



Influence of nitrogen on the tribological properties of a-C:H layers on the polycarbonate substrates

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Abstract

Polycarbonate (PC) possesses many commercial applications. However, PC is still limited to non-abrasive and chemical-free environments due to its low hardness, low scratching resistance and high susceptibility to chemical attacks. To overcome this limitation, PC can be coated by hydrogenated amorphous carbon layers. The a-C:H layers have very attractive properties such as high hardness, infrared transparency, chemical inertness, low friction coefficients, and biocompatibility. Addition of nitrogen in the structure allows lowering internal stress and improve tribological properties of a-C:H layers. In this work, a-C:N:H layers were deposited from mixture CH_4/N_2 gases by RF PECVD method. Effects of the nitrogen incorporation on structure and tribological properties of deposited layers were investigated. The structure of layers were characterized by Fourier Transform Infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The friction coefficient, wear resistance of a-C:H:N layers were estimated by tribometer in ball-on-disc configuration. The IR spectra of the obtained layers have demonstrated a presence of nitrogen bonded both to carbon and to hydrogen. A formation of the following bonds has been confirmed: $-C\equiv N$, $-NH_2$, $-C-NH_2$, $>C=NH$. They are all typical for a-C:N:H layers. The tribological tests have shown that the layers reduce the friction coefficient of the polycarbonate (up to 50 %) and considerably improve wear resistance.

Keywords: nitrogen incorporation, a-C:H:N films, plasma-enhanced chemical vapour deposition (PECVD), polycarbonate

1. Introduction

Plastics form a class of very important materials which in many applications can replace traditional ceramics and glasses. They can be produced on a big scale and with low costs. They are light and easy to be formed. Especially wide range of possible applications characterizes a family of polycarbonates (PC). They have perfect transparency that allows them to substitute glass in such uses like: automotive headlamps [1], window safe shield or corrective lenses [2]. Unfortunately polycarbonates are not as hard as glass and have low scratch resistance. They may be easily destructed by chemical substances and UV radiation. This is why the use of polycarbonates is limited to environments without abrasives and free of substances causing chemical

corrosion. Thus, an improvement of usable properties of polycarbonates should come down to a modification of a surface of the product. The desirable effects may be achieved throughout application of overcoats carefully designed to meet the expectations.

Polycarbonates are generally known as untoward materials when used as substrates in the thin layer technology [3]. This is because of their low thermal stability, weak adhesion of the layers and a presence of interface tensions. The most optimal conditions that allow reducing these limitations are offered by plasma-enhanced chemical vapour deposition technique with plasma generated by radio waves (RF-PECVD) [4,5]. This method is successful in obtaining amorphous carbon layers of a-C:H and a-C:N:H types, which are very promising as overcoats applied to modify polycarbonate surface [6]. The layers of this type exhibit a series of exceptional properties such as high hardness, good transparen-

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cy, chemical inertness, low friction coefficient and biocompatibility [7,8]. Their unique properties make them good candidates for wear-protective and antireflective coatings providing a gas permeation barrier for a variety of different applications [9–11].

This work contains the results of the studies aimed at obtaining good quality and well adhesive a-C:N:H layers on polycarbonate substrates. In the series of the experiments, performed with application of RF-PECVD technique, various quantities of nitrogen precursor were introduced to the reactive gas mixture. An influence of nitrogen on the layer structure and composition was examined with Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Friction coefficient and wear resistance were evaluated in tribological tests.

II. Experimental

The a-C:N:H layers were deposited on polycarbonate substrates with plasma enhanced RF CVD technique (13.56 MHz, 300 W). The substrates were placed in the processing chamber onto the cathode biased to -325 V. Before each deposition process the PC substrates were properly modified by Ar⁺ and He⁺ ion bombardment during 10 minutes (8 W of plasma generator power, 15 sccm of Ar flow and 15 sccm of He flow). The layers were synthesized using mixtures of pure reactive gases: CH₄ and N₂ with inert Ar. The gases were introduced into the reactor chamber at different proportions. For the purpose of structural studies a simultaneous deposition was made on Si (100) substrate. The synthesis parameters used in the respective experiments were following: 22.6 Pa of gas pressure in the reactive chamber, 80 W of plasma generator power and 1.5 h of the deposition time. The substrate temperature was below 80°C. Few series of the samples were grown for various gas-flow ratios. The N₂ flow was varied between 0 and 60 sccm, while CH₄ and Ar flow were kept constant at 8 and 50 sccm, respectively. The structure of the obtained layers was studied from FTIR absorption spectra recorded within the wavenumber range 1800–4000 cm⁻¹, with resolution 4 cm⁻¹ (FTS-60V Bio-Rad spectrometer). The quantitative analysis was evaluated of the X-ray photoelectron spectroscopy (XPS) with the use of the X-ray with aluminum anode and quartz monochromator, from the area approximately 0.8 mm in diameter. The friction coefficient and wear resistance were determined in the rotary motion test by using the tribotester of “ball-on-disc”. The measurements were made according to the ASTM G 99-05, ISO 20808:2004 norms, using steel and Al₂O₃ balls, both of 1 mm in diameter. The following test parameters were applied: normal load $F_n = 1.5$ N, rotary speed $\nu = 60$ rot/min, number of cycles $N = 2000$, radius friction trajectory $R = 4$ mm.

III. Results and Discussion

Infrared spectra recorded for the a-C:N:H layers grown with application of various concentrations of nitrogen in the reactive gas mixtures are shown in Fig. 1. The spectrum of the a-C:H layer deposited from CH₄ is given for comparison.

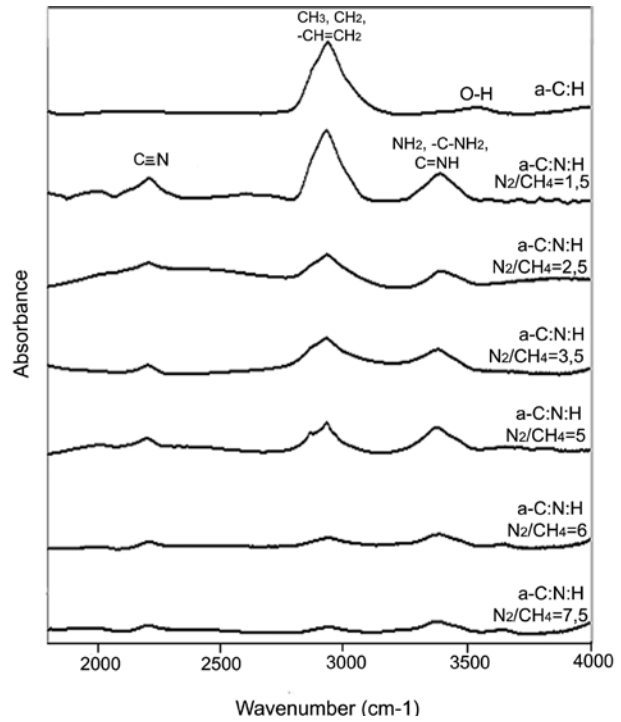


Figure 1. Transmission FT IR spectra recorded for the a-C:H and a-C:N:H layers deposited from different gas mixtures

The measurements were made within the wavenumber ranging between 1800 and 4000 cm⁻¹. The FTIR spectrum taken for the a-C:H layer exhibits a presence of a strong band at 2800–3000 cm⁻¹, which can be assigned to the vibrations in -CH₃, -CH₂ and -CH=CH₂ groups [12,13]. For higher energies (above 3500 cm⁻¹) a weak band related to the vibrations of the O–H bonds can be seen. Its presence results from an adsorption of water on the surface of the layer. The spectra of the nitrogenated a-C:N:H layers contain additional absorption bands at about 2200 cm⁻¹ and 3350–3410 cm⁻¹. They come from the vibrations in C≡N, NH₂, -C–NH₂ and C=NH groups [14,15]. There is no longer the band due to O–H vibrations. The spectra for the layers deposited at various N₂/CH₄ ratios do not reveal any qualitative differences. The only effect concerns intensities of the respective bands. In particular, the intensities of the bands assigned to CH₃, CH₂, -CH=CH₂ (in the region 2800–3000 cm⁻¹) clearly decrease with increase of N₂ content in the gas mixture. Simultaneously, the intensity of the bands coming from the bonds formed with participation of the nitrogen (at 2200 and 3350–3410 cm⁻¹) lowers insignificantly.

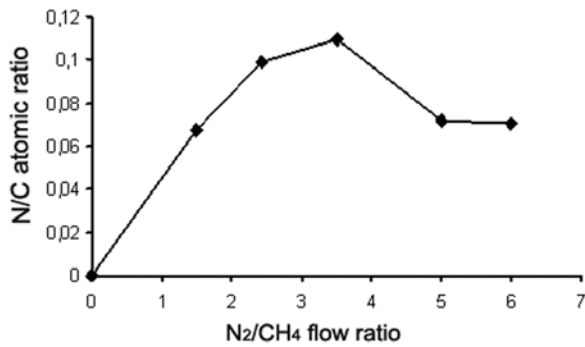


Figure 2. Evolution of the N/C ratio in the films as the function of the N₂/CH₄ flow ratio

The chemical composition of the layers was determined using XPS method. The results are presented in Fig. 2. An increase of N₂/CH₄ ratio up to 3.5 causes the rise of nitrogen content, calculated as N/C, up to atomic 12%. Further increase of N₂ flow is followed by decrease of N content in the layers (down to atomic 7%). This effect may be a consequence of the chemical desorption of N₂ molecules formed in the reactions between nitrogen atoms from the surface and gas phase. Thus, higher N₂ concentration in the gaseous mixture increases a probability of such reactions [16]. Simultaneously, one observes a decrease of the layer thickness, which is in agreement with lowering of the intensities of FTIR absorption bands (Fig. 1).

The obtained layers are well adhesive to the polycarbonate substrate. No acoustic effects have been registered in the scratch-test that could be related to a potential crack or a delamination of the layer from the substrate.

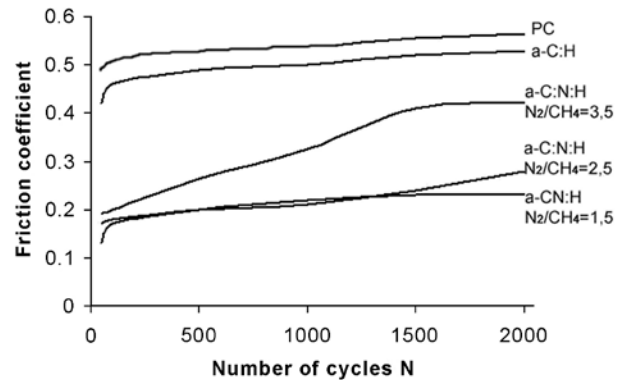


Figure 3. An average value of the friction coefficient measured at the contact of the layer with the Al₂O₃ (1 mm) ball during 50, 100, 500, 1000, 1500 and 2000 cycle ($F_n = 1.5$ N; $n = 60$ rot/min; $R = 4$ mm)

In Fig. 3 the values of friction coefficients measured in rotary motion during 2000 cycles are shown. The values for a-C:H and a-C:N:H layers are given. In the experiment, the Al₂O₃ ball was used instead of the steel one. The results of the measurements performed with the use of the steel ball were difficult to detect. The lowest friction (0.2) coefficients characterise the a-C:N:H layers deposited from the reagent-mixture ratio N₂/CH₄ equal to 1.5 and 2.5. At the initial stage of the contact the friction coefficients were lower, i.e. 0.12 and 0.18 for the a-C:N:H layers deposited from the reagent-mixture ratio N₂/CH₄ equal to 1.5 and 2.5, respectively. The respective value for the sample formed at N₂/CH₄ = 3.5 changes from 0.2 to 0.42, which is connected with a destruction of the layer (after about 1200 cycles). A destruction of the a-C:H took place after a few cycles. The respective friction coefficient has been 0.5.

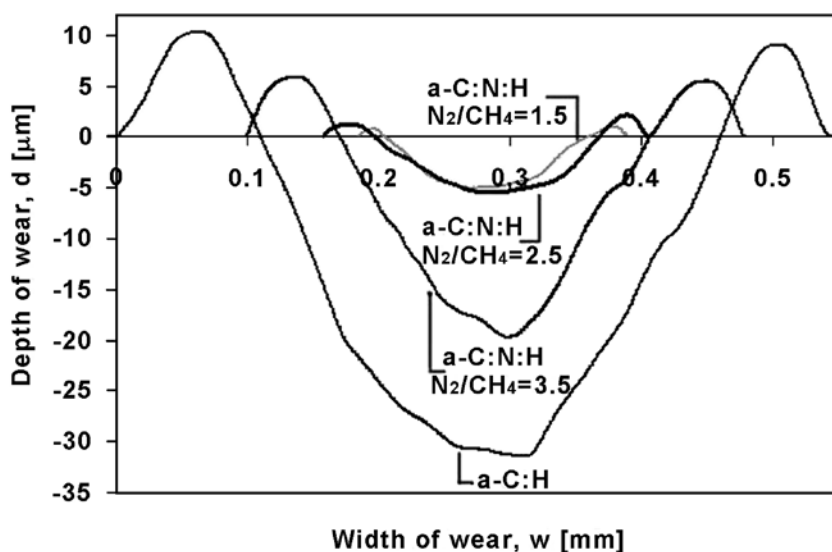


Figure 4. Cross-section profiles of the typical grooves observed for the samples covered with the layers. The results of the friction test performed with the use of the Al₂O₃ ball ($F_n = 1.5$ N; $n = 60$ rot/min; $R = 4$ mm; $N = 2000$ cycles)

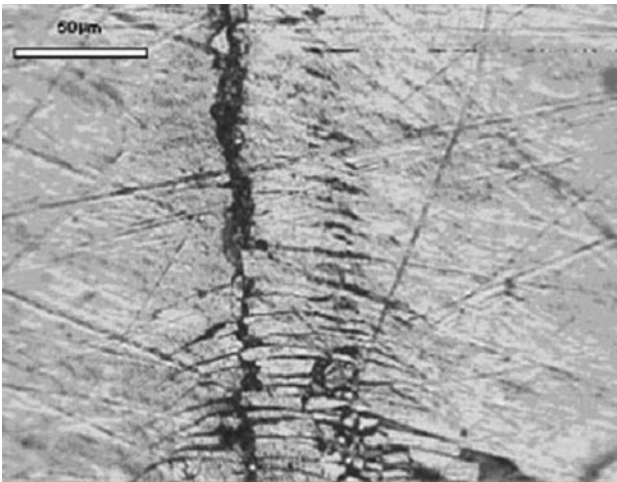


Figure 5. The surface of the sample covered with the a-C:N:H ($N_2/CH_4 = 1,5$) layer. The characteristic cracks can be seen. The picture made after the friction test performed with application of the Al_2O_3 ball ($F_n = 1,5$ N; $n = 60$ rot/min; $R = 4$ mm; $N = 2000$ cycles).

In the case of the contact with the Al_2O_3 ball there can be seen grooves. A cross-section of such groove is shown in Fig. 4. The typical piles occurring at the groove sides can be also seen. The grooves appearing in the samples after the contact with the Al_2O_3 ball under the 1.5 N of the weight have characteristic cyclic sills and hollows (Fig. 5). The samples covered with the a-C:N:H layers show the wear resistance few times higher than the samples with a-C:H layers. The highest resistance is typical for the layer deposited from the $N_2/CH_4 = 1.5$ mixture, but characteristic at $N_2/CH_4 = 2.5$ is a little worse (Fig. 6).

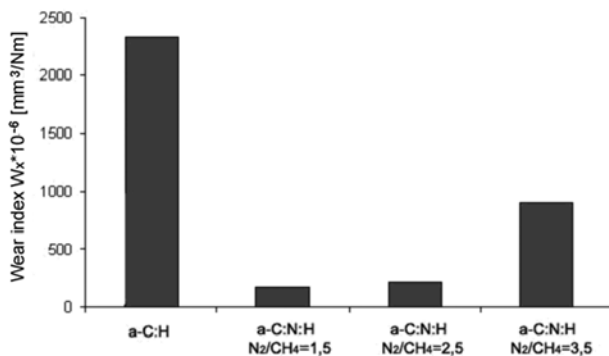


Figure 6. Wear indexes for the samples after the friction test performed with the use of the Al_2O_3 ball ($F_n = 1,5$ N; $n = 60$ rot/min; $R = 4$ mm; $N = 2000$ cycles)

VI. Conclusions

The application of plasma enhanced RF-CVD technique allows obtaining the a-C:N:H layers well adhesive to the PC substrate. The IR spectra recorded for the deposited layers are of typical shape and confirm a presence, in the structure, of the groups containing nitrogen: $C \equiv N$ and NH_2 , $-C-NH_2$, $C=NH$. The intensities

of the bands decrease with rising nitrogen content in the gas mixture.

The compositions analysis allowed to determine the quantity of built-in nitrogen in the layer in dependence of the flow of nitrogen. The quantity of nitrogen in the layer was limited and increase of the N_2/CH_4 ratio, in the reactionary mixture, to the certain level even causes the lowering of its content.

Simultaneously the incorporation of the nitrogen causes a significant improvement in the tribological properties of the PC covered with the layer. The friction coefficient decreases almost twice and the wear resistance significantly improves (up to 10 times for the a-C:N:H layers deposited at $N_2/CH_4 = 1.5$).

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