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Wear, Corrosion and Tribocorrosion Behavior of Polyurethane and Polyvinylpyrrolidone Blends as Coating for Corrosion Protection of AISI 316L Stainless Steel

Muharrem Taşdemir^{1,2,*}, Fatih Şenaslan^{1,2}, Ayhan Çelik²

¹ Department of Mechanical Engineering, Gumushane University, 29100, Gumushane, Turkey
 ² Department of Mechanical Engineering, Atatürk University, 25030, Erzurum, Turkey.
 *E-mail: <u>mtasdemir@gumushane.edu.tr</u>

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Polyurethanes (PUs) are used across a widely from biomaterials to industrial applications due to their versatile properties. Polyurethane is blended with other polymers to improve their physical and thermal properties. In this study, different concentrations of polyurethane and polyvinylpyrrolidone (PVP) blends were applied to AISI 316L stainless steel using the dip coating method as protection against wear and corrosion. The effects of different concentrations of blends on the mechanical, corrosion and tribocorrosion properties of the AISI 316L stainless steel were investigated. The phase structure of polymer coatings were investigated by X-ray diffraction (XRD), and their surfaces were examined by scanning electron microscopy (SEM). Corrosion and tribocorrosion tests of the polymer coated samples were carried out in 3.5% NaCl solutions. The surface roughness and nanohardness of the polymeric coated samples were also measured. It was found that surface roughness and friction coefficient increased with raised concentration of PVP, while wear and corrosion resistance decreased with the increased of PVP concentration in the coating. As the penetration depth of the PU coated sample increased, the nanohardness and elasticity modulus decreased. Coatings containing PVP up to 25% protected the substrate surface under tribocorrosion conditions in NaCl solutions.

Keywords: polyurethane, polymer coatings, nanohardness, corrosion, wear

1. INTRODUCTION

Polyurethanes (PUs) are commonly used in numerous sectors from biomaterials to industrial applications due to their versatile properties [1, 2]. Polyurethanes have weak physical and thermal properties. Therefore, polyurethanes are blended with other polymers to overcome their deficiency. The polymer blending process is the combination of two or more different polymer types at various concentration [3-5]. This process is used to obtain new polymer with improved polymer characteristics in practice [6]. Polyvinylpyrrolidone (PVP) is one of the polymers used for the development of thermal

and physical properties of polyurethane. Moreover; PVP has good environmental stability, a high glass transition temperature and exhibits chemical and thermal resistance thanks to the presence of rigid pyrrolidone rings [7, 8]. Additionally; PVP is commonly preferred in a variety of industrial applications, such as adhesives and coatings due to its good film forming and adhesive character [9, 10] Polymer coating is applied to the substrate surface by various deposition methods such as spray coating, spin coating, and dip coating [11-13]. Among these methods, dip coating is widely used due to uniform and high quality coatings can be obtained [14].

Thermal and hydrophilic properties of polyurethane and polyvinylpyrrolidone coated materials were generally investigated by scientists in the literature [15-17]. However; there is no study on mechanical wear, corrosion and tribocorrosion behavior of PU-PVP polymer blends coated in NaCl aqueous solution. Thus, this study will fill an important deficiency for industrial applications. In this study, different concentrations of PU-PVP polymer blends were applied to the surface of AISI 316L stainless steel using the dip coating method. The effect of polymer concentrations were investigated on mechanical wear, corrosion and tribocorrosion tests in NaCl solution.

2. MATERIALS AND METHODS

In this study, AISI 316L stainless steel was used as substrate material and its chemical composition is given in Table 1. Polyurethane Pellethane 2363-90A was supplied from Lubrizol. The density of the polyurethane was 1.14 gr/cm³. PVP 10 was purchased from Sigma Aldrich. Dimethylacematide was used to dissolve PU and PVP. PU and PVP were continuously stirred on magnetic stirrer for 1 day to make the solution homogeneous. The preparded solution contained 10% (w/w) PU/PVP polymer in dimethylacetamide. The polymer coating process was carried out by dipping the stainless steel samples into the prepared solution. The schematic representation of the dip coating process is given in Figure 1. The process includes the steps of dipping sample into the solution, then coating and evaporating. The coatings were cured at 60 °C for 5 hours in a heating furnace. The coating was carried out under vacuum conditions to prevent air bubbles in the samples. XRD analysis of samples were conducted by Cu-K α radiation in a scanning range of $2\theta = 10$ to 60° at a scanning rate of 2°/min using a Panalytical Empyrean diffractometer. The tribological behavior of coatings was performed under reciprocating conditions using Turkyus wear test equipment. Wear tests were done under the frequency 1 Hz, 3 N normal load during 3600 seconds. The Surface morphology of samples was examined with a Zeiss Sigma 300 scanning electronic microscope. The corrosion tests were performed with a standard three-electrode cell using a Gamry Series G750 potensiostat/galvanostat in 3.5% NaCl aqueous solution. The coating sample (working electrode), Ag/AgCl (reference electrode) and graphite (counter electrode) was used for electrochemical measurement. Polarization measurements were carried out at a scan rate of 1 mVs⁻¹ in a range -1 to +2 V_{ref} . Tribocorrosion tests were conducted in experimental equipment obtained by combining a corrosion tester with tribometer device. Tribocorrosion tests were done with an open circuit potential (OCP) wear test in a 3.5% NaCl solution. The samples of polymers blended in the ratio of 3: 1, 1: 1, 1: 3 were called as PU75/PVP25, PU50 / PVP50, PU25 / PVP 75, respectively in this study



 Table 1. Chemical composition of AISI 316L stainless steel

Figure 1. Steps of the dip coating process

3. RESULTS AND DISCUSSION

3.1.XRD Results

XRD is a crucial, non-destructive process that determines detailed information about the crystallographic structure of polymers [7]. The XRD graphs of the PU/PVP polymer coated samples are shown in Figure 2. The XRD peaks of PU and PVP are quite wide since their structures are amorphous. The spectrum of PU shows at $2\theta = 20.6^{\circ}$, which is the microcrystalline area of the hard segment of the polyurethane. This peak is very wide because of polyurethane consists of two segments. The XRD peak position of PVP corresponds $2\theta = 20.1^{\circ}$ [18]. This peak position shifted to the right with the increasing of PU concentration in PU/PVP blends. The gradual shift rise following the incorporation of PVP confirmed the uniform miscibility of both PU and PVP. The XRD results obtained for both PU and PVP are consistent with the studies in published literature [19, 20].



3.2. Surface views of PU/PVP



Figure 3. The surface images of PU/PVP coatings a) PU, b) PU75/PVP25, c) PU50/PVP50 and d) PU25/PVP75

The surface images with its details of gradually blended PU/PVP coated samples are shown in Figure 3. Figure 3a shows the branch structures in polyurethane. Figure 3b exhibits PVP stably penetrated PU as the concentration of PVP increased in the PU/PVP blends. Figure 3c and 3d show the surface area of this formation expanded with increased PVP concentration in the coating. The cross-sectional view of PU/PVP polymer coated samples is given in Fig. 4. This image shows that the

PU/PVP polymer films are coated homogeneous and good adhere to the stainless steel surface. The film thickness was determined to be approximately 20 μ m in the measurements taken from the cross-sectional view of samples.



Figure 4. The cross-sectional view of PU/PVP polymer coatings a) PU, b) PU50-PVP50 and c) PVP

3.3. Tribological Analysis

The friction coefficient graph of AISI 316L coated with PU/PVP polymers are given in Figure. 5. The friction coefficient curve for all polymer coatings showed a fluctuating course due to the stick-slip effect.



Figure 5. The friction coefficient graph of AISI 316L coated with PU/PVP polymers

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The friction coefficients of the PU, PU50/PVP50 and PVP coated samples was 0.2, 0.3 and 0.55, respectively. The friction coefficient of PU coated sample decreased behaving like a lubricating agent on the substrate surface during wear. The friction coefficients of polymer coated samples increased with increasing PVP concentration in the PU/PVP blending due to the low mechanical properties of PVP. The friction coefficient of PVP was very high from the beginning to the end of the experiment depending on the loss of surface protection feature of the PVP coating. This shows that in coatings containing up to 50% PVP, the wear remains in the coating layer. The mechanical properties of the blending including yield strength, modulus of elasticity decreased with the addition of PVP to PU [19, 21].



Figure 6. Wear surface images of AISI 316L coated with PU/PVP polymers

Wear surface images of AISI 316L coated with PU/PVP polymers are shown in Figure 6. The wear scar of PU is quite narrow and shallow. The wear scar significantly increased with the amount of PVP added in the PU/PVP blends coatings. During sliding, the PU coated sample was removed locally

from the surface and smeared to other wear scar region. Wear mechanism of the PU75/PVP25 coated material was abrasive. The PU25/PVP75 and PVP polymer layer was broken due to the weak mechanical properties of the PVP in the coating. This phenomenon caused an increase in total wear volume. It was seen that the mechanical properties of the polymer decreased with the increased amount of PVP in the polyurethane [21]. Considering wear and friction together the coating containing up to 50% PVP protected the substrate surface and the friction of coefficient was low. However, wear in the PU25-PVP75 and PVP coated samples went down to the substrate material and therefore the friction coefficient increased with effect of metallic surface. The wear volume of AISI 316L coated with PU/PVP polymers are shown in Figure 7. The lowest wear volume was observed in PU coated sample. The reason for this is due to its good mechanical and lubricating properties. High an amount of PVP can result in weaker structures in blending [8].



Figure 7. The wear volume of AISI 316L coated with PU/PVP polymers

The wear volume dramatically increased with adding PVP concentration in the coatings due to the weak mechanical properties of PVP. Surface roughness values for PU/PVP polymer coated samples are given in Table 2. The surface roughness of the PU and PVP coated samples was low owing to surface of coatings was more homogenous. Surface roughness also increased with the adding PVP concentration in the coatings. This situation was attributed to phase separation within the polymer blend. The surface roughness of polymer coated sample increased the addition of inorganic and organic material to polyurethane [22, 23].

Table 2. Surface roughness values for PU/PVP polymer coatings

Material	PU	PVP	PU75/PVP25	PU50/PVP50	PU25/PVP75
Surface Roughness, Ra (µm)	0.070	0.031	0.117	0.151	0.226

3.4. Nanohardness

Nanohardness tests of the coatings were performed under 0.1 mN loads. The nanohardness, elasticity modulus and load displacement of PU coatings are shown in Figure 8. The elasticity modulus and nanohardness dramatically decreased up to a penetration depth of 25 nm. Figure 8a shows that the decrease in elasticity modulus and nanohardness is less after a 25 nm penetration depth.

Coating	Penetration Depth (nm)	Modulus of Elasticity, E (MPa)	Nanohardness (MPa)
PU	9.8 ± 2.4	1081.4 ± 109.8	430.674 ± 8.9
PU	30.8 ± 4.8	250.1 ± 33.8	96.5 ± 2.4
PU	235.3 ± 7.1	100.223 ± 6.5	18.7 ± 0.6



Figure 8. Nanohardness and elasticity modulus of Polyurethane

The nanohardness and elasticity modulus of polyurethane are given in Table 3. The elasticity modulus and surface hardness of polyurethane was found to be 100.223 ± 6.597 MPa and 18.7 ± 0.613 MPa, respectively, at a penetration depth of 240 nm. The nanohardness and elasticity modulus of polyurethane changed depending on the penetration depth and the applied load. The results for the elasticity modulus and surface hardness of polyurethane are seen to be quite similar with the results in the reference study [24, 25].

3.5. Corrosion Analysis

Potentiodynamic curves for AISI 316L coated with PU/PVP polymers in a 3.5 wt% NaCl solution are shown in Figure 9. Different surface modifications affected passivation and polarization of the samples. PU/PVP coated samples led to the formation of a protective film on the metal/solution interface. Corrosion potential values of all polymer coated samples presented a more inert than AISI

316 L sample indicating reduced corrosion kinetics due to polymer coatings. Ecorr of AISI 316L stainless steel are -452 mV vs V_{Ref.} Ecorr values of PVP, PU25/PVP75, PU50/PVP50, PU75/PVP25, PU polymer coated samples are -138, -119, -114, -106, -69 mV vs V_{Ref}, respectively. Ecorr values of polymer coated samples shifted towards positive values and displayed a more noble behavior than bare stainless steel. Ecorr decreased with increasing polyurethane concentration in blending. PU, PU75-PVP25 coated samples protected the substrate surface by acting as a barrier and exhibited a lower current density in anodic and cathodic region. This results suggests that PU and PU75-PVP25 polymer films that are correspondingly less susceptible to localized pitting. PU50/PVP50 coated sample reduced its protection feature by breaking the polymer layer at 400 mV (vs V_{ref}) levels in the anodic region. The PU25-PVP75 and PVP coated samples did not show effective protection of the substrate material due to electrolyte leakage and, thus, these polymer films exhibited a higher current density above 500 mV vs V_{Ref} in the anodic region. The addition of PVP caused an increase in the anodic and cathodic tafel slopes, which indicated that the PVP affects the iron dissolution and anodic-cathodic reaction. PU coated sample provided a better corrosion resistance than PU/PVP polymer blending coated samples due to its hydrophobic character in anodic and cathodic region that block the metal surface and do not permit the corrosion to occur. PVP is a good corrosion inhibitor for steel in NaCl solutions which makes PVP a promising polymer in the drilling industry [26]. PDMS and PEG coated AISI 316L improved the corrosion resistance comparing with the untreated sample in the published literature [27].



Figure 9. Potentiodynamic curves for AISI 316L coated with PU/PVP polymers in 3.5 wt% NaCl solution

Corrosion parameters calculated from potentiodynamic measurements is given in Table 4. Icorr values of PVP, PU25/PVP75, PU50/PVP50, PU75/PVP25, PU polymer coated samples are 1.39×10^{-4} , 1.62×10^{-4} , 7.22×10^{-5} , 1.44×10^{-4} , 1.87×10^{-5} (A/cm²), respectively. Polarisation resistance of PVP, PU25/PVP75, PU50/PVP50, PU75/PVP25, PU polymer coated samples are 1848, 1361, 3319, 1328, 14312 (Ω /cm²), respectively. The Polarisation resistance and corrosion rate of polymer coated samples were found to be higher than untreated AISI 316L stainless steel, confirms that polymer films provide the block the metal surface [28]. This is indicative of high chemical stability of the polymer coated samples [29]. The increasing of PU concentration in blending leads to superior corrosion properties. Higher polarization resistance and lower corrosion rate was obtained in PU coated sample in potentiodynamic tests.

Sample	Ecorr (mV)	İcorr (A/cm ²)	Rp (Ω/cm^2)	Vcorr (mpy)
AISI 316L	-452	9.16×10 ⁻⁴	147	3.875
PVP	-138	1.39×10^{-4}	1848	0.588
PU25/PVP75	-119	1.62×10^{-4}	1361	0.685
PU50/PVP50	-114	7.22×10 ⁻⁵	3319	0.305
PU75/PVP25	-106	1.44×10^{-4}	1328	0.609
PU	-69	1.87×10^{-5}	14312	0.079

Table 4. Corrosion parameters calculated from potentiodynamic measurements

3.6. Open circuit potential (OCP) Wear

Open circuit potential (OCP) wear of AISI 316L coated with PU/PVP polymers in 3.5 wt% NaCl solution is shown in Figure 10. The sliding time was fixed to 3000 seconds for all samples. The samples were stabilized for 1000 seconds before and after sliding. OCP values of all polymer coated samples are -0.2 V vs V_{Ref} at the beginning of test. When sliding started, OCP values of PU and PU75/PVP25 coated samples shifted to a more positive direction compared to the beginning, this continued until the end of the experiment. This positive shift indicates that the surface is thermodynamically stable with the protective effect. This situation shows that the mechanical wear occurs only in the polymer layer and did not contact the substrate material. Thus these coatings can be used safely in applications under tribocorrosion conditions. The PU50/PVP50 coated sample protected the substrate surface at the beginning of the test; however, this layer then lost its protective properties by deteriorating from the middle of the test. The sudden potential decline in PU25/PVP75 and PVP coated samples differed from others. With the onset of sliding, OCP values of PU25/PVP75 and PVP shifted the negative direction abruptly. OCP values of PU25/PVP75 and PVP coated samples are nearly -0.4 V vs V_{Ref} during sliding. This drop can be explained by the mechanical wear partial disruption of the polymer film. This value is very close to the OCP value of AISI 316L stainless steel $(0.45 \text{ V vs V}_{\text{Ref}})$ in figure 9 but slightly more positive. This phenomenon indicates that the surfaces of these coatings are thermodynamically less stable with a weakened protective effect. [30] The potential rise of PU25/PVP75 and PVP coated samples was approximately 50 mV vs V_{Ref} during sliding. This states the predominance of electrochemical repassivation over the mechanical depassivation [31]. It can be deduced that these coatings can reduce the corrosion rate of the substrate material [32]. OCP measured values for damaged and non-damaged parts of PU25-PVP75 and PVP during sliding. When sliding stopped, OCP values for PU25-PVP75 and PVP increased under the effect of surface repassivation. Also, PVP polymers can be used as corrosion inhibitors.



Figure 10. OCP wear of AISI 316L coated with PU/PVP polymers in 3.5 wt% NaCl solution

The low OCP value generally means high degradation material under tribocorrosion tests. In our study, both potendiodynamic and tribocorrosion tests confirmed that superior properties of PU and PU75/PVP25 coated samples compared to PU25/PVP75 and PVP coated samples under %3.5 NaCl solutions. The friction coefficients of and PU and PU75-PVP25 polymer coated samples are 0.2. Lower friction coefficients were obtained in PU and PU75-PVP25 coated samples because

polyurethane behaved as a lubricating agent under tribocorrosion conditions. The friction coefficients of PU25-PVP75 and PVP polymer coated samples are 0.4 due to the weak mechanical properties of PVP. The highest friction coefficient was obtained from the PVP coated sample. Considering OCP and friction coefficient together, it was determined that OCP values of PU and PU75/PVP25 coated samples are more positive and friction coefficients are lower under tribocorrosion conditions. On the contrary, OCP values of PVP and PU25/PVP75 coated samples are negative and friction coefficients are very high. Previous studies have reported the lower friction coefficient of polymer coated samples can be explained by the self lubricating capacity of the polymer [33-35].

4. CONCLUSIONS

In this study, corrosion and tribocorrosion behavior of PU/PVP polymeric blends coated AISI 316L stainless steel was investigated in a NaCl solution for industrial applications. The results are given below:

Wear and corrosion resistance increased with the increasing PU concentration in the coating. The highest wear and corrosion resistance was obtained in PU coated sample under tribocorrosion tests. The friction coefficient and surface roughness considerably increased with the rising PVP concentration in the polymer coating. The lowest friction coefficient was obtained from the PU coated sample under wear test. The nanohardness and elasticity modulus of the polyurethane film decreased with increased penetration depth. Coatings containing PVP up to 25% protected the AISI 316L stainless steel in NaCl solutions under tribocorrosion conditions.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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