

Amorphous carbon layers on polymeric substrates

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Materials

ABSTRACT

Purpose: This paper is aimed to study an effect of nitrogen incorporation on the structure and tribological properties of amorphous a-C:N:H layers grown on polycarbonate substrates.

Design/methodology/approach: Series of the layers were deposited from CH₄ + N₂ gas mixture with application of Plasma Enhanced Chemical Vapour Deposition technique assisted by radio waves (RF PE CVD). An analysis of atomic-level structure of the layers was made using FT IR technique. The samples were subjected to investigations of friction coefficient and wear resistance. The respective measurements were performed using Micro-Combi-Tester and a tribometer in ball-on-disc configuration.

Findings: 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≡N, -NH₂, -C-NH₂, >C=NH. All they are 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 abrasion resistance.

Research limitations/implications: Further studies in order to find relations between growing conditions and the properties of the layers should be performed. A role of the chemical composition and structure should be carefully analyzed.

Practical implications: An application of carbon overcoats on polycarbonates may improve the usable properties of plastic components (hardness, scratch resistance, UV radiation resistance). This will make polycarbonates attractive materials of wide spectrum of possible applications.

Originality/value: It has been shown in this research that application of RF PE CVD technique allows obtaining the a-C:N:H layers improving usable properties of plastics. The layers well adhesive to the substrate may be obtained at the temperatures below 80°C.

Keywords: Amorphous materials; Engineering polymers; C:N:H layers; PA CVD; Tribology

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 for 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 PE CVD) [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 transparency, 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 [9,10,11].

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 PE CVD technique, various quantities of nitrogen precursor were introduced to the reactive gas mixture. An influence of nitrogen on the layer structure was examined with Fourier transform infrared spectroscopy (FTIR). Friction coefficient and wear resistance were evaluated in tribological tests.

2. 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 min. 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 was kept constant at 8 and 50 sccm respectively.

The structure of the obtained layers was studied from FTIR absorption spectra recorded within the wavelength range 400 - 4000 cm⁻¹, resolution 4 cm⁻¹ (FTS-60V Bio-Rad spectrometer). The friction coefficient and wear resistance were determined both in reciprocating and rotary motion of the sample. The reciprocating motion test was performed with a Micro-Combi-Tester CMES according to the guidelines given in the norms: ASTM G99-90, DIN 50324E and ASTM G133-02. A steel ball of 1mm of the diameter was used for the measurements. The other

parameters were following: normal load $F_n = 0,5$ N, linear speed $v = 5$ mm/min, track length $s = 2$ mm, number of the cycles $N = 100$. In the rotary motion test, the tribotester of "ball-on-disc" type was used. The measurements were made according to the ASTM G 99-05, ISO 20808:2004 norms, using steel and Al₂O₃ balls, both of 1mm of the diameter. The following test parameters were applied: normal load $F_n = 1,5$ N, rotary speed $v = 60$ rot/min, number of cycles $N = 2000$, radius friction trajectory $R = 4$ mm.

3. Results and discussion

3.1. FT IR spectra

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.

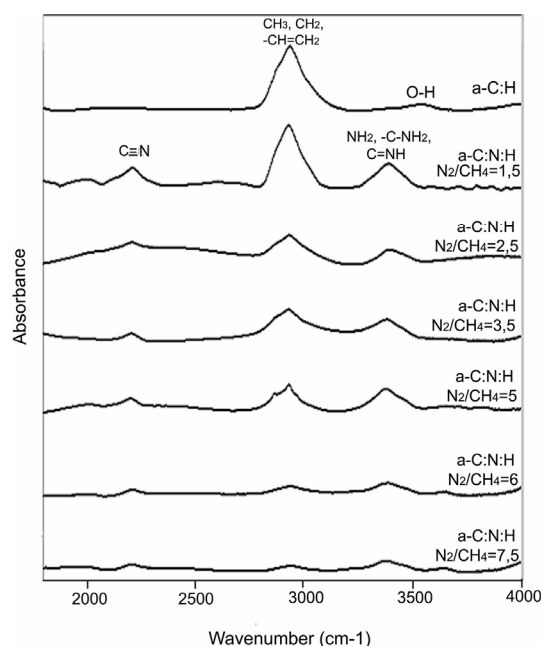


Fig.1. Transmission FT IR spectra recorded for the a-C:H and a-C:N:H layers deposited from different gas mixtures

The measurements were made within the wavelength 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 - 3000cm⁻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 N_2/CH_4 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 CH_3 , CH_2 , $-CH=CH_2$ (in the region $2800-3000\text{ cm}^{-1}$) clearly decrease with increase of N_2 content in the gas mixture. Simultaneously, the intensity of the bands coming from the bonds formed with participation of the nitrogen (at 2200 and $3350-3410\text{ cm}^{-1}$) lowers insignificantly.

3.2. Tribological properties

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. The results of the measurements of friction coefficients performed in the progressive and repayable motion are presented in Fig. 2 and 3. At the initial stadium of the friction test, small instabilities of tangent force have been observed. They can be put down to a formation of a contact between the co-operating surfaces.

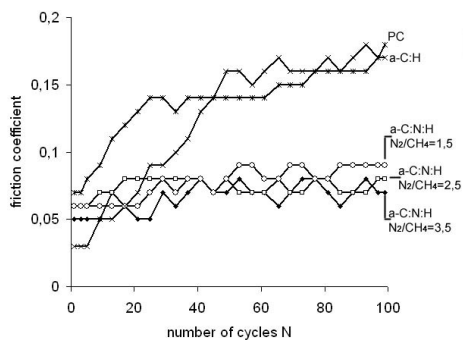


Fig. 2. Friction coefficient measured in progressive motion after 100 cycles for: $F_n = 0,5\text{ N}$, $v = 5\text{ mm/min}$, $s = 2\text{ mm}$

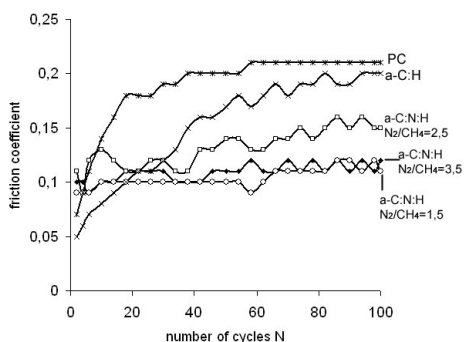


Fig.3. Friction coefficient measured in repayable motion after 100 cycles for: $F_n = 0,5\text{ N}$, $v = 5\text{ mm/min}$, $s = 2\text{ mm}$

For all samples the values of the friction coefficient in the progressive motion are lower than the respective values measured in the repayable motion. A comparison of the friction coefficients for the a-C:N:H layers deposited from various gas mixtures indicates that the

lowest values (about 0,09) are characteristic for the samples deposited at $N_2/CH_4 = 1,5$ and $N_2/CH_4 = 3,5$. Somewhat higher (0,11) is the coefficient of the layer deposited at $N_2/CH_4 = 2,5$. The friction coefficient of the bare PC equals 0,2. In the measurement of the friction coefficient of a-C:H layer its variation is observed. It initially increases and then stabilises at about 0,2. Such behaviour indicates a rapid destruction of the layer and eventual contact of the ball with the substrate. In the contradiction to this, a behaviour of a-C:N:H layers remains. During the measurements performed with the weight of 0,5 N at 100 cycles no layers' wear has been observed. Only a small wear of the ball takes place.

In Fig. 4 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 Al_2O_3 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 N_2/CH_4 equal to 1,5 and 2,5. At the initial stage of the contact the friction coefficient has been lower and equalled 0,12 and then 0,18. The respective value for the sample formed at $N_2/CH_4 = 3,5$ 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.

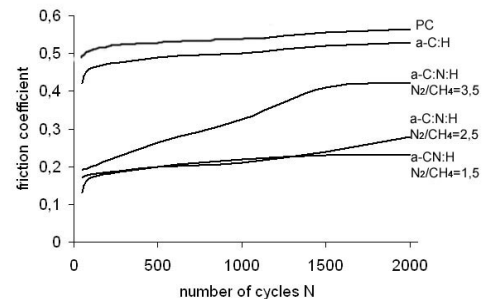


Fig. 4. An average value of the friction coefficient measured with a use of Al_2O_3 (1 mm) ball after 50, 100, 500, 1000, 1500 i 2000 cycles ($F_n = 1,5\text{ N}$; $n = 60\text{ rot/min}$; $R = 4\text{ mm}$)

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.5. 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.6). 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, a little worse is characteristic at $N_2/CH_4 = 2,5$ (Fig. 7).

4. Conclusions

The application of 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: $C=N$ and

NH_2 , $-\text{C}-\text{NH}_2$, $\text{C}=\text{NH}$. The intensities of the bands decrease with rising nitrogen content in the gas mixture. Simultaneously the incorporation of the nitrogen causes a significant improvement of 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 $\text{N}_2/\text{CH}_4 = 1,5$).

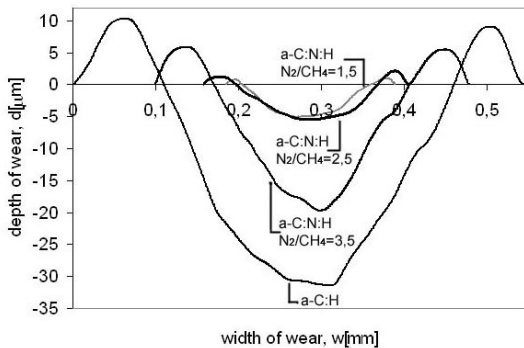


Fig. 5. A cross-section profiles of the typical grooves observed for the samples covered with the layers. The results of the friction test performed with the use of the Al_2O_3 ball ($F_n = 1,5 \text{ N}$; $n = 60 \text{ rot/min}$; $N = 2000 \text{ cycles}$; $R = 4 \text{ mm}$)

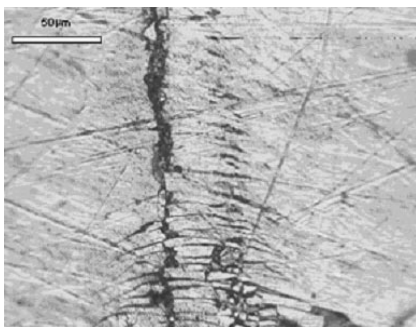


Fig. 6. The surface of the sample covered with the a-C:N:H ($\text{N}_2/\text{CH}_4=1,5$) layer. The characteristic cracks can be seen. The picture made after the friction test performed with application of the Al_2O_3 ball ($F_n = 1,5 \text{ N}$; $n = 60 \text{ rot/min}$; $R = 4 \text{ mm}$, $N = 2000 \text{ cycles}$)

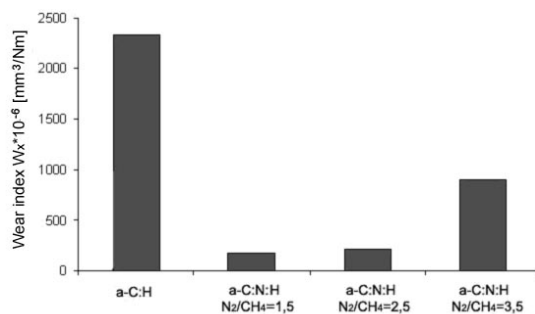


Fig. 7. Wear indexes for the samples after the friction test performed with a use of the Al_2O_3 ball ($F_n = 1,5 \text{ N}$; $n = 60 \text{ rot/min}$; $N = 2000 \text{ cycles}$; $R = 4 \text{ mm}$)

Acknowledgements

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References

- [1] T. Schmauder, K.D. Nauenburg, K. Kruse, G. Ickes, Hard coatings by plasma CVD on polycarbonate for automotive and optical applications, *Thin Solid Films* 502 (2006) 270-274.
- [2] M. Kuhr, S. Bauer, U. Rothhaar, D. Wolff, Coatings on plastics with the PICVD technology, *Thin Solid Films* 442 (2003) 107-116.
- [3] U. Schulz, N. Kaiser, Vacuum coatings of plastic optics, *Progress in Surface Science* 81 (2006) 387-401.
- [4] J. Zajickova, V. Bursikova, V. Perina, A. Mackova, D. Subedi, J. Janca, S. Smirnova, Plasma modification of polycarbonates, *Surface and Coatings Technology* 142-144 (2001) 449-454.
- [5] J. Robertson, *Materials Science and Engineering, Diamond-like amorphous carbon* 37 (2002) 129-281.
- [6] N. K. Cuong, M. Tahara, N. Yamauchi, T. Sone, Effects of nitrogen incorporation on structure of a-C:H films deposited on polycarbonate by plasma CVD, *Surface and Coating Technology* 193 (2005) 283-287.
- [7] J. Takadom, J.Y. Rauch, J.M. Cattenot, N. Martin, Comparative study of mechanical and tribological properties of CN_x and DLC films deposited by PECVD technique, *Surface and Coatings Technology* 174-175 (2003) 427-433.
- [8] B.P. McNamara, H. Murphy, M.M. Morshed, Adhesion properties of diamond-like coated orthopaedic biomaterials, *Diamond and Related Materials* 10 (2001) 1098-1102.
- [9] Y.C. Wang, K.J. Shieh, M.S. Shyu, F.L. Shyu, J.S. Shyu, W.C. Hwang, Diamond-like carbon film overcoats for phase-change optical recording discs, *Surface and Coating Technology* 165 (2003) 140-145.
- [10] A. Shirakura, M. Nakaya, Y. Koga, H. Kodama, T. Hasebe, T. Suzuki, Diamond-like carbon films for PET bottles and medical applications, *Thin Solid Films* 494 (2006) 84-91.
- [11] S. Zang, M.J. Tang, P. Hing, H. Xie, H.L. Wong, W.L. Ng, Nitrogenated carbon layer on magnetic recording discs, *Journal of Materials Processing Technology* 89-90 (1999) 556-560.
- [12] S.E. Rodil, Infrared spectra of amorphous carbon based materials, *Diamond and Related Materials* 14 (2005) 928-933.
- [13] G. Lazar, I. Lazar, IR characterization of a-C:N:H films sputtered in $\text{Ar}/\text{CH}_4/\text{N}_2$ plasma, *Journal Non-Crystalline Solids* 331 (2003) 70-78.
- [14] J.Ju, Y.Xia, W.Zhang, L.Wang, D.Tang, Infrared optical properties of amorphous hydrogenated carbon nitride film, *Journal of Non-Crystalline Solids* 278 (2000) 213-217.
- [15] S. Jonas, I. Łagosz, C. Paluszkiwicz, W. Ptak, Low temperature IR spectra of a-C:N:H layers, *Journal of Molecular Structure* 596 (2001) 101-108.