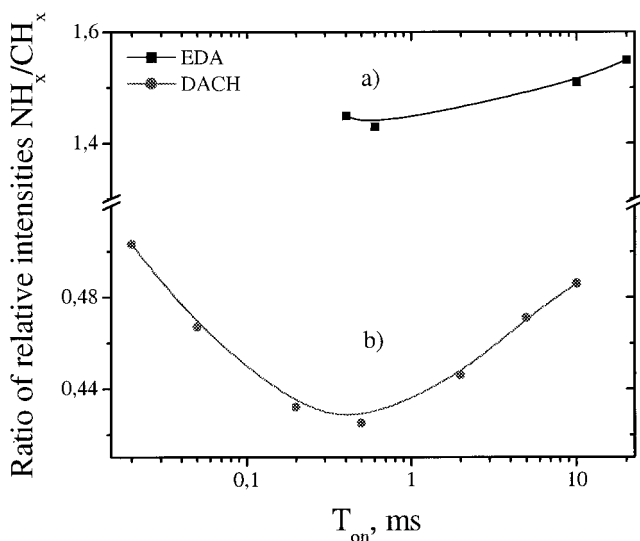


Figure 9 Dependence of the relative concentration of NH_x groups on t_{on}: (a) EDA plasma polymer, P_{av} = 20 W, D = 0.5; (b) DACH plasma polymer, P_{av} = 15 W, D = 0.1

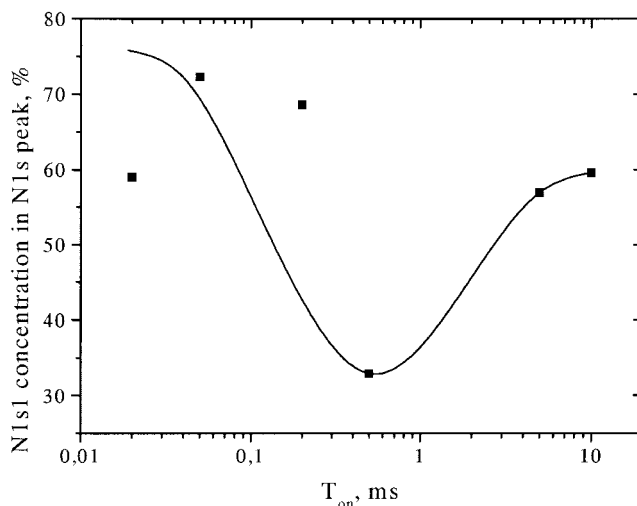


Figure 10 Dependence of concentration of amine groups in pulsed plasma-polymerized DACH (ESCA measurements, 15 W, D = 0.1).

identify the third nitrogen component exactly. It may correspond to complex double-bond structures, for example, O=C—N—C=O functionality. It is interesting to notice that amines constitute only a small part of the nitrogen bonds.

The oxygen peaks are fit by two very broad (more than 2 eV) components, which are shifted by 1 eV with respect to each other. In general, the ~531 eV component might be attributed to the oxygen-carbon with predominant double bonds, and the ~532 eV one, to single-bound oxygen. Both spectra are asymmetric. The EDA spectrum has the higher binding energy tail, while the situation is opposite in the DACH case. Probably a lesser amount of nitrogen in a carbon-oxygen-bound environment for DACH reduces the first component and is responsible for this effect.

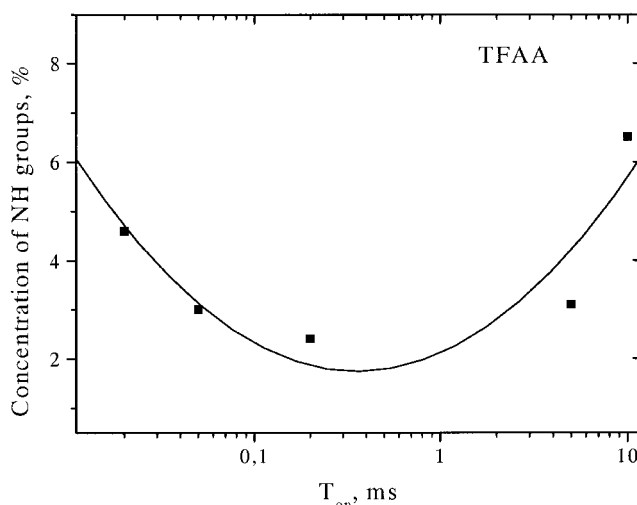


Figure 11 Results of chemical derivatization of DACH plasma polymers by TFAA (15 W, D = 0.1).

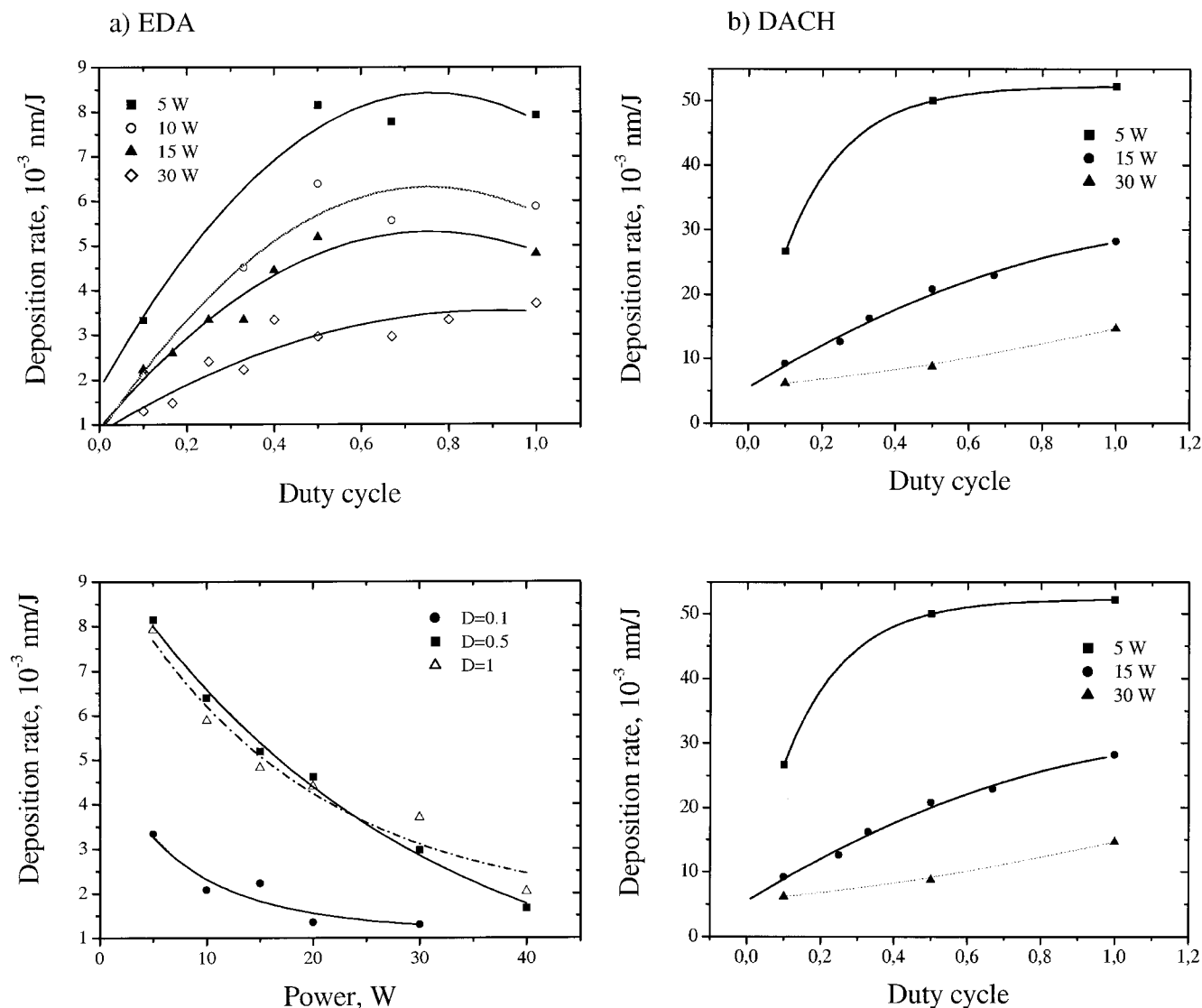


Figure 12 Dependence of the deposition rate of plasma polymers on deposition parameters: (a) EDA, flow rate 2.5 sccm, $t_{\text{on}} = 2$ ms; (b) DACH, flow rate 0.85 sccm, $t_{\text{on}} = 2$ ms.

The C 1s XPS spectra of samples prepared by plasma polymerization of EDA at various powers in CW and pulsed modes are given in Figure 6, and Figure 7 demonstrates the trends in behavior of different deconvoluted peaks in dependence on the power and deposition modes. There is no significant difference between plasma polymers prepared in the CW and pulse modes. Both types of spectra behave similarly in dependence on the power. The power reduction results in an increase of the second and decrease of the first and third carbon components. Following the above-mentioned assignments, the lower discharge powers lead to formation of films with a lower amide concentration and a higher concentration of ordinary C—N bonds. EDA plasma polymers reveal a wider range of compositional changes than those of DACH. In fact, it is difficult to notice any changes in the

C 1s spectra of plasma-polymerized DACH. Figure 7 shows that these changes exist. However, the range in which the composition of the coating can be adjusted is rather small in the CW case and almost negligible in the pulse mode. From this point of view, EDA is a much more preferable monomer, because the composition of the films are much more easily controlled.

To estimate the concentration of amines in the resulting films, the chemical-derivatization technique was applied. TFBA and TFAA were chosen for the detection of primary and secondary amine groups. It should be mentioned that TFAA can react with hydroxyl groups (OH) as well. As a consequence, the NH concentration may be overestimated, provided that there is a certain amount of OH groups on the surface. Still the error cannot be too large. (The oxygen concentration is about 5–10% versus 30–60% of nitrogen.)

The amine concentration has the highest values at the lowest powers applied (Fig. 8). In both EDA and DACH plasma polymers, the concentration of primary amines (NH₂) is much lower than that of secondary amines (NH). Apparently, the monomer molecules are fragmented more extremely in the high-power discharge and the flow sweeps away the NH₂ parts, not allowing them to get into the polymer matrix. EDA produces films with a higher amine concentration and that coincides with the FTIR-ATR results. The pulsing does not produce any considerable effect on the retention of amine groups in the film, in our case. The concentration of NH₂ groups in pulse plasma-polymerized EDA is only a little more than in the CW case for lower powers. In DACH plasma polymers, it is even less for pulsing than for CW. The concentration of secondary amines is also nearly the same for the pulse and CW modes. DACH plasma polymers prepared at lower powers in the pulse mode seem to have more NH groups than do the CW plasma polymer. The pulse mode seems to work ineffectively with the chosen monomers and parameters.

Influence of t_{on} on Film Composition

The further step of our research was to investigate the deposition process with t_{on} as a single variable parameter, others being held constant. Before measurements, the samples were kept in open air for 1 month. The range of t_{on} variation was chosen from 0.02 to 10 ms. The character of the FTIR spectra is the same as of those in Figure 2 regarding the location of the absorption bands, which indicates that no new bonding environment occurs in a mentioned range of parameters. However, if intensities of individual peaks are compared, one may notice that this ratio somewhat changes. To make it clearer, the ratio of intensities of the NH_x and CH_x asymmetric vibrations are plotted in Figure 9 as a function of t_{on} . This ratio may serve as a semiquantitative value of NH_x concentration with respect to CH_x. It may be observed that t_{on} values of about 0.5 ms correspond to films with a lesser concentration of amine/amide groups.

The results of N 1s XPS spectra deconvolution indicate that the amine/amide ratio is minimal in that region (Fig. 10). It is reported¹³ that aging of amine-containing films runs predominantly through the oxidation of carbon atoms bound to amine groups, which results in the formation of amides. From that viewpoint, our films prepared at the lowest and highest t_{on} are more stable to oxidation processes than those obtained at t_{on} of about 0.5 ms. DACH samples treated with TFAA reveal a minimum in amine concentration (Fig. 11). The fragmentation of the monomer molecules does not result in effective retention of NH_x groups into the film in that region. The reason of that effect is still unclear.

Dependence of Deposition Rate on the Deposition Parameters

The deposition rate was calculated as follows: $Dr = l / (Pt)$, where l is the thickness of the film (nm); P , the average discharge power (W); and t , the time of the deposition (s). It was assumed that the time dependence of the deposition rate is linear. The curves in Figure 12 illustrate that the highest deposition rates are accessible at lower powers and in the CW mode.

The chosen value of $t_{on} = 2$ ms is, probably, too large for this kind of deposition. It seems that the polymerization process ends in quite a short time after the discharge has been turned off. In the rest of the t_{off} time, there is no polymerization at all and reduction of the duty cycle (increase of t_{off}) leads to a significant slowing of the process. Thus, the deposition process is preferably to be performed at lower t_{on} and t_{off} (Fig. 13). The effect of the deposition rate dependence on the duration of t_{on} and t_{off} (at a constant duty cycle)

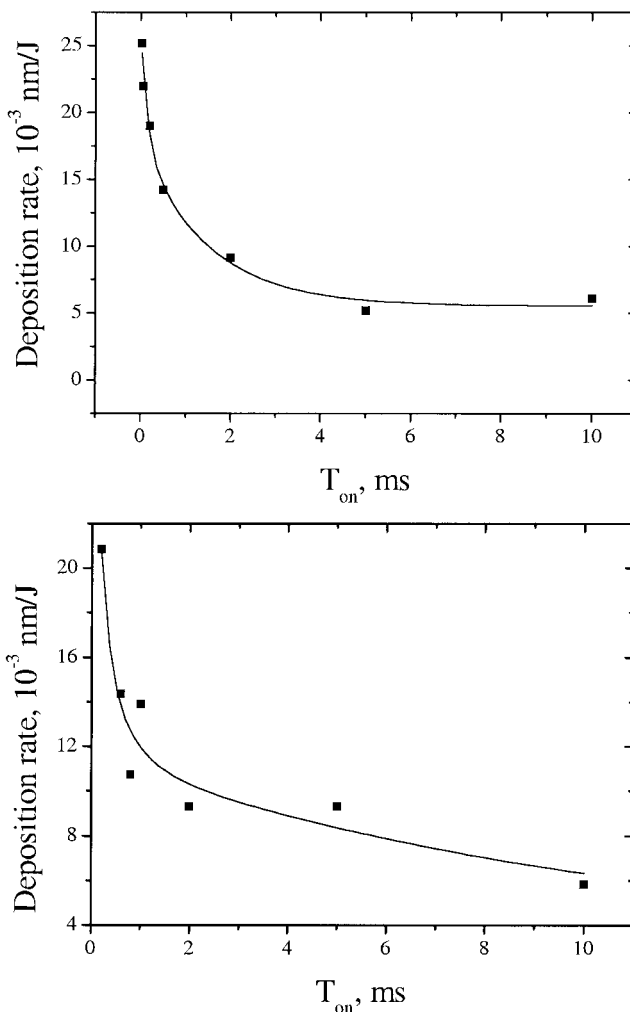


Figure 13 Dependence of the deposition rate of the plasma polymers on t_{on} : (a) DACH, 15 W, D = 0.1, 0.85 sccm; (b) EDA, 5 W, D = 0.2, 0.5 sccm.

was noted for fluorocarbon monomers.¹⁴ In our case, the deposition rate, being nearly constant in the millisecond range, increases rapidly, approaching the microsecond region, when the frequency of the on- and off-time interchange is higher. In that case, the supply of the polymerizing species is more intensive and polymerization runs effectively through the whole period of t_{off} . Hence, when choosing the parameters of deposition, attention should be paid to the right choice of the duty cycle, power, and duration of t_{on} .

The reason of the higher deposition rate of the DACH plasma polymer is in the lower flow rate of that monomer compared to EDA. It is assumed that at lower flow rates the active species have a longer time for anchoring at the surface. The deposition rate would be expected to decrease at the very small values of the flow rate because of the lack in supply of the fresh monomer¹⁵; however, we did not reach this region.

CONCLUSIONS

The amine-containing coatings were prepared in a wide range of conditions from different monomers. It is shown that plasma polymers have little in common with the traditional polymers and possess unique features. Two chosen monomers produce very different films. EDA is more effective than is DACH, if the ability to produce the higher amine concentration is considered. The nitrogen concentration in EDA plasma polymers is about twice higher than that of DACH. Oxygen incorporates into the polymer during both the polymerization process as a result of the reaction with carbon radicals and, after the deposition, due to aging in the air. Lower discharge powers pro-

duce films with a higher concentration of amine groups and with higher deposition rates. Duty-cycle variation does not significantly influence the composition of the resulting films. However, the duration of the t_{on} time is a very important parameter, which affects the kinetics of the deposition process.

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References

1. Rinsch, C. L.; Chen, X.; Panchalingam, V.; Eberhart, R. C.; Wang, J.-H.; Timmons, R. B. *Langmuir* 1996, 12, 2995.
2. Han, L. M.; Timmons, R. B. *Chem Mater* 1998, 10, 1422.
3. Calderon, J.; Timmons, R. B. *Macromolecules* 1998, 31, 3216.
4. Mackie, N. M.; Castner, D. G.; Fisher, E. R. *Langmuir* 1998, 14, 1227.
5. Leich, M. A.; Mackie, N. M.; Williams, K. L.; Fisher, E. R. *Macromolecules* 1998, 31, 7618.
6. Haddow, D. B.; Beck, A. J.; France, R. M.; Fraser, S.; Whittle, J. D.; Short, R. D. *J Vac Sci Technol A* 2000, 18, 3008.
7. Limb, S. J.; Gleason, K. K.; Edell, D. J.; Gleason, E. F. *J Vac Sci Technol A* 1997, 15, 1814.
8. Labelle, C. B.; Limb, S. J.; Gleason, K. K. *J Appl Phys* 1997, 82, 1784.
9. Chance, J. J.; Purdy, W. C. *Thin Solid Films* 1998, 335, 237.
10. Muller, M.; Oehr, C. *Surf Coat Technol* 1999, 116–119, 802.
11. Biederman, H.; Boyaci, I. H.; Bilkova, P.; Slavinska, D.; Mutlu, S.; Zemek, J.; Trchova, M.; Klimovic, J.; Mutlu, M. *J Appl Polym Sci* 2001, 81, 1341.
12. Pearse, R. W. B.; Gaydon, A. G. *The Identification of Molecular Spectra*, 4th ed.; Wiley: New York, 1976.
13. Gengenbach, T. R.; Chatelier, R. C.; Griesser, H. J. *Surf Interf Anal* 1996, 24, 611.
14. Labelle, C. B.; Gleason, K. K. *J Vac Sci Technol A* 1999, 17, 445.
15. Biederman, H.; Osada, Y. *Plasma Polymerization Processes*; Elsevier: Amsterdam, 1992.