SURFACE MODIFICATION OF HIPS USING MULTICOMPONENT THIN FILMS DEPOSITED BY PULSED DC MAGNETRON SPUTTERING

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https://doi.org/10.37904/metal.2026.5292

Abstract

Surface modification of polymeric materials represents an effective strategy for tailoring their properties without the need to synthesize new material systems, thereby significantly expanding their application potential. In this context, advanced plasma technologies have emerged as a promising tool for the controlled deposition of functional coatings on polymer substrates. The present study focuses on the deposition of thin films on high-impact polystyrene (HIPS) using pulsed direct current magnetron sputtering. Targets based on titanium, silicon, zirconium, and nickel were employed, while different magnetron power duty cycles were applied (45/20/20/15%, 100/100/100/100%, and 45/20/20/100%). Characterization of the modified surfaces includes analysis of surface morphology, the chemical composition, and the height roughness parameters of the deposited films. Tribological properties were assessed using the Ball-on-Flat method, showing a reduction (15.4-21.1%) in the dynamic coefficient of friction compared to the reference material. In addition, surface wettability was analyzed, revealing an increase in the contact angle after thin film deposition; the highest increase (22.6%) was observed for the sample prepared at a duty cycle of 45/20/20/15%. The results confirm that pulsed DC magnetron sputtering is an effective approach for enhancing the functional properties of polymeric materials.

Keywords: Thin film, pulsed DC magnetron sputtering, surface modification, HIPS, functional properties

1. INTRODUCTION

High Impact Polystyrene (HIPS) is an amorphous polymer produced by grafting a small amount of butadiene-styrene rubber during the polymerization of polystyrene (PS). The combination of these two components results in a material that offers the rigidity and ease of processing of polystyrene together with the toughness and impact resistance of polybutadiene. Its advantages include good mechanical, chemical, and barrier properties. However, the increased impact resistance is achieved at the expense of a reduction in other properties, such as modulus of elasticity and tensile strength. Therefore, for specific applications, it is necessary to find an appropriate compromise. This can be achieved by adjusting the rubber content. Another option is to blend PS with HIPS in suitable ratios. [1–3]

Surface modification of polymers is a way to deliberately alter a material's functional properties without affecting its bulk properties. In general, surface modifications can be classified into chemical, physical, and physicochemical methods. Common techniques include plasma activation, corona discharge, grafting, and thin film deposition. These approaches enable tailoring of surface energy, wettability (for surface activation), surface morphology, chemical reactivity, biological properties, and optical properties. [4–6] For

polymers, it is necessary to use technologies operating at lower temperatures to reduce the risk of thermal degradation. Standard polystyrene (PS) exhibits negligible creep under typical conditions and has a maximum service temperature of approximately 80 °C. Compared to PS, HIPS has lower thermal stability and heat resistance, which must be taken into account during processing and application. [1, 2, 7]

Magnetron sputtering is a modification of conventional sputtering in which a planar magnetron increases theefficiency of the process. A glow discharge is generated in the plasma, whose ions bombard the target, and the released atoms subsequently deposit on the substrate as a thin film. This method is widely used for thin film deposition and is also suitable for temperature-sensitive materials due to its relatively low thermal impact on the substrate. [7–10] Pulsed DC power supply enables better plasma stabilization (e.g., by suppressing arcing) and enhanced control of the deposition process through adjustment of frequency and duty cycle. This approach reduces the overall energy input into the system and minimizes damage to the thin film. [11]

The aim of this research is to develop and analyze TiSiZrNi thin films deposited on HIPS substrates, with particular emphasis on their chemical composition, morphology, tribological performance, and wettability.

2. MATERIALS AND METHODS

2.1 Samples Preparation

High Impact Polyester (HIPS) in the form of a film with a thickness of 0.2 mm was used as the substrate, commercially available under the trade name STYRON A-TECH™ 1200. This material has a Vicat softening temperature of 100 °C (ISO 306/A120) and a heat deflection temperature of 73 °C (ISO 75-2/A).

The surface of the base material was modified by thin film deposition using PVD, specifically DC magnetron sputtering with pulse-width modulation (PWM). The process was performed on an NP 70 coating system (KWS CZ s.r.o., TUL). Thin films were prepared from titanium (Ti, 99.99% purity), silicon (Si, 99.999% purity), zirconium (Zr, 99.5% purity), and nickel (Ni, 99.99% purity) targets, with four targets operated simultaneously and duty cycles distributed according to the PWM scheme (**Table 1**). A base pressure of ≤ 0.001 Pa was maintained. Deposition was carried out at 100 Hz using argon (40 sccm) and a power of 1.5 kW. Samples were placed 120 mm from the targets on a rotating substrate holder (40°·s^{-1}) for 10 minutes.

Table 1 Deposition parameters

Sample	Duty cycle (%)				Working pressure (Pa)
	Ti	Si	Zr	Ni	
TiSiZrNi_4515	45	20	20	15	0.22
TiSiZrNi_100	100	100	100	100	0.22
TiSiZrNi_45100	45	20	20	100	0.23

2.2 Evaluation Methods

The samples were characterized in terms of thin film thickness, surface morphology, chemical composition, surface roughness, tribological behavior and wettability.

The thickness of the thin films was measured using a SENSOFAR S Neox confocal microscope, based on the step height between the coating and substrate created by masking part of the substrate during deposition.

Surface morphology and chemical composition were analyzed by scanning electron microscopy (SEM) at 5000× magnification at CXI TUL. Thin-film-coated samples were examined using a Helios 5 PFIB Cxe microscope at an accelerating voltage of 2 kV, while the substrate was analyzed with a Zeiss ULTRA PLUS microscope at 1 kV, which is more suitable for charge-sensitive materials.

Surface height roughness parameters were determined using a non-contact optical 3D profilometer (S Neox) in accordance with ISO 25178 at 20× magnification. The evaluated parameters included the arithmetic mean height, Sa (µm), and the maximum height, Sz (µm).

Tribological properties were evaluated using the Anton Paar TRB^3 tribometer with the Ball-on-Flat method under linear reciprocating motion to assess friction behavior and coating adhesion. The dynamic coefficient of friction, including mean value and standard deviation, was determined for each measurement. Wear track was analyzed using a SENSOFAR S Neox confocal microscope. Tests were performed under dry sliding conditions using a Si_3N_4 spherical counterbody (diameter 6 mm, hardness <1600 HV10, density 3.21 g/cm³), over a sliding distance of 3 m (track length 12 mm), at a maximum speed of 5.0 cm/s and a load of 0.5 N.

Surface wettability was evaluated by the sessile drop method using a Surface Energy Evaluation System. During the measurement, a 3 µl droplet of distilled water was applied to the sample surface using a pipette.

3. RESULTS AND DISCUSSION

The obtained data were processed and analyzed using Microsoft Excel and OriginPro.

The chemical composition of the thin films (**Table 2**) does not show a linear dependence on the duty cycle, indicating different deposition efficiencies of the elements. In the TiSiZrNi_4515 sample, a high Ni content (33.0 at%) was observed despite a low duty cycle, while Si remains low (7.5 at%). In the TiSiZrNi_100 sample, a non-uniform composition is also present, with elevated Zr (41.9 at%), Ti and Ni around 26 at%, and low Si (4.8 at%). The TiSiZrNi_45100 sample is dominated by Ni (79.0 at%). Overall, the film composition is governed not only by the duty cycle but also by material-specific and process-related factors.

The thickness of the prepared thin films (**Table 2**) ranges from 147 ± 24 nm (TiSiZrNi_4515) to 187 ± 16 nm (TiSiZrNi_100) and up to 212 ± 28 nm (TiSiZrNi_45100). The greatest thickness was observed for the TiSiZrNi_45100 sample, which has the highest duty cycle set on the Ni target, while the lowest thickness corresponds to the sample with the lowest duty cycle on Ni (TiSiZrNi_4515). This indicates a higher contribution of Ni to film growth. In contrast, lower thicknesses are associated with a higher proportion of elements with lower deposition efficiency, particularly Si.

Table 2 Results of the chemical composition and thickness of thin films

Sample	Chemical composition	Ti (at%)	Si (at%)	Zr (at%)	Ni (at%)	Thickness of thin films	Thickness (nm)
TiSiZrNi_4515		31.4	7.5	28.1	33.0		147 ± 24
TiSiZrNi_100		26.6	4.8	41.9	26.7		187 ± 16
TiSiZrNi_45100		11.4	2.1	7.5	79.0		212 ± 28

Surface topography varied according to the sample's characteristics (**Figure 1).** Samples with deposited thin films are electrically conductive, resulting in well-focused images (**Figures 1b–d**). The substrate (**Figure 1a**) exhibits a homogeneous, compact surface with visible features. After thin film deposition, changes in surface topography are observed across all samples. The TiSiZrNi_4515 sample (**Figure 1b**) shows only slight texturing and uniformly distributed features, with no significant defects, indicating relatively uniform and continuous surface coverage. In contrast, TiSiZrNi_100 (**Figure 1c**) exhibits increased structural complexity, with the presence of clusters and irregular features. The most pronounced changes are observed in the TiSiZrNi_45100 sample (**Figure 1d**), which shows irregular morphological features and defects, indicating a less compact coating structure. Overall, a trend of decreasing surface homogeneity and film quality can be observed from TiSiZrNi_4515 to TiSiZrNi_45100.

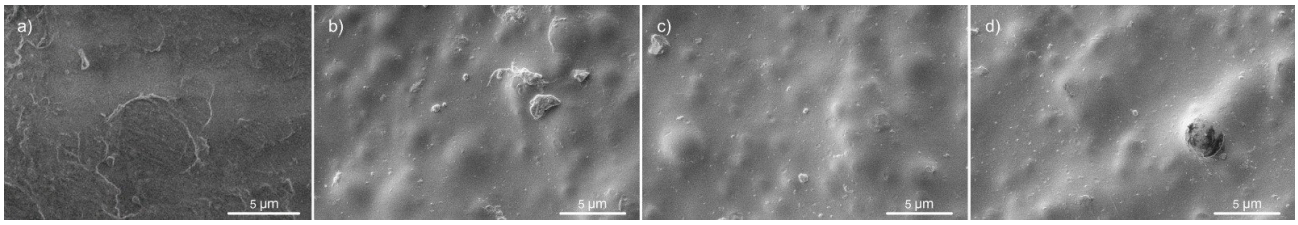


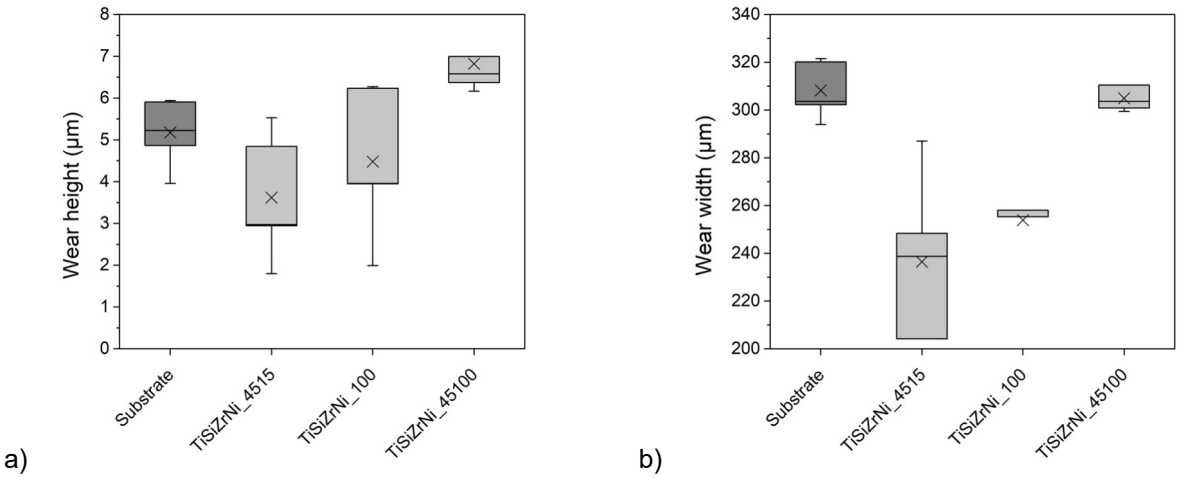
Figure 1 SEM analysis: (a) substrate (HIPS), (b) TiSiZrNi_4515, (c) TiSiZrNi_100, (d) TiSiZrNi_45100

The results of the surface morphology analysis indicate that both parameters decreased significantly in the coated samples compared to the substrate. The Sa parameter (**Table 3**) shows the highest values for the substrate (approximately 1.35–1.71 µm), while all coated samples exhibit a substantial reduction to approximately 0.73–1.08 µm, indicating surface smoothing after film deposition. Differences among the individual coatings are small, although the TiSiZrNi_4515 sample shows slightly higher variability. A similar trend is observed for the Sz parameter (**Table 3**), where the substrate reaches significantly higher values (approximately 35–45 µm), while the coated samples range only between approximately 5–7 µm. This confirms a marked reduction in surface height variations following thin film deposition. Overall, it can be concluded that film deposition results in a significant decrease in surface roughness, with only minor differences among the individual samples.

The substrate shows an average coefficient of friction of 0.61 ± 0.97 (**Table 3**), while all coated samples exhibit lower values, with the lowest recorded for TiSiZrNi_45100 (0.48 ± 0.09). However, the best wear resistance is observed for TiSiZrNi_4515, which shows a significant reduction in wear track depth and width compared to the substrate (**Figure 2**). The TiSiZrNi_100 sample exhibits intermediate behavior, whereas TiSiZrNi_45100, despite its lowest friction, shows increased wear comparable to the substrate.

Table 3 Results of surface roughness parameters and the dynamic coefficient of friction

	Substrate	**TiSiZrNi_4515**	**TiSiZrNi_100**	**TiSiZrNi_45100**
Arithmetical mean height, Sa (µm)	1.51±0.11	0.87±0.11	0.83±0.02	0.90±0.05
Maximum height, Sz (µm)	38.49±3.67	6.25±0.54	6.32±0.31	6.63±0.37
Average coefficient of friction µ (-)	0.61±0.97	0.52±0.06	0.50±0.10	0.48±0.09



a) b)

Figure 2 Tribological wear: (a) height, (b) width

The HIPS substrate shows a contact angle (**Figure 3**) of 64–78° (average 73–75°), indicating a slightly hydrophilic surface. After thin film deposition, all samples exhibit increased contact angles, reflecting reduced wettability and increased hydrophobicity. The highest values are observed for TiSiZrNi_4515

(~87-95°, avg. ~90°), followed by TiSiZrNi_100 (~79–91°, avg. ~83–85°), while TiSiZrNi_45100 shows the lowest values (~75–85°, avg. ~82°).

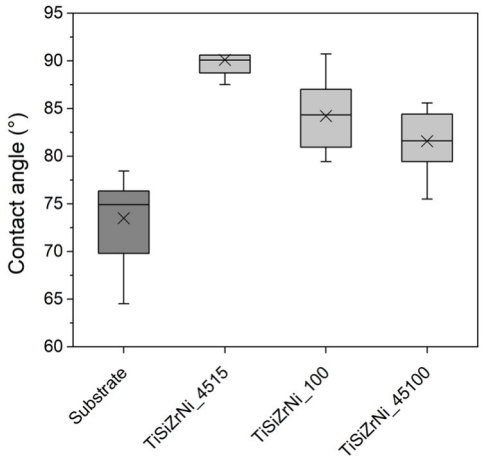


Figure 3 Contact angle

Based on the chemical composition and thin film thickness results, a deposition efficiency trend of Ni > Zr > Ti > Si was observed, corresponding to differences in sputtering yields. A full description of the process requires detailed knowledge of plasma conditions, including atom transport and deposition dynamics (see [12]). Thus, the duty cycle represents only one of several parameters influencing the final film properties. Higher Ni content also leads to increased film thickness, confirming its greater contribution to film growth.

The substrate topography observed in SEM may be related to a dispersed phase or preparation artifacts, as reported in the literature [12]. Changes in modified samples correlate with composition and thickness variations, where higher Ni content may lead to partial amorphization or segregation. This, together with increasing Ni content and film thickness (146–212 nm), may reduce thin film structural integrity. The reduction in roughness parameters confirms coverage of the substrate by a compact coating layer.

Tribological results show that coating deposition reduces the coefficient of friction; however, lower friction does not necessarily correspond to higher wear resistance, as demonstrated by the TiSiZrNi_45100 sample, where increased inhomogeneity and reduced cohesion likely lead to poorer wear performance.

After deposition, the contact angle increased for all coated samples compared to HIPS, despite the high surface energy of the deposited elements. The highest values were observed for TiSiZrNi_4515, while more morphologically complex samples (TiSiZrNi_100 and TiSiZrNi_45100) showed lower contact angles, indicating the influence of both composition and surface morphology on wettability. All coated samples exhibited reduced surface roughness, which is consistent with the literature [13], where increased roughness of silicon oxide thin films led to higher hydrophilicity.

4. CONCLUSION

This study investigated TiSiZrNi thin films prepared by pulsed DC magnetron sputtering and their structural, tribological, and wetting properties. The results show that film composition does not scale linearly with the duty cycle, indicating different deposition efficiencies of the elements (Ni > Zr > Ti > Si), which also affects film thickness. Film deposition led to surface smoothing and a significant reduction in roughness, although coating homogeneity decreased with higher Ni content.

Tribological testing showed a reduced coefficient of friction after coating deposition, but wear resistance did not directly correlate with friction, with the most inhomogeneous sample showing the best wear performance.

Wettability increased for all coated samples, with more homogeneous coatings exhibiting higher contact angles. Overall, the results demonstrate that the functional properties of the films are governed by a complex interplay between composition, microstructure, and deposition conditions.

ACKNOWLEDGEMENTS

This publication was supported by the Student Grant Competition of the Technical University of Liberec within the project SGS-2026-5606 and project No. FW09020103, "Design and modification of surface layers for bio-applications using innovative plasma technologies," which is co-financed with state support from the TA CR within the TREND Programme, subprogramme 2

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