Surface & Coatings Technology 258 (2014) 677–690

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

On the deposition and properties of DLC protective coatings on elastomers: A critical review

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ARTICLE INFO

Article history:
Received 5 March 2014
Accepted in revised form 5 August 2014
Available online 14 August 2014

Keywords:
Friction
Protection
Rubber
Adhesion
Carbon
Polymer

ABSTRACT

In this paper we will critically review various strategies for a successful deposition of highly adherent protective coatings on elastomers and rubbers. Emphasis will be placed on the differences with traditional approaches that are explored on rigid substrates (e.g. steel or silicon). Although we will focus on protective coatings, the generic ideas are also applicable for the deposition of any thin film on flexible polymers. The method for fine tuning the coating microstructure via a proper selection of the deposition conditions will be elucidated afterwards. Since the protection of rubber substrate is the major application of these coatings, the performance as protective films will be discussed in detail. Particular attention will be given to the friction coefficient and the influence of the viscoelastic properties of substrate. A comprehensive model explaining the influence of the parameter set is presented. Finally, the main conclusions of the work and the open questions for future explorations are briefly outlined. In general, an excellent adhesion is the critical requirement to reach optimal protection of the substrate. The frictional performance can be optimized depending on the viscoelastic properties of the rubber, the microstructure of the coating and the conditions of the contact.

Contents

1. Introduction

It goes without saying that polymeric materials experienced great momentum over the last decade because on the one hand of the increased scarcity of the metals and alloys and on the other with the development of carbon-based substances like carbon nanotubes [1–3], graphene [4,5] and of organic light emitting diodes (OLEDs) [6–8], among others. Deposition technologies are typically used to tune the surface properties of any material without altering the 'bulk' response. Physical and chemical vapor deposition techniques (PVD and CVD) are the most employed in order to obtain controlled films with tailored properties. However, successful deposition on these sensitive and/or flexible polymeric substrates entails some new opportunities, but also exciting new challenges. This statement is particularly true for

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http://dx.doi.org/10.1016/j.surfcoat.2014.08.016
0257-8972/

protective applications, since in that case the film must show an excellent adhesion to the substrate in order to accomplish its function. However, highly energetic assistance (e.g. biasing, pulses or implantation techniques) has to be used with extreme care during plasma deposition, since these types of substrates are very sensitive to heating (e.g. maximum operation temperature can be lower than 150 °C, [9]), and their properties have to be kept invariant.

Among polymers, elastomers are probably the most difficult to work with. In addition to temperature sensitivity, they show great deformation capability, which forces the deposited coating to be flexible and adherent. However, traditional solutions used for coating rigid substrates, like deposition of ductile metallic interlayers, are not applicable due to the non-metallic character of the substrate and the requirement of flexibility to the complete materials system. Another issue is that rubbers show high roughness and polishing is not possible, in contrast for instance to rigid thermoplastics. Moreover, in many cases the presence of filler particles increases the complexity of the situation, since they may create adhesion problems in particular sites on the surface. Finally, rubbers are typically 'dirty' substrates to operate with. For instance, waxes like stearamide are known to be added to improve the processability of the rubber, which can migrate to the surface during ageing after the deposition of a coating [10]. Sometimes, even other residues can be found, due to the manufacturing and production. Therefore, proper cleaning is mandatory in order to achieve good adhesion. However, chemicals have to be used with care, since polymers may be modified when using organic solvents (for instance, the typically used acetone or ethanol).

In this work, we revise the deposition of adherent DLC-based films on rubber. The description of the cleaning and deposition protocols comes first, and the influence of different deposition conditions on the film microstructure is also explained. Then, their behavior in protective applications is explored, with particular attention to the relationship between viscoelasticity and frictional performance. Finally, the most remarkable ideas for further research are indicated and some conclusions are outlined.

2. Deposition, growth and microstructure

Table 1 summarizes the characteristics of different approaches for the deposition of DLC-based films on rubber. It can be seen that the research was concentrated mainly in the last decade, although some papers not easily accessible were presented earlier by T. Nakahigashi et al. [11–14] and Takikawa et al. [15] before their publications in 2004 [16–18]. Several authors, up to 2007 exclusively from Japan, contributed to this topic with experimental results obtained by Y. Aoki et al. [19], D. Tusbone et al. [20], S. Yoshida et al. [21], L. Martinez et al. [22], J. M Lackner et al. [23], I. Masami et al. [24], and Nagashima et al. [25]. In addition, another set of contributions came from the group of De Hosson [26–40], and groups of Moon [41–43] and Lubwama [44–47]. Papers published so far from these units present also a theoretical approach to understand the frictional and mechanical performance [48,49], or the formation of the coating microstructure [50].

In general we may say that the deposition of protective DLC films on rubber substrates embrace different applications; for instance, the wear

Table 1
Deposition details and some characteristics of DLC related coatings on elastomers.

Year	Deposition details						Characteristics			Ref.
	Elastomer substrates [1]	Film	Technique [2]	Gases and precursors	Cleaning, Pretreatment	Interlayer	Dep. Rate (nm/s)	Roughness (nm)	Contact angle (º)	
2004	CR, NBR, EPT, Q, PU, PV	DLC	RF PACVD	CH_4	H_2 plasma		0.3–0.7		90	[16]
	EPDM, Q	DLC	T-FAD (graphite)	none, H_2, Ar, C_2H_2, C_2H_4, CH_4	Water		0.6–1.2	50–350 [R_a][3]	110–120	[17,18]
	Butyl rubber	DLC	RF PACVD	CH_4	Acetone Ar plasma		0.9			[19]
2007	PE, PET, SIS, PDMS, PP	DLC, $F_{(11\%)}$–DLC	RF PACVD	C_2H_2, C_2H_2/C_2F_2			3.3			[20]
	Q	DLC	PLD	Frozen $C_5H_{11}OH$			0.5			[21]
2008	FKM, HNBR, ACM	$W_{(20\%)}$–DLC	MS (WC)	C_2H_2	Ethanol	Cr (optional), W–C				[26,27]
	HNBR	$Ti_{(19\%)}$–DLC	DC MS (Ti) p-DC bias	C_2H_2			0.1–0.3			[28]
2009	HNBR	DLC	DC MS (graphite) P-DC bias	C_2H_2	Soap, hot water in ultrasounds Ar plasma					[29]
	NBRs (x3), HNBR	DLC	RF PACVD	C_2H_2	Ar plasma	Organosilicon	0.3	131 [R_a][4] 32 [RMS][4]	85–115	[22]
	TPU	DLC	RF MS (graphite)	C_4H_{10}, C_2H_2	Ethanol		0.2–3			[23]
2010	PDMS	SiO_x–DLC	RF PACVD	$(Si(CH_3)_3)_2O$			1.5	6–200 [4]	100–120	[41]
	PDMS	DLC	GLAD by Ar gun	C_2H_2	Ar plasma					[42]
2010–13	ACM, HNBR	DLC	P-DC PACVD	C_2H_2	Soap, hot water in ultrasounds Ar, Ar/H_2 plasmas		0.05–0.1			[30–39]
2011	Fluoro rubber (Togawa V-100)	Si–DLC	P-PBII	$Si(CH_3)_4$	Ethanol, UV light Ar plasma		0.3–0.5			[24]
2012	Grooved PDMS	DLC	RF PACVD	C_2H_2	Ar plasma		4			[25]
	PDMS	DLC	RF PACVD	CH_4	O_2 plasma		0.05–0.1	55–110 [RMS][4]		[43]
2012–14	NBR	DLC, $Si_{(2.9–4\%)}$-DLC	DC MS (Si) P-DC PACVD	C_4H_{10}	Ar plasma	Si–C (optional)	0.2–0.3	1500–2200 [5]	100–106	[44–47]
2014	NBR	DLC	ETP	C_2H_2	Soap, hot water in ultrasounds Ar plasma		3.5–5	97–133 [RMS][4]		[40]

[1] ACM (alkyl acrylate copolymer), CR (polychoroprene), EPDM (ethylene propylene diene monomer), EPT (ethylene–propylene), FKM (fluorocarbon terpolymer), HNBR (hydrogenated acrylonitrile–butadiene), NBR (acrylonitrile–butadiene), PDMS (polydimethylsiloxane), PE (polyethylene), PET (polyethylene terephthalate), PP (polypropyrene), PU (polyurethane), PV (polyvinyl), Q (silicone), SIS (polystyrene–block–polysoprene–block–polystyrene copolymer).
[2] RF (radiofrequency), DC (direct current), P-DC (pulsed DC), T-FAD (T-shaped filtered arc deposition), PACVD (plasma assisted chemical vapor deposition), PLD (pulsed laser deposition), PBII (pulsed plasma based ion implantation), GLAD (glancing angle depositon), ETP (expanded thermal plasma).
[3] laser microscopy; [4] AFM; [5] profilometry.