Substrate surface temperature as a decisive parameter for diamond-like carbon film adhesion to polyethylene substrates

I.Sh. Trakhtenberg [a], O.M. Bakunin [a], I.N. Korneyev [a], S.A. Plotnikov [a],
A.P. Rubshtein [a,*], K. Uemura [b]

[a] *Institute of Metal Physics, Ural Branch RAS, Ekaterinburg, Russia*
[b] *Tomsk Polytechnic University, Tomsk, Japan*

Abstract

Protective diamond-like carbon coatings (DLCs) deposited on polymer substrates represent a promising means for modification of the substrate surface. Application of strong DLCs on these substrates is rendered difficult due to a large difference in their thermal expansion coefficients, and also to the low heat resistance and thermal conductivity of most polymers. Vacuum pulsed sputtering of graphite is among the methods which show greatest promise for creation of DLCs on such substrates. In this method it is possible to adjust, within broad limits, the mean sputtering rate, and consequently control the thermal load on the substrate during sputtering.

We measured the temperature distribution in bulky high-density polyethylene (PE) substrates depending on the pulse repetition rate and the number of pulses in the carbon source. The data were used to determine optimal conditions for deposition of DLCs on PE. DLCs almost 0.1 μm thick were deposited in two stages. In the first stage, when the best adhesion was provided, the source power was a maximum. In the second stage the source power was an order of magnitude lower.

Adhesion of the DLCs to the substrates was evaluated using the standard adhesive tape test and by resistance to thermal cycling in the intervals from 77 to 287 K and 77 to 373 K. Adhesion of the DLCs to PE was shown to be strongly dependent on the substrate temperature at the start of sputtering. The best result was achieved when the substrate temperature was nearly equal to, but did not exceed, the PE melting point. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Adhesion; Diamond-like coating; Polymer substrate; Vacuum pulsed sputtering

1. Introduction

Deposition of wear-resistant protective (including optical) coatings on the surface of polymer products is undoubtedly of practical significance. These products have a relatively low resistance to external effects.

In this respect DLCs are most favorable candidates since they possess high hardness, large wear resistance and low friction coefficients. DLCs can be deposited on substrates with widely varying temperatures. The last factor is of special significance if one takes into account the low heat resistance of most commercial polymers.

Attempts have been made recently to deposit DLCs on substrates such as PE terephthalate [1,2], PE [3], polypropylene [1], polycarbonate [4–6], and polyimide [7].

Those papers were focused on the adhesion of DLCs to the substrate. Adhesion was evaluated by the scratch test [1,3], the adhesive tape test [2] and resistance to thermal cycling [7] considering pre-treatment of the substrate surface [1,3,6] and coating deposition conditions [3]. However, the effect of the substrate temperature on coating adhesion has not yet been analyzed in sufficient detail.

On the one hand, DLCs should be deposited on substrates whose temperature is minimized. This is because their thermal expansion coefficients are largely different ($\sim 10^{-6} \, \mathrm{K}^{-1}$ for DLCs and $\sim 10^{-3} \, \mathrm{K}^{-1}$ for most polymers). Otherwise, the sputtered coating peels off the substrate under the action of stresses arising in the coating on cooling.

On the other hand, adhesion of DLCs to substrates a priori should depend on the substrate temperature at

* Corresponding author. Tel.: +7-3432-499366;
fax: +7-3432-7455244.
E-mail address: a_rubshtein@mail.ru (A.P. Rubshtein)

the moment the first atomic layers of the coating are formed. This dependence may be especially pronounced for most polymer substrates whose physical and chemical properties change to a great extent within a narrow temperature interval.

One more significant feature of polymer materials is their low thermal conductivity. Thanks to this feature, a considerable temperature gradient may appear across the substrate depth during sputtering. As a result, the whole volume of the sample is not heated when several initial layers of the coating are formed. The surface temperature can be controlled over broad limits by changing the power setting of the pulsed arc carbon source. If the power setting of the carbon source is minimized after a thin DLC layer is formed on the substrate, the substrate temperature does not elevate as the DLC is sputtered further. Consequently, the problems associated with widely differing thermal expansion coefficients of the coating and the substrate, and also thermal instability of polymers, are eliminated.

This paper deals with the effect of the surface temperature of polymer substrates on DLC adhesion. Bulky samples of high density PE were taken as an example.

2. Experimental Technique

PE samples $20 \times 20 \times 20$ mm were used as substrates. DLCs were sputtered on the untreated surface, which was formed during the molding of the PE pellets.

The substrate temperature was measured using chromel–alumel thermocouples, which were placed in blind holes of the required depth. The junction of the thermocouple was pressed snug to the hole and was fixed with silicon sealing compound.

DLCs were deposited by vacuum pulsed sputtering of graphite [8]. The thickness of the sputtered coatings was calculated from the dependence of the DLC thickness on the number of pulses generated by the source. The dependence was determined beforehand by the weighing method. The sputtering rate was 0.038 nm and 0.024 nm of carbon per pulse when the sample was spaced 10 cm and 25 cm from the source respectively.

DLCs were sputtered in two stages. In the first stage the carbon source was set to the maximum power (30 Hz), the sample was spaced 10 cm from the source, and 50 to 212 pulses were applied. Under these conditions the surface temperature of the substrate depended on the number of pulses because the substrate had a low thermal conductivity. In the second stage the source power was decreased abruptly (5 Hz), the sample was moved away from the source to a distance of 25 cm, and 4000 pulses were applied additionally. The temperature of the sample did not rise in the second stage.

The adhesion of DLCs to the substrates was evaluated by two methods. In the first standard method, an X-cut

was made in the coating with the angle between the cuts equal to 30°. A cellophane adhesive tape was carefully attached to the coating at room temperature. The tape was pulled off sharply after 2 min. In accordance with the standard: the evaluation point number was 10 in the absence of peeling; 8 if no peeling occurred at the intersect and little peeling was observed at the X-cut; 6 if peeling occurred within 1.5 mm in either direction from the intersect of the X-cut; 4 if peeling occurred within 3.0 mm in either direction from the intersect of the X-cut; 2 if most of the X-cut peeled off with the adhesive tape; and 0 if the peeling area was larger than the X-cut.

In the second method, coated samples were immersed first in liquid nitrogen for 10 s and then in water for 10 s at room temperature and at boiling point. Subsequent to the thermal cycling treatment, the adhesion of the coatings was first assessed under an optical microscope at $\times 100$ magnification. If no peeling was observed, the samples were dried carefully and underwent the adhesive tape test.

3. Results and discussion

Fig. 1 illustrates typical dependences of the substrate temperature on the number of pulses from the carbon source (DLC thickness). These dependences were determined at the maximum power of the source (30 Hz) and a sample–source distance of 10 cm. The thermocouple was positioned differently relative the sputtered surface. It is seen that a considerable temperature gradient, which is due to low thermal conductivity of PE, exists across the depth of the substrate. Fig. 1 suggests that under the given conditions the temperature gradient near the surface in a layer 0.1 mm thick can be estimated at 200 K/mm. The substrate temperature shows a linear dependence on the distance to the surface in semilogarithmic coordinates (after 500 pulses, Fig. 2) and there-
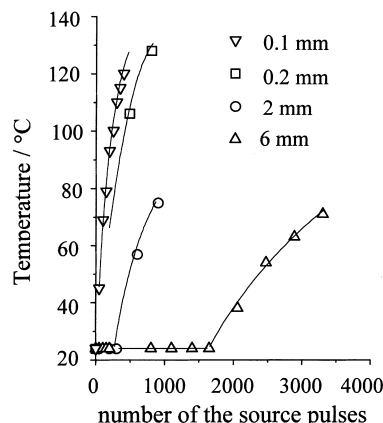

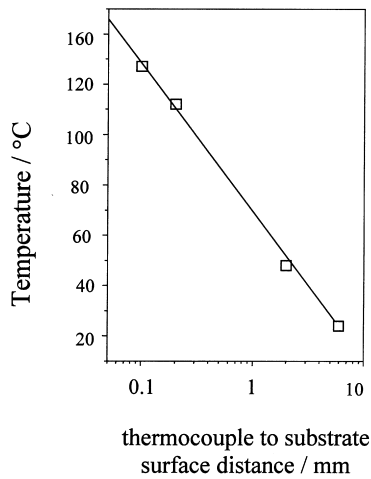Fig. 1. Substrate temperature during DLC deposition. The thermocouple to surface distance is as indicated.

Fig. 2. Temperature distribution in a PE substrate during DLC deposition. Maximum source power, 500 pulses.
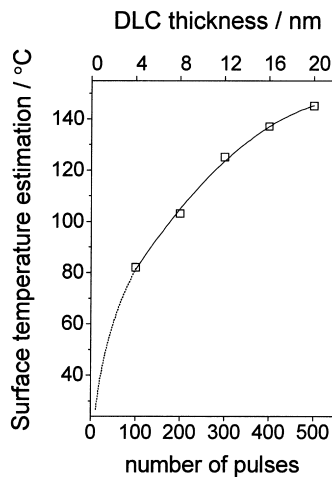

Fig. 3. Estimation of the PE surface temperature during DLC deposition at maximum source power.

Fig. 4. X-cut tape test results for DLC on PE after deposition.
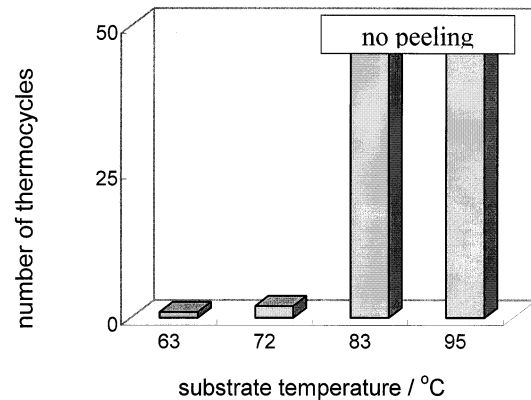
Fig. 5. Spontaneous DLC on PE peeling during thermocycling 77–287 K.

fore it is possible to evaluate the surface temperature. Fig. 3 gives the true temperature estimate of the PE surface depending on the number of pulses from the carbon source and the DLC thickness. The estimate was made on the strength of the data in Figs. 1 and 2 at the maximum power setting of the source. From Fig. 3 it follows that the melting temperature of 376–383 K is
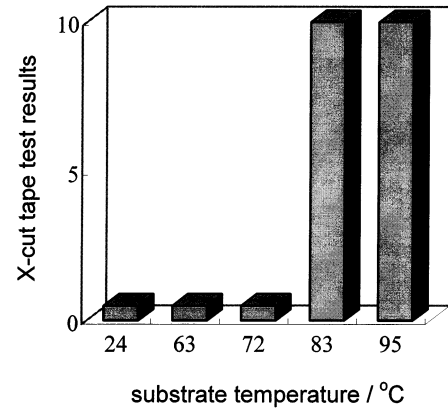
achieved after 200–230 pulses, which correspond to a DLC thickness of 7.5–9 nm. Table 1 gives the sputtering conditions for the test samples.

DLCs on all the samples, except No. 6, were smooth and uniform as seen in an optical microscope. The surface of the sample No. 6 was covered with a network of deep cracks formed as a result of PE melting.

The results of the X-cut tape test of the coated samples are given in Fig. 4. If the surface temperature of the substrate is below 353 K in the first stage, the DLCs readily peel off the substrates. At higher temperatures adhesion is sharply enhanced. Fig. 5 shows the

Table 1
DLC sputtering conditions

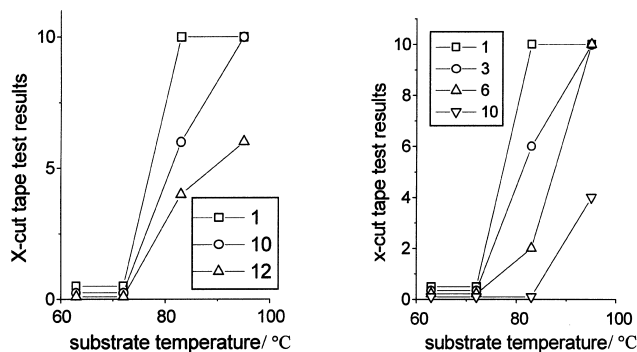| Ord. no.	Number of pulses at the first stage	Thickness of DLC in the first stage (nm)	Maximum temperature of the substrate (K)	Total thickness (nm)
1	0	0	297	96
2	50	2	336	98
3	75	3	345	99
4	106	4	356	100
5	158	6	368	102
6	212	8	376	104

Fig. 6. X-cut tape test results. Left: thermocycling 77–287 K; right: 77–373 K. The number of thermocycles is indicated on the plots.

test results for coatings which underwent thermal cycling between the liquid nitrogen temperature and room temperature. Similar to the X-cut tape test, coatings deposited on substrates having temperatures below 353 K peeled off spontaneously after one or two thermal cycles. On the contrary, coatings deposited at higher temperatures did not peel off even after 50 thermal cycles.

Fig. 6 gives the X-cut tape test results for the samples which underwent different numbers of thermal cycles, including the liquid nitrogen temperature, room temperature and water boiling point. It is seen that in this case, too, good adhesion is achieved when the substrate temperature exceeds 353 K. Excellent results were obtained when the substrate temperature was 368 K, i.e. close to the PE melting point.

4. Conclusion

Considering that PE possesses a low thermal conductivity and low heat resistance, DLC sputtering conditions should allow for the substrate temperature.

Adhesion of DLCs to PE substrates depends strongly on the substrate temperature during sputtering. The optimal temperature falls within the interval from 353 to 373 K. Coatings deposited under optimal conditions withstand thermal cycling and adhesive tape tests.

References

[1] B. Ollivier, A. Matthews, J. Adhesion Sci. Technol. 8 (6) (1994) 651.
[2] G.D. Vaughn, B.G. Frushour, W.C. Dale, J. Adhesion Sci. Technol. 8 (6) (1994) 635.
[3] J. Lankford, C.R. Blanchard, C.M. Agrawal, D.M. Micallef, G. Dearnaley, A.R. McCabe, Nucl. Instr. and Meth. 80 (1993) 1441.
[4] B.R. Mehta, E.A. Ogryzlo, Diamond Relat. Mater. 13 (1994) 10.
[5] A.J. Hsieh, P. Huang, S.K. Venkataraman, D.L. Kohlstedt, Thin Films 308 (1993) 653.
[6] H.C. Ong, R.P.H. Chang, N. Baker, W.C. Oliver, Surf. Coat. Technol. 89 (1997) 38.
[7] M.J. Freeman, D.R. Harding, J. Polym. Sci. B 32 (1994) 1377.
[8] A.I. Maslov, G.K. Dmitriev, Yu.D. Chistyakov, Prib. Tekh. Exp. 3 (1985) 146.